Feasibility of polymer enhanced ultrafiltration (PEUF) for heavy metals retention under competitive conditions.

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FEASIBILITY OF *POLYMER ENHANCED ULTRAFILTRATION (PEUF)* FOR HEAVY METALS RETENTION UNDER COMPETITIVE CONDITIONS

by

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the Requirements for the Degree Of

DOCTOR OF PHILOSOPHY (Ph.D.)

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d Almutairi

Summary

Heavy metals are valuable resources for the modern world; however, they are potentially hazardous. Contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operations, and tanneries. The soils surrounding many military and industrial sites are also contaminated and pose a risk of metals groundwater and surface water contamination. Some metals associated with these activities are cadmium, chromium, lead, and mercury. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. However, heavy metals have a high commercial value if they can be recovered in pure form.

Polymer enhanced ultrafiltration (PEUF) was investigated because it offers the potential to selectively recover metals rapidly from solutions containing low concentrations. However, the major drawback (complex solutions containing other chelators and competitors) of these processes have not been investigated in detail and a fundamental understanding of these processes in real systems is required to truly assess and exploit their potential.

The aim of this project was to investigate the performance of PEUF for metal ions filtration in batch mode and continuous feeding using metals, individual and in mixtures, metal binding chelator and competitor. A variety of feed compositions were used, and metal ions retention profiles were determined. The competition from other chelators or competitors for metal ions was investigated in the presence of PEI. The binding mechanisms of metal ions were explored and the ability of the Langmuir isotherm model to describe these systems using a batch and continuous feed was determined. Based on the principal of mass balance and Langmuir adsorption isotherms, a mathematical model describing the continuous feed of PEUF was developed.

Ultrafiltration experiments were carried out in the stirred dead-end ultrafiltration cell and cross flow ultrafiltration systems. The metals investigated were: Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+}.

The results showed that adding PEI to metal ion solutions significantly increases the retention of the metal ions in the solution to greater than 90% at its best. However, the addition of the polymer significantly reduces the flux of the process (by approximately 50%) for equivalent solution conditions. Membrane surface charge is also a factor which is critical to the process performance. In general, the highest retention of metal ions occurred when the membrane had its highest negative charge.

The results of the binding studies showed that the Langmuir isotherm offers a better description of the binding process than the Freundlich isotherm.

The work reported here showed that competition for ions from other chelators or competitors is possible and change the performance compared to ideal simple systems. It also showed some potential advantages of this approach by changing capacity and selectivity of the separation based on PEUF processes. Under competitive conditions with chelators and competitors, maximum capacities of metal ions bind to PEI using Langmuir isotherm in continuous feed of PEUF were greater than those obtained from batch system, they were similar for Cu^{2+}-PEI complex in single and mixed metals solutions of both systems. The model developed in this project showed good predictions of the experimental results with minor exception in the case of strongly competitive situations.

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Chapter 1 Introduction

Metals in the environment and heavy metals recovery processes

1.1. An overview of metals in the environment

Metals in the environment may be present in the solid, liquid or gaseous state. They may be present as individual elements, and as organic and inorganic compounds. The movement of metals between environmental reservoirs may or may not involve changes of state. The geosphere is the original source of all metals (except those that enter the atmosphere from space in the form of meteorites and cosmic dust). Within the geosphere, metals may be present in minerals, glasses, and melts. In the hydrosphere, metals occur as dissolved ions and complexes, colloids, and suspended solids. In the atmosphere, metals may be present as gaseous elements and compounds and as particulates and aerosols [1].

Of all the elements on the periodic table, metals make up about 75% and they are found as ions and complex compounds throughout the hydrosphere. Metals in the hydrosphere are of environmental interest and important because of their interactions with solid phase materials of geological origin and also because of their influence on biological processes. Metal such as potassium and calcium are important nutrients required in substantial amounts by plants, animals, and microorganisms. Other metals such as copper and zinc are also nutrients, but the amounts required by organisms are very small. These metals, if present in excessive amounts can be toxic, so there is a range of concentrations, sometimes narrow, that are suitable for supporting life processes [2]. Because of the combination of a widespread possibility for human exposure coupled with an extremely high toxicity, certain heavy metals are a particular concern with regard to their toxic effects and even very small concentrations can be toxic to many living organisms. These metals are chromium, cadmium, mercury and lead [3, 4].

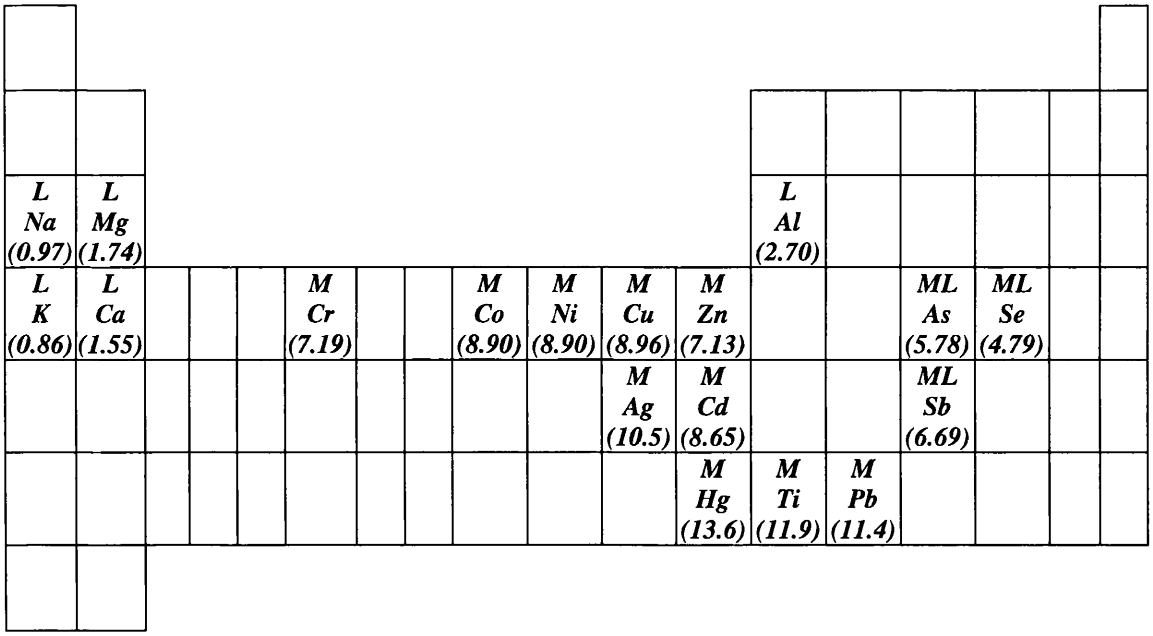
Sources of metals also include domestic and industrial effluents, the atmosphere, runoff and the lithosphere. The metals can adsorb onto soil, runoff into rivers or lakes or leach into groundwater, an important source of drinking water. Exposure to the heavy metals through ingestion or uptake of drinking water (particularly where water is reused) and foods can lead to accumulation in animals, plants and humans. Over the past years, use of metals such as copper, cadmium and zinc have increased substantially (table 1.1). Copper is produced more than any other metal, whereas more zinc reaches the soil than any other metal. Lead use has decreased due to toxicity concerns [5].

***Table 1.1** Global production of metals, and the rate of metals reaching the soil (10^3 ton/year)[5].*

Metal	***1975***	***1980***	***1985***	***1990***	***Emission to the soil in the 1980s***
Cd	15.2	18.2	19.1	20.2	22
Cu	6739	7204	7870	8814	954
Pb	3432.2	3448.2	3431.2	3367.2	796
Zn	3975.4	4030.3	4723.1	5570.9	1372

1.2. Principles of Heavy Metals

The term "heavy metal," in spite of its widespread usage among professionals and laymen, does not have a rigorous scientific basis or a chemical definition. Although many of the elements listed under "heavy metals" have specific gravities greater than five, major exceptions to this rule remain. In hindsight, this group should preferably have been referred to as "toxic elements", for they are all included in the United States Environmental Protection Agency's (USEPA's) listed of priority pollutants. Figure (1.1) shows the periodic table containing the heavy metals that are of significant environmental concern. Strictly from a chemical viewpoint, heavy metals constitute transition and post-transition elements along with metalloids, namely, arsenic and selenium. They are indeed significantly heavier (i.e., higher specific gravities) than sodium, calcium and other light metals. These heavy metal elements often exist in different oxidation states in soil, water and air. The reactivities, ionic charges and solubilities of these metals in water vary widely. For their short-term and long-term toxic effects, the maximum permissible concentrations of these heavy metals in drinking water as well as in municipal and industrial discharges are closely regulated through legislation [4].



Number in parenthesis represents the specific gravity of each element letters at the top middle of each cell denote

L: Commonly occurring LIGHT metals.

M: USEPA regulated HEAVY metals.

ML: USEPA regulated METALLOIDS

Figure 1.1 *A modified periodic table showing commonly encountered regulated heavy metals, metalloids and regulated light metals [4].*

1.3. Environmental concerns

Pollution by heavy metals is of considerable concern as these metals have found widespread use in electroplating, leather tanning, metal finishing, nuclear power plant, and textile industries [6]. The major toxic metal ions hazardous to humans as well as other forms of life are Cr, Fe, Se, V, Cu, Co, Ni, Cd, Hg, As, Pb, Zn etc. These heavy metals are of specific concern due to their toxicity, bio-accumulation tendency and persistency in nature [7].

Nowadays, governments introduce and progressively enforce stricter legislation with regard to the metal discharges into water and wastewater particularly from industrial operations. (UK and EU environmental legislations are covered in details in Appendix 1). However, controlling heavy metal discharges and removing toxic heavy metals from aqueous solutions has become a challenge for the 21st century [8]. In many countries, industry and other consumers are obliged to reduce their water consumption. Therefore, the recycling of process and rinsing water, and as a consequence, the removal and recovery of heavy metal ions from these sources, take on great importance. In accordance with low toxic heavy metal ions must be removed from water before its delivery to sewage plants [9, 10].

In order for a metal to be given high priority for removal it should meet the following criteria. One is that the metal should be present in quantities that pose a serious health threat to humans. A second is that the targeted metal has sufficient commercial value that its resale can recover the costs of the extraction process. As a result, studies focused on metal ion removal from both aqueous solutions and soils, either for pollution control or for raw material separation and recovery, have become of increasing importance in recent years. This is particularly true for metals that have both high toxicity and a high commercial value if they can be recovered in pure form [3].

1.4. The Role of Separation Technologies

Environmental technologies were defined: as those that reduce or eliminate emissions and discharges of water and pollutants from current practice, or reduce the risk to human health and the environment from past emissions and discharges.

Environmental technologies have three important attributes:

1. They must satisfy appropriate regulatory goals.
2. They should be designed from multimedia perspectives, that is, accounting for their effects on air, water, and soil.
3. They should reduce risk not only to human health, but also to the ecosystems.

The dominant environmental problems in which separation methods may play a role are shown in table (1.2).

***Table 1.2** Environmental problems: risk to human health and the ecosystems [11].*

Air Pollution	VOCs, SOx, NOx, CO, Ozone, CO2, heavy metals (for instance, Hg, Pb, Cr).
Water Pollution	Organics, metals, pathogens.
Land Pollution	Toxic metals, organics.

In the environmental context, separation technologies are "enabling technologies." They provide a means to isolate or concentrate pollutants so that recycle/reuse or control/disposal methods can be efficiently implemented, providing an economic incentive for their use. Additionally, they are a means of strategically positioning efficient separation methods in a process flow sheet so that waste generation can be reduced or avoided, and/or resource use, such as that of clean water, can be minimized.

These separation technologies have two unique attributes. First, most environmental problems of relevance to separations represent very dilute contaminated matrices, which pose special challenges to process designers and risk assessors. Second, separation technologies alone do not solve many environmental problems. They generally complement other technologies, such as further processing to recover the pollutants for recycling and reuse, or converting them to a form suitable for ultimate disposal [11].

1.5. Remediation Techniques

The selection of the most appropriate water and soil remediation method depends on the site characteristics, concentration, types of pollutants to be removed, and the end use of the contaminated medium [5]. It is well known, for example, that heavy metals, which are toxic to most organisms, have found their way into the water system from different processes. The production of nuclear weapons has also resulted in dangerous waste problems. The Hanford Reservation (Richland, WA, USA) stores 65 million gallons of radioactive waste from nuclear weapons production in 177 underground tanks. Sixty seven of the tanks have either leaked, or are presumed to have leaked. There are estimates that over 3 million sites in the United States, including municipal and industrial landfills, require remediation at a cost ranging from 250 billion to 1 trillion dollars. In addition, there is a growing interest in recovering precious metals and metal catalysts due to both environmental and economic reasons. A serious problem encountered in the removal of the metal ions is that the target species are usually in low concentrations and exist in complex mixtures. Radioactive waste, for example, can contain not only radionuclildes, but environmentally benign ions such as sodium, potassium, and calcium in higher concentrations. The innocuous ions can saturate the extractants before they can effectively remove the toxic ions [12].

A variety of methods for remediation of both solid and liquid media such as water, groundwater, industrial wastewater, soils, sediments, and sludges are known. To give a general overview of different technologies it is most convenient to divide them into three major categories: first, physical methods, second biological methods, third chemical methods (Fig. 1.2).

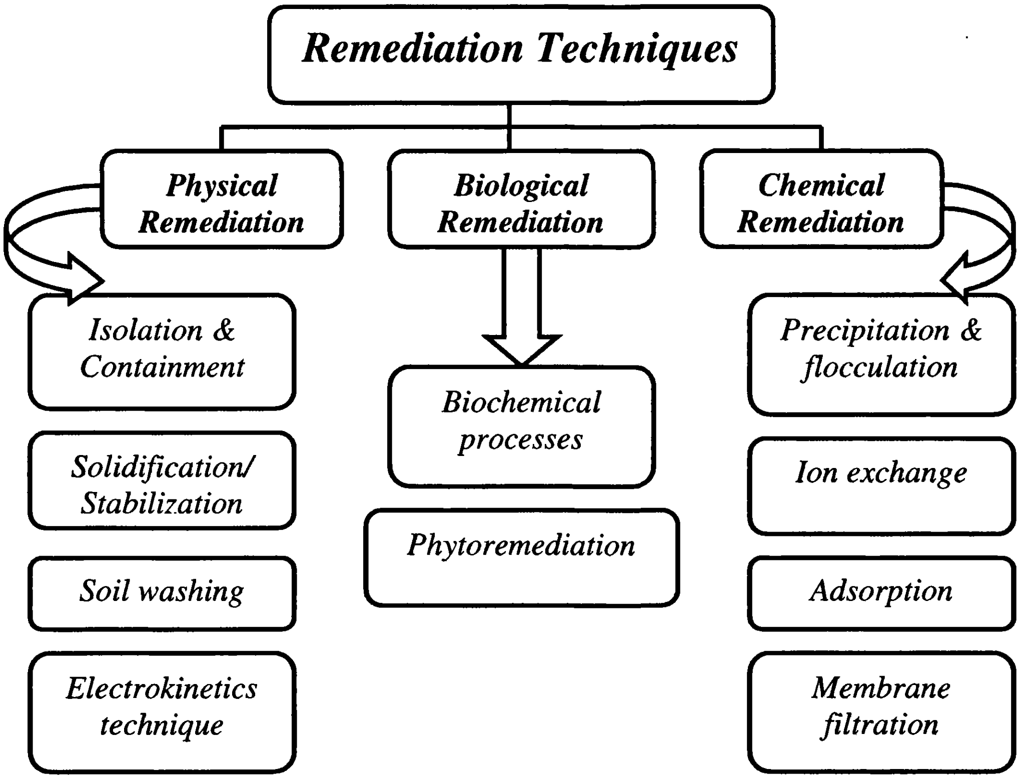


Figure 1.2 *Remediation process types of heavy metal removal from soil and liquid media*

1.5.1 Physical Remediation Techniques

Physical remediation techniques include Isolation and Containment, Solidification/ Stabilization, soil washing (Chemical Leaching) and electrokinetics technique.

1.5.1.1 Isolation and Containment

Contaminants can be isolated and contained, to prevent further movement, to reduce the permeability of the waste and to increase the strength or bearing capacity of the waste. Physical barriers made of steel, cement, bentonite and grout walls can be used for capping, vertical and horizontal containment. Capping is a site-specific proven technology to reduce water infiltration. Synthetic membranes can be used for this purpose. Vertical barriers reduce the movement of contaminated groundwater or uncontaminated ground water through a contaminated area. Horizontal barriers within the soil are under development and have not been demonstrated as effective but are potentially useful in restricting downward movement of metal contaminants by acting as underlying liners without the requirement for excavation [5].

1.5.1.2 Solidification / Stabilization

Solidification/stabilization technologies are very common as they contain the contaminants, not the contaminated area like physical barriers. They are treatment processes that reduce the mobility of contaminants by trapping or immobilizing them within the soil through chemical and/or physical means. Solidification is physical encapsulation of the contaminants in a solid matrix while stabilization includes chemical reactions to reduce contaminants mobility. Solidification/stabilization is a proven technology for the treatment of liquids, soils, and sludges contaminated with heavy metals. Some metals such as arsenic, chromium (VI) and mercury are not suitable for this type of treatment since they do not form hydroxides that are not highly soluble. Liquid monomers that polymerize, pozzolans, bitumen, fly ash and cement are injected to encapsulate the soils. Soils can be treated in situ or after excavation. In situ solidification/ stabilization techniques are preferred since labor and energy cost are lower but site conditions such as bedrock, large boulders, clays and oily patches may cause mixing problems. These solidification/stabilization processes are suitable for contamination in shallow depths and of large volume [5, 13].

1.5.1.3 Soil washing (Chemical Leaching)

The basic principle of soil washing is the transfer of the heavy metals which are bound to the soil, via desoprtion or solubilization. Heavy metals can be removed from soils using various agents added to the soil. This can be done in reactors or as heap leaching. These agents are: inorganic acids such as sulfuric and citric acids (pH not less than 4), chelating agents such as ethylenediamine tetraacetic acid (EDTA) and nitrilotriacetate (NTA), and various combinations of the above. The cleaned soil can then be returned to the original site. Soils with less than 10-20% clay and organic content (i.e. sandy soils) are most effectively remediated with these extractions. Both organics and metals are removed.

Despite of the advantages of the soil washing there is a serious problem that the washing effluent containing heavy metals should be released and treated for discharge [5, 13, 14]. The feasibility of using biodegradable biosurfactants to remove heavy metal from an oil-contaminated soil was demonstrated by laboratory scale batch washes with surfactin, a rhamnolipid and a sophorolipid. The first two agents are produced by bacteria while the last is produced by a yeast. Since these agents are biodegradable, can enhance hydrocarbon removal and can potentially be produced in situ, they have a great potential for soil washing and soil flushing applications [5].

1.5.1.4 Electrokinetics

Electrokinetic process involve passing a low intensity electric current between a cathode and an anode imbedded in the contaminated soil. Ions and small charged particles, in addition to water, are transported between the electrodes. Anions move towards the positive electrode and cations towards the negative. An electric gradient initiates movement by electromigration (charged chemicals movement), electro-osmosis (movement of fluids), electrophoresis (charged chemicals movement) and electrolysis (chemical reactions due to electric field). Buffer solutions are used to maintain the pH at the electrodes. The metals can be removed by electroplating or precipitation/co-precipitation at the electrodes, using ion exchange resins or recovering the metals by pumping the waste to the surface. Metals as soluble ions and bound to soils as oxides, hydroxides and carbonates are removed by this method. Other non-ionic components can also be transported due to the flow. Large metal objects, rocks, foundations, rubble or other obstacles can interfere with the process. Unlike soil washing, this process is effective with clay soils of low permeability [5, 13].

1.5.2. Biological Remediation Techniques

Environmental biotechnology includes any specific applications that reduce pollution. Methods might use organisms to break down or sequester pollutants (sometimes producing useful products along the way, or replace existing activities that pollute with those that do not. In this way, bioremediation consists of using naturally occurring or laboratory cultivated microorganisms to reduce or eliminate toxic pollutants. Therefore, bioremediation – from bio (living) and remediate (to fix or cure) – is a branch of biotechnology that uses bacteria and other microorganisms to clean up pollution [15]. Biological Remediation Techniques include biochemical processes for the extraction of metal by microbiological means, and phytoremediation which use plants to remove heavy metals.

1.5.2.1 Biochemical Process

Techniques for the extraction of metal by microbiological means include bioleaching and oxidation/reduction reactions. Bioleaching involves thiobacillus sp. bacteria under aerobic and acidic conditions (pH4) at temperature between 15 and 55 °C, depending on the strain. Leaching can be performed by direct means, oxidation of metal sulfides to produce sulfuric acid, which then can desorb the metals on the soil by substitution of protons. Indirect leaching involves conversion of Fe^{2+} to Fe^{3+} which in turn oxidizes sulfur minerals to Fe^{2+} producing acidity. Another leaching technique that has potential for remediation of metal-contaminated soil is through the production of citric and gluconic acids by the fungus Aspergillus niger can produce citric and gluconic acids. They can act as acids (pH 3.5) and chelating agents for the removal of metals such as copper from oxide mining residues. Inexpensive carbon substrates will be required to decrease the costs of this process.

Biosorption is a biological treatment method which involves the adsorption of metals into biomass such as algal or bacterial cells that can be dead or alive. This method is mainly applicable for removal of low concentrations of metals in water.

Microorganisms are also known to oxidize and reduce metal contaminants. Mercury and cadmium can be oxidized whole arsenic and iron can be reduced by microorganisms. Cr (VI) can be oxidized to Cr (III) that is less mobile and less toxic [5].

1.5.2.2 Phytoremediation

Phytoremediation is defined as the use of green plants to remove pollutants from the environment or to render them harmless. Plants such as Thlaspi, Urtica, Chenopodium, Polygonum sachalase and Alyssim have the capability to accumulate cadmium, copper, lead, nickel and zinc and can be therefore be considered as an indirect method of treating contaminated soils. This method is limited to shallow depths of contamination. The plants will have to be isolated from wildlife and agricultural lands. The climatic conditions and bioavailability of the metals must be taken into consideration when using this method. Once contaminated, the plants will have to be disposed of in an appropriate fashion. The main disadvantage of this method is that longer times are required compared to other methods [5, 13, 16].

1.5.3. Chemical Remediation Techniques

Chemical remediation techniques for the removal of heavy metals in contaminated groundwater and wastewater include precipitation of dissolved metals, flocculation, ion exchange, adsorption, and membrane filtration processes such as micro-and ultrafiltration. In fluid media, heavy metals occur as dissolved ions or bound to colloidal particles.

1.5.3.1 Precipitation and flocculation processes

A basic distinction must be made between precipitation and flocculation processes. Precipitation is a process, in which there is a phase transfer of soluble, ionic components into a non-soluble ionic phase. Flocculation is a process, in which small undissolved solids of colloidal size are aggregated into larger solid flocs. These flocs are then separated mechanically from the fluid by sedimentation, centrifugation, or flotation [17]. Solidification aims at the reduction of heavy metal mobility by trapping or immobilizing them within the soil by injecting or mixing immobilizing agents into the contaminated soil. Besides reducing chemical solubility, stabilization and solidification processes can be used to increase mechanical strength and reduction of soil permeability.

In precipitation, dissolved metal ions react with added precipitants by forming insoluble compounds. These solid sediments can be removed from the supernatant liquid by different solid/liquid separation techniques. The main chemical parameters, which are of importance in the precipitation process, are pH and concentration. In general, heavy metals tend to be present in ionic form at low pH levels, while they tend to precipitate when pH is raised. Heavy metals can be precipitated as insoluble hydroxides, sulfides, carbonates, and others [13].

There is a variety of precipitating agents such as digested sludge, Fe salts, calcium hydroxide, and Al salts. (Table 1.3) lists the effect of these different agents on the elimination of heavy metals [17].

Table 1.3 *Effect of different precipitating agents on the elimination of heavy metals [17].*

Precipitating Agent	High Effectiveness	Low Effectiveness
Digested sludge	Cu, Pb, Zn, Cd	Ni
Precipitation with Fe salts	Ag, Cr, Pb, Cd, Hg, Sn	Mn, Co, Sb, Se
Precipitation with CaOH	Ag, Co, Cr, Pb, Ni, Cd	Sb, Se, As
Precipitation with Al salts	Ag, Be, hg, Cr, Cd, Pb	Zn, Mn, Ni

Flocculation is used to transform the suspended colloidal particles in a form so that they can be separated mechanically from the supernatant solution with the help of flocculants. Primary colloidal particles have a typical particle diameter in the range between 10^{-4} to 10^{-7} cm.

In principle there are two classes of colloidal systems: hydrophilic and hydrophobic colloids. Hydrophobic colloids are dispersions of solid particles in a liquid. They are characterized by the large interface between the two components. The properties of the particle surfaces are of great importance for the system properties. Hydrophilic colloids consist of macromolecular components and water. They are in fact genuine solutions of macromolecules in water and are called macromolecular colloids. Their colloid chemical properties are caused by the size of their molecules and ions. An important difference between the two classes consists in their reaction toward salt addition. Hydrophobic colloids flocculate immediately when salt is added. In contrast, macromolecular colloids react relatively insensitive when salt is added, but large salt addition influences the solubility of the macromolecules, which then precipitate.

The main inorganic flocculation chemicals are calcium hydroxide, Fe(II) and Fe(III) salts, and Al salts [13].

1.5.3.2 Ion Exchange

Ion exchange is a chemical reaction where ions from solutions are exchanged for ions attached to chemically active functional groups on ion exchange resins. Ion exchange resins are typically classified as cation exchange resins or anion exchange resins. Cation resins usually exchange sodium or hydrogen ions for positively charged cations such as nickel, copper and sodium. Anion resins typically exchange hydroxyl ions for negatively charged ions such as chromates, sulfates and chlorides. Cation and anion exchange resins are both produced from three-dimensional, organic polymer networks. However, they have different ionizable functional group attachments that provide different ion exchange properties. Ion exchange resins have varying ion-specific selectivities (preferences for removal).

Ion exchange systems typically consist of columns loaded with ion exchange resin beads, process solutions are pumped through the columns for treatment. Resins can be regenerated, whereby acidic solutions are typically used to remover metals from cation exchange resins, and caustic solutions are typically used to remove resin-bound salts. Rinse solutions are used to remove excess regenerations fluids from the columns.

Ion exchange has been used commercially for many years in water deionization, water softening applications, and waste water treatment applications. There are widespread applications for rinse water recovery and metals recovery in the surface finishing industry. The most common applications include recovery of copper (from acid copper solutions), nickel and precious metal, from plating rinse water [18].

1.5.3.3 Adsorption

Adsorption occurs when a dissolved solute is bound to a solid adsorbent. A typical process involves four steps. First, a feed solution is added to the adsorbent. Second, adsorption occurs, a process which may be both selective and slow. Third, the spent feed solution is withdrawn. Fourth, the adsorbed solute is eluted, often using a different solvent.

Adsorption requires adsorbents, solid materials to which solutes of interest bind reversibly. While a large number of adsorbents are used industrially, only two major groups are used for biological molecules: carbons and synthetic resins. The carbons used are commercial products and are not manufactured specifically for bioseparations. A wide variety of products is available, with varying porosity and capacity. The more effective are made from vegetable sources like sawdust or fruit pits; carbons made from mineral sources can contain inorganic impurities which catalyze degradation of some solutes.

Ion exchange resins are largely based on synthetic polymers. The polymers usually contain fixed charges like $-SO_3^-$, $-COO^-$, or $-NR_3^+$; however, they can effectively adsorb both ionic and nonionic solutes. Resins made from styrene and divinylbenzene often adsorb nonpolar solutes most strongly; resins based on acrylic esters tend to be more effective for hydrophilic solutes. Adsorbents based on hydrogels are often made of polyacrylamides, which are the mainstay of gel electrophoresis. Resin manufacturers are eager to synthesize custom adsorbents, which are expensive and often do not last as long as expected [19].

1.5.4. Membrane Filtration Processes

Membrane separation technology is a novel and highly innovative process engineering operation. Membrane filtration processes are nowadays used as an alternative to conventional industrial separation methods. Membrane separation processes have found wide application for most of the fluid separations encountered in industry. They potentially offer the advantages of separation without any auxiliary materials, ambient temperature operation, usually no phase changes, continuous and automatic operation, economical operation also in small units, modular construction and simple integration in existing production processes, as well as relatively low capital and running costs [20]. The former advantages make membrane processes even more interesting for certain types of materials which have been inherently difficult and expensive to separate, such as,

- Finely dispersed solids, especially those which are compressible, have a density close to that of the liquid phase, have high viscosity, or are gelatinous.
- Low molecular weight, non-volatile organics or pharmaceuticals and dissolved salts.
- Biological materials, which often fall in the colloidal size range and are very sensitive to their physical and chemical environment [20, 21].

The various membrane separation methods can be divided according to their separation characteristics which may be classified by the size range of materials separated. These four types of membrane processes, as used in pressure driven force separation, are microfiltration, ultrafiltration, nanofiltration and reverse osmosis (figure 1.3). Ultrafiltration is probably the most widely used of these pressure driven membrane separation processes, and used to retain solutes and colloidal particles of the size of ~ 2-100 nm range [22].

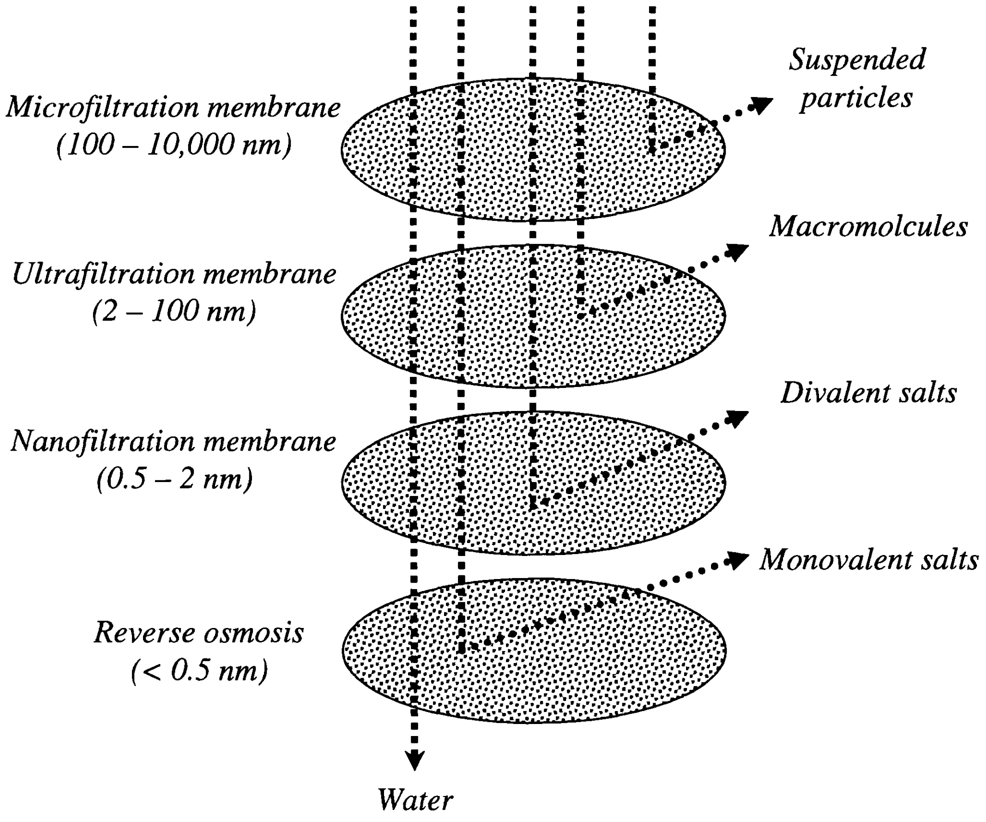


Figure 1.3 *Schematic representation of rejection behavior of membrane filtration.*

1.5.4.1. Theory of Ultrafiltration

Ultrafiltration is a pressure-driven membrane process by which macro-molecular solutes and/or colloidal particles are separated from a solvent, usually water. The relationship between the applied ultrafiltration pressure and the rate of permeation (flux) for a pure solvent feed flowing under laminar conditions in tortuous membrane channels may be described by the Carman-Kozeny equation:

$$J = \frac{|\Delta p|}{\mu R_m} \qquad \text{.......................... } (equation\ 1.1)$$

Where J is the flux (volumetric rate per unit area), Δp the transmembrane pressure difference, μ the solvent viscosity and R_m the membrane resistance, the general approach to describe ultrafiltration in the presence of a solute is given by:

$$J = \frac{|\Delta p| - |\Delta \pi|}{\mu (R_m + R_s)} \qquad \text{.......................................} (equation\ 1.2)$$

Where $\Delta\pi$ is the difference in osmotic pressure across the membrane and Rs represents reversible (concentrated layer, filter cake) and sometimes irreversible (foulants) deposition of solute (or solids) onto the membrane surface.

Operational performance of membrane systems are generally assessed by efficiency in retention of the required solutes, and permeate flux.

Important operating variables affecting permeate flux are:

- Applied transmembrane pressure
- Cross-flow velocity through the membrane module.
- Flow regime of fluid through the membrane

The effect of these operating variables on permeate flux (Fig. 1.4) have been observed by many workers. Permeate flux increases with applied transmembrane pressure (Fig. 1.4 A) up to a critical transmembrane pressure (Δp). Above this pressure, which has to be experimentally determined for each application, permeate flux becomes insensitive to pressure increases. In fact, too high a pressure may aggravate fouling of the membrane, and decrease permeate flux. Increasing cross flow velocity of the feed stream increases permeate flux (fig.1.4 B), and the effect of the flow regime (fig. 1.4 C) intensifies the effect of cross flow velocity [21].

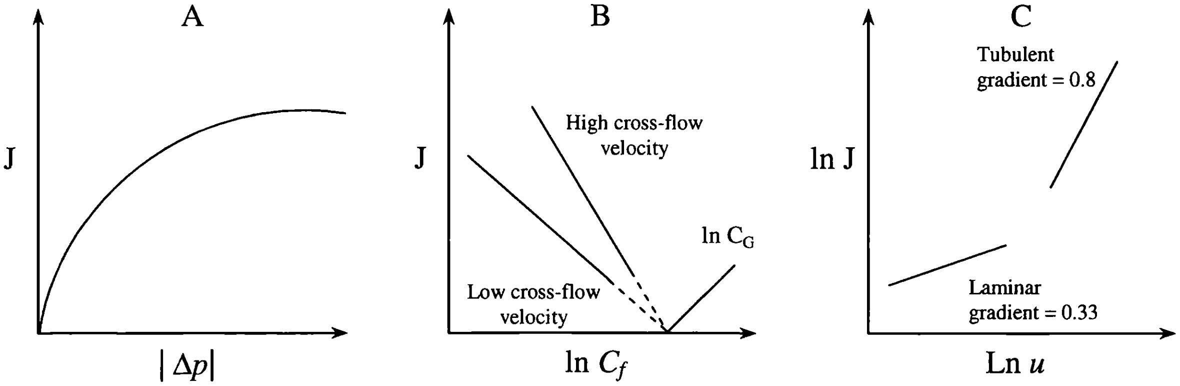


Figure 1.4 *Observed effects of operating variables on permeate flux(J), transmembrane pressure (A), feed stream velocity (B), and flow regime of the feed stream (C). [Δp: applied pressure difference, C_f: feed solute concentration, u: cross flow velocity and C_G: the concentration of solute in the gel-layer [21].*

1.5.4.2. Fouling and Concentration Polarization

Fouling is another of the limiting factors of membrane technologies, which cause an irreversible decrease in permeates flux with operation time. It is due to deposition or accumulation of solutes over membrane surface and/or into the pores as a result of physical and chemical interactions between solute and membrane.

Concentration Polarization (CP) is the phenomenon that more strongly affects these UF processes, since it cause deterioration in process design parameters: decline in permeate flux and metal rejection coefficients [23]. The separation of solute and solvent takes place at the membrane surface where the solvent passes through the membrane and the retained solute causes the local concentration to increase, an effect which is known as concentration polarization. Thereby a concentration profile is established within a boundary film generated by the hydrodynamic conditions (fig. 1.5).

With the higher concentration at the membrane surface, there will be a tendency of solute to diffuse back into the bulk solution according to Fick's law of diffusion. A solute mass balance above the membrane surface at steady state condition and with the assumption that:

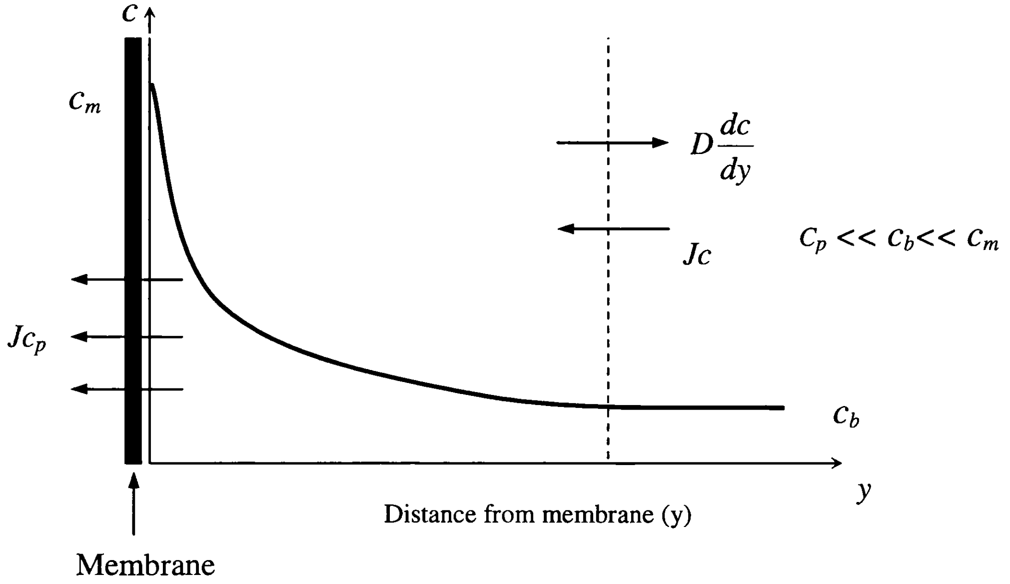


Figure 1.5 *Concentration polarizations at a membrane surface. (The separation of process liquid and solute that takes place at the membrane during ultrafiltration gives rise to an increase in solute concentration close to the membrane surface) [20].*

1. solvent and solute densities are similar,
2. the diffusion coefficient is constant and
3. concentration gradients parallel to the membrane are negligible compared with the concentration gradients orthogonal to the membrane, gives the rate of convective transport of solute towards the membrane surface equal to the rate of solute leakage through the membrane plus the rate of solute due to back-diffusion,

$$Jc = D\frac{dc}{dy} + J\,c_p \qquad \text{..........................}(\textit{equation 1.3})$$

where C and Cp are solute concentrations in the boundary layer and in the permeate, respectively and D is the diffusion coefficient of the solute in the solvent. An integration of Eq. (3) over the boundary layer thickness (δ) with the boundary conditions

$C(y = \delta) = C_b \qquad C(y = 0) = C_m$

gives the well-known film model relationship:

$$J = k_s \ln\left(\frac{c_m - c_p)}{c_b - c_p}\right) \qquad \text{..........................}(\textit{equation 1.4})$$

Where $k_s = D/\delta$, the overall mass transfer coefficient of the solute in the boundary layer, and C_m is the concentration at the membrane surface.

The overall mass transfer coefficient is usually obtained from correlations of the form:

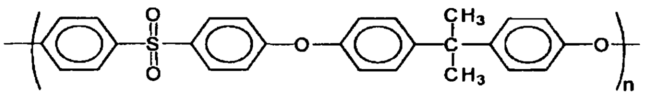
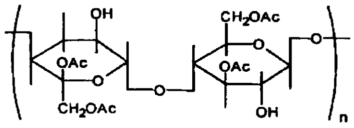
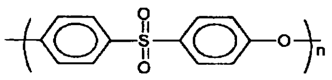
$$Sh = \frac{k_s d_h}{D} = K\,Re^a\, Sc^b \left(\frac{d_h}{L}\right)^c \qquad \text{..........................(equation 1.5)}$$

where the constants K, a, b, c vary with the flow regime. The above boundary layer theory applies to mass transfer controlled systems where the permeate flux is independent of pressure (no pressure term in the model) [20].

1.5.4.3. Ultrafiltration Membrane Modules

The most common UF membranes are based on cellulose acetate (CA), polysulfone (PS), poly (ether sulfone) (PES), polyacrylonitril (PAN) and polyvinyldiene (PVD) as shown in (table 1.4). Although CA-based membranes are less prone to fouling and typically have a higher flux than PS membrane at equivalent rejection, PS membranes are used in many applications because of higher stability [24].

***Table 1.4** Molecular structure of ultrafiltration membranes [24].*

Name	Molecular structure
Poly(sulfone)	
Cellulose acetate	
Poly(ethersulfone)	
Poly(ethylene)	$—(CH_2)_n—$
Poly(vinyldiene fluoride)	$—(CH_2CF_2)_n—$

Membranes used in ultrafiltration should have high fluxes, a separation characteristic tailored to the required separation, a sharp molecular weight cut-off, (which means a narrow pore size distribution), and good mechanical, chemical, and thermal stability, which in general provides good flux stability and high life expectancy [25]. The properties of the principal ultrafiltration membranes are summarized in Table 1.5.

***Table 1.5** Polymers Used for Manufacturing of Ultrafiltration Membranes [25].*

Polymer	Typical achievable (MWCO)	pH Operating range	Maximum operating temp. (°C)	Chlorine resistance	Organic solvent resistance	Membrane configuration
Cellulose acetate	1,000-50,000	3.5-7	35	Good	Poor	Flat sheets, tubes
Polysulfone	5,000-50,000	0-10	50	Good	Fair	Flat sheets, tubes, capillaries
Aromatic polyamides	1,000-50,00	2-12	80	Poor	Fair	Flat sheets,tubes, capillaries
Polyacrylonitrile,poly (vinyl chloride), copolymer	30,000-100,000	2-12	50	Fair	Fair	Flat sheets, tubes, capillaries

For the successful application of ultrafiltration as an efficient mass-separation process, the design of the module used to contain the membrane and the layout of the system in which the module is installed are as important as the selection of the proper membrane. This is because of concentration polarization that leads to gel- or cake-layer formation on the membrane surfaces. This gel layer, which can drastically alter the ultrafiltration properties of the membrane, is sensitive to the module design. In addition to affecting the economics of the process by reducing the filtration rate, gel-layer formation on the membrane surface can also change the separation characteristics of the membrane. Several membrane module designs have been used having significant differences in the feed flow distribution, operating pressure and capital and operating costs [21, 25].

Table 1.6 summarizes and compares the remediation techniques for heavy metal removal from waste streams. Among the treatments presented in the table, some of them have been tested successfully in the laboratory or even on a pilot scale. However, no individual process has been found to be significantly effective and applicable for the removal of metal ions from solution containing low concentration of metals. As future regulations focus upon the ability of industrial users to comply with the legal requirements of the residual metal concentration in discharge, it would be very beneficial to investigate various treatments, which can assist industrial users to comply with the environmental legislation (Appendix 1). As results, a selective separation of metals using polymer enhanced ultrafiltration process PEUF was considered for further study.

***Table 1.6** Comparison of remediation techniques for heavy metal removal.*

Technology		***Advantages***	***Disadvantages***	***Comments***
Isolation & Containment		Simple process, low cost	Environmental risk	Barriers used like steel and cement.
Solidification/ Stabilization		Labor and energy cost are lower.	Site condition may cause mixing problems	Suitable for large volume contamination in shallow depths.
Soil washing		Remove metals and organics, biodegradable biosurfactnts can be used	Washing effluent should be treated.	In effective with clay soils of low permeabilty
Electrokinetics technique		Effective with clay soils of low permeabilty	Large metal objects, rocks can interfere with the process.	Not commonly used.
Biochemical processes		Most cost efficient	Extended treatment time, monitoring difficulties.	The microorganisms can alter the chemical properties of metals.
Phytoremediation		Phytoremediation is well suited for use at very large field sites.	Long duration of time for remediation, contamination of the food chain.	Phytoremediation is relatively new technique.
Precipitation & flocculation		Simple process, inexpensive equipment requirement, convenient and safe operation.	Process not sufficiently efficient, higher operational cost due to chemical consumption, large amount of sludges.	Treat inorganic effluent with a high metal concentration. pH is the major parameter that effects the process, pH ranging from 11-11.5.
Ion exchange		Highly effective, no sludges generation, good capacity, easy to operate.	Sensitive to particles, not selective, expensive	Resins have different effective pH ranges.
Adsorption		Conventional sorbents, high adsorption capacity.	Adsorbent disposal, cost, not for metal.	Adsorption is a mass transfer process.
Membrane filtration	***MF&UF***	Low pressure (energy costs are lower),	Low salt rejection,	Operation of membrane system is simple, Membranes are suffered from fouling and degradation, pretreatment is required in some cases, no chemicals are needed, recycling of selected waste streams within a plant.
	NF&RO	High salt rejection, high water flux	High pressure (high energy consumption), not selective,	
	PEUF	High selectivity, low driving force (energy costs are lower), effective for small ions separation.	No specific polymer designed to be used in this process.	

Chapter 2 Literature review

Polymer Enhanced Ultrafiltration (PEUF)

2.1. Introduction

Toxic heavy metals appear in low concentrations in industrial and wastewater discharges. Potential adverse health impact and environmental concern have resulted in stricter environmental legislation regarding effluent quality standards [26, 27].

Conventional methods for heavy metals removal include the use of liquid-liquid extraction, ion-exchange, adsorption and precipitation reagents. All have been successfully used, however, these techniques offer significant disadvantages related to heterogeneous reactions, incomplete removal, high energy requirement or chemical consumption and generating toxic sludge or solid waste that also require expensive disposal [28-30]. On the other hand, membrane separations are efficient and widely applied separation processes that are comparable to other separation techniques in terms of technical and economical feasibility [31]. Many commercial separation problems are being solved by membrane processes, which can be successfully used to treat industrial wastes [32]. The main disadvantage in using membrane processes for treatment of effluents with heavy metals is the size of the dissolved metallic salts. These hydrated ions or low molecular weight complexes, pass easily through most membranes with the exception of reverse osmosis and nanofiltration membranes. However, as these membranes are relatively non selective, all the metallic ions are retained together with alkaline and alkaline-earth ions [33]. Selective separation, recovery and purification of heavy metals can be achieved by using polymeric reagents containing selective ligand groups and termed “polychelatogens” in combination with membrane filtration [9, 24, 31-34]. A soluble polymer reagent with chelating groups is characterized by two main components: the polymer backbone, which provides the solubility and stability of the reagent, and the functional groups, which are necessary for the selective reactivity of the polymer [35].

The combination of the two phenomena; binding of metal ions to a water soluble polymer, and ultrafiltration has been termed Polymer Enhanced Ultrafiltration (PEUF), and includes complexation of metallic ions with polymers. Separation of metal ions bound to the soluble polymers from non-bound metals is achieved using an ultrafiltration membrane. This produces a permeate solution almost free of metal ions and a retentate with high metal content [9, 24, 32-38]. The concentrate metal is recovered from polymer allowing the polymer to be reused.

In the PEUF process, complexation of metals with polymers occurs in the homogenous phase, hence avoiding difficulties relating to heterogeneous reactions, interface transfer, and long contact time problems of multiphase separation processes [36, 39]. Another potential advantage of PEUF is the low energy requirements involved in ultrafiltration process [34]. However, economical feasibility study for a similar process [40], demonstrated favorable cost compared to other processes.

2.2. PEUF Process description

A variety of terms have been used in the literature for the combination of ultrafiltration with chelation including polymer-supported ultrafiltration (PSU) (9, 30), liquid-phase polymer-based retention (LPR) (24, 32-34, 41-45, 46-49), polymer-assisted ultrafiltration (PAUF) (10, 30, 50-54) and polymer (or polyelectrolyte) enhanced ultrafiltration (PEUF) (23, 36, 38, 40, 55-65).

The Polymer Enhanced Ultrafiltration process combines proprietary polymers with size exclusion ultrafiltration to remove metal ions from aqueous streams. Polymers used in the process are water-soluble and have specific chelating functionalities that allow for selective binding of the targeted metal ion(s). The polymers are precisely sized such that they will not pass through an ultrafiltration membrane, which are typically have pore sizes in the 0.002–1.0 micron (20–10,000 A) range [39].

Process descriptions are presented in figure 2.1, the first stage of PEUF is a metal-polymer complexation; in this stage the process stream (metal ions solution) is added to the polymer solution and the conditions adjusted for optimal binding of target metal ions to the polymer. The metal polymer complex solution is then pumped through an ultrafiltration membrane in the second stage of PEUF , where the solution with non target metal ions not bound to the polymer passes through the membrane to the permeate stream, while the macromolecular complexes of target metal ions and polymer are retained by the membrane (termed retentate). The retentate in this stage becomes more concentrated as more solution is processed.

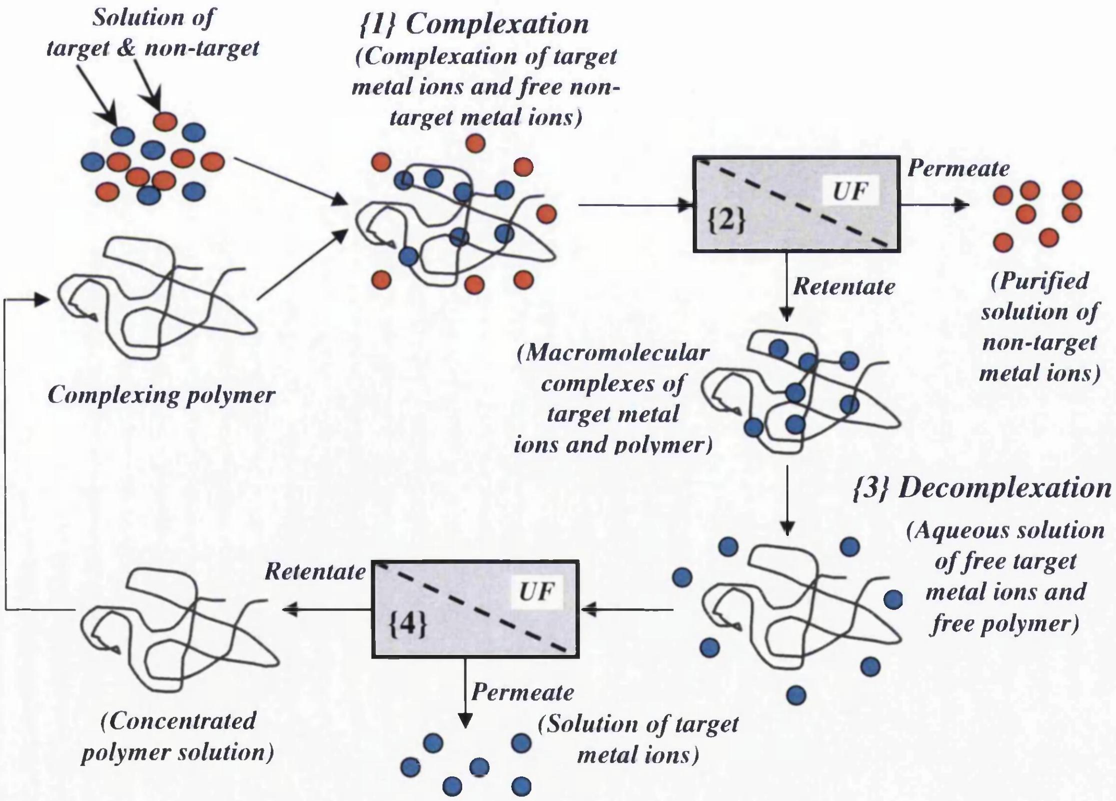


Figure 2.1 *Schematic diagram of the PFUF process. Note the various stages that allow selective separation, concentration of metals plus recycling of the polymer.*

When the polymer-metal complex is concentrated to the desired level, the pH of retentate solution is decreased to break the polymer-metal complexes (decomplexation occurred in the third stage of process), producing an aqueous solution of free target metal ions and free polymer. Separation of this solution can be achieved in the last stage of PEUF using ultrafiltration membrane, where the target metals ions will pass into the permeate stream and the retentate of concentrated polymer solution (regenerated polymer) can be reused for further complexation processes.

Geckeler [32, 66] described the general function of the polymeric complexing agents in the liquid-phase retention separation procedure as it is illustrated in (figure 2.2).

As shown there, several steps can be discerned when employing this process:

- Preparation of the polymer reagent from a monomeric precursor by polyreaction or by polymer-analogous functionalization from a performed polymer;
- Interaction with the metal ions in the homogeneous phase (aqueous solution), predominantly based on complexation, with the formation of the interaction product with the target metal ions;
- Separation of the polymer-metal complex from non-bound metal ions using the membrane separation techniques;
- Cleavage and removal of the target metal ions yielding the polymer reagent.

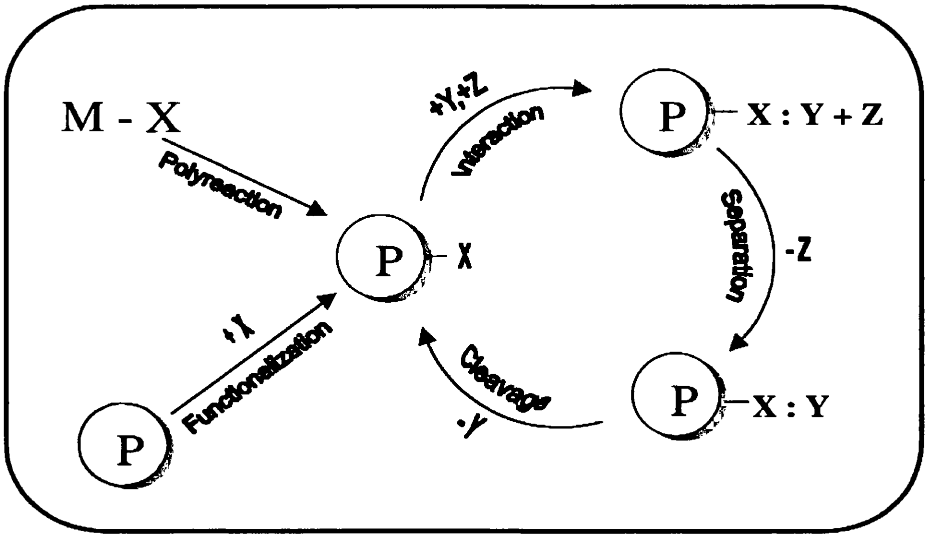


Figure 2.2 Functionalization or polyreaction, interaction with metal ions, separation, and cleavage from water- soluble polymers using the liquid-phase retention separation. P = Polymer, X = Functional molecule or group, P-X=Polymer ligand, Y = Target metal ion, Z = Non-target metal ion, P-X:Y = Polymer-metal complex [21, 30].

2.3. Water Soluble Polymers

The concept of using water-soluble polymers (WSP) to retain small ionic solutes in this way was first discussed by Michaels [67]. There are now reviews on the use of this technology for metal ion separations [4, 68] as well as more focused work on the removal of specific ions from solution [69], where there are three distinct advantages of using water-soluble polymers:

1) The metal bound to the polymer in solution can be easily concentrated by UF;

2) The metal subsequently released from the WSP can be easily segregated by UF to allow for recycle of the extraction agent and disposal of the metal;

3) Commercially available polymers can be modified to selectively bind the target metal ions [69].

The separation process of metal ions will be successful, if the complexing agent employed in PEUF meet the following requirements [68, 70]:

- High affinity towards the target metal ion,
- Inactivity towards the nontarget metal ion
- Good solubility
- High molecular weight
- Possibility of regeneration
- Stability of complexes
- Low-toxicity, and low cost.

Three main groups of polymers can be classified:

- Basic polymers, such as poly(ethylenimine), poly(vinylamine), poly (allylamine), and other amino or imino group-containing polymers;
- Neutral polymers, such as polyglycols, polyalcohols, polyethers;
- Acidic polymers, such as poly(acrylic acid), poly(vinylsulfonic acid), poly (styrene-sulfonic acid) [31, 68].

Water soluble polymer that have been investigated for their ability to bind different metal ions in PEUF studies include:

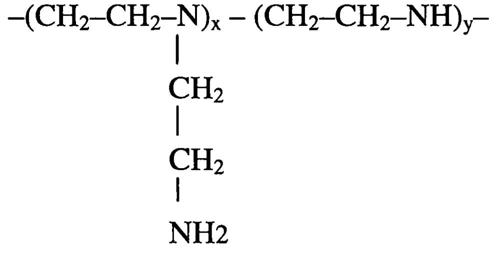
Poly(ethyleneimine) (PEI) [10, 23, 24, 30, 31, 36-38, 50, 51, 53, 56, 60, 62, 64, 69-76]
Poly(acrylic acid) (PAA) [10, 23, 31, 34, 46, 47, 52, 55, 58, 70, 77, 78]
Poly(sodium 4-styrenesulfonate) (PSS) [4, 79]
Poly(allylamine) (PALA) [79]
Poly(acrylamide-co-1-vinyl-2- pyrrolidone) [42]
Poly(*N,N*-dimethylacrylamide-co-1-vinyl-2-pyrrolidone) [42]
Poly(*N*-acetyl-α-acrylic acid) [43]
Poly(*N*-acryloyl piperazine) [44]
poly(*N*-acryloyl-*N*-methylpiperazine) [80]

Poly(*N*-acryloyl-*N*-methylpiperazine-co-*N*-acetyl-α-aminoacrylic acid) [45]
Poly(methacrylic acid) (PMA) [24, 34, 46]
Poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (PAMPSA) [24, 34, 46, 80]
Poly[(2-hydroxyethyl)-DL-aspartamide] [33]
Poly(2-acrylamido-2-methyl-1-propane sulfonic acid-co- methacrylic acid) [46]
Poly(styrene sulfonic acid-co-maleic acid) [81]
Poly(acrylic acid-co-maleic acid) [81]
Poly(vinyl sulfonic acid) (PVS) [47]
Poly[acrylamide-co-1-(2-hydroxyethyl)aziridine] [48, 82]
Poly(vinylphosphonic acid) [34]
Poly(ethyleneimine epichlorohydrin) (PEIE) [37]
Poly(dimethylamine-co-epichlorohydrin) (PDMA-co-E) [37]
Poly(vinylalcohol) (PVA) [4, 73, 75, 83, 84]
Poly(acrylic acid sodium salt) (PAASS) [10, 57, 85]
Poly(dimethylarnine-co-epichlorohydrin-coethylene-diamine) (PDEHED) [10]
Poly[(N-maleoylglycine)-co-(hydroxyethyl methacrylate)], P(MG-co-HEMA) [49]
Poly(carboxylic acid) (PC) [72]
Chitosan [50, 60, 62, 86, 87]
Poly(diallyldimethylammonium chloride) (PDADMAC) [50, 65]
Poly(acrylic acid–maleic anhydride) sodium salt (PAM-Na) [59]
Pectin [60]

Beauvais *et al.* [12] reviewed various polymeric ligands that display different affinities toward metal ions these include: heterocyclic amines; amidoximes; dithizone; hydroxamic acid; crown ethers; phenolics and phosphorus-based ligands.

Polyethylenimine (PEI) reported in many PEUF studies [10, 23, 24, 37, 60, 69, 70] as a good polychelatogen in the separation of metal ions in aqueous solutions, which possess a number of advantages such as good water solubility, high affinity to target metal ions, less affinity to non target metal ions, a high concentration of functional groups, possibility of regeneration, chemical and mechanical stability, low toxicity and low cost [23, 37, 76].

It is possible to find PEI in two forms: LPEI (linear) and BPEI (branched). This branched form contains primary, secondary and tertiary amines (figure 2.3), while, linear form contains only secondary amines (figure 2.4). PEI has a very strong heavy metal complexing ability since it contains primary, secondary and tertiary imine groups in the 1:2:1 ratio [24, 38, 88]. PEI has an extremely high cationic charge density owing to the protonation of amine groups as a function of pH. This relationship between pH and charge is useful when PEI takes part in complex formation with metal ions, where the efficiency rises, as amine groups are deprotonated. Nevertheless, this polymer does not interact with alkaline or alkaline-earth metal ions [50, 68]. These features of PEI as polychelatogen were considered of choosing this polymer in this study for further investigations.



$$-(\mathrm{CH_2{-}CH_2{-}}\underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{NH2}}}{\mathrm{N}})_x-(\mathrm{CH_2{-}CH_2{-}NH})_y-$$

***Figure 2.3** PEI Branched [48]*

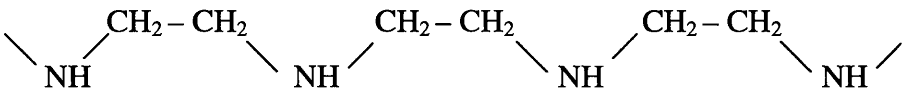


***Figure 2.4** PEI Linear [10]*

2.4. Modes of Operation

Different modes of operation of polymer enhanced ultrafiltration process were reported in the available literature as follow:

1. The batch method of PEUF [9, 23, 31, 35, 39, 50, 52, 62, 72, 83, 87, 89, 90]
2. The recycled method of PEUF [36, 38, 52, 56, 59, 63, 64, 71, 78, 91]
3. The washing method of PEUF [4, 33, 37, 41, 43, 44, 79, 80, 81]
4. The continuous feed method of PEUF [46, 55, 82]

In batch method of PEUF (figure 2.5), the solutions of the metal ions and the polymer were loaded into the feed reservoir. Then, the solutions were pumped and circulated through an ultrafiltration membrane. The complexes of polymer and target metal ions were rejected from membrane and recycled back to the reservoir while the non-target metal ions solution freely permeated through the membrane. Therefore, a continuous reduction of the volume of solution inside the system results in an increase of the concentration of the target metal ions and the polymer.

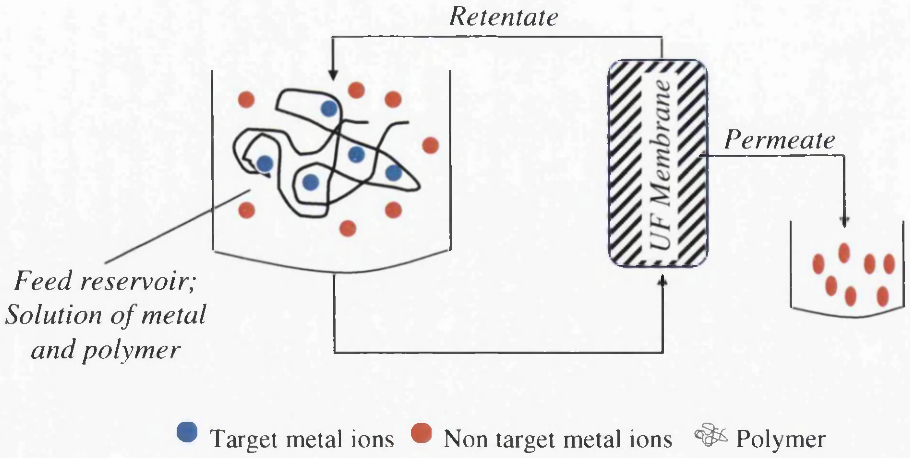


Figure 2.5 *Schematic diagram of the batch mode configuration for selective absorption in polymer enhanced ultrafiltration process. [In this mode, a continuous reduction of the volume of complex solution resulting a permeate solution with non target metal ions and retentate complexes with high concentrations of target metal ions].*

When the polymer-metal complex is concentrated, the polymer can be regenerate by adjusting the pH of the retentate solution to break down the polymer-metal complex into metal ions and regenerated polymer. At this stage, the diafiltration mode (figure 2.6) can be applied to remove the metal ions from the polymer. In this process, pure water was added to the retentate at the same rate that permeate was collected from the permeate stream in order to maintain constant reservoir volume. After having passed a certain volume of fresh water through the feed reservoir, the retentate was washed free of the metal ions and then regenerated polymer capable of being used again in further PEUF process.

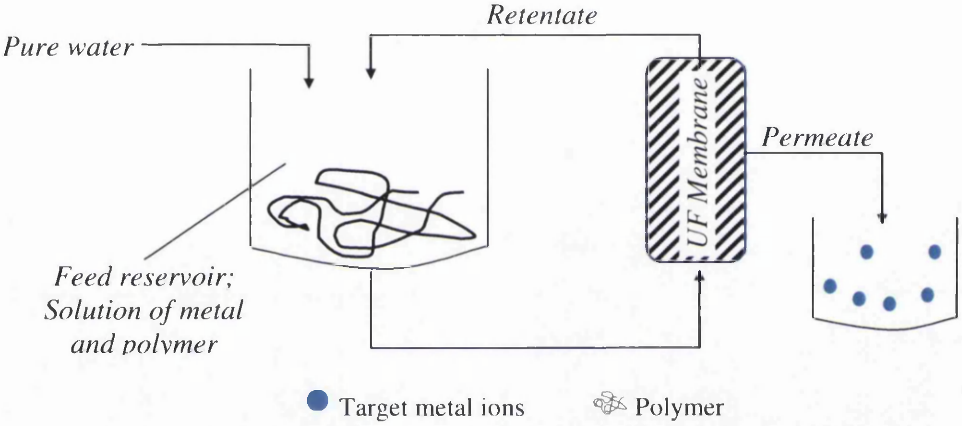


Figure 2.6 *Schematic diagram of the diafiltration/washing of released metal mode configuration in polymer enhanced ultrafiltration process. [In this mode, the concentrated target metal ions were released from the polymer by decreasing the solution pH and then diafiltred/washed using continuous pure water].*

The recycled method was similar to the batch method, with the exception that both retentate and permeate solutions were returned back to the feed reservoir to keep the concentration of the feed solution constant throughout the experiments. At certain time intervals, relatively small samples from both permeate and feed solutions were taken without effecting process solution volume or concentrations.

The washing method of PEUF process (figure 2.7) is a batch like method with a significant difference that the amount of permeate collected from the permeate stream was replaced using wash solution from the secondary reservoir, resulting a constant primary reservoir fluid volume. This process can be run in two types of operation; (i) washing method at constant ionic strength and (ii) washing method at variable ionic strength. In the case of washing method at constant ionic strength, a similar amount of electrolyte can be added to the metal-polymer solution in the primary reservoir and the washing solution in the secondary reservoir, giving both solutions the same ionic strength. In the washing method at variable ionic strength, pure water was used as wash solution without the addition of an electrolyte, so that, it's ionic strength is very low.

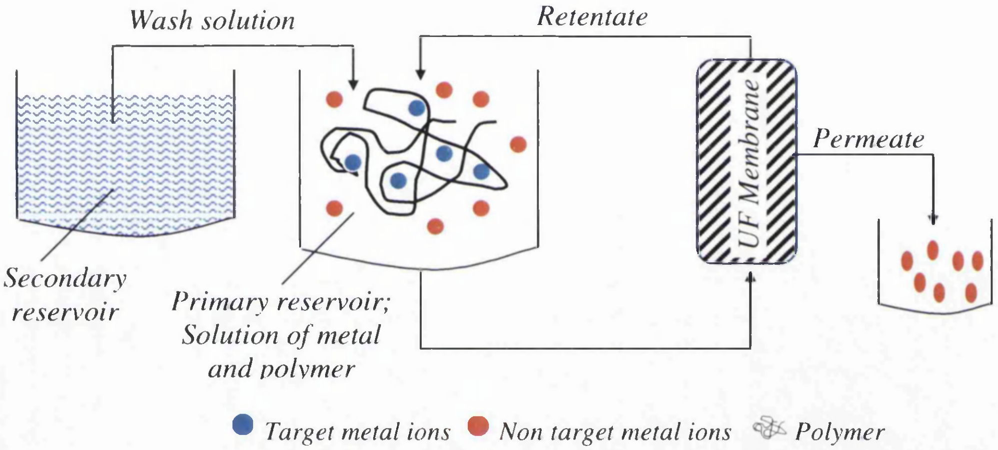


Figure 2.7 *Schematic diagram of the washing method configuration for polymer enhanced ultrafiltration process. [In this mode, the complexes of metal polymer solution were placed in the primary reservoir and then washed using wash solution; non target metals passed through the membrane while the polymer with target metals were rejected.*

Different mode of operation of PEUF was observed in the continuous feeding method (figure 2.8). In this process, a polymer solution is placed in the primary reservoir and a metal solution is placed in the secondary reservoir. To achieve capture of metal ions, the solution of metal ions from secondary reservoir is passed through the polymer solution in the secondary reservoir. The volume of complex metal-polymer solution in the primary reservoir is kept constant by continuous feeding of metal solution at the same rate as permeate is collected from the permeate stream, resulting an uptake of metal in the primary reservoir until saturation is achieved.

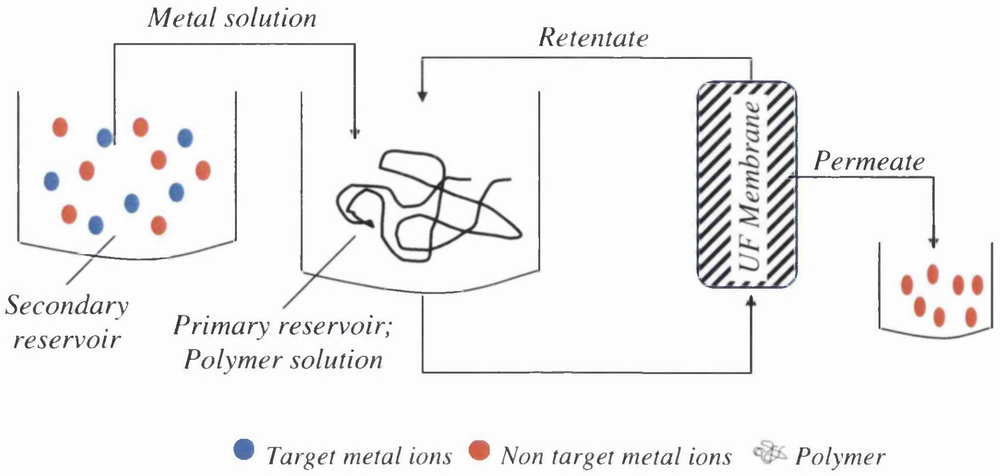


***Figure 2.8** Schematic diagram of the continuous feeding method configuration in polymer enhanced ultrafiltration process. [In this method, the solution of metal ions passed through the polymer solution, resulting permeate with non target metal ions and retentate containing a complex of target metal ions with polymer].*

Villoslada *et al.* [82] developed a graphical analysis concerning the metal ion enrichment of water-soluble polymers by the ultrafiltration technique. It assumed that the polymer does not affect the diffusion of metal ions since this phenomenon is faster than the flow rate. Also, the steady state approximation is assumed so that the polymer and metal ions achieve an equilibrium situation in every instant. Plotting of the metal concentration in the filtrate as a function of filtration factor showed four different curves as shown in (figure 2.9). A blank experiment curve was obtained in the absence of the polymer showing the diffusion controlled process as it shown in (figure 2.9 a). If only an irreversible uptake of metal ions by the water-soluble polymer is carried out, a parallel curve to the plot of the blank experiment will appear at a higher filtration factor value (figure 2.9 b). As polymer–metal ion interactions are processes in equilibrium, it is normally found a lower slope in the rate of increase of the metal concentration in the filtrate (figure 2.9 c and d). In curve c, the case of the unique existence of an equilibrium situation is shown, while curve d shows the combination of the two effects, the existence of an equilibrium situation and an irreversible uptake of metal.

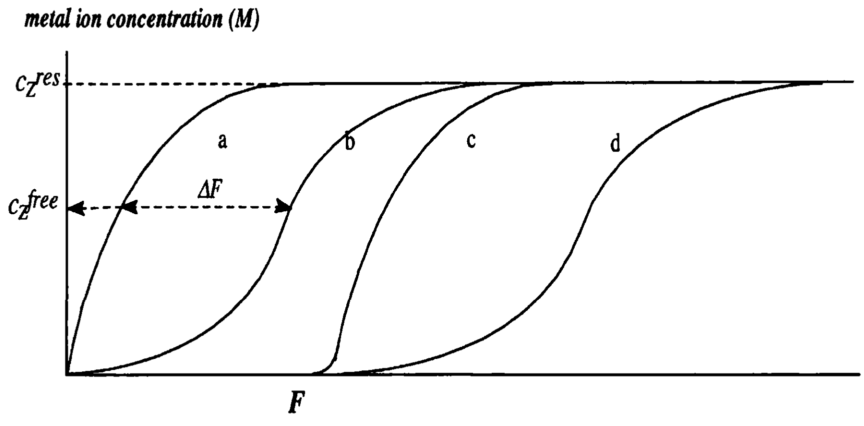


***Figure 2.9** Shape of the curves in enrichment ultrafiltration experiments. [(a) a blank experiment curve in the absence of polymer, (b) irreversible uptake of metal ions by the polymer, (c) the case of the unique existence of an equilibrium situation, (d) the existence of an equilibrium situation and an irreversible uptake of metal ions].*

The amounts of metal ions bound to the polymer and free in the solution can be calculated from these graphs. It is assumed that

$$C_Z^{filtrate} = K_Z^m \; C_Z^{free} \qquad \text{.................................... equation 2.1}$$

Where, $C_Z^{filtrate}$ is the metal ion concentration of the filtrate solution at a given instant, C_Z^{free} is the value of the molarity of metal ions not bound to the polymer chains and the subscript z always refers the valence of the metal ion. K_Z^m is the coefficient of membrane retardation which reflects the influence of the membrane on the retention of the metal ions. The constant can be experimentally calculated and it is normally found that it equals one for most metal ions. $C_Z^m = 1$, then C_Z^{free} is directly readable from experiments curves. If C_Z^{bound} is the concentration of metal ions bound to the polymer, its value is given by the formula:

$$C_Z^{bound} = \Delta F \; C_Z^{res} \qquad \text{.................................. equation 2.2}$$

Where C_Z^{res} is the metal ion concentration of the solution in the reservoir, and ΔF is given in figure 2.9 above.

In those cases, the dimensionless enrichment factor (E) is defined as [18]:

$$E = C[P]/c_Z^{res} = V_f^{sat}/V_o = F^{sat} \qquad \text{.................................} \; \textit{equation 2.3}$$

Where C is the maximum capacity; $[P]$, the polymer concentration in g/l, V_f^{sat} is the total volume of the filtrate when the saturation of the polymer is achieved; and V_o is the volume of the polymer solution in the cell. The filtration factor (F) is defined as the volume ratio of the filtrate (V_f) versus the volume in the cell (V_o). So, E can be defined as the filtration factor in conditions of saturation of the polymer.

2.5. Polymer-metal Ion Interaction Mechanism

Interactions of metal ions with water-soluble polymers are mainly due to electrostatic forces and the formation of coordinating bonds. Other weak interactions may appear as trapping metal ions in the bulk of the polymer phase [24, 92].

The type of polymer/metal-ion interaction depends on the chemical nature (ionization potential and electronic affinity) of the functional groups. The variables that affect the interaction are classified into two groups: Intrinsic to the polymer and extrinsic to the polymer. The former includes the polymer structure in terms of the composition and geometry, which affect the flexibility of the chains in solution, the branches of the chain, the chemical nature of the functional groups, their distribution at the polymer chain, and so forth. The second group includes the charge and type of the metal ion, the pH of the solution, the ionic strength, the temperature, and the dielectric constant of the medium [81, 92]. The chemical interaction between the polymer and the metal ion(s) can be ionic or covalent in nature. Ionic interactions do not typically exhibit high selectivity. However, chelating groups with multiple donor atoms arranged in specific geometries can bind metal ions very selectively. The presence of multiple donor atoms on the polymer leads to a very strong binding interaction between the polymer and the metal ions, and thus, very low concentration of "free" metal ions will be present in solution. Due to the high stability of the polymer-metal complex and the fast reaction times, extremely dilute solutions can be effectively treated. The polymers can be chemically modified to target different metal ions or to favor the binding of one metal over another [12, 39].

Polyelectrolytes may be distinguished from chelating polymers (polychelatogens). The former have charged groups, or easily ionizable groups in aqueous solution, while the latter bears functional groups with the ability to form coordination bonds [24]. Rivas *et al.* [80, 92] concluded that the interactions between polyelectrolytes and metal ions are very dependent on the ionic strength, and low interaction rate are found when the ionic strength is high. The interaction rates increase rapidly increasing the pH, and high retention values are found for divalent and trivalent metal ions at pH above 3. On the contrary, when interactions occur by formation of coordinating bonds, the nature of the metal ions and the effect of the pH may induce differences in the retention profiles of like charged metal ions and changes in metal selectivity. However, the nature of interaction of metal ions with both polyelectrolytes and chelating polymers does not affect appreciably the retention profiles of each metal ion considered individually, and some specific tendencies are found when comparing the retention profiles of mixtures of metal ions ultrafiltered under different conditions. At a molecular level, polyelectrolytes are assumed to bind counterions nonspecifically, while bonds of metal ions to chelating polymers are site-specific [79].

The most investigated ligands present in the polychelatogens are amines, carboxylic acids, amides, alcohols, aminoacids, pyridines, thioureas, iminos, etc. The most studied polyelectrolytes include those with carboxylic acid, phosphoric acid, sulfonic acid, or amino groups in their structure. Rivas *et al.* [24, 34, 81] reported that the polymer-metal ion interaction mechanism is strongly related to the dissociation degree of the polychelatogens. Thus, for Poly(etheleneimine) (PEI) and Poly(methacrylic acid) (PMA), at pH 5 most of the ligand groups are as free amine, and carboxylate respectively. Therefore, these groups form polymer-metal complexes, which are shown in (figure 2.10a) and (figure 2.10b). Poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (PAPSA) is deprotonated at lower pH than that of carboxylic acid and therefore showed a higher metal ion retention capability. For this polychelatogen, the polymer-metal ion interaction is only an electrostatic type (figure 2.10c).

In terms of Pearson's concept of hard and soft acids and bases, carboxylate and amine groups are soft bases, whereas sulfonate groups are relatively hard bases. As a general rule, hard acids coordinate better with hard bases, and soft acids coordinate better with soft bases [81].

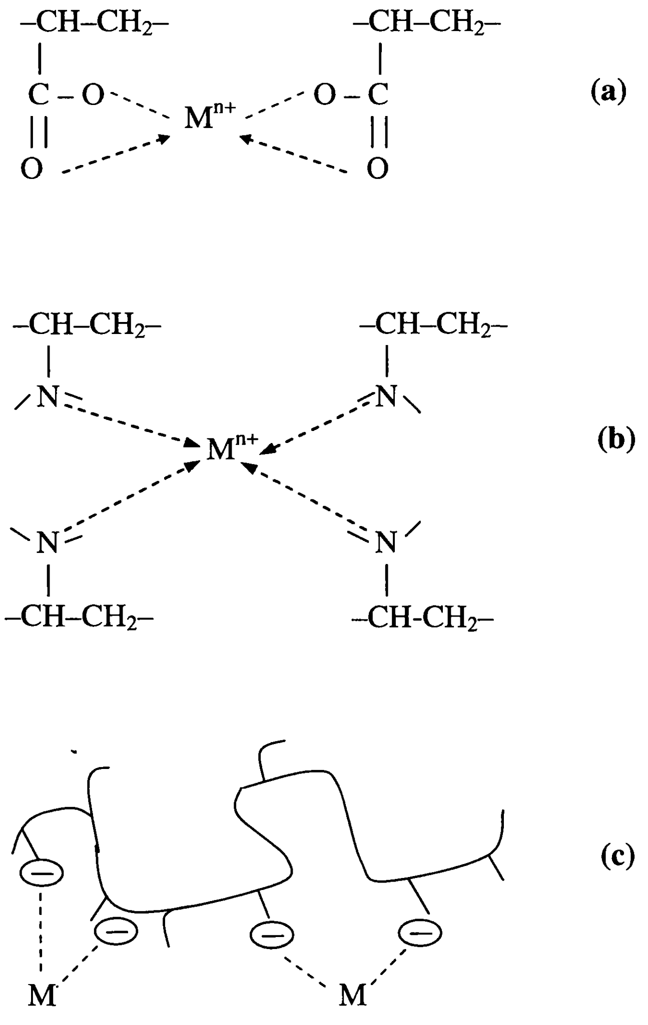


Figure 2.10 Possible polymer-metal ion interaction mechanisms, *a) carboxylate group (complex formation), b) amine type complex, and c) sulfonate group (electrostatic interaction)[24, 34, 81].*

2.6. Effect of operating parameters on the PEUF process

The performance of polymer enhanced ultrafiltration (PEUF) process in the removal of the considered metal ions is revealed by each of permeate flux and metal ions rejection. Permeate flux (*J*) is defined as the volume of permeate flowing through the membrane per unit time per unit membrane area, while the metal ion rejection (*R*) measures the membrane's capabilities. Evidently, a number of factors influenced the metal ion separation and process efficiency, including:

1). Solution pH
2). Loading ratio of metal/ polymer complex
3). ionic strength of solution
4). Effect of the temperature
5). Polymer concentration
6). Polymer regeneration

2.6.1 Effect of the pH

Indeed, the pH is one of the most important factors in the separation of metal ions using a PEUF process. As the pH increases, the affinity of the different ligand groups of polychelatogen to bind metal ions also increases [10, 24, 37, 43-45, 60, 81]. Thus, the removal of mercury and cadmium in the presence of PEI in binary mixtures solution [36] showed that decreasing the pH resulted in decreasing the retention of both metals. Also, the retention of cadmium is much more sensitive to the pH and the critical value for cadmium is much higher than that of mercury. This enables selective separation of two metals at selected pH, as it also observed in study [58] for the separation of lead from aqueous solution in the presence of calcium using polyacrylic acid (PAA) as chelating agent, resulting an optimum pH value at 4 where the retention of lead and calcium (97% and 15%, respectively). Water-soluble poly[(N-maleoylglycine)-co-(hydroxyethyl methacrylate)] [49] was employed for the separation of a series of metal ions in the aqueous phase at different pH. High retention of all metal ions was observed at pH 5 and pH 7 while lower retention occurred at pH 3 for all metal ions investigated. The same observation was noticed in study [71], high retention of mercury (R > 95) in aqueous solution with PEI was obtained for pH higher than 4, while for pH lower than 4 retention decreased as the pH of solution decreased and was nearly zero at pH 1. In this lower pH range the electro-donating imino groups of PEI become positively charged due to protonation, and are unable to form complexes with mercury ions. Poly(acrylic acid sodium salt) was used in study [85] as complexing agent, the separation process performed in the acid medium (pH 2 and pH 4) enabled a retention of only 20–40% of Zn(II) ions and 10–30% of Ni(II) ions, indicating competition of H^+ with divalent metal ions to condense on the polymer surface [92]. An increase in pH up to 8, very high retention of both metal ions was obtained. Similar observation reported by Molinari *et al.* [10] and Cañizares *et al.* [57] for the retention of Cu^{2+}, suggesting that carboxylic functional groups (COOH) of polymer at low pH would not be dissociated, when pH of solution grows, carboxylic groups of polymer start dissociating and presence of carboxylate anions (COO^-) is more important. Effect of the solution pH on permeate flux and retention of Cu^{2+} ions using chitosan [86, 87] showed that flux decreased and retention increased with an increase of pH value. However, it should be noted that many heavy metals form hydroxides complexes with very low solubility at high pH regions, and this is vary from metal to metal [50, 86, 90, 92, 93].

2.6.2 Effect of loading ratio

Loading ratio in PEUF can be described as ratio of the polymer concentration to the total concentrations of metal ions in the aqueous solution. In general, the higher binding capacity of metal ion by a polymer, the higher of the metal ion retention [68].

Yilmaz *et al.* [38] studied the effect of metal-polymer loading ratio on the retention of mercury using PEI in continuous mode of PEUF process. Constant retention value of 0.98 was observed until the mercury-to-PEI ratio of unity, after which retention decreased linearly. It was also found that retention of mercury was dependent on the mercury-to-PEI ratio rather than their concentrations. Also, the authors reported in study [36] a similar trend of retention as a function of loading ratio of mercury and cadmium in the presence of PEI in binary mixtures solution. In total recirculation mode, study [55] employed a constant polyacrylic acid concentration and increasing quantities of metals, Lead and cadmium, added to the reactor at pH 5 to investigate the permeate flux and loading ratio for both metals. It showed that variation in metal concentration in the reactor does not affect permeate flux in the essayed interval. Lead concentrations in permeate increase linearly with loading ratio, whereas cadmium concentrations increase exponentially. For a constant loading ratio, metal concentrations in permeate for cadmium are always higher than those for lead. Furthermore, decreases in polymer concentration lead to an increase in permeate flux, because solution viscosity and density are lower.

2.6.3 Effect of solution ionic strength

The ionic strength of aqueous solutions may greatly influence the effectiveness of the PEUF process. The ionic strength, ψ, is a characteristic of the solution and is defined as:

$$\psi = 0.5 \sum_i [M]\, Z_i^2 \qquad \text{.................................... } \textit{equation 2.4}$$

where $[M]$ is the molar concentration of the ith ion, Z_i is ion valence, and the summation extends over all the ions in the solution [94].

However, in studies with poly(ethyleneimine) as complexing polymer, loss of metal retention was observed when the salt concentration and thus the ionic strength was increased [64, 71, 90]. in study [47], a significant impact of the solution ionic strength was observed on the retention profiles for Ni(II) and Cu(II) in contact with poly(acrylic acid) (PAA) and poly(vinyl sulfonic acid) (PVS). Retention of both metal ions decrease when the concentration of $NaNO_3$ in the solution increase from 0.01 M to 0.1 M, and the great difference appears in the retention profiles of Cu(II) and Ni(II) by PAA. Suggesting that an increase in the salt concentration causes a compression of the electrical double layer and thus the electrostatic attraction between metal ions and charged polymers is reduced [87, 90, 95]. As a result, significant amount of unbound metal ions pass through the membrane pores leading to lower retention. Also, similar observations reported in study [65] when deep decreases of chromate retention was observed with the addition of NaCl using poly(diallyldimethylammonium chloride) (PDADMAC) as water-soluble polymer, indicating that higher concentration of salt displaces the complex formation equilibrium of PDADMAC-Chromate to its decomposition. However, it was observed in [9] that the retention of copper and nickel was not significantly influenced by the added sodium nitrate salt to the complex solutions of copper and nickel ions in the presence of the benzoylthiourea modified polyamidoamine dendrimer. On the other hand, Ionic strength of the feed solution influenced the flux through the membrane when aqueous solutions of PVA-Cu(II) macrocomplex with various concentrations of KCl are ultrafiltred [83], resulting a noticeable reduction of the flux with the increase of the concentration of KCl. It is on the contrary affected by an increase of the ionic strength of the medium which acts in favour of a reduction in the viscosity of the medium but also in favour of the increase of the phenomenon of formation of concentration polarization layer. Precipitation may also occur when the ionic strength of the solution is high as polymer solubility is reduced [68, 96]

2.6.4 Effect of the temperature

Temperature is an operational parameter which may affect both retention of metals and permeate flux in PEUF process. Yilmaz *et al.* [36] looked at the effect of temperature variation on the retention of mercury using PEI, and permeate flux also was investigated. The results showed that increasing the temperature results in a decrease in retention of mercury and increase in permeate flux. Expansion in membrane pore size and/or decrease in feed solution viscosity were suggested as the reasons for the linear increase in the permeate flux and why the retention of mercury decreases when the temperature increases.

2.6.5 Polymer concentration

The concentration of the water-soluble polymer in solution typically ranges from 0.001% w/v to 20% w/v of final concentrated solution. It is sufficient, and in some cases desirable, to have only enough polymer in solution such that the polymer's solute loading approaches 90-100%; use of higher concentrations of the water-soluble polymer results in lower flux rate through the UF membrane during the concentration stage. The use of a high initial polymer concentration can sometimes cause aggregation of the polymer and reduce binding capacity. In this case, operation at lower initial polymer concentration can allow more complete solute binding, and the polymer can be concentrated to higher final concentration with overall improved performance [4]. Therefore, the polymer concentration should be a compromise mainly between the extent of binding and the flux [68]. On the other hand, the molecular weight and concentration of water-soluble polymer must be high enough to assure an efficient separation of target metal ions and a complete rejection in accordance to membrane molecular weight cut-off (MWCO). If molecular weight and/or concentration of water-soluble polymer are too high, it will result in high viscosity of solution and high concentration polarization, which reduces permeate flux and increases process cost [23].

2.6.6 Polymer regeneration

The process of polymer enhanced ultrafiltration appears to be a more economical process if the polymer can be regenerated and reused, in particular when it is necessary to use an expensive polymer. In PEUF, a metal-polymer complex (retentate) coming from the ultrafiltration unit can be decomposed by two methods: protolysis and electrolysis.

In protolysis [30, 50, 57, 69, 72, 90], chemical decomplexation is obtained by lowering the pH of the retentate solution down to 2 (acidified) allowing unbound metal ions to pass through the ultrafiltration membrane while the polymer is retained. On the other hand, the electrolysis [50, 76] of the retentate results in a deposition of the metal ions on the cathode, whereas the polymer reagent remains in the solution. In comparison of two methods, electrochemical regeneration appears to be more energy-consuming than the chemical one [68]. It was reported in study [50] that the electrolysis regeneration of the used polymers from a retentate was not practicable, but was satisfactory by acidification. On the other hand, the loss of regenerated polymer was estimated at 2% in the treatment of large volumes of effluent containing Ni (II) at a low concentration using a polycarboxylate and an ultrafiltration membrane [72]. However, polymer losses in PEUF process is unacceptable from a number of process perspectives: (1) the polymer must remain in the system to maintain its working concentration, (2) polymer contamination in the permeate may create downstream contamination problems, (3) loss of solute-loaded polymer that would carry bound solutes into the permeate can result in failure to achieve target discharge limits, and (4) valuable soluble-polymer complexes would be lost from the system [4].

2.7. Modeling the PEUF process

In this section, proposed model descriptions of polymer enhanced ultrafiltration for metal ions retention in aqueous solutions from the available literature are reviewed.

Complexation in PEUF processes is largely based on equilibrium reactions. In this situation the complexation of metal ions is proportional to the ratio of the concentrations of free metal ions to the complexed metal ions. However, concentrations of complexed metal ions in PEUF change with the process time, due to the reduction of fluid volume or degree of filtration. The degree of filtration is given by the filtration factor (*F*):

$$F = V_p / V_0 \qquad \text{............ .... equation 2.5}$$

Where F is the filtration factor, V_p is the permeate volume and V_0 is the initial volume.

The formation of complexes under different conditions of reactions include the protonation of polymer, the metal polymer binding and the formation of metal hydroxide complexes can be described by the following equations:

$$H + L \leftrightarrow HL; \qquad K_p = \frac{[HL]}{[H][L]} \qquad \text{............... equation 2.6}$$

$$M + nL \leftrightarrow MLn; \qquad K_b = \frac{[MLn]}{[M][L]^n} \qquad \text{.............. equation 2.7}$$

$$M + mOH \leftrightarrow M(OH)_m; \qquad K_m = \frac{[M(OH)_m]}{[M][OH]^m} \qquad \text{................ equation 2.8}$$

Where n is the average coordination number of polymer ligands bound to one metal ion and m is the number of hydroxide ions in one soluble metal hydroxyl complex. [*HL*] is then non-dissociated polymer form, [*H*] the proton concentration, [*L*] the dissociated polymer form, [*M*] the free metal concentration, [*ML*] and [ML_n] are the complex concentration, K_a the polymer dissociation constant, K_p and K_m are the complex formation constant. Charges have been omitted since they are not significant for the modeling process [23, 55, 95-97].

Volchek *et al.* [96] suggested a model of metal retention in a multicomponent solution containing the ions of several metals using a polymeric complexing agent. The reaction occurring in the solution includes the formation of metal-polymeric complexes, hydrolysis of the metals and the protonation of the polymer. Thus, the value of R_i for each metal is influnced by the following factors:

- The stability constants of the polymer complexes of all metals present in the solution
- The ability of the i^{th} metal to be hydrolysed
- The pH of the solution
- The retention by the membrane of the polymer and hydroxide the i^{th} metal.

In the case that the insoluble hydroxide does not form, then

Stepwise complex formation:

$$R_i = \frac{\sum_{j=1}^{n}\prod_{j=1}^{n} K_{ij}[L]^j}{1+\sum_{i=1}^{m}\sum_{j=1}^{n}\prod_{j=1}^{n} K_{ij}[L]^j + \sum_{i=1}^{m}\sum_{k=1}^{p}\prod_{k=1}^{p} K_{ik}^{(h)}[OH]^k} R_L \qquad \text{...................equation 2.9}$$

Non-stepwise formation:

$$R_i = \frac{K_i[L]}{n_i\left(1+\sum_{i=1}^{m}\sum_{k=1}^{p}\prod_{k=1}^{p}K_{ik}^{(h)}[OH]_k+\sum_{i=1}^{m}K_i[L]\right)}R_L \qquad \text{.......................} \textit{equation 2.10}$$

Where $[L]$ can be calculated using equations (2.11) and (2.12) for stepwise and non-stepwise complex formation, respectively:

$$[L]_t = [L]+K_P[L][H]+\sum_{i=1}^{m}\frac{[M_i]_t\sum_{j=1}^{n}\prod_{j=1}^{n}K_{ij}[L]^j}{1+\sum_{k=1}^{p}\prod_{k=1}^{p}K_{ik}^{(h)}[OH]^k+\sum_{j=1}^{n}\prod_{j=1}^{m}K_{ij}[L]^j} \qquad \text{.........} \textit{equation 2.11}$$

$$[L]_t = [L]+K_P[L][H]+\sum_{i=1}^{m}\frac{n_iK_i[L][M_i]_t}{n_i\left(1+\sum_{k=1}^{p}\prod_{k=1}^{p}K_{ik}^{(h)}[OH]^k\right)+K_i[L]} \qquad \text{.............} \textit{equation 2.12}$$

If the insoluble hydroxide forms, then

Stepwise complex formation:

$$R_i = R_i^{(h)}-[M_i]^{(h)}\times\left\{\left(1+\sum_{k=1}^{p}\prod_{k=1}^{p}K_{ik}^{(h)}[OH]^k\right)\times R_i^{(h)}+\sum\prod K_{ij}[L]^j\left(R_i^{(h)}-R_L\right)\right\} \text{.............}$$

$$\text{..........................} \textit{equation 2.13}$$

Non-stepwise formation:

$$R_i = R_i^{(h)}-[M_i]^{(h)}\times\left\{\left(1+\sum_{k=1}^{p}\prod_{k=1}^{p}K_{ik}^{(h)}[OH]^k\right)\times R_i^{(h)}+\frac{K_i[L]}{n_i}\left(R_i^{(h)}-R_L\right)\right\} \text{......} \textit{equation 2.14}$$

$[L]$ can be calculated using equations (2.15) and (2.16) for stepwise and non-stepwise complex formation, respectively:

$$[L]_t = [L] + K_P[L][H] + \sum_{i=1}^{m}[M_i]\prod_{j=1}^{n}K_{ij}[L]^j$$

....*equation 2.15*

$$[L]_t = [L] + K_P[L][H] + \sum_{i=1}^{m}\frac{K_i[M_i][L]}{n_i}$$

....*equation 2.16*

Where:

K_{ij} : Stepwise complex formation constant of the i^{th} metal

K_i : Non-stepwise complex formation constant of the i^{th} metal

$K_{ik}^{(h)}$: Stability constant of the hydroxyl complexes of the i^{th} metal

K_P : Protonation constant for a polymer

$[M_i]_t$, $[L]_t$: Total concentrations of a metal and a polymer (mol/L)

$[M_i]$, $[L]$: Concentrations of free metal ions and a free polymer (mol/L)

$[M_iL_j]$: Concentration of a macromolecular complex of the i^{th} metal containing j groups per metal ion (mol/L)

$[M_i(OH)_k]$: Concentration of a hydroxy complex of the i^{th} metal containing k OH groups

R_i : Retention of the i^{th} metal by a membrane

R_L : Retention of a polymer by a membrane

$R_i^{(h)}$: Retention of a metal hydroxide by a membrane

$i = 1,\ldots m$: Number of a metal in a multicomponent solution

$j = 1,\ldots n$: Number of ligand groups coordinated with a metal ion in a macromolecular complex

$k = 1,\ldots p$: Number of OH groups coordinated with a metal ion in a soluble hydroxyl complex.

The following assumptions were considered in this model:

1) The complexing groups in a polymer are thermodynamically independent
2) Protonated forms of the polymeric agent are excluded from the metal-polymer complexation equilibrium

3) Passivated forms of a metal (hydroxyl complexes and any solid hydroxide phase if it is formed) are not capable of forming complexes
4) Thermodynamic constants of the polymer do not depend on the pH and the metal concentration
5) Retention of a macromolecular complex is the same as that of the polymer
6) Free metal ions and hydroxyl complexes do not interact with a membrane

Juang *et al.* [95] described the retention data in the pH range of 3.0-3.8 for the investigation of binding equilibria as follow:

$$Log\{((1-R_i)/R_i)(\beta-nR_i)^n\}=nLog(K_P/K_b[M]_0)-npH \qquad \text{................}\textit{equation 2.17}$$

Where β is the initial concentration ratio of polymer to metal ions and $[M]_0$ is the initial metal concentration. If the values of K_P and K_b do not depend on solution pH, the value of n can be determined from the slope of the straight line of left side of the equation as a function of pH, and should be corrected by a trial and error method.

If the values of equilibrium constant depend on solution pH, then equation 2.17 above become:

$$[M]_0(\beta-nR_i)((1-R_i)/R_i)^{1/n}=K_b^n+K_PK_b^n[H^+] \qquad \text{................ ....}\textit{equation 2.18}$$

Once the value of n is known, the values of K_P and K_b can be found from the plots of left side of equation 2.18 as a function of $[H^+]$. It should be noted that the effect of the formation of soluble metal hydroxyl complexes was ignored in this model.

The analytical expressions of the retention profiles of metal ions using water soluble polymer based on adsorption isotherms were deduced (Villoslada *et al.* [79]). Considering the expressions of Langmuir and Freundlich, the systems of poly(sodium 4-styrenesulfonate) (PSS)/Cd^{2+} and poly(allylamine) (PALA)/Ni^{2+} was evaluated and correlations were found between theory and experiments under the washing method at constant ionic strength. In this model, theoretical values derived from Freundlich isotherms showed a better adjustment of the retention values with the experimental data compared to Langmuir isotherms.

Based on Langmuir isotherms, the retention of metal ion as a function of filtration factor was calculated from the following expression:

$$Ln\,R_Z = \frac{-a\,Ln\left(b + c\exp(-jF) + 1\right)}{c(b+1)} + \frac{abF}{b+1} + K_1 \qquad \text{.................}\textit{equation 2.19}$$

Based on Freundlich isotherms,

$$Ln\,R_Z = \frac{a}{j(n-1)} Ln\left\{1 + m\exp\left[-j(n-1)F\right]\right\} + aF + K_2 \qquad \text{..................}\textit{equation 2.20}$$

Where:

$$K_1 = \frac{a\,Ln(b+c+1)}{c(b+1)}$$

$$K_2 = \frac{-a}{j(n-1)} Ln(1+m)$$

$$a = -k_Z^m \text{ , } b = \left(Q_Z^{\max} K_Z^L c^P\right)^{-1} \text{ , } c = C_Z^{init}\left(Q_Z^{\max} c^P\right)^{-1} \text{and } m = k\left(C_Z^{init}\right)^{n-1} c^P$$

R_Z : Retention of metal ions of valence Z

F : Filtration factor

k_Z^m : Coefficient of membrane retardation

K_Z^L : Apparent thermodynamic constant drived from Langmuir isotherm (mol^{-1}l)

k : The Freundlich equilibrium constant

C_Z^{init} : The initial metal ion concentration (mol l^{-1})

c^{P} : Polymer concentration (mol of monomeric unit l^{-1})

$Q_{Z}^{\max}$: Maximum amount of metal ions that may condense on the polymer surface per monomeric unit

The following assumptions were considered in the model to predict the experimental results:

1) Coefficient of membrane retardation (k_{Z}^{m}) is considered to be equal to 1 (there is no metal retention produced by the membrane)
2) The ultrafiltration system can be considered a steady state mixed flow reactor, so that the polymer and metal ions achieve an equilibrium situation in every instant during the filtration.
3) All metal ions are considered to be free in solution or bound to the polymer.
4) Polarization phenomena are neglected as the flow rate is slow.

Rivas *et al.* [4] developed a model to predict the retention values at high filtration factor of washing experiments performed under variable initial ionic strength. This model was applied to the results of two single experiments performed with poly(sodium 4-styrenesulfonte) (PSS) in the presence of Cd^{2+}, and poly(vinyl alcohol) (PVA) in the presence of Pb^{2+} with variable amounts of Na^{+} [98]. The retention of the different metal ions of valence z, by the polymer during filtration with pure water can be adjusted to the plot of a function of the type:

$$R_{Z} = u_{Z} + v_{Z} \exp(-k_{Z} F) \qquad \text{............................} \textit{equation 2.21}$$

Where:

R_{Z} : Retention value

F : Filtration factor

u_{z}, v_{z}, k_{z} : Retention parameters

For a mixture of a divalent metal ion species in the presence of an excess of a monovalent metal ion, two retention profiles of PEUF can be expressed:

$$R_1 = u_1 + v_1 \exp(-k_1 F) \qquad \text{.....equation 2.22}$$

$$R_2 = u_2 + v_2 \exp(-k_2 F) \qquad \text{.....equation 2.23}$$

The authors proposed the possibility of prediction of the experimental retention profiles from a single experiment in a wide range of initial ionic strength conditions, according to the following assumptions [98]:

- The values of the coefficients of membrane retardation are equal to one, which means that nor the divalent neither the monovalent metal ions interact with the membrane.
- The interactions of the monovalent metal ions with the polymer are negligible.

In this model, the retention value at high filtration factor for any experiment 'b' may be calculated from the retention parameters obtained in an experiment 'a', and the values of the initial ionic strengths using the following expressions:

$$\frac{k_2^a}{k_1^a} = \frac{k_2^b}{k_1^a} \qquad \text{.....equation 2.24}$$

$$\frac{u_2^b}{v_2^b} = \frac{u_2^a}{v_2^a}\left(\frac{C_1^{ia}}{C_1^{ib}}\right)^{k_2} \qquad \text{.....equation 2.25}$$

$$u_2^b = \frac{\left(u_2^a/v_2^a\right)\left(C_1^{ia}/C_1^{ib}\right)^{k_2}}{\left(1+\left(u_2^a/v_2^a\right)\left(C_1^{ia}/C_1^{ib}\right)^{k_2}\right)} \qquad \text{.....equation 2.26}$$

Where C_1^{ia} and C_1^{ib} are the initial metal ion concentration in experiments 'a' and 'b' respectively.

Geckeler *et al.* [99] proposed a mathematical model of metal retention profiles in aqueous solution by soluble polymer during membrane filtration process in both the washing and enrichment methods. The kinetics theory of chemical reactions that occur in partially open systems was applied.

The logarithm of metal retention as a function of filtration factor using washing methods can be investigated as a system of differential equations:

$$\partial R_1/\partial F = k_2^{'}T\,R_2 - k_1^{'}T\,R_1 - k_m^{'}\,R_1 \qquad \text{.............................} \textit{equation 2.27}$$

$$\partial R_2/\partial F = k_1^{'}T\,R_1 - k_2^{'}T\,R_2 \qquad \text{.............................} \textit{equation 2.28}$$

A differential form of the total retention can be obtained from equations (2.27) and (2.28)

$$\partial Ln\,R/\partial F = -k_m^{'}a \qquad \text{.............................} \textit{equation 2.29}$$

Where:

R_1 and R_2 are retention values for the metal (M) and metal polymer complex (ML)

$k_1^{'}$ and $k_2^{'}$ are the dissociation constants

$k_m^{'}$: is the coefficient of membrane retardation

F : is the filtration factor, expressed as filtrate volume to the volume of washing fluid

T : is the time necessary for a washing fluid volume to pass through the cell

a : represents the free metal fraction of the total metal concentration in the cell solution

However, the model proposed and the parameters obtained were used to calculate enrichment factor (*E*) for metal ions concentrated by using the differential form of the enrichment function:

$$\partial E/\partial F = 1 - k_m^{'}\,a\,E \qquad \text{.............................} \textit{equation 2.30}$$

where the enrichment factor (E) can be expressed as a ratio of metal concentrations in feed and in retentate.
As results, a good agreement was obtained between the experimental results and the values evaluated from the calculated functions in both methods of experiments.

On the other hand, Strathmann [100] reported a mathematical model for the selective removal of heavy metal ions from aqueous solution by diafiltration of macromolecular complexes. In this study, the chemistry of the metal polymer interaction was not considered and the model was applicable when the retention (R_i) is already known and fixed. However, In the case of complete binding of metal ions to the polymer, the enrichment factor can be determined as follows:

$$E = \frac{1 - \exp\left[-V_f / V_r\right](1 - R_i)}{1 - R_i} \qquad \text{......................equation 2.31}$$

Where V_f and V_r are the volumes of the feed solution and the retentate, respectively.

2.8 Aims of the project

As reviewed above, heavy metals are often found in very low but significant concentrations in industrial and municipal effluents are potentially both valuable and hazardous materials. Separation and recovery of metals from these streams are important objectives in reducing health and environmental risk or for an economical purpose. As a result, the effectiveness of polymer enhanced ultrafiltraion (PEUF) as selective process on metal ions retention and binding from various aqueous solutions was investigated. In this study, Copper (II), Zinc (II), Chromium (VI), Cobalt (II), Cadmium (II) and Nickel (II) have been selected due to their economic and environmental importance. Polyethylenimine (PEI) with molecular weight 750,000 (branched chain) has been selected as a suitable polychelatogen for further investigation. The modes of operation chosen to investigate the PEUF process were batch and continuous feed. These modes can be used to extract and purify metals from complex mixture at low concentrations.

The aims of this work are therefore:

- to investigate the retention and binding conditions of metal ions in dilute solutions by processes involving the membrane filtration of metal complexes,
- to study the more complex situations where competitions for metal binding site on PEI,
- to investigate the performance of the polymer enhanced ultrafiltration (PEUF) process under competitive conditions of metal ions-chelate to the PEI and,
- to determine the viability and ability of adsorption isotherms to analysis and model the PEUF process.

In order to achieve these aims, the following objectives were considered:

1. Devise a suitable experimental equipment to study in batch (i.e. stirred cell ultrafiltration unit) and in continuous (i.e. cross flow ultrafiltration rig) operation of PEUF process. These methods are described in Chapter 3.

2. Development and implementation of analytical systems for the measurement of ion mixtures at low concentrations. (namely they are Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)). These methods are described in Chapter 3.

3. For single metal solutions, batch mode PEUF experiments were performed in the presence and absence of polyethylenimine (PEI) at different pH's using stirred dead-end ultrafiltration cell. The retention and flux of aqueous solutions of heavy metals were investigated. Streaming potential measurements have also been performed at a variety of different pH values in order to characterise the membranes used. These data have then been used to analyse the PEUF performance. The retention profiles of mixed metal ions in the presence of PEI at pH 5.5 were determined and an investigation and comparison of the binding of single metal ions and mixtures of metal ions with PEI were also reported. The data are applied to the Langmuir and Freundlich isotherms. The effects of the competition between metal ions binding to the polymer and the retention of these metal ions in the PEUF process are also investigated. These results are described in Chapter 4.

4. Lack of data using industrial or model industrial mixtures (i.e. landfill leachate, mining waste streams). In real industrial waste streams, more than one metal ion exists and some complexing agents are released as effluents. Therefore, the influences of different chelators competitors on metal ions retention with PEI were investigated. This is done using mixture of metal solutions with PEI in the presence of various solutes and chelators in batch mode operation using a stirred dead-end ultrafiltration cell. The chelating competitors used in these investigations were: Ammonium sulfate, Ammonium chloride, Sodium acetate, Ethylenediaminetetra acetic acid (EDTA) and Nitrilotriacetic acid (NTA). Then, the binding characteristics of PEI with these systems were also investigated by applying Langmuir adsorption isotherm and the maximum binding of metal ions was determined under competitive conditions using this model. These results are described in Chapter 5.

5. The performance of PEUF process for metal ion filtration was investigated using a continuous feed of this process rather than batch mode. A variety of feed compositions were used, and metal ion retention and binding were determined. First, the retention of metals in the absence of polymer was investigated as the metals and their salt interact directly with the membrane. Secondly, the retention characteristics of single metal ions and mixed metal ions with PEI were studied. Then, the competition effects of the chelating competitors on metal ions retention to PEI in mixture solutions was investigated using a continuous feed process. Finally, the binding mechanisms of metal ions were explored and the ability of the Langmuir isotherm model to describe these systems using a continuous feed was determined. These results are described in Chapter 6.

6. The mathematical modeling for describing the continuous feed of a PEUF process was developed. Based on the principal of mass balance and Langmuir adsorption isotherm, the applicability of this model for three systems of complex solutions were determined. These results are described in Chapter 7.

From these aims and objectives a greater understanding and novel approaches to metal removal and recovery can be made using PEUF process.

Chapter 3

Experimental materials and methods

This chapter presents details of the materials, equipment and methods that were used in the experiments and discussed in this work.

3.1. Introduction

The aim of this present work was to investigate the retention and binding of metal ions in aqueous solution by using polymer enhanced ultrafiltration (PEUF) with a variety of feed processes. These ranged from solutions of single and mixtures of metal ion to more complex and competitive mixtures including organic compounds. Both batch mode and continuous ultrafiltration processes were investigated.

Suitable analytical equipment was employed to perform ultrafiltration experiments and to analyse them. Two ultrafiltration rigs were used: a stirred cell ultrafiltration unit and a cross flow ultrafiltration rig. An Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) was used for the measurement of metal ions concentrations in aqueous solutions. Streaming potential and the zeta potential have been performed to characterize the polysulphone ultrafiltration membrane used in this study. The essential features and operation of the ultrafiltration equipment used in this work are described in more detail.
Additionally, details of experimental methods employed during this work are presented and discussed in this section.

3.2. Materials

3.2.1 Metal solutions

Individual stock metal solutions of 1000 mg/l were prepared by the addition of metal salts (Fischer Scientific chemicals, laboratory grade) as shown in table (3.1) to a suitable volume of purified water. For this purpose, the following salts, reagent grade, were used: ($CuSO_4.5H_2O$; $ZnCl_2$; $K_2Cr_2O_7$; $NiCl_2.6H_2O$; $CoCl_2.6H_2O$; and $3CdSO_4.8H_2O$). The aqueous metal solutions used in all experiments were produced by the addition of the correct amount of stock metal solutions to high purity water obtained from Millipore Unit with conductivity lower than 1μS/cm.

Certified solutions of 1000 ppm Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+} in (1M HNO_3) supplied by Fisher chemicals were diluted as required to produce calibration standard curves.

Stock Metal Solutions	
Metal Salt	***Metal Salt Added (g)***
$CuSO_4. 5H_2O$	3.8
$ZnCl_2$	2.085
$NiCl_2. 6H_2O$	4.00
$K_2Cr_2O_7$	5.65
$CoCl_2. 6H_2O$	4.57
$3CdSO_4. 8H_2O$	2.28

***Table 3.1**: Metal salts, and quantities used to produce stock metal solutions used for all experiments.*

3.2.2 Polyethylenimine solutions

The polychelatogen polyethylenimine (PEI), was received as a 50% solution from Aldrich (Cat.: 18,197-8, lot.: 16118DD-235, CAS: 25987-06-8). This was a branched chain form of the polymer with an average molecular weight of 750,000; the polymer has primary, secondary and tertiary amine groups. Stock solutions of the polymer were produced, as required, by the addition of the correct amount of the PEI solution to purified water. Sufficient HCl (1M) and/or KOH (1M) were added to produce the required pH.

3.2.3 Preparation of other solutions used

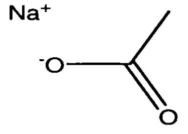
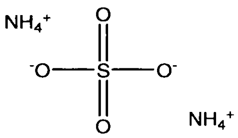
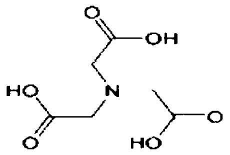
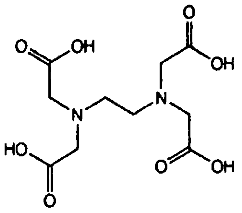
1M HCl stock solutions were produced by the addition of 110.49 ml (Fischer scientific laboratory reagent grade) of a 33% solution HCl made up to 1 L with pure water. Stock KOH solutions were produced by the addition of 56 g KOH from Fisher chemicals, made up to 1 L pure water. Buffer solutions of 10 mM were produced by the addition of 1.36g KH_2PO_4 from [Riedel-deHaen,] to 1L purified water. Ammonium sulfate solution

($(NH_4)_2SO_4$) of 100 mM, Ammonium chloride solution (NH_4Cl) of 100 mM from BDH chemicals and Sodium acetate solution ($C_2H_3O_2Na$) of 100 mM from SIGMA were produced by the addition of 13.2g, 5.399g and 8.203g respectively, made up to 1L of with purified water. EDTA (Ethylenediaminetetra acetic acid) solutions of 100 mM from [AnalaR] were produced by the addition of 37.224g made up to 1L with pure water. NTA (Nitrilotriacetic acid) solutions of 100 mM from [ACROS ORGANICS] were produced by the addition of 191.14g made up to 1L of purified water.

3.2.4 Chemical structures of complexing agents

The presence of complexing agents in industrial effluent streams is common and thus potentially impacts the complexation of heavy metals ions with polyethylenimine in polymer enhanced ultrafiltration system. For this purpose, chemicals in table 3.2 were chosen in this present work as potential complexing agents and the details of their chemical formula, structure, properties and other facts of reactions are shown in table 3.2.

Table 3.2 Chemical compounds used in this work as complexing agents

Chemical	***Structure***	***Properties***	***Reaction***
Sodium acetate ($C_2H_3O_2Na$)	 sodium acetate	White powder Density: 1.45 g/cm^3 Solubility: 76g/100ml	Produced by the reaction of acetic acid with Sodium bases
Ammonium sulfate ($(NH_4)_2SO_4$)	 ammonium sulfate	Density: 1.77 g/cm^3 White fine crystals, Solubility: 70.6g/100ml	Prepared by reacting ammonia with sulfuric acid
Nitrilotriacetic acid (NTA) ($C_6H_9NO_6$)		White crystalline powder, pH 1.7-2.7 easily biodegradable	EDTA and NTA are synthesized from ethylenediamine, formaldehyde, and a source of cyanide (HCN or NaCN)
Ethylenediaminetetra acetic acid (EDTA) $[CH_2.N(CH_2.COOH).CH_2.COONa]_2.2H2O$		Density: 0.86 g/cm^3 White powder, poor biodegrability	
Ammonium chloride (NH_4Cl)	$[NH_4^+] [Cl^-]$	White crystal salt Density: 1.53 g/cm^3 Solubility:29.7g/100ml	Prepared by reacting ammonia with hydrochloric acid
Polyethylenimine (PEI)	See Chp.2, Fig.2.3	See Chp.2, Sec.2.3,	---

3.3. Equipment

Two type of membrane equipment were used: (a) stirred cell & (b) cross flow membrane module, allowed different methods of determining the polymer binding kinetics.

- Stirred cell ultrafiltration was easy to use and allows small experiment to characterize the nature of PEI-metal interaction and set condition.

- Cross flow rig could be used on a large scale and with many practical configurations using commercial membrane modules.

3.3.1 Stirred cell ultrafiltration unit

The stirred cell ultrafiltration unit used for the work reported in this thesis was an Amicon ultrafiltration stirred cell Model 8050 (figure 3.1). This unit was used to perform batch mode ultrafiltration experiments. The measurements were carried out in the ultrafiltration stirred cell of 50 ml capacity which held a membrane disc of 44.5 mm in diameter and the effective membrane area is 13.4 cm^2, and the maximum operating pressure is 5 bar. The membrane holder and cell body are made of a polysulphone material and the O-rings are made from silicone rubber. Ultrafiltration stirred cell can be easily dismantled for ease of maintenance and cleaning. Once assembled, the cap is simply pushed on to the top of the main body of the filtration cell, under pressure the cap is then held in place by the retaining stand.

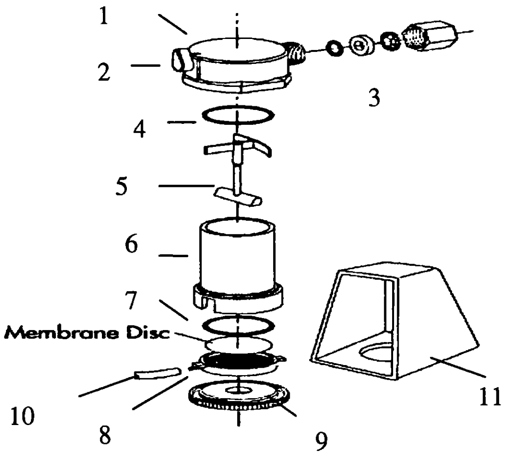


Figure 3.1 Schematic diagram of Amicon ultrafiltration stirred cell (Model 8050).
(1) cap, (2) pressure relief valve, (3) pressure tube fitting assembly, (4) top o-ring, provides seal to maintain pressure in the unit, (5) magnetic impeller, provides cross flow conditions, (6) main body of the stirred cell, (7) bottom o-ring, provides seal to maintain pressure in the unit and prevent loss of sample, (8) base with outlet permeate, (9) screw in bottom to secure base in the main body, (10) permeate tube line and (11) retaining stand, prevents displacement of cap when pressure is used in the unit.

3.3.2 Membranes used in batch ultrafiltration

The membranes used in all batch ultrafiltration experiments employing the stirred cell ultrafiltration unit were: Intersep-Nadir polysulphone with a molecular weight cut off (MWCO) of 30K Dalton and were supplied as a sheet form. The Nadir membranes are made from a blend of highly resistant polymers and exhibit high hydrophilicity (and thus have a low tendency towards adsorption). The membrane can be used up to a maximum temperature of 50°C and in a pH range from 1 to 10. Before the membranes were used in streaming potential or polymer enhanced ultrafiltration experiments, the pieces of new polysulphone membrane were cut to appropriate size and kept in distilled water (conductivity less than 1μS/cm) for 24 hrs to allow them to become fully hydrated.

KCl solution with 0.001 M concentration and pH ($10 > pH > 3$) was used as electrolyte to measure the streaming potential, and the solution pH was adjusted with dilute HCl or NaOH. Streaming potential measurements were carried out along the membrane surface tangential streaming potential (TSP) using EKA-Electrokinetic's Analyzer (Anton Paar, Graz, Austria). Membrane charge was measured and plotted as a function of pH, variation profile of the membrane charge provides useful information about the membrane surface properties.

3.3.3 Batch mode ultrafiltration setup

A batch mode ultrafiltration system set up is shown in Figure 3.2, the ultrafiltration stirred cell was pressurised with free nitrogen gas, which was controlled by the reducing valve at the gauge of the nitrogen cylinder. The applied pressure was determined by means of digital pressure gauge. All experiments were carried out at a constant pressure of 3 bar. A water jacket around the filtration cell body was connected to a recirculation thermostatically controlled water bath where the temperature was kept constant at 25°C. The total filtration time was coupled to the amount of permeate collected. The amount of permeate collected was determined by continuously weighting the filtrate on an electronic balance linked to a computer where the weight was recorded. Experiments were stopped after 25 ml of permeate was collected.

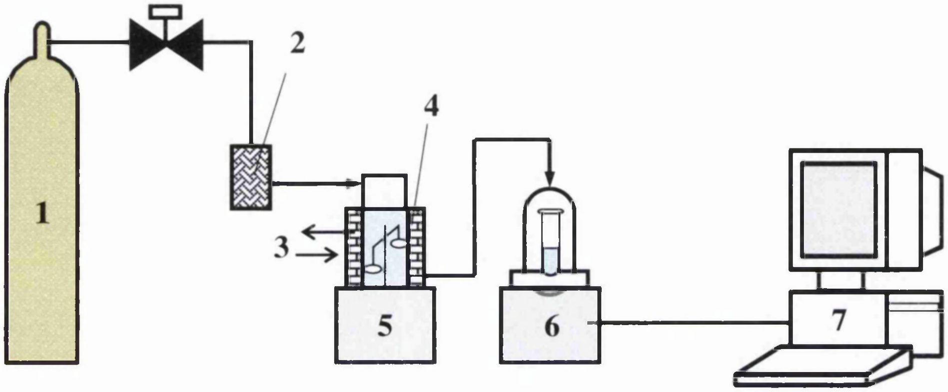


Fig. 3.2 Schematic diagram of batch mode ultrafiltration system.

(1) nitrogen flask, (2) pressure gauge, (3) water jacket, (4) ultrafiltration cell, (5) magnetic stirrer, (6) electronic balance, (7) personal computer

3.3.3.1 Batch mode ultrafiltration operation

In batch mode ultrafiltration, the ultrafiltration cell was filled with 50 ml solution using a 50 ml volumetric flask. The ultrafiltration cell was placed inside the retaining stand above a magnetic stirrer. The magnetic stirrer speed was ~ 300 rpm to simulate cross flow conditions within the ultrafiltration cell, and an overpressure of 3 bar with high purity nitrogen applied. The first 5 ml of permeate was discarded and the following 20 ml collected for analysis by using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), the ICP spectrometer (Spectro Ciros) used for metals analysis and detailed descriptions of the instrument and operating procedures can be found elsewhere [20]. During ultrafiltration processes, the PC automatically recorded the weight at time intervals from which the permeate flux was calculated. The ultrafiltration procedure was stopped when 50 % of the volume was filtered.

3.3.4 Cross flow ultrafiltration rig

Continuous mode or enrichment ultrafiltration experiments were conducted using a cross flow ultrafiltration rig (figures 3.3 and 3.4). This equipment was used to investigate ultrafiltration experiments in continuous mode which reflects the actual operation process of ultrafitration on an industrial scale. The system consists of a 9 L volume capacity reservoir, stainless steel piping with an inside diameter of 22 mm, feed and recirculated pumps (Stuart Turner Ltd, type 254, 2800 rev/min), pressure gauges, diaphragm valves, clamp fittings, membrane module and heat exchanger. All connection sections in the system were made by clamp fittings to provide easy changes in rig design for alternative operations. The hollow fiber cartridge membrane of 50 kDa molecular weight cut-off (MWCO) (Koch Romicon hollow fiber cartridge 1" HF 1.0-43-PM50, S/N: KM867825-7001) was used in continuous ultrafiltration experiments. The membrane was efficient within the pH range of 1.5 -10, maximum inlet pressure of 2.7 bar and maximum temperature of 60 °C. This polysulphone membrane has a slightly negative charge with a length of 457 mm, diameter of about 25.4 mm and an membrane area of 0.036 m^2. The transmembrane pressure was measured by means of pressure gauges located at the inlet and outlet of the membrane (P1 and P2). The heat exchanger was connected with main cold water supply and the temperature of process fluid in the reservoir was maintained manually by altering the cold water flow rate. Aqueous solution pH was measured using a Fischer scientific Hydrus 300 pH meter. The system was controlled at constant pressure and constant permeate flow rate. The flow rate of the permeate pump (Watson-Marlow Ltd., Model 501 U) was set up on the outlet permeate line to keep the permeate flow rate constant in continuous ultrafiltration experiments. The accuracy of the permeate pump reading during these experiments was also checked by continuously weighting the filtrate on an electronic balance (type Sartorious AG Gottingen, Germany CP4202S, Supplied by Jencons-Pls.), the time of collection was measured using a stopwatch and recorded. The volume of liquid in the reservoir was kept constant using an automatic level controller unit (made in the electrical engineering workshop), continuous feed solution of 5 l capacity vessel is passing via electro valve located in this unit and connected to a level sensor set up in the reservoir tank. The level control was based upon a 3 contact conductively circuit that could be set by altering the level of metal rod located in the reservoir.

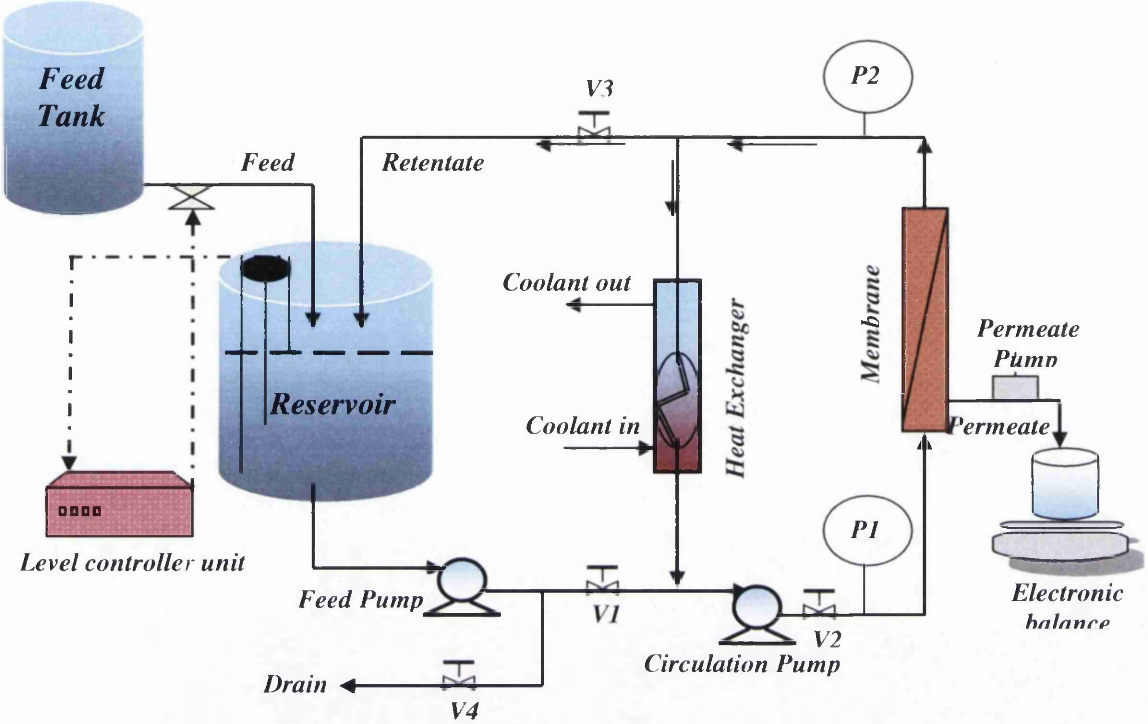


Figure 3.3 *Sechematic diagram of the cross flow ultrafiltration rig.*

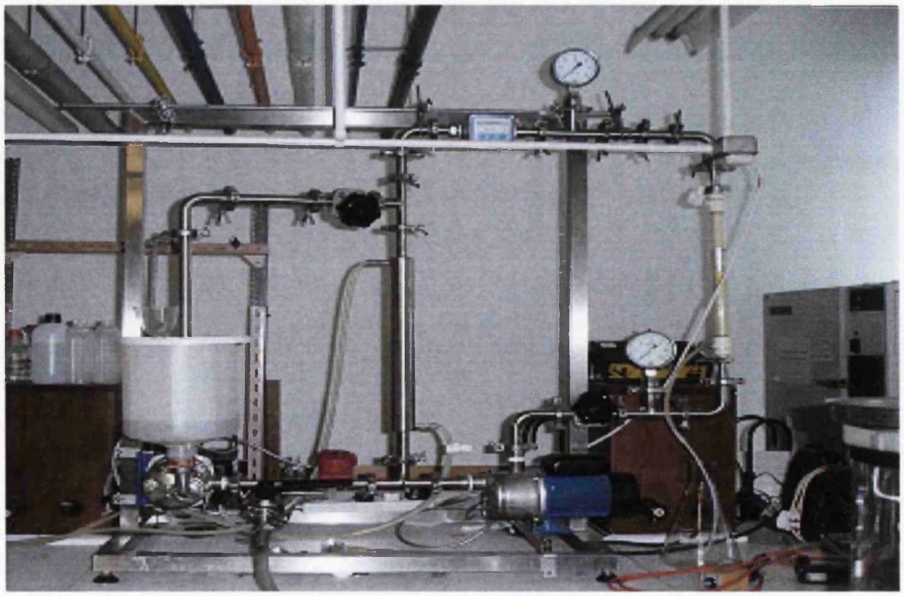


Figure 3.4 *Photograph of the cross flow ultrafiltration rig.*

3.3.4.1 Operation of the cross flow ultrafiltration rig

Prior to loading the process fluid and starting ultrafiltration experiments using the cross flow rig (figure 3.3), the diaphragm valves (V1, V2 and V4) were closed and diaphragm valve (V3) was fully opened. The desired solutions were loaded into the system, and Pump 1 was then started. Valve 1 was slowly opened until steady process flow was reached, thus allowing control of the rate of fluid drawn from the reservoir and to minimize pump cavitations during the experiment. Then, pump 2 was started and valve (V2) slowly opened to protect the membrane from possible damage of high pressure shock. Valve (V3) was then slowly closed until the required pressure within the system was achieved. The feed solution was supplied from the feed tank to the reservoir through the level controller unit, which directly controlled the level inside the reservoir tank. Constant permeate flow rate was achieved by means of the permeate pump, and constant temperature was regulated using cold water through the heat exchanger. The separation process occurred when the process solution was passed through the membrane; the permeate was collected for further analysis while the retentate solution returned back to the system. At the end of each experiment, the process fluid was drained from the system using valve (V4).

3.3.5 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

The Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) was used for the measurement of metal ions concentrations during the experimental work of this study. ICP-OES is a technique that can provide extremely rapid analysis of a number of chemical elements using Argon plasma flame. The analysis using this instrument occurred when each element emits energy at specific wavelengths. In this case, the Spectro Ciros ICP software was used for the selection of the suitable wavelength for each metal as follow: Cu^{2+} (324.754), Zn^{2+} (213.856), Ni^{2+} (221.648), Cr^{6+} (284.325), Co^{2+} (228.615), Cd^{2+} (214.438), Pb^{2+} (220.351) and Sn^{2+} (175.8). Further information of method development and operating procedures can be found in Spectro Ciros ICP-OES User manual.

Prior to sample analysis with the ICP-OES, a calibration is required for each metal. The calibration curves were produced using Certified solutions of 1000 ppm Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+}, Cd^{2+}, Pb^{2+}, and Sn^{2+} in (1M HNO_3) supplied by Fisher chemicals. Five samples at different concentrations (10, 5, 1, 0.1 and 0.01 ppm) were prepared for each metal solution by the addition of correct amount of 1000 ppm stock metal solutions to distilled water. Then, calibration curves using ICP-OES were achieved by measuring the amount of emission (response) at each metal concentration. (See Appendix 2)

3.4. Experimental Methods

3.4.1. Single metal retention and flux measurements in batch mode ultrafiltration

A study was undertaken to investigate the retention characteristics of different metals during ultrafiltration of aqueous solutions of individual metals, in the absence and presence of the polyethylenimine at different pH.

Using the 50 ml membrane stirred cell (Figure 3.1), experiments were carried out and the flux and metal content were determined. Retention of metals by the membrane can be observed in the absence of polymer where the metals and its salts interact directly with the membrane. In the presence of polymer when solutions of single metal ions are contacted with polymer solution, complexes of metal ions with polymer are thus prevented from passing through the membrane. Retention profiles of the different metal ions by the polychelatogen (PEI) during the ultrfiltration processes can be used as an indication of the degree of metal-polymer complexation.

Individual aqueous solutions of six metals (Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+}, and Cd^{2+}) were produced over range of pH 2 to pH 6.5. Solutions were prepared by the addition of 10 mg/l stock metal solution to 1 g/l polyethylenimine (PEI) in 10 mM buffer solution (KH_2PO_4) using a 50 ml volumetric flask. Solution pH was adjusted as required using 1 M HCl or 1 M KOH. Aqueous solutions containing individual metals, in the absence of polyethylenimine were produced in a similar way; with the exception that PEI was not added to these.

50 ml of individual metal solution with or without PEI was subjected to batch mode ultrafiltration using batch mode ultrafiltration apparatus as described in section (3.3.1). In the experiments, metal ion concentrations of both feed and permeate were analyzed by means of ICP (section 3.3.5) and the results of the selected metal ions allowed calculation of the retention value of each metal (R_i) by using the following expression:

$$R_i = \left(1 - \frac{C_{pi}}{C_{fi}}\right) \times 100 \text{ .... } \textit{equation 3.1}$$

Where C_{pi} is the concentration of metal *i* in the permeate and C_{fi} is the concentration of metal ion *i* in the feed.

In addition to the above experiments where the average of permeates fluxes were calculated for individual metal solutions at different pH, typically measurement was made triplicate with ±5% error after this method of measurement. Two types of solutions were prepared as standards, one consisting of buffer solution of 10 mM KH_2PO_4 and the other containing buffer plus the PEI (1 g/l) over range of pH 2 – pH 6.5. The permeate data was recorded during batch mode ultrafiltration process (as described above) and permeate flux through the membrane was calculated as follows:

$$Flux = \left(\frac{Volume\ of\ permeate\ (m^3)}{Membrane\ area\ (m^2) \times Time\ (hr)}\right) \text{ .... } \textit{equation 3.2}$$

3.4.2. Binding studies and analysis of single/ mixture metals in batch mode UF

Individual aqueous solutions of single metal (Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+}, and Cd^{2+}) were produced by the addition of various concentrations (from 2 to 60 mg/l) of the required

1000 mg/l stock metal solution to 1 g/l PEI in buffer solution KH_2PO_4 (10 mM) at pH 5.5 with total volume of 50 ml. pH was adjusted as required using 1M HCl or 1M KOH. The batch mode ultrafiltration apparatus (described above) was used for all experiments. Samples from permeate and retentate were measured via ICP, binding and retention studies at pH5.5 were investigated according to Langmuir and Freundlich isotherm theories. Also the investigation for binding studies of mixture metals in batch mode PEUF were produced in a similar way as described for single metal solutions, with the exception that all six metals (equal concentration) were put in each solution. Under competitive conditions, the amount of metal bound to the PEI, retention values, and binding isotherms according to Langmuir and Freundlich isotherms were investigated.

The use of Langmuir and Freundlich isotherms to describe the complexation process of binding metal to the polymer was investigated using the following equations:
The form of Langmuir isotherm equation is given by:

$$Q = \frac{Q_{\max}\, Y_i}{K_L + Y_i} \quad \text{.................} \quad \textit{equation 3.3}$$

Where: Q : is the amount of metal bound (mg metal/g polymer).
Q_{max} : is the maximum capacity of polymer (mg metal/g polymer).
Y_i : is the metal free in solution (mg/l).
K_L : is the Langmuir equilibrium constant (mg/l).

Taking reciprocals of both sides of the Langmuir equation gives a linear form:

$$\frac{1}{Q} = \frac{K_L}{Q_{\max}} \frac{1}{Y_i} + \frac{1}{Q_{\max}} \quad \text{.........} \quad \textit{equation 3.4}$$

If plots of $1/Q$ versus $1/Y_i$ give a straight line then the values of $Q_{\max}$ and K_L can be calculated from the intercept and slope of the plots, respectively.

The Freundlich isotherm equation is given by:

$$Q = K_F \, Y_i^n \quad \text{....................}\textit{equation 3.5}$$

Where: Q : is the amount of metal bound (mg metal/g polymer).

K_F : is the Freundlich equilibrium constant ($\mathrm{mg^{1-n}\,g^{-1}l^{n}}$).

Y_i : is the metal free in solution (mg/l).

n : is a constant.

Taking logs of both sides of the Freundlich equation gives a linear form:

$$L_n\, Q = n\, L_n\, Y_i + L_n\, K_F \quad \text{...........}\ \textit{equation 3.6}$$

According to this equation if the plot of $L_n\, Q$ versus $L_n\, Y_i$ gives a straight line then K_F and n values can be calculated from the intercept and slope of this straight line, respectively.

3.4.3. Competition studies in batch mode ultrafiltration

This section presents details of batch mode polymer (PEI) enhanced ultrafiltration experiments in the presence of various solutes and other chelators using the stirred cell ultrafiltration equipments described in (sections 3.3.1 and 3.3.3). The solutes and chelators used were: Ammonium sulfate (AS), Ammonium chloride (AC), Sodium acetate (SA), Nitrilotriacetic acid (NTA) and Ethylenediaminetetra acetic acid (EDTA). The effect of these compounds on metal ions retention and binding during polymer enhanced ultrafiltration experiments was investigated.

3.4.3.1 Competition study with Ethylenediaminetetra acetic acid (EDTA)

Aqueous solutions containing mixtures of six metals (Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+}) were prepared in a range of metals concentrations while maintaining a constant polymer concentration. Solutions of mixted metal ions were placed in 50 ml capacity flasks with various concentrations (from 2 to 60 ppm) of the required 1000 ppm stock metal solutions. The 10 mM phosphate buffer solutions containing 1g/1 PEI were prepared and used in all experimental solutions at different metal feed concentrations. Then, 1 ml of (10 mM and 100 mM) EDTA stock solutions was added to the 50 ml of prepared solutions to give required concentrations of EDTA at 0.2 and 2 mM, respectively. Using the two concentrations of EDTA, six solution containing mixtures of metals over the range 2 - 60 ppm of each metal were prepared at pH5.5. Aqueous solutions containing six metals, in the absence of PEI were produced in a similar way, and 2 mM of EDTA concentration was used in these experiments. Also, aqueous solutions containing two metals (Cu^{2+}, Zn^{2+}) in the absence of PEI were produced in a similar way, and the concentration of EDTA in these solutions was set at 2 mM. Each solution was prepared using a 50 ml flask and the solution pH in these experiments was adjusted to pH 5.5. Approximately 50 ml of each solution was applied to the ultrafiltration stirred cell unit and using batch mode ultrafiltration system (section 3.3.3). 15 ml samples of the relevant metal from permeate and retentate were collected and measured via ICP (Section 3.3.5). The effect of EDTA on the rejection and binding of metal ions to PEI was observed experimentally using batch mode ultrafiltration. Also, the rejection of metals-EDTA chelate in the 2 component and 6 components of mixed metal solutions were investigated in the absence of polymer. Using the data obtained from these experiments, Langmuir and Freundlich isotherms models (equations 3.3 and 3.5) were investigated to describe the maximum binding of different metal ions during PEUF using PEI under competitive condition with EDTA.

3.4.3.2 Competition study with Sodium acetate

Aqueous solutions containing mixtures of six metals (Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+}) were prepared in a range of metals concentrations while maintaining a constant polymer concentration. The 10 mM phosphate buffer solutions containing 1g/l PEI were prepared and placed in 50 ml capacity flask, then the various concentrations of metal (from 2 to 60 ppm) were added. 1 ml of (10 mM and 100 mM) sodium acetate stock solutions was added to the 50 ml of these prepared solutions to give required concentrations at 0.2 and 2 mM, respectively. Using the two concentrations of sodium acetate, six solution containing mixtures of metals over the range 2 - 60 ppm of each metal were prepared at pH5.5. Approximately 50 ml of each solution was applied to the ultrafiltration stirred cell unit using batch mode ultrafiltration apparatus (sections 3.3.1 and 3.3.3). 15 ml samples of the relevant metal from permeate and retentate were collected and measured via ICP (Section 3.3.5). The effect of adding Sodium acetate on the rejection and binding of metal ions to the PEI was observed experimentally using batch mode ultrafiltration. Langmuir and Freundlich isotherms models (equations 3.3 and 3.5) were investigated to describe the maximum binding of metal ions during polymer enhanced ultrafiltration using PEI under competitive condition.

3.4.3.3 Competition study with Ammonium sulfate

Ammonium sulfate was investigated as a competitor to PEI chelation of metals. The experimental method was as described in section 3.4.3.2., except the appropriate concentrations of ammonium sulfate were used instead of sodium acetate.

3.4.3.4 Competition study with Ammonium Chloride

Ammonium chloride was investigated as a competitor to PEI chelation of metals. The experimental method was as described in section 3.4.3.2., except the appropriate concentrations of ammonium chloride were used instead of sodium acetate.

3.4.3.5 Competition study with NTA (Nitrilotriacetic acid)

NTA was investigated as a competitor to PEI chelation of metals. The experimental method was as described in section 3.4.3.2., except the appropriate concentrations of NTA were used instead of sodium acetate.

3.5. Continuous feed experiments using the cross flow ultrafiltration rig

In addition to the experiments of batch mode PEUF using ultrafiltration stirred cell (as mentioned above), cross flow ultrafiltration rig described in section 3.3.4 was used in continuous feed experiments to investigate the following aspects:

- Membrane performance and its retention to metal ions in aqueous solutions,
- Single metal ions retention and binding in the presence of PEI,
- Retention characteristics and binding of mixture of metal ions in the presence of PEI,
- Mixed metal ion retention and binding with PEI in the presence of various chelating agents.

3.5.1 Membrane performance in cross flow ultrafiltration process

3.5.1.1 Membrane flux measurements

The performance of the ultrafiltration membrane in the removal of metal ions from aqueous solutions was measured by permeate flux and metal ion rejection was determined. The hollow fiber cartridge membrane of 50 kDa molecular weight cut-off (MWCO) was used in all enrichment ultrafiltration experiments using cross flow ultrafiltration rig. The membrane operates within the pH range of 1.5 -10, maximum inlet pressure of 2.7 bar and maximum temperature of 60°C. The polysulphone membrane has a slight negative charge. The module length of 457 mm, diameter of about 25.4 mm and an membrane area of 0.036 m^2 in the form of 1 mm hollow fiber. Before experiments were conducted, the new membrane was filled with deionized water and allowed to equilibrate overnight. Then, membrane permeability was measured for pure distilled water at different pressures using the cross flow ultrafiltration rig (section 3.3.4). Moreover, the membrane fluxes were measured in the presence of various PEI concentrations (1g/l, 2g/l, 4g/l and 6g/l) at pH 5.5. Indeed, using (equation 3.2) allowed calculation of the membrane flux and the results are shown in (figure 3.5). It was observed that the membrane flux of pure water was higher than those of PEI solutions and the flux decreased with increasing PEI concentrations in the solution. The reduction of membrane flux was due to the increase of solution viscosity with increasing polymer concentration.

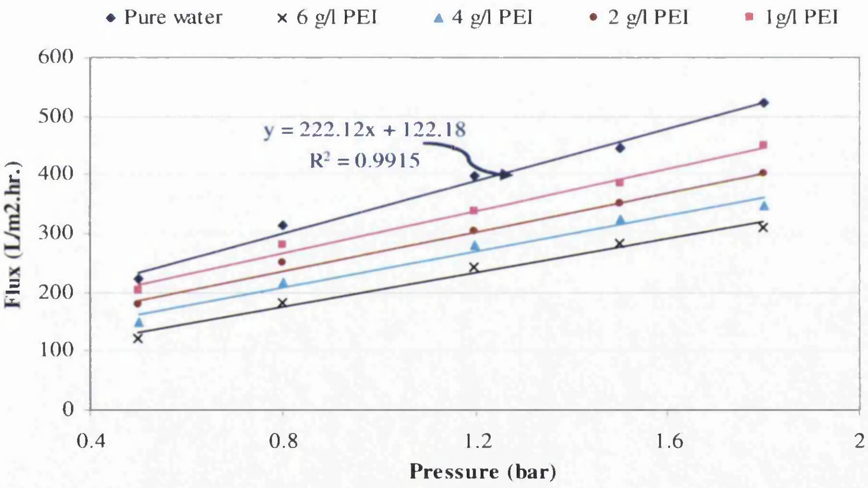


Figure 3.5 *Experimental flux of pure water as a function of pressure at various feed concentrations of PEI using cross flow ultrafiltration rig. [pH 5.5 and temp. 25°C]*

However, when pure water is filtered, the permeate flux follows the equation 1.1. When polymer solution is filtered, the permeate flux follows the equation 1.2 (see chpt.1).

Membrane resistance (*Rm*) determination can only be done for pure water as polymer will significantly alter the viscosity, so value for *Rs* and solution viscosity could be differentiated with the measurements made here (static head also potential problem). Positive *Rm* due to static pressure of fluid in the membrane ~ 0.5 m (see fgure 3.3 & 3.4).

3.5.1.2 Membrane rejection

To examine the ability of the membrane to reject various metal ions using the cross flow ultrafiltration rig (section 3.3.4), aqueous solutions containing mixtures of six metals (Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+}) was prepared as feed solutions. The required amount of each metal was added to 16 l distilled water to give required individual metal concentrations of 14 mg/l. The reservoir tank was filled with 5 l distilled water. The pH was adjusted for both solutions at pH 5.5. The experimental start up procedures was described in detail in section (3.3.4.1). Constant permeate flow rate (5 l/hr) and constant operating temperature at about 25 °C was applied during this experiment. Permeate samples (20 ml) were collected in regular intervals of time and the metal ions concentrations in each sample were measured via ICP. Then, the ability of membrane to reject different metal ions was determined and the results are shown in figure 3.6.

Plotting the metals concentrations in the permeate as function of process time showed that the metal ions concentrations in the permeate were increased with increasing the time of process feeding. Thus, the maximum rejection was noticed for Copper and Chromium ions among other metals in the solution. In contrast, little rejection by membrane was observed for Cadmium, Zinc, Nickel and Cobalt in the mixture of metal solution.

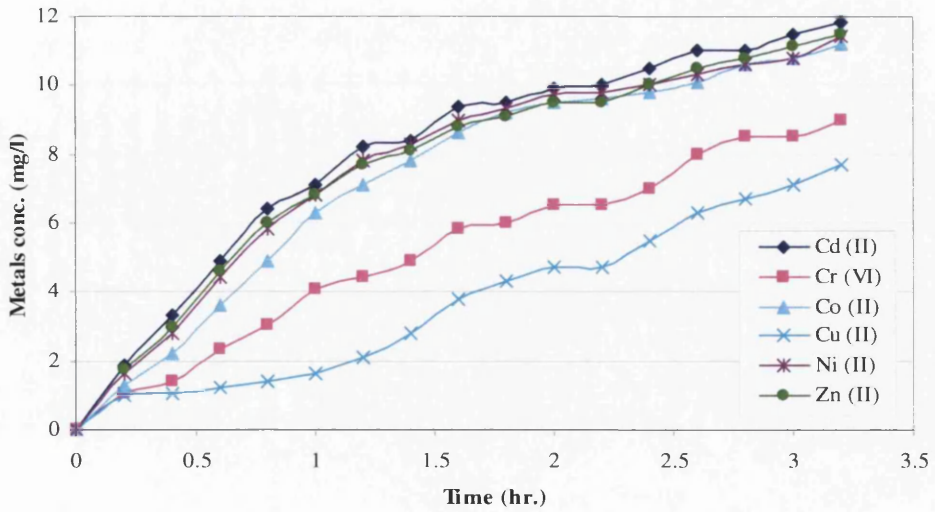


Figure 3.6 *Metal ions concentration in the permeate as function of filtration factor for PM50 ultrafiltration membrane using cross flow UF rig.*

3.5.1.3 Cleaning the membrane

In ultrafiltration processes, inorganic fouling can exist due to concentration polarization of metal precipitates on the membrane surface or due to interactions between metal ions and the polymer via chemical bonds. Permeate flux decline and, eventually, retention decrease results from accumulation of these fouling materials. In cross flow ultrafiltration experiments, the membrane was cleaned after each experiment to insure the same experimental performance and conditions. The cleaning procedures were started by pumping 3 l of distilled water through the membrane without pressure to rinse out the residual metals and polymer for 10 minutes before drainage. Then, 5 l solution of 0.05 M citric acid (10.5 g/l) was used to clean the membrane and the solution was circulated in the system for 20 minutes at low pressure (0.5 bar). The system was then drained and filled with 5 l solution of 0.1 M NaOH (4 g/l), which was circulated through the membrane for about 20 minutes. At last, 3 l of the distilled water was recycled at 0.5 bar for 10 minutes.

The effect of using the above cleaning procedures on membrane flux was measured and the results are shown in (figure 3.7). Pure distilled water was used after each cleaning and the flux was measured as function of pressure.

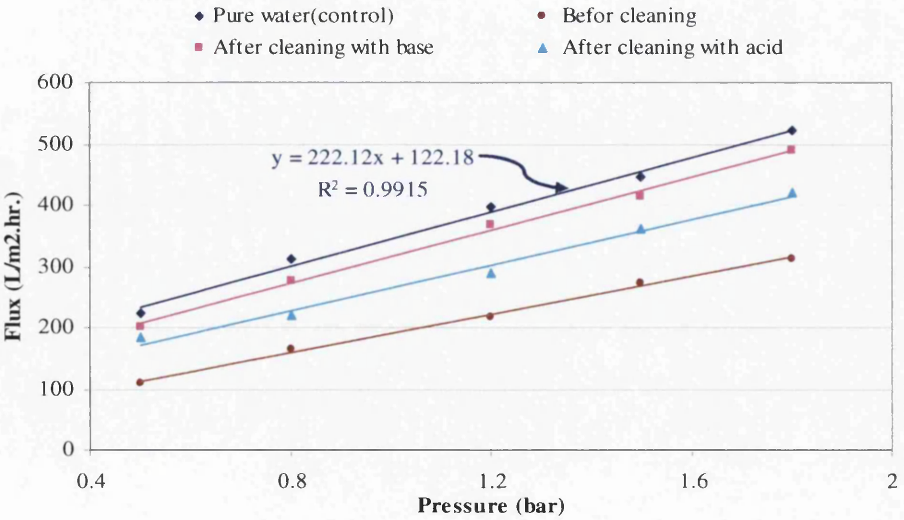


***Figure 3.7** Flux measurements as a function of pressure at different membrane cleaning stages.*

3.5.2 Filtration experiments of single metal ions in the presence of PEI

The retention and binding affinity of single metal ions to PEI were investigated. Individual aqueous solutions of single metal ion (Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+}) were prepared. Each solution was produced in 25 l distilled water, and the required amount of 1000 mg/l stock metal solution was added to give the required metal concentrations (70 mg/l). Then, the solution of single metal was placed in the feed tank and the pH adjusted to 5.5 using 1M HCl or 1M KOH. Required amount of PEI was added to 5 l distilled water to give 1 g/l PEI concentration. To ensure complete mixing of PEI, the solution was stirred for about 15 minutes. The solution was then put in the reservoir tank and the pH adjusted to 5.5. Experiments were conducted using continuous mode ultrafiltration apparatus as described in (section 3.3.4.1). The operation procedures were started by feeding the individual metal solutions from the feed tank to the reservoir using a peristaltic pump. Then, the complxing metal polymer solution was pumped up through the membrane and was separated there. The polymer with bound metal ions was rejected by the membrane and recycled back to the system, while the non-bound metal ions permeated through the membrane. The system was controlled at constant permeate flow rate (5 l/hr) and constant operating temperature at 25 °C. Therefore, the volume of complex solution in the reservoir remained constant by a continuous feed of metal solution controlled by the level controller unit.

Experiments were run for 5 hr. and samples (20 ml) were collected from every 1 L of the permeate. The affinity of PEI to bind metal ions was determined by measuring the metal ions concentrations in the permeate at different content of feed solutions using ICP. The retention of single metal due to the complexation to PEI was determined using (equation 3.1), Then, Langmuir and Freundlich isotherms models (equations 3.3 and 3.5) were investigated to best describe the binding of different metal ions during polymer enhanced ultrafiltration using PEI.

3.5.3 Filtration experiments of mixture metals in the presence of PEI

To investigate the metal ions retention and binding in competitive conditions with PEI, aqueous solutions of mixture six metal ions (Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+}) were prepared. Solution was produced in 25 l distilled water, and the required amounts of 1000 mg/l stock metal solutions were added to give the required metal concentrations (14 mg/l). Then, the solution was placed in feed tank and the pH adjusted to 5.5 using 1M HCl or 1M KOH. Required amount of PEI was added to 5 l distilled water to give 1 g/l PEI concentration. To ensure complete mixing of PEI, the solution was stirred for about 15 minutes. The solution was then put in the reservoir tank and the pH adjusted at pH 5.5. Continuous mode ultrafiltration apparatus was applied as described in section 3.3.4.1. The operation procedures were started by feeding the metal solution from the feed tank to the reservoir using a peristaltic pump. Then, the complexing metal polymer solution was pumped up through the membrane system and separated there. The polymer with bound metal ions were rejected by the membrane and recycled back to the system, while the non-bound metal ions permeated through the membrane. The system was controlled at constant permeate flow rate (5 l/hr) at an operating temperature at 25 °C and a constant volume by level controller unit.

Samples (20 ml) from the permeate line were collected at regular intervals (every 12 minutes) during ultrafiltration experiments and the metal concentrations were measured using ICP. The performance of the polymer enhanced ultrafiltration process at competitive condition of metal ions was investigated, and the maximum binding of metal ions determined using Langmuir and Freundlich isotherms models (Equations 3.3 and 3.5). Also, the retention value of each metal was calculated using (equation 3.1).

3.5.4 Competitive binding of metals-chelates to the PEI using continuous feeding system

This section describes the methods followed during the enrichment experiments of adding various chelators to aqueous solutions of complex metal/ polymer. The retention and binding of metal ions using PEI were investigated in the presence of: Ammonium sulfate (AS), Ammonium chloride (AC), Sodium acetate (SA), Nitrilotriacetic acid (NTA) and Ethylenediaminetetra acetic acid (EDTA). The cross flow ultrafiltration rig apparatus fitted with the PM50 membrane (section 3.3.4) was used for each of the competitive studies described in the following sub-sections.

3.5.4.1 Competitive effects of Ammonium sulfate

In competitive condition of metal-chelate to the polymer, the effect of adding ammonium sulfate to the complex of metals/ PEI was investigated. Mixture of six metal ions (Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+}) was prepared in 25 l distilled water using the required amounts of 1000 mg/l stock metal solutions, to give the required metal concentrations (14 mg/l). The amount of 6.6 g ammonium sulfate was added to solution to give the required concentration of ammonium sulfate at 2 mM. Then, the mixted solution was placed in feed tank and the pH adjusted to 5.5 using 1M HCl or 1M KOH. Another solution was prepared containing 1 g/l PEI concentration, and then the amount of 1.32 g of ammonium sulfate was added to give the required concentration at 2 mM. To ensure complete mixing of PEI, the solution was stirred for about 15 minutes. The solution was then put in the reservoir tank and the pH adjusted at pH 5.5. Continuous mode ultrafiltration apparatus was applied as described in section 3.3.4.1. The operation procedures were started by feeding the mixture metal-chelate solution from the feed tank to the reservoir using a peristaltic pump. Then, the complxing solution was pumped up through the membrane system. The polymer with bound metal ions was rejected by the membrane and recycled back to the system, while the non-bound metal ions permeated through the membrane. The system was controlled at constant permeate flow rate (5 l/hr) and constant operating temperature at 25 °C. Therefore, the volume of complex solution in the reservoir remained constant by continuous feeding of metal solution and controlled by level controller unit.

20 ml samples from permeate line were collected in regular intervals time during ultrafiltration experiments and the metal concentrations were measured using ICP. The

performance of the polymer enhanced ultrafiltration process for metal ions retention at competitive condition of metal ions-chelate to the PEI was investigated experimentally, and the maximum binding of each metal ion was determined using Langmuir isotherms model (equations 3.3 and 3.5).

3.5.4.2 Competitive effects of Ammonium chloride

Ammonium chloride was investigated as a competitor to PEI chelation of metals using a continuous feeding system. The experimental method was as described in section 3.5.4.1, except that 2 mM ammonium chloride was added instead of ammonium sulfate. (The amount of 2.675 g and 0.535 g of ammonium chloride were added to metals and polymer solutions, respectively).

3.5.4.3 Competitive effects of Sodium acetate

Sodium acetate was investigated as a competitor to PEI chelation of metals using a continuous feeding system. The experimental method was as described in section 3.5.4.1, except that 2 mM sodium acetate was added instead of ammonium sulfate. (The amount of 4.1 g and 0.82 g of sodium acetate were added to metals and polymer solutions, respectively).

3.5.4.4 Competitive effects of Nitrilotriacetic acid (NTA)

NTA was investigated as a competitor to PEI chelation of metals using a continuous feeding system. The experimental method was as described in section 3.5.4.1, except that 2 mM NTA was added instead of ammonium sulfate. (The amount of 9.56 g and 1.91 g of NTA were added to metals and polymer solutions, respectively).

3.5.4.5 Competitive effects of Ethylenediaminetetra acetic acid (EDTA)

EDTA was investigated as a competitor to PEI chelation of metals using a continuous feeding system. The experimental method was as described in section 3.5.4.1, except that 2 mM EDTA was added instead of ammonium sulfate. (The amount of 14.89 g and 3.72 g of EDTA were added to metals and polymer solutions, respectively).

Chapter 4

Batch mode UF of individual and mixed metal solutions in the presence and absence of PEI

4.1. Introduction

In this chapter, a study was undertaken to investigate the retention characteristics of different metals during ultrafiltration of aqueous solutions of individual metals, in the absence and presence of the polyethylenimine (PEI) at different pH. The binding characteristics of PEI with single and mixed metal ion were also investigated.
Experiments were carried out in batch mode ultrafiltration cell (section 3.3.1), the permeate flux and metal content of the permeate were determined.

First, the retention of metals in the absence of polymer was investigated as the metals and their salt interact directly with the membrane. Secondly, in the presence of polymer, solutions of single metal ions are contacted with polymer solutions, complexes of metal ions with polymer prevent the metals passing through the membrane. Retention profiles of the different metal ions by the polychelatogen during the ultrfiltration processes can be used as an indication of the degree of metal-polymer complexation. Finally, the maximum binding of single and mixture metal ions was used to describe the affinity of polymer to bind different metal ions in competitive processes.

4.2. Membrane characterization

The membranes used in all batch ultrafiltration experiments were Intersep Nadir polysulphone with a molecular weight cut off (MWCO) of 30K Dalton. Before the membranes were used in streaming potential or PEUF experiments, the pieces of new polysulphone membrane were kept on distilled water during 24 hr (water conductivity less than 1μS/cm) to allow them to become fully hydrated.

Streaming potential measurements were performed at a variety of pH values in order to characterise the membranes used (section 3.3.2). These data have then been used to analyse the PEUF performance.

A plot of the zeta potential versus pH for the NADIR polyethersulphone membranes in 0.001 M KCl showed that the isoelectric point of the membrane, at the given experimental conditions, occurs at approximately pH 3.9. The membrane is negatively charged for pH values above pH 3.9 and positively charged for pH values below pH 3.9. The membrane zeta potential plateaus out at approximately pH 6.5 – pH 7. Once the pH is higher than this no significant increase in zeta potential, and thus membrane charge, is observed. Therefore, the maximum surface charge on the membrane during the ultrafiltration experiments occurs at pH 6.5 and falls as the pH is reduced until it reaches zero at pH 3.9.

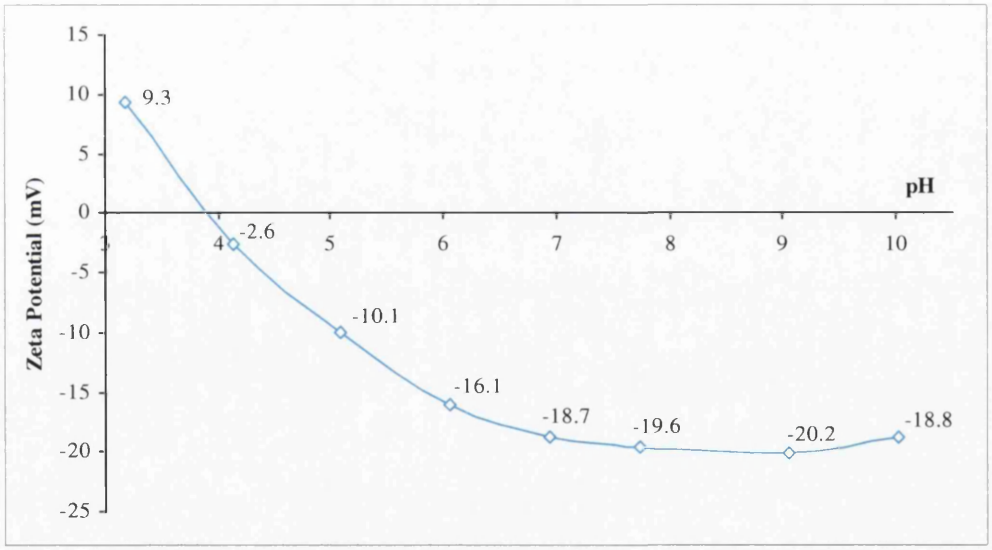


Figure 4.1 *Zeta potential of the polysulphone membrane (30K MWCO) as a function of pH in 0.001 M KCl solution.*

4.3. Filtration of single metal ions in the presence and absence of PEI

This section presents the effect of pH on metal retention values and permeates fluxes during the batch mode ultrafiltration experiments, in the absence and presence of PEI. Individual aqueous solutions of six metals (Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+}) were produced over range of pH 2 to pH 6.5. Retention profiles were investigated in the absence and presence of PEI by using batch mode ultrafiltration process (Section 3.3.3). Subsequently, analysis of permeate and retentate samples for the relevant metal, via ICP was carried out (Section 3.3.5), allowed calculation of the retention value of each metal using equation 3.1. (Further details on experimental methods are available in section 3.4.1).

Plotting metal ions retention as a function of pH allowed exploration of retention characteristics of these solutions, in the absence and presence of polymer. Figure 4.2 compares rejection in the presence and absence of PEI for Cu^{2+}, the plot shows retention against pH in the absence of PEI. At low pH (below 4) where the membrane is positively charged, a slight high retention was observed compared to a little retention of Cu^{2+} up to ~ pH 5. Conversely, more retention of Cu^{2+} was observed above pH 5.5 with an approximate average of 53% at pH 6 and pH 6.5, this appears to be retention of the metal ion due to precipitation of Copper hydroxides. Hence as solution pH increases the formation of insoluble hydroxides is likely to become the major mechanism responsible for metal ions retention. This retention observed for Cu^{2+} agrees with the results reported by Rivas et al [92]. Clearly this scenario of Cu^{2+} retention in the absence of PEI was also observed in the retention profiles of other metals in this study. In contrast, the relationship between Cu^{2+} retention values and pH in the presence of PEI was completely different; the retention values were very high from pH 3 up to pH 6 with an average of 90% approximately and the minimum retention of Cu^{2+} was obtained at pH 2 (37 ± 5 %).

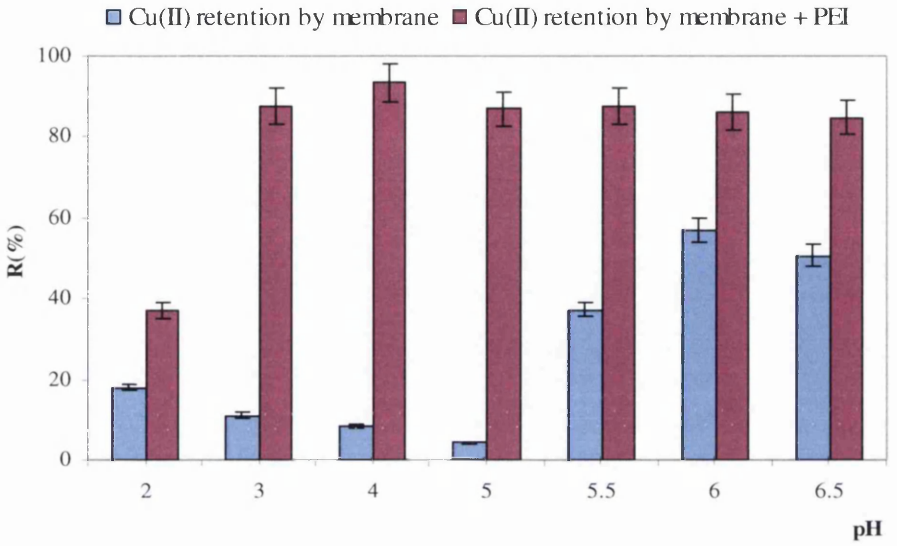


Figure 4.2 *Cu^{2+} retention profiles in the presence and absence of PEI as function of pH in batch mode ultrafiltration, using single metal solution with 10 mg/l and 1 g/l PEI.*

A similar retention pattern to Cu^{2+} ions was also observed for Zn^{2+} (Figure 4.3), little retention of Zn^{2+} occurred up to pH 5.5 in the absence of PEI and the retention was very low at pH 4 where the charge of the membrane is zero, while at pH 6 and pH 6.5 more retention occurred with an average of 42% most probably due to the formation of insoluble Zinc hydroxides in this range of pH.

Retention values for Zn^{2+} from solutions in the presence of PEI increased with pH. At pH 5.5 the highest retention (94 ± 3 %) was obtained for Zn^{2+} while the lowest retention was observed at pH 2 and pH 3 respectively.

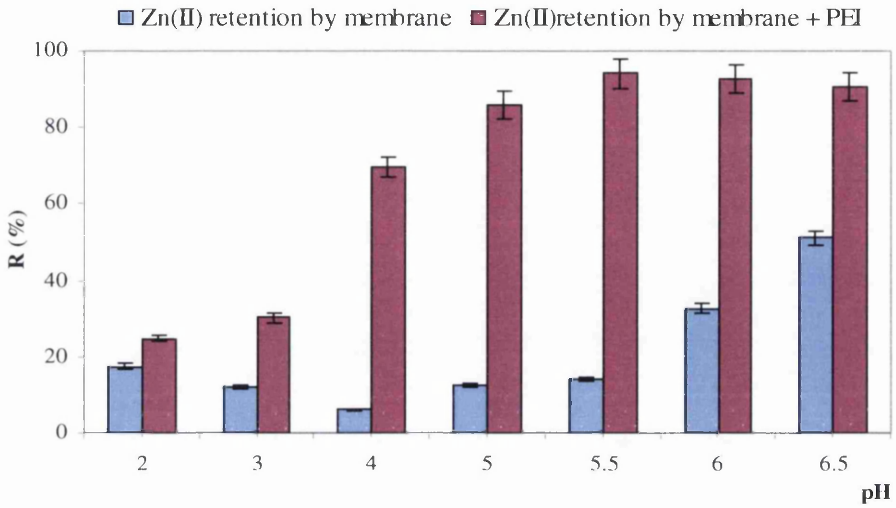


Figure 4.3 *Zn^{2+} retention profiles in the presence and absence of PEI as function of pH in batch mode ultrafiltration, using single metal solution with 10 mg/l and 1 g/l PEI.*

Retention of Cr^{6+} plotted as function of pH for aqueous Cr^{6+} solution (Figure 4.4) showed little or no retention of Cr^{6+} occurred for all pH in the absence of PEI. On the other hand, PEI showed high capability for Cr^{6+} retention at all pH investigated.

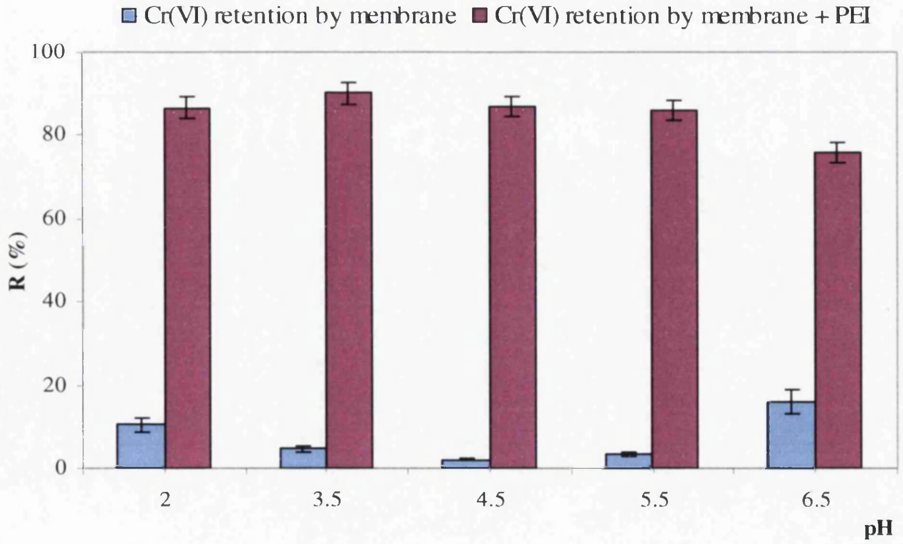


Figure 4.4 *Cr^{6+} retention profiles in the presence and absence of PEI as function of pH in batch mode ultrafiltration, using single metal solution with 10 mg/l and 1 g/l PEI.*

The plot of retention against pH for aqueous Ni^{2+} solutions in the absence of PEI (Figure 4.5) showed little or no retention of Ni^{2+} occurred for all pH investigated. However, in the presence of PEI, a maximum retention of Ni^{2+} was achieved at pH 5.5, pH 6.5 with an approximate average of 94 %.

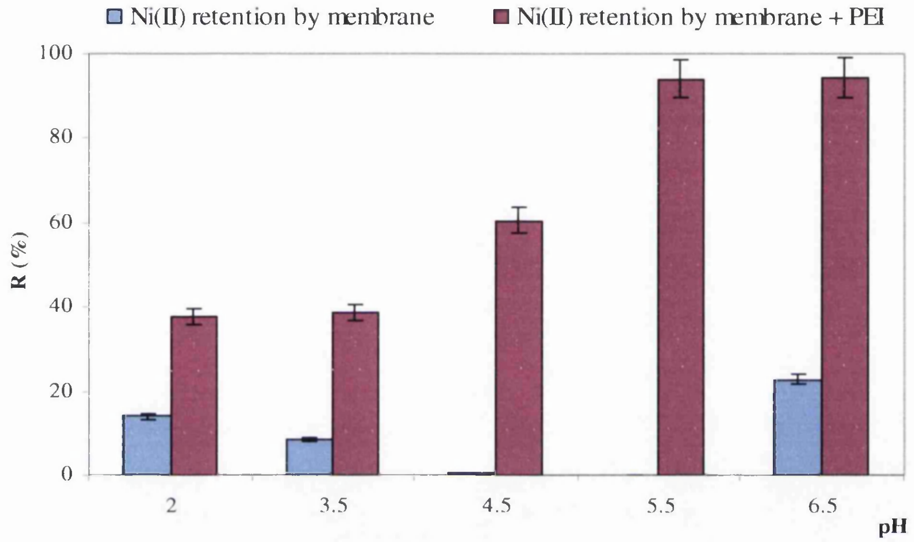


Figure 4.5 *Ni^{2+} retention profiles in the presence and absence of PEI as function of pH in batch mode ultrafiltration, using single metal solution with 10 mg/l and 1 g/l PEI.*

Cd^{2+} retention was studied in the absence of PEI (Figure 4.6), suggesting little or no retention of Cd^{2+} was observed from pH 2 to pH 5.5. Maximum retention (52 ± 9 %) was obtained at pH 6.5; precipitation of Cadmium hydroxides at pH 6.5 was likely to have been responsible for the observed retention. In the presence of PEI, little retention of Cd^{2+} was observed from pH 2 to pH 4.5. A maximum retention of Cd^{2+} was obtained at pH 5.5, and pH 6.5 with an average retention values of (71±3 %) and (91±5 %) respectively.

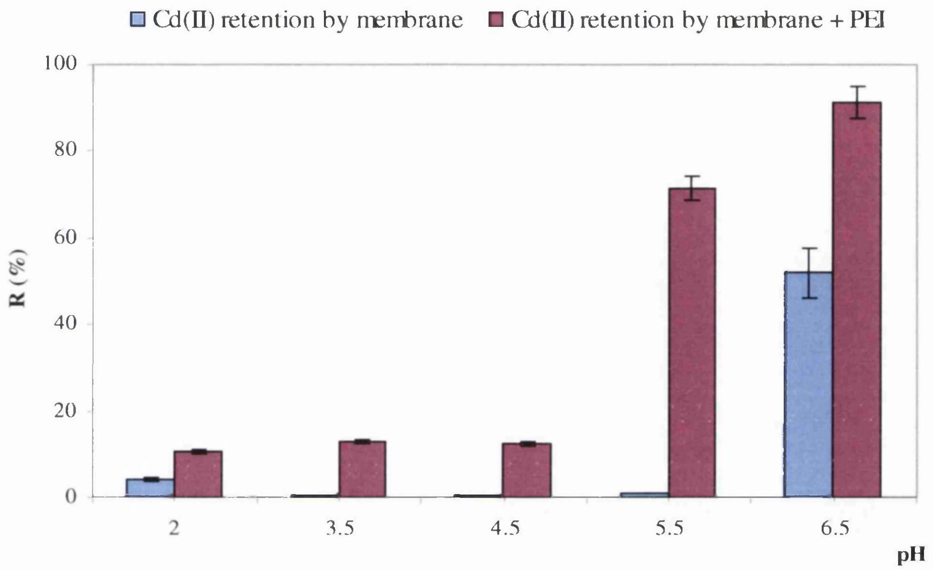


Figure 4.6 *Cd^{2+} retention profiles in the presence and absence of PEI as function of pH in batch mode ultrafiltration, using single metal solution with 10 mg/l and 1 g/l PEI.*

Retention of Co^{2+} plotted against solution pH for aqueous Co^{2+} solutions (Figure 4.7) showed little retention of Co^{2+} occurred for the pH range investigated in the absence of PEI. However, the polychelatogen PEI had a good affinity for binding Co^{2+} at pH 5.5 and pH 6.5 with retention values of (88 ± 5 %) and (96 ± 4 %) respectively.

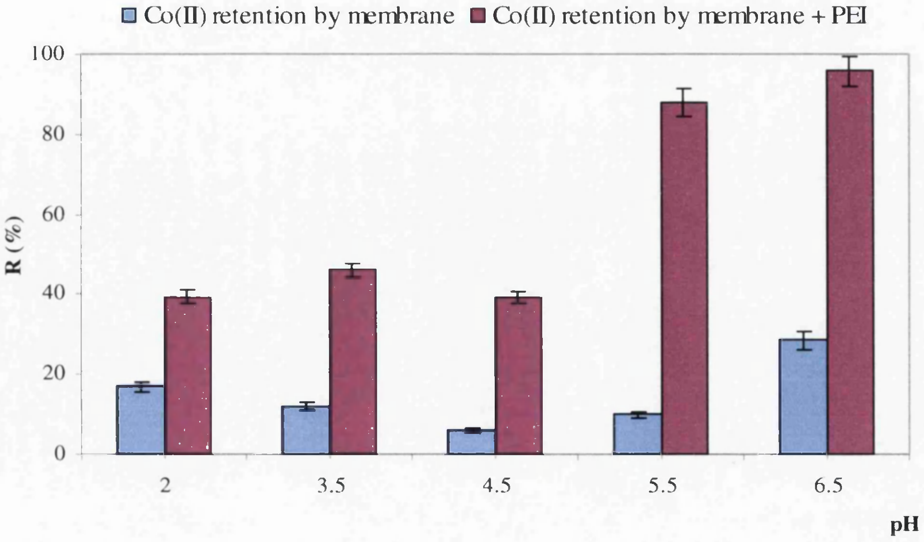


Figure 4.7 *Co^{2+} retention profiles in the presence and absence of PEI as function of pH in batch mode ultrafiltration, using single metal solution with 10 mg/l and 1 g/l PEI.*

Data gathered from ultrafiltration of aqueous solutions containing single metal ions in the absence and presence of polyethylenimine (Figures. 4.2 to 4.7), showed the retention of metals in the absence of polymer at low pH was relatively high for the positive values of membrane zeta potential. When the pH of solution reached the isoelectric point of the membrane (zeta potential = 0), the retention was very low and then increased for the pH value where the membrane is negatively charged and it is thought that the precipitation of hydroxyl salts occurs. In the case of metal ultrfiltration in the presence of polymer, significant increases in the retention of Cu^{2+}, Zn^{2+} and Cr^{6+} due to strong complexation of these metals by PEI polymer. However, PEI showed a lower affinity to form complexes with Ni^{2+}, Co^{2+}, and Cd^{2+} metals especially at low pH where the increase of H^+ concentration favours protonation of the metal binding sites on the polymer which prevents metal ions binding at that site. As pH increases, the retention of metal ions increases due to the greater availability of binding sites on the polymer together with the precipitation of metal hydroxides on the membrane surface at $pH \geq 6$.

In Figures 4.8 and 4.9, the flux vs. pH measured during the course of the UF experiments of metal solutions in the absence and presence of PEI are shown.

Figure 4.8 shows the average flux versus pH for solutions without PEI added. The pure buffer solution flux was used as a reference solution for these experiments. It can be seen that the pure buffer solution flux (Fig 4.8) was similar to the average pure water flux (0.096 m^3/m^2 hr) for the membrane at low pH values, but decreases away from this value as the pH was increased. The lowest flux for the reference solution was seen to occur when the membrane surface charge was at its highest value i.e. at pH 6.5. This likely to be due to the electroviscous effect which causes an increase in the fluid viscosity within a charged capillary or pore [101] resulting in a decrease in flux. When metal ions were added to the pure buffer solution (metal concentration 10 mg/l) some interesting trends were observed. Cu^{2+} and Zn^{2+} ions reduce the flux of the solution in comparison with the pure buffer flux. This corresponds to the data in figures (4.2 - 4.7), as these ions show higher retention values which would result in some concentration polarization at the membrane surface which will reduce the flux (especially at higher pH values).Again the electroviscous effect [101] may also reduce the flux at these conditions. Cd^{2+} and Cr^{6+}

ions have little effect on the flux of the solution as these ions pass relatively easily through the membrane at the conditions investigated. The retention of these metal ions is extremely low until the pH exceeds a value of 6. However, Co^{2+} and Ni^{2+} ions actually enhance the flux of the solutions in comparison to the reference solution. Flux enhancement remains to be explained. There is some evidence to suggest that flux may be reduced by interaction of the metal ion with a cellophane membrane [102] but enhancement of flux may also possible. Trivunac and Stevanovic [103] have presented data to show that pure metal salt solutions substantially alter the flux through the membrane (Versapor 200 UF membrane). The explanation may be that the ions in the buffer interact differently with the metals ions so allowing both reduction and enhancement of the flux over the phosphate buffer control.

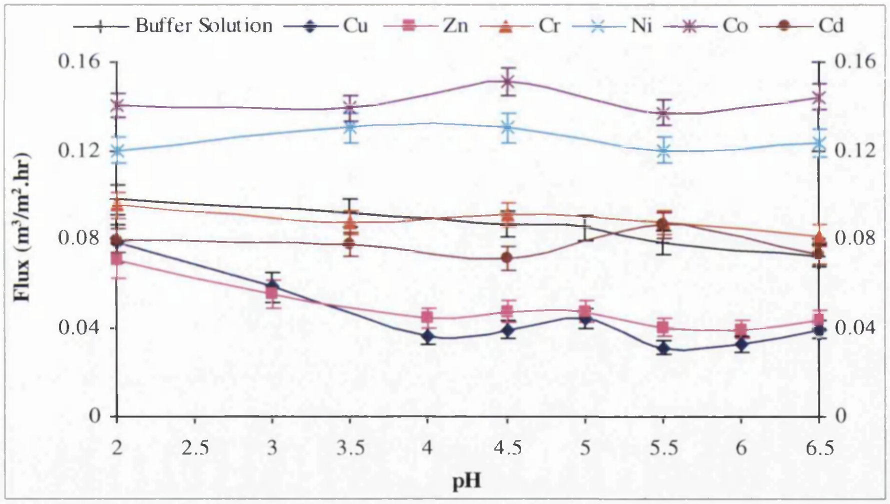


Figure 4.8 *The effects of pH on permeate flux for different single metal ions in the absence of PEI at constant temperature (25 ℃) and pressure (3 bar) using 30 kDa polysulphone ultrafiltration membrane.*

Figure 4.9 shows the average flux versus pH for solutions with 1g/l PEI added. In this case the reference solution used was the pure buffer solution with PEI added until the solution concentration was 1g/l. Similar trends to those seen for metal ion buffer solutions without PEI added were observed. However, the fluxes observed in all cases when PEI was added were significantly reduced from the fluxes without PEI (reduced by about 50%). This is due to the metal ion and polymer forming a complex which cannot pass through the membrane resulting in concentration polarization at the membrane surface which reduces the flux.

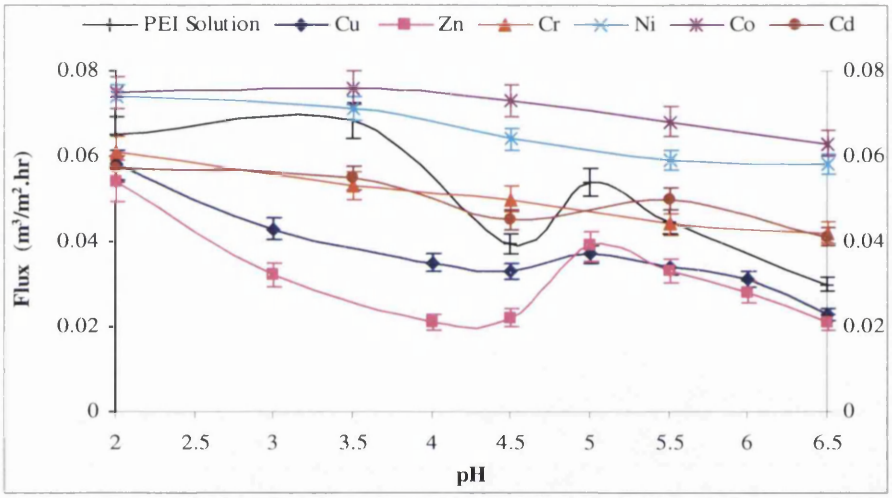


Figure 4.9 The effects of pH on permeate flux for different single metal ions in the presence of PEI at constant temperature (25 °C) and pressure (3 bar) using 30 kDa polysulphone ultrafiltration membrane.

4.4. Binding studies of single and mixture metals based on adsorption isotherms

The binding conditions and retention of single and mixtures of metal ions (Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+}) at different metal concentrations in the presence of PEI were studied. The maximum polymer binding (Q_{max}) of single and mixed metal ions was determined according to Langmuir and Freundlich isotherms. A clear indication of the importance of solution pH to the complexation of metal ions by the polymer was observed from the retention experiments results (section 4.3). At lower pH values, the active sites of the polymer are less available for the metal ions due to protonation of the active sites at acid pH (< 4) causing low metal retention. At pH values (4.0–6.0), a significant reduction in the protonation of binding sites and retention of the metal ions is increased. In this pH range, it is believed that the complex formation processes is the major mechanism for removal of metal ions from solution. At pH values higher than 6.0, both complex formation and precipitation of metal hydroxides may become significant mechanisms in the metal retention process. For this reason, the optimum pH value of metal retention was chosen at pH 5.5 to study the binding condition of single and mixed species ions.

4.4.1 Results of binding single metal ions with PEI in batch mode PEUF

Binding studies were carried out for individual aqueous solutions of single metals in batch mode PEUF. The amount of metal bound to the polymer was determined experimentally at pH 5.5 for each single metal by measurement of the concentration of the filterable metal ions. Then, the applicability of the Langmuir and Freundlich isotherms to describe these systems was explored, using the linear form of the Langmuir equation (equation 3.4) and the linear form of the Freundlich equation (equation 3.6) the data was fitted by linear regression.

Plotting the amount of metal bound to the polymer (PEI) for various feed concentrations of single metal solutions (Figure 4.10), showed a good fit of langmuir model (equations 3.3 and 3.4) comparing to the batch mode ultrafiltration experimental results, and that the maximum binding to PEI was observed for Cu^{2+}, Cr^{6+} and Zn^{2+}, respectively. In contrast, PEI showed lower affinity to complex Ni^{2+}, Co^{2+}, and Cd^{2+}.

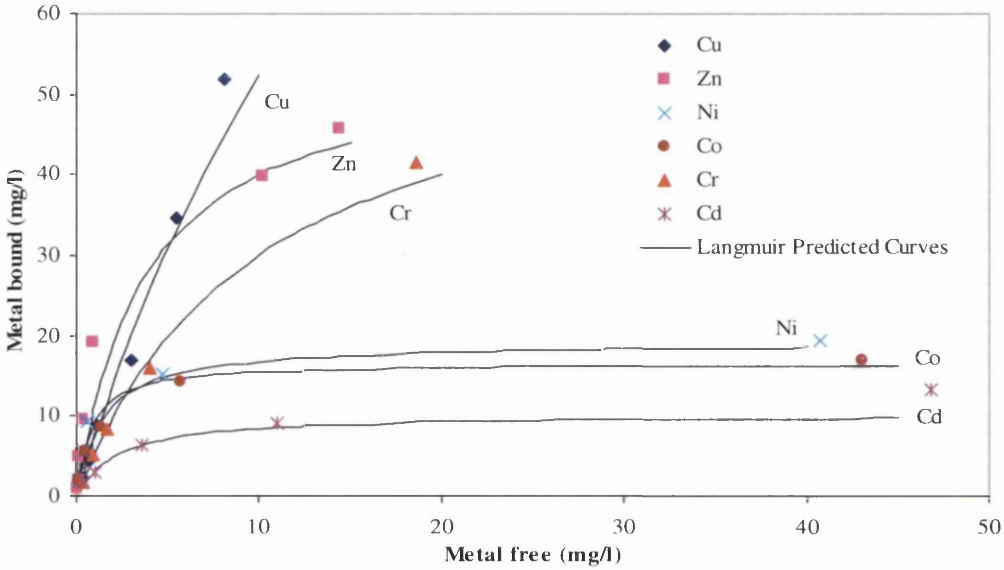


Figure 4.10 *Results of binding of single metal ions to PEI in batch mode PEUF process, experiments (points) and using Langmuir model (lines) at pH 5.5, 1 g/l PEI, and different feed concentrations*

Figure 4.11 compares the predicted data of single metal ions (Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+}, and Cd^{2+}) with the experimental data of these metals using Freundlich isotherms model (equations 3.5 and 3.6). It is seen that the model showed a good fit for the experimental results of Cu^{2+}. The model successfully fitted the data of Cr^{6+} and Cd^{2+} at low concentrations, but less accuracy of model predicting was observed for the experimental data of Zn^{2+}, Ni^{2+} and Co^{2+}.

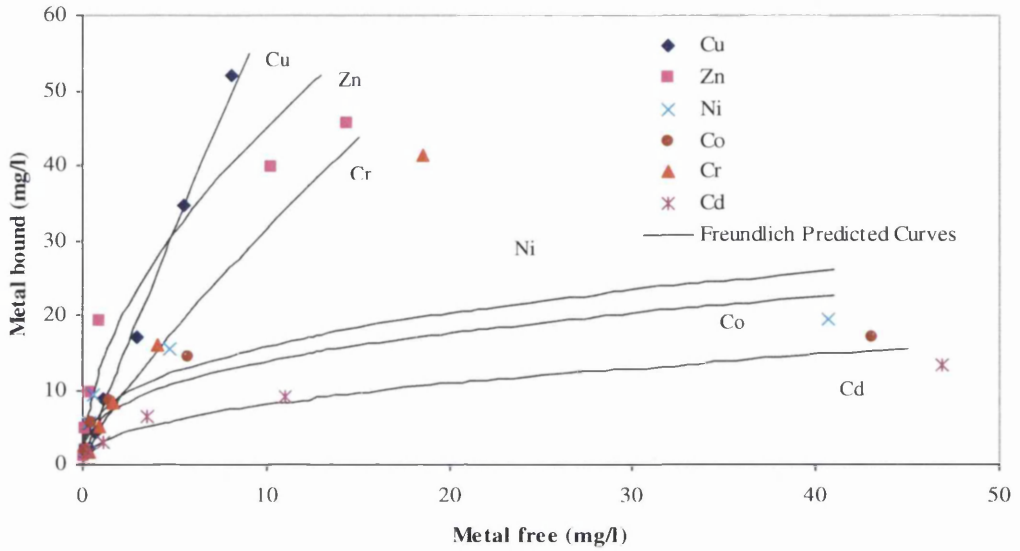


Figure 4.11 *Results of binding of single metal ions to PEI in batch mode PEUF process, experiments (points) and using Freundlich model (lines) at pH 5.5, 1 g/l PEI, and different feed concentrations*

The Langmuir isotherms allowed estimation of maximum capacity of the polymer for metal ions (Q_{max}), and the equilibrium constant (K_L) at pH 5.5. Plots of the linear form of the Langmuir isotherm showed that much of the data gave a fairly good fits to the Langmuir model, this is clear from the values of square linear regression (R^2) and the maximum capacity of the polymer for metal ions are shown in (table 4.1). The linear form of the Freundlich isotherm also proved to fit the data reasonably well at pH 5.5 for all metal used with the values of n<1 (favorable sorption) and square linear regression (R^2) not less than 0.88 (table 4.1). However, the values of (R^2) in single metal solutions indicate that the results obtained with Langmuir isotherm appeared to offer the better description of the binding conditions than those obtained with Freundlich isotherm.

The Langmuir data showed that the Q_{max} for Cu^{2+} was 169.5 mg/g$_{PEI}$ (2.67 mmol/g), for Cr^{6+} was 60.6 (1.16), for Zn^{2+} was 55.2 (0.84), for Ni^{2+} was 19.2 (0.327), for Co^{2+} was 16.6 (0.28) and for Cd^{2+} was 10.3 (0.092). While the equilibrium constants were in the following order: Co^{2+} (0.76 mg/l), Ni^{2+} (1.43), Zn^{2+} (1.56), Cd^{2+} (2.1), Cr^{6+} (10.2) and Cu^{2+} (22.3). These data suggest possible different mechanisms of binding metal ions to the polymer.

***Table 4.1** Data derived from applying Langmuir and Freundlich isotherms for single metal ions in batch mode PEUF process, the data were fitted to linearised form of these experiments.*

Langmuir Isotherm								**Freundlich Isotherm**			
Exp.	**Slope** K_L/Q_{max}	**Intercept** $1/Q_{max}$	Q_{max}		K_L		R^2	**Intercept** (Ln K_F)	*n*	K_F (mg^{1-n} $g^{-1}l^{n}$)	R^2
			(mg/ g_{PEI})	(mmol/ g_{PEI})	(mg/ l)	(mmol/ l)					
Cu^{2+}/ PEI	0.132	0.0059	169.5	2.67	22.3	0.35	0.998	1.95	0.93	7.0	0.995
Cr^{6+} / PEI	0.169	0.0165	60.6	1.16	10.2	0.19	0.999	1.62	0.79	5.1	0.994
Zn^{2} / PEI	0.028	0.018	55.2	0.84	1.56	0.024	0.997	2.59	0.53	13.3	0.937
Co^{2} / PEI	0.046	0.060	16.6	0.28	0.76	0.013	0.989	1.93	0.49	6.9	0.983
Ni^{2+} / PEI	0.074	0.052	19.2	0.327	1.43	0.024	0.996	2.10	0.49	8.17	0.883
Cd^{2} / PEI	0.201	0.097	10.3	0.092	2.08	0.018	0.985	1.07	0.44	2.92	0.958

The retention profiles of single metal solution (Figure 4.12) showed that the highest retention of Zn^{2+} with (95 ± 3 %) at low metal concentration up to 20 mg/l. At high concentration where the polymer becomes saturated the metal retention by the membrane becomes lower. Overall metal concentrations studied, the retention values for Cu^{2+} and Cr^{6+} remain constant above 80 ± 4 %. For other metal ions, the drop in retention values were observed between metals concentration of 10 and 60 mg/l with an approximate reduction of 50%.

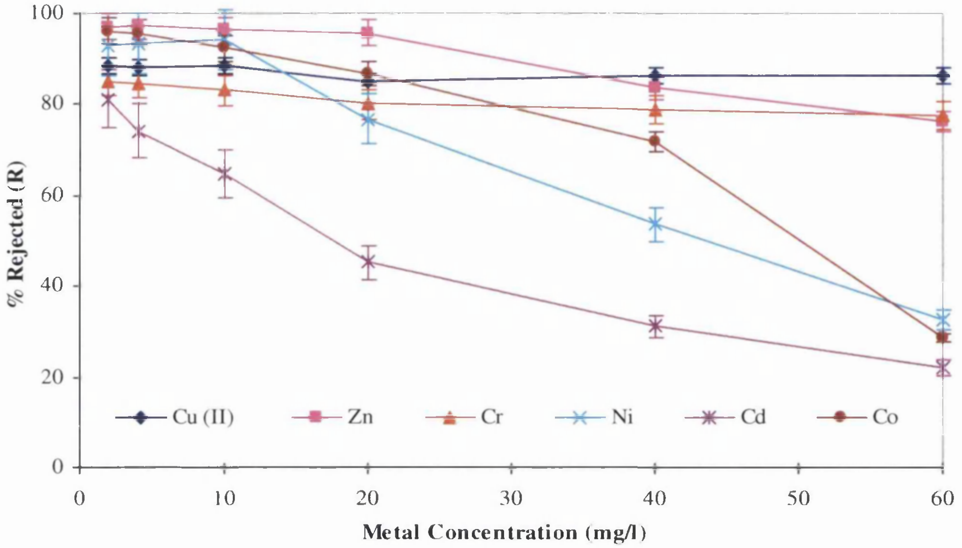


Figure 4.12 *Retention values of single metal ions at pH 5.5 in the presence of 1 g/l PEI for different feed metal concentrations using batch mode of PEUF.*

4.4.2 Binding mixed species of metal ions with PEI in batch mode PEUF

Results from binding studies of single metal solutions have indicated the ability of achieving a maximum binding of metal to the polymer using batch mode PEUF with PEI as a polychelatogen. As an extension, to the work carried out on simple aqueous solutions of single metal, the competition effect of mixture metals in batch mode PEUF was investigated.

Plotting the amount of metal bound to the polymer (PEI) for various feed concentrations of mixture metal solutions (Figure 4.13), showed also a good fit of Langmuir curves to the experiments result with a different trend to those observed previously of single metal solutions. The effect of metal competition on the shape of binding curves shows that all were altered significantly. In figure (4.14), reasonable fit of Freundlich isotherm model to the experimental data was observed, with less accuracy of fitting data compared to the Langmuir isotherms except for $Cd2^+$. This was clear from the values of square linear regression (R^2) shown in table (4.2).

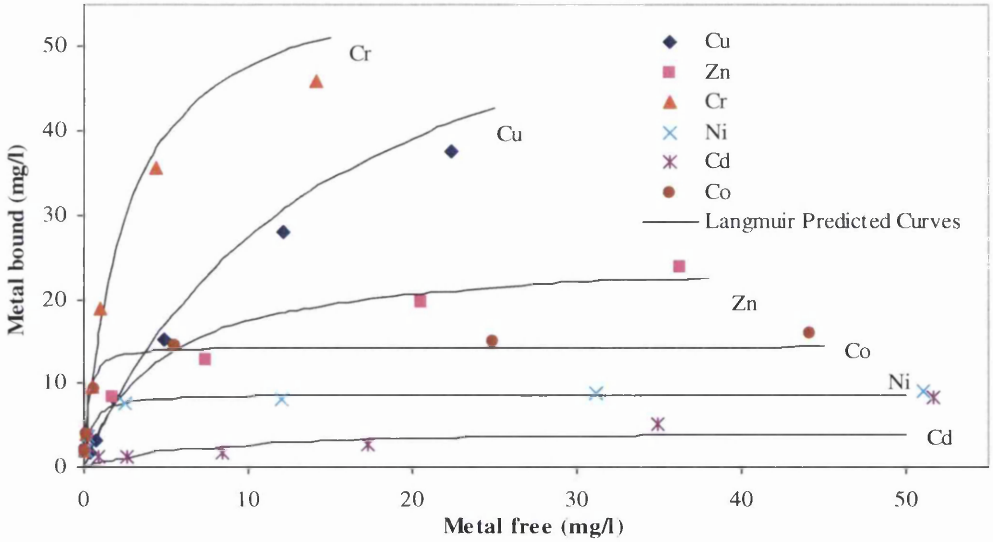


Figure 4.13 *Results of binding of mixture metal ions to PEI in batch mode PEUF, [experiments results (points) and using Langmuir model (lines) at pH 5.5, 1 g/l PEI, and different feed concentrations]*

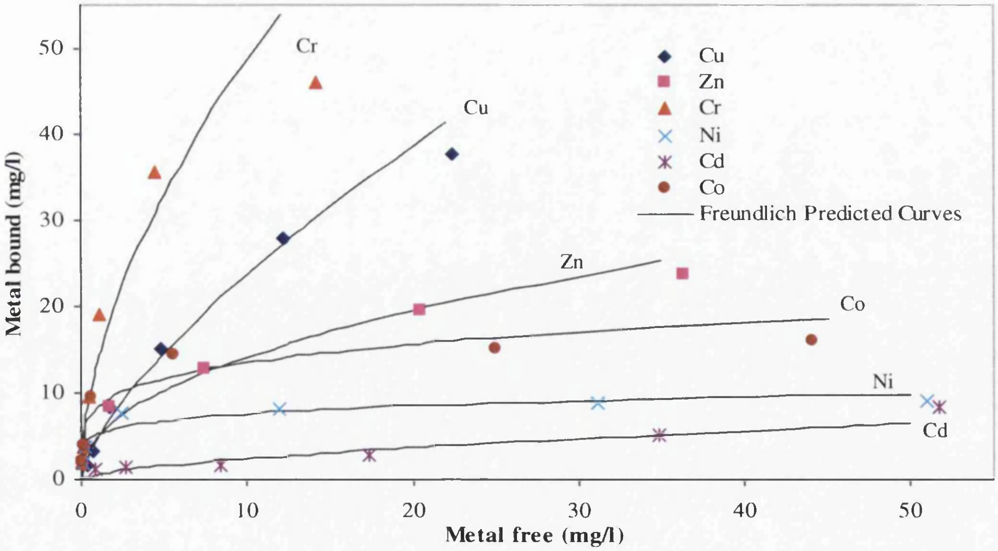


Figure 4.14 *Results of binding of mixture metal ions to PEI in batch mode PEUF, [experiments results (points) and using Freundlich model (lines) at pH 5.5, 1 g/l PEI, and different feed concentrations]*

Langmuir and Freundlich isotherms were explored under competitive conditions of mixed metal solutions with PEI using batch mode PEUF. Plots of the linear form of the Langmuir isotherm at pH 5.5 showed that data fitted the isotherms reasonably well and the results from the application of the linear form of Langmuir isotherm allowed estimation of maximum capacity of the polymer for metal ions (Q_{max}) under competitive of metal (table 4.2). The Langmuir data showed that the Q_{max} for Cu^{2+} was 68.03 mg/g_{PEI} (1.07 mmol/g), for Cr^{6+} was 59.88 (1.15), for Zn^{2+} was 25.32 (0.387), for Co^{2+} was 14.43 (0.245), for Ni^{2+} was 8.75 (0.149) and for Cd^{2+} was 4.62 (0.041). While the equilibrium constants were in the following order: Co^{2+} (0.19 mg/l), Ni^{2+} (0.36), Cr^{6+} (2.56), Zn^{2+} (4.52), Cd^{2+} (7.44) and Cu^{2+} (14.73). These data suggest that Cr^{6+} and Co^{2+} binding were not significantly altered while Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} were significantly lower in mixture solutions, indicating the binding competition of Cr^{6+} and Co^{2+} have different binding mechanisms than Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} due to the interactions between metal ions for binding sites. However, Cd^{2+} is poorly complexed by PEI in both systems and this is clear from the lower values of Q_{max} (10.3 and 4.62 mg/g_{PEI}) in single and mixed metal solutions, respectively.

Table 4.2 *Data derived from applying Langmuir and Freundlich isotherms for mixture metal ions in batch mode PEUF process, the data were fitted to linearised form of these experiments.*

Langmuir Isotherm								***Freundlich Isotherm***			
Exp.	***Slope*** ***K_L/Q_{max}***	***Intercept*** ***$1/Q_{max}$***	***Q_{max}***		***K_L***		***R^2***	***Intercept*** ***($Ln\ K_F$)***	***n***	***K_F*** ***(mg^{1-n} $g^{-1}l^n$)***	***R^2***
			(mg/ g_{PEI})	***(mmol/ g_{PEI})***	***(mg/ l)***	***(mmol/ l)***					
Cu^{2+}/ PEI	0.217	0.0147	68.03	1.07	14.73	0.232	0.991	1.54	0.7	4.7	0.979
Cr^{6+}/ PEI	0.043	0.0167	59.88	1.15	2.56	0.049	0.999	2.59	0.56	13.4	0.935
Zn^{2}/ PEI	0.179	0.0395	25.32	0.387	4.52	0.069	0.981	1.59	0.46	4.9	0.944
Co^{2}/ PEI	0.013	0.0693	14.43	0.245	0.19	0.003	0.989	2.12	0.21	8.35	0.886
Ni^{2+}/ PEI	0.041	0.1143	8.75	0.149	0. 36	0.006	0.996	1.66	0.16	5.26	0.862
Cd^{2}/ PEI	1.611	0.2164	4.62	0.041	7.44	0.066	0.774	-0.57	0.62	0.57	0.909

The retention values with the metal concentrations under competitive conditions (Figure 4.15) showed that the highest retention was for Cr^{6+} for most competitive metal concentrations investigated with an average retention value of ~ 90%, suggesting that no significant impact of metals competition on Cr^{6+} retention. Also the retention of Cu^{2+} ions in the competition process remains nearly constant between 70-80%. For other metals, the highest retention was observed at low metal concentration, with increasing of metal concentrations the retention dramatically dropped for Zn^{2+}, Co^{2+} and Ni^{2+}. However, little retention of Cd^{2+} was observed under all competitive metals concentrations studied.

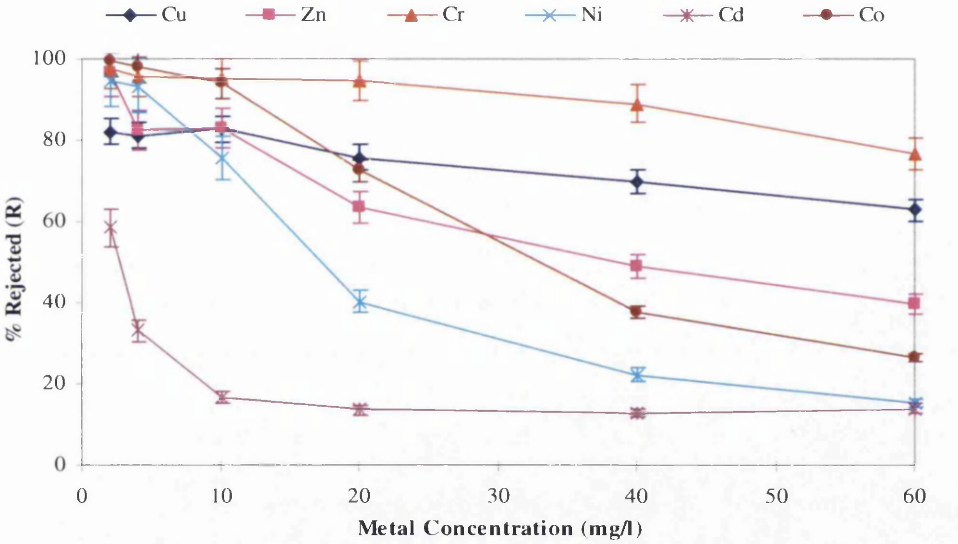


Figure 4.15 *Retention values of mixture metal ions at pH 5.5 in the presence of 1 g/l PEI for different feed metal concentrations using batch mode of PEUF.*

4.5. Conclusions

PEUF process allows good retention for metal ions investigated by using PEI at different pH and that metal ions retention is dependent on many factors including their chemical properties in solution as well as their interaction with PEI and the membrane. The main aim of this study was to determine the rejection of PEUF using zeta potential and to identify the effect of metals competition on binding conditions in PEUF process. Since the charge of membrane surface is critical to the process performance, it was concluded the membrane material and pore size are two other possible factors to affect the process.

Comparison of the data from ultrafiltration experiments in the absence and presence of polymer, clearly suggested that the presence of PEI had a very significant impact on the retention values of metal ions and the affinity of PEI to metal ions depended on the pH. The observed retention in the absence of PEI was variation with the polysulphone ultrafiltraion membrane charge. For the positive charge of zeta potential, the potential retention of metal ions was slightly high in comparison with the negative charge of zeta potential at acid pH, and the retention was very low where the charge of the membrane is equal to zero. However, high metals rejection by membrane was observed at pH ≥ 6 due to the formation of insoluble metal compound. Retention profiles with respect to pH in the presence of PEI during these experiments can be explained by the formation of strong metal-polymer complexes which can be retained by ultrafiltration membrane, and the formation of insoluble metal compound (hydroxides) too large to pass through ultrafiltration membrane. At low pH, the retention of metal ions by the polymer was low due to the high proton concentration resulting in a low affinity of the metal ions for the polymer. In contrast, the retention of metal ions by the polymer increases as pH increases, a significant reduction in the protonation of binding sites was expected with an increasing in the availability of metal binding sites.

Although reduction of flux was anticipated by the addition of 1 g/l PEI (reduced by about 50% as compared to pure controls), the addition of small quantities of metals (10 mg/l) also significantly affected the flux and that this was metal ion dependent. Flux was enhanced by up to 40% by addition of Co^{2+} and Ni^{2+}, while the Cr^{6+} and Cd^{2+} had neutral effect on flux and that Zn^{2+} and Cu^{2+} were lower, especially above pH 4 and that this may be caused either by formation of small insoluble material. However, the transmission of these metals through membrane was good. This suggests that these metals significantly interact with membrane and membrane pores. The influence of the polymer shows a reduction of flux as the pH is increased from 2 to 6.5. In the presence of PEI similar trends were observed as compared to the metal/buffer solutions flux. However, Zn^{2+} in the presence of polymer at pH 5 shows enhanced up to a similar to the polymer/buffer control. Cu^{2+} also follows the trend by less significantly.

In an attempt to identify the effect of metals competition on binding conditions in PEUF process, experiments in the presence of PEI for single and mixture metal solutions have been carried out and fitted to the Langmuir and Freundlich isotherms. The results obtained with Langmuir isotherm are better fit for the data than those obtained with Freundlich isotherm as indicated by the high values of R^2. However, it was observed that the amount of metal ions bound to the polymer in solutions containing mixed metals were less than those of single metals for all metals investigated, indicating a reduction in binding capacity and equilibrium constant resulting from metals competition for binding sites on the polymer. These data also suggest that the binding sites of Cr^{6+} and Co^{2+} remain constant in competition while Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} show change in both binding capacity and equilibrium constant. The competition and effectiveness of the PEUF process is heavily dependent on the concentration of competiting metal ions, influencing both capacity and selectivity of these systems.

Chapter 5

Batch mode PEUF for metal ions filtration in the presence of various competing solutes and chelators

5.1. Introduction

In the previous chapter, the filtration of individual or mixed metal solutions was investigated in the presence and absence of PEI. This chapter set out to study the more complex situations where competitions for metal binding site on PEI are investigated. This was done in two ways. The first was to investigate common competing solutes while the second was to investigate competing chelating agents. To evaluate the retention profiles more correctly, batch mode ultrafiltration experiments were first carried out to investigate the retention of mixed metal ions (Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+}, and Cd^{2+}) using PEI. Then, batch mode ultrafiltration experiments were carried out in the two experimental schemes; (i) varying the concentration of metal ions with 1 g/l PEI at fixed concentration of individual solutes and chelators (0.2 mM). (ii) Varying the concentration of metal ions with 1 g/l PEI at fixed concentrations of individual solutes and chelators (2 mM). In addition, the performance of the polymer enhanced ultrafiltration process at competitive conditions of metal ions-chelate to the PEI was investigated, and the maximum binding of metal ions was determined using Langmuir isotherms model. However, the processes of metal binding to chelation agents in the presence of PEI were expressed by the following reactions:

1- Competitive reaction:

In competitive reaction, chelating agent combines with metals in a manner that prevents metal ions binding due to a true competition for the available site of PEI.

$$\begin{tikzcd}
Me + PEI \arrow[r, leftarrow, shift left, "K_{PEI}"] \arrow[r, shift right] \arrow[d, bend right] & PEI\ Me \\
+\ Ce \arrow[r, leftarrow, shift left, "K_C"] \arrow[r, shift right] & Me\ Ce
\end{tikzcd}$$

...........*Equation 5.1*

Where PEI is polymer, Me is metal, Ce is chelating agent and K_{PEI}, K_C are equilibrium constants for the formation of $PEI\ Me$ and $Me\ Ce$, respectively.

Equilibrium constants are:

$$K_{PEI} = \frac{[PEI][Me]}{[PEI\ Me]}, \quad \text{and} \quad K_C = \frac{[Me][Ce]}{[Me\ Ce]}$$

2- Noncompetitive reaction:

In noncompetitive reaction, chelator agent has less effect on metal ions binding to the PEI, and the interaction to the available site assumed to be independently, assuming that metals binding to chelator/ PEI complex are independent.

$$\begin{tikzcd}
PEI + Me \arrow[r, leftarrow, shift left, "K_{PEI}"] \arrow[r, shift right] & PEI\ Me \\
+ & + \\
Ce \arrow[d, leftarrow, shift left] \arrow[d, shift right, "K_C"'] & Ce \arrow[d, leftarrow, shift left] \arrow[d, shift right, "K_C"'] \\
PEI\ Ce + Me \arrow[r, leftarrow, shift left, "K_{PEI}"] \arrow[r, shift right] & PEI\ Me\ Ce
\end{tikzcd}$$

...........*Equation 5.2*

Equilibrium constants are:

$$K_{PEI} = \frac{[PEI][Me]}{[PEI\ Me]} = \frac{[PEI\ Ce][Me]}{[PEI\ Me\ Ce]},$$

and

$$K_C = \frac{[PEI][Ce]}{[PEI\ Ce]} = \frac{[PEI\ Me][Ce]}{[PEI\ Me\ Ce]}$$

5.2. Metal ions retention in the presence of PEI and various chelating agents

Plotting the observed retention values as function of metals concentration at pH 5.5 (figures. 5.1-5.12), affords a convenient way to investigate the effect of adding Ethylenediaminetetra acetic acid, Nitrilotriacetic acid, Sodium acetate, Ammonium chloride and Ammonium sulphate (which were designated as EDTA, NTA, SA, AC and AS respectively) to the system where a complex of metals/ PEI was undertaken. (Details of the experiments have been described previously in section 3.4.3).

5.2.1 Retention profile with 0.2 mM chelating agents

We begin with the result for the first experimental scheme, where the retention of metal ions can be obtained within 1 g/l PEI and 0.2 mM chelating agent in mixture metals solutions. In figure (5.1), the retention of Cu^{2+} in the presence of different solutes and chelators shows some differences compared with the retention of Cu^{2+} using PEI only (no additive added to the mixture metal solutions). In general, similar trends in separation efficiencies among five solutes and chelators are observed except for the presence of EDTA in the solution at low Cu^{2+} concentration (2 mg/l). It was observed that the retention of Cu^{2+} in the absence and presence of various solutes and chelators is kept constant at about 80% until the feed concentrations reach 20 mg/l, then the retention of Cu^{2+} decreases with increasing the feed concentration. Thus, the observed retention of Cu^{2+} was believed to have been largely due to complexation with PEI. Also, no significant effect of adding solutes or chelators to the complex except for the addition of EDTA to low Cu^{2+} concentration where the retention was about 32% at 2 mg/l feed concentration. Clearly these changes in metal ions retention suggested an inhibition effect of different chelators to the system and less binding of metal ions to the PEI is expected.

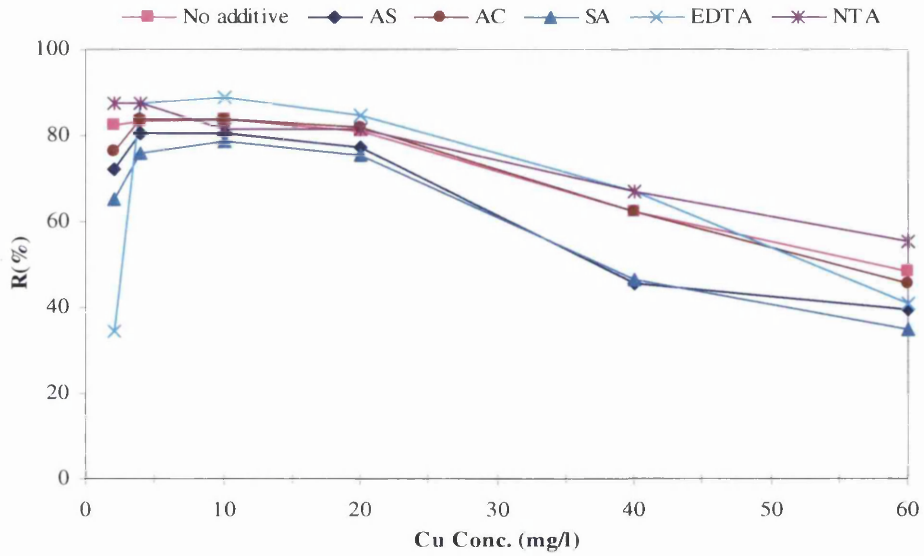


Figure 5.1 *Cu^{2+} retention in the presence of PEI and various chelating agents as function of mixture feed metal concentrations (1 g/l PEI, 0.2 mM chelating agents, pH 5.5).*

In figure (5.2), very similar trend of retention profile for Zn^{2+} was observed either for the absence or presence of solutes and chelators. Thus, the observed retention of Zn^{2+} was believed to have been largely due to binding with PEI and no significant effect of adding solutes or chelators to the complex except for the addition of EDTA or NTA at low Zn^{2+} feed concentration.

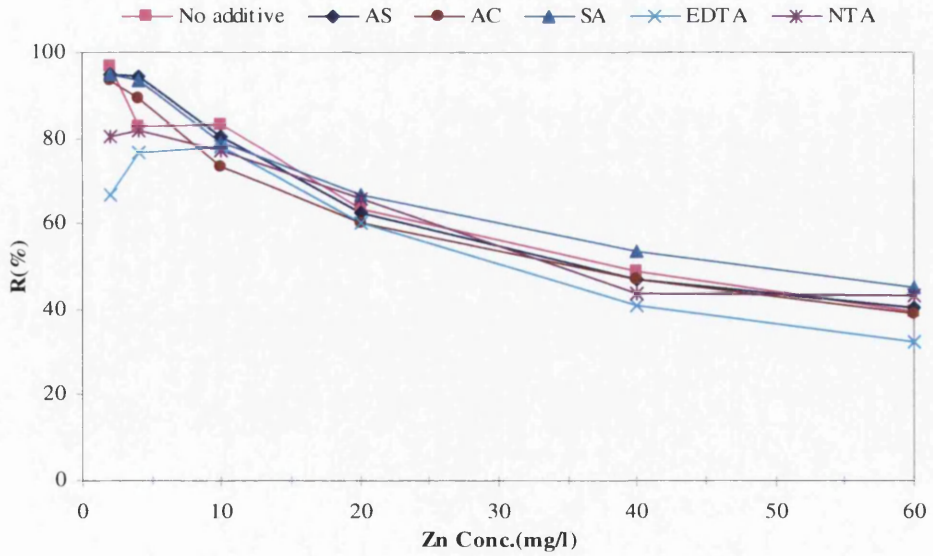


Figure 5.2 *Zn^{2+} retention in the presence of PEI and various chelating agents as function of mixture feed metal concentrations (1 g/l PEI, 0.2 mM chelating agents, pH 5.5).*

In figure (5.3), the retention of Cr^{6+} in mixture metal solutions with the presence of PEI was effected by the addition of EDTA or NTA to the complex of metal/ PEI solution at low concentrations (2- 10 mg/l) and high feed concentrations (60 g/l). However, no significant impact on the retention of Cr^{6+} when adding AS, AC and SA to the metal/ polymer complexes except for AS at 60 mg/l feed concentration (R< 75%).

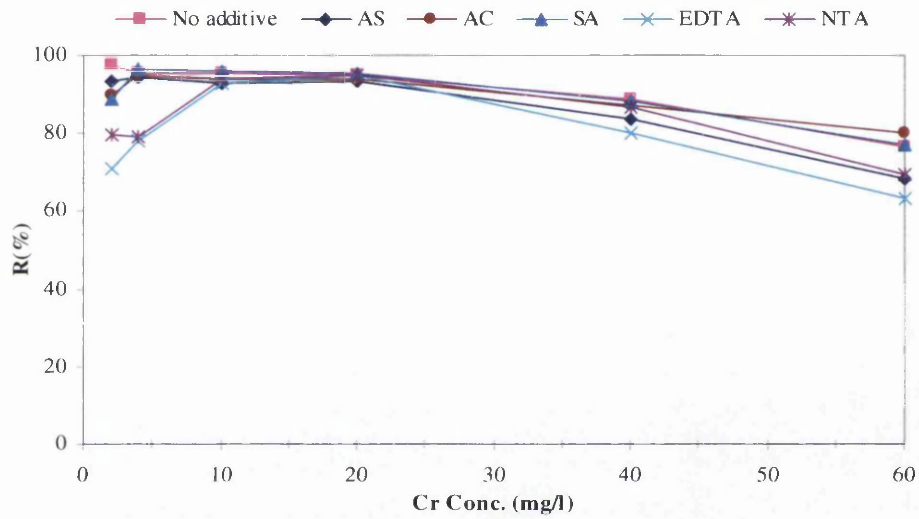


Figure 5.3 *Cr^{6+} retention in the presence PEI and various chelating agents as function of mixture feed metal concentrations. (1 g/l PEI, 0.2 mM chelating agents, pH 5.5).*

Figure (5.4) illustrates the retention of Ni^{2+} in the presence of PEI and various chelators. A significant reduction of Ni^{2+} retention (about 40%) by the addition of NTA to the system was observed. On the other hand, no significant impact for the presence of other chelators into Ni^{2+}/ PEI complex except the observed low retention by adding EDTA at low feed concentration (< 10 mg/l).

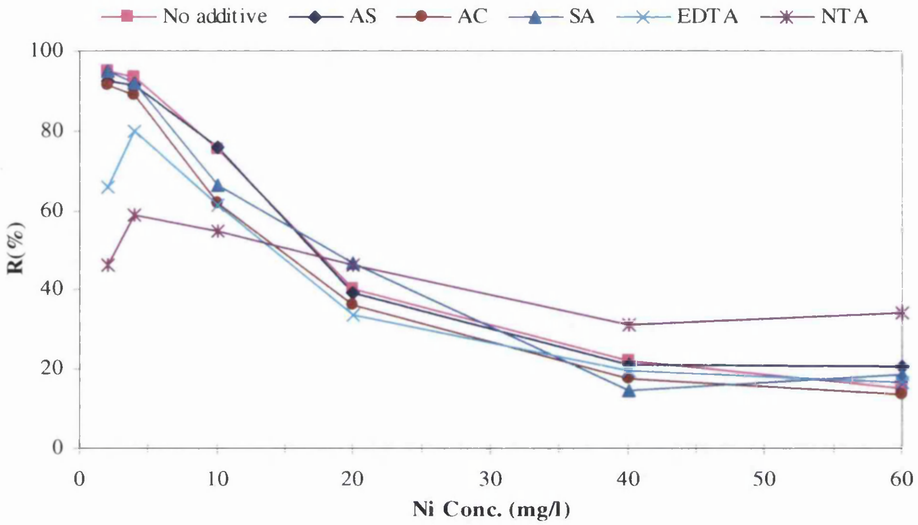


Figure 5.4 *Ni^{2+} retention in the presence of PEI and various chelating agents as function of mixture feed metal concentrations. (1 g/l PEI, 0.2 mM chelating agents, pH 5.5).*

The plot of Co^{2+} retention in the presence of solutes and chelators (figure 5.5), exhibited almost constant retention up to ~ 10 mg/l feed concentration with an average retention about 90 %. Conversely, Co^{2+} retention values in the presence of EDTA increased in an approximately linear relationship with metals concentration in the feed (from 30 % at 2 mg/l to 80% at 10 mg/l). Beyond the 10 mg/l feed concentration, the retention of Co^{2+} became insensitive to the presence of chelators and exhibited an approximately linear decrease from 80% to 20% retention at 60 mg/l feed concentration. It should be noted that an enhancement of the retention of Co^{2+} is obtained by NTA in this range of concentrations.

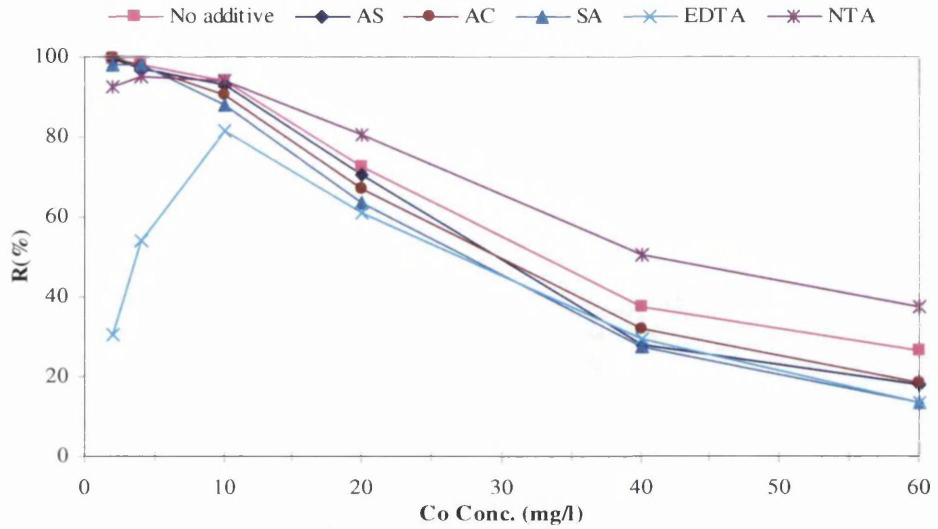


Figure 5.5 Co^{2+} *retention in the presence of PEI and various chelating agents as function of mixture feed metal concentrations. (1 g/l PEI, 0.2 mM chelating agents, pH 5.5).*

Retention of Cd^{2+} in the presence of solutes and chelators (figure 5.6), showed less affinity of PEI to complex Cd^{2+} and no real retention observed at high Cd^{2+} concentration in the feed solutions ($Cd^{2+} > 10$ mg/l). However, little enhancement of Cd^{2+} retention was observed by the addition of chelators in the following order: EDTA> NTA >AS >SA.

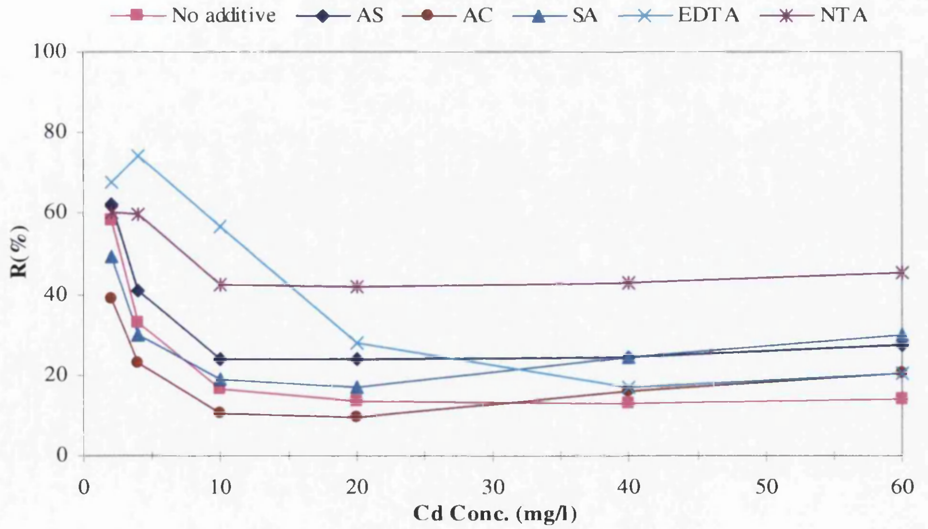


Figure 5.6 Cd^{2+} *retention in the presence PEI and various chelating agents as function of mixture feed metal concentrations. (1 g/l PEI, 0.2 mM chelating agents, pH 5.5).*

5.2.2 Retention profile with 2 mM chelating agents

For the second experimental scheme when the concentration of solutes or chelators was increased from 0.2 mM to 2 mM, the results showed a significant change to the retention of metal ions (figs. 5.7- 5.12).

Figure (5.7) shows the retention profile of Cu^{2+} in the absence and presence of various chelators. The maximum retention of Cu^{2+} was determined in Cu^{2+}/ PEI complex (no additive) or in the presence of additive chelating agents over the entire range of concentration. Due to the competition of Cu^{2+} and PEI with such chelators, the retention of Cu^{2+} decreases in the presence of various chelators in the following order: SA > AC > AS > NTA > EDTA. It is seen from figure (5.7) that Cu^{2+} retention decreases by raising the feed concentration except when the EDTA appears in the complex solutions. However, PEI showed poor affinity to bind Cu^{2+} in the presence of EDTA and such differences become significant at lower feed concentration.

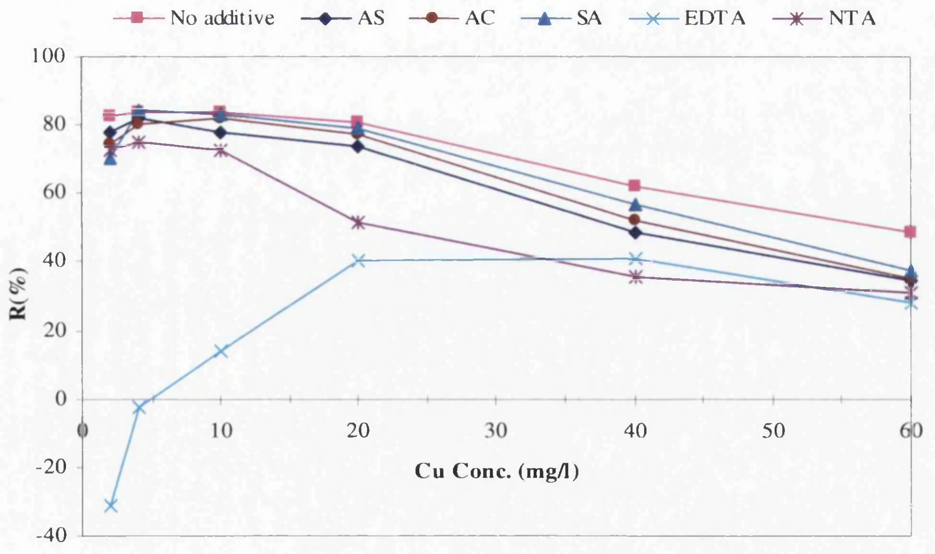


Figure 5.7 *Cu^{2+} retention in the presence PEI and various chelating agents as function of mixture feed metal concentrations. (1 g/l PEI, 2 mM chelating agents, pH 5.5).*

As shown in figure (5.8), the presence of EDTA or NTA in the solutions of metal/ PEI caused a significant reduction on Zn^{2+} retention. Thus, the average retention was observed at 50%. Also, it should be noted that an enhancement of the retention of Zn^{2+} (about 12%) is obtained by the addition of SA to the complex solution.

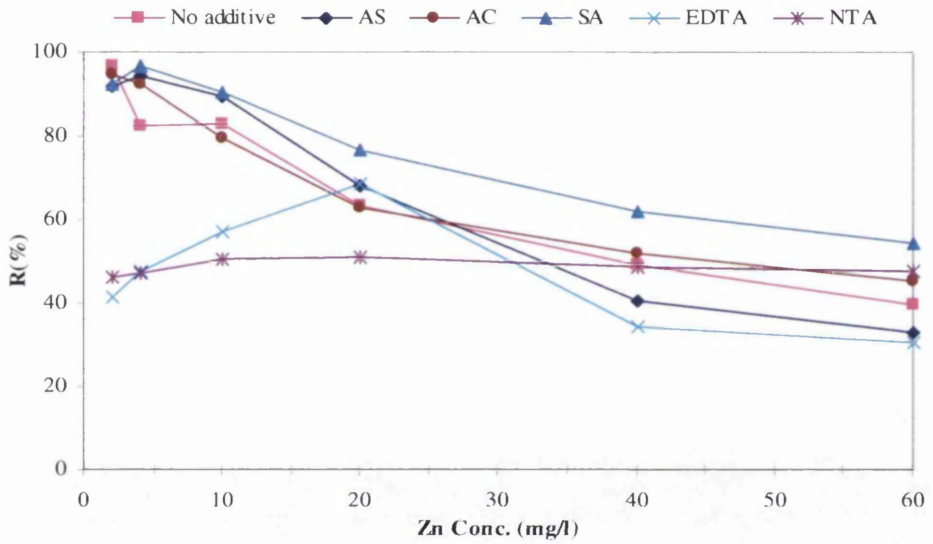


Figure 5.8 Zn^{2+} *retention in the presence PEI and various chelating agents as function of mixture feed metal concentrations. (1 g/l PEI, 2 mM chelating agents, pH 5.5).*

The plot of Cr^{6+} retention under competition of chelators with metal/ polymer complex (figure 5.9), showed almost low and constant retention of Cr^{6+} in the presence of EDTA or NTA by (45%, 70%) respectively. However, similar trend of retention profile was observed for other chelators in the following order: SA > AC > AS.

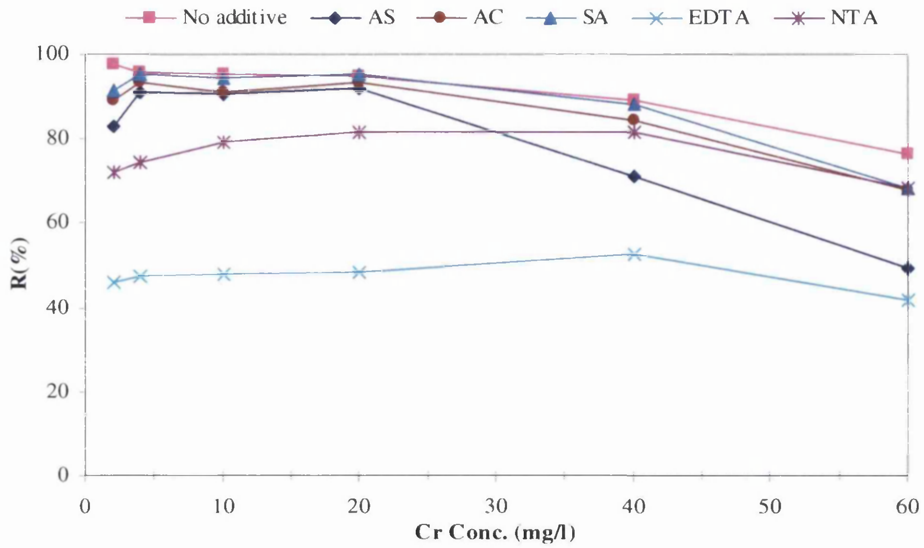


Figure 5.9 *Cr^{6+} retention in the presence PEI and various chelating agents as function of mixture feed metal concentrations. (1 g/l PEI, 2 mM chelating agents, pH 5.5).*

In Figure (5.10), the presence of EDTA or NTA in the complex solutions showed a significant impact of Ni^{2+} retention. At low feed concentrations, the observed retention of Ni^{2+} was low due to strong competition of EDTA or NTA on the available site of the polymer. In contrast, AS and SA showed a better performance of Ni^{2+} retention by about 20% in the entire range of feed concentration between 10 and 30 mg/l.

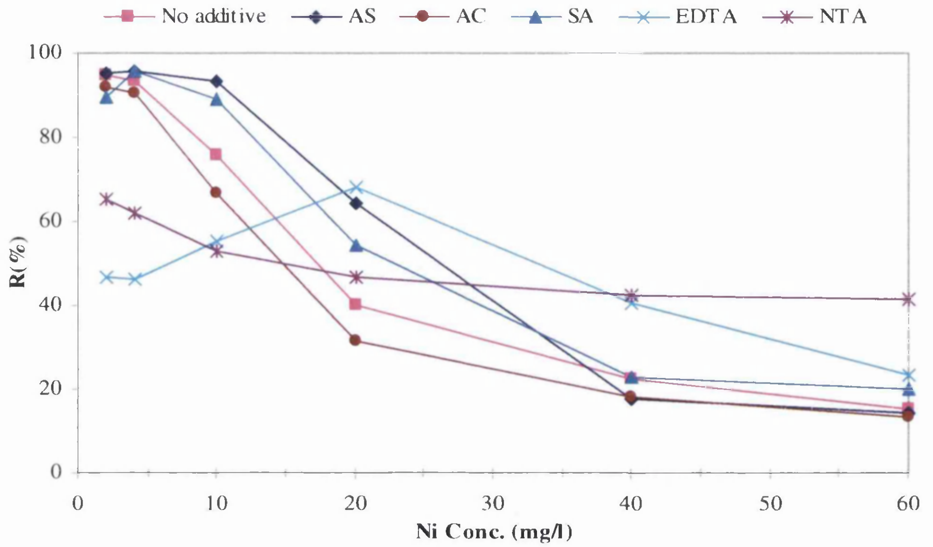


Figure 5.10 *Ni^{2+} retention in the presence PEI and various chelating agents as function of mixture feed metal concentrations. (1 g/l PEI, 2 mM chelating agents, pH 5.5).*

The addition of EDTA to the metal/ polymer complex (figure 5.11), showed a poor retention of Co^{2+} (~ 20%) in the entire metal concentrations range considered in this experiment. Also, variations of the retention were small in the presence of various chelating agents except with NTA at high feed concentration where the Co^{2+} retention was increased by 20%.

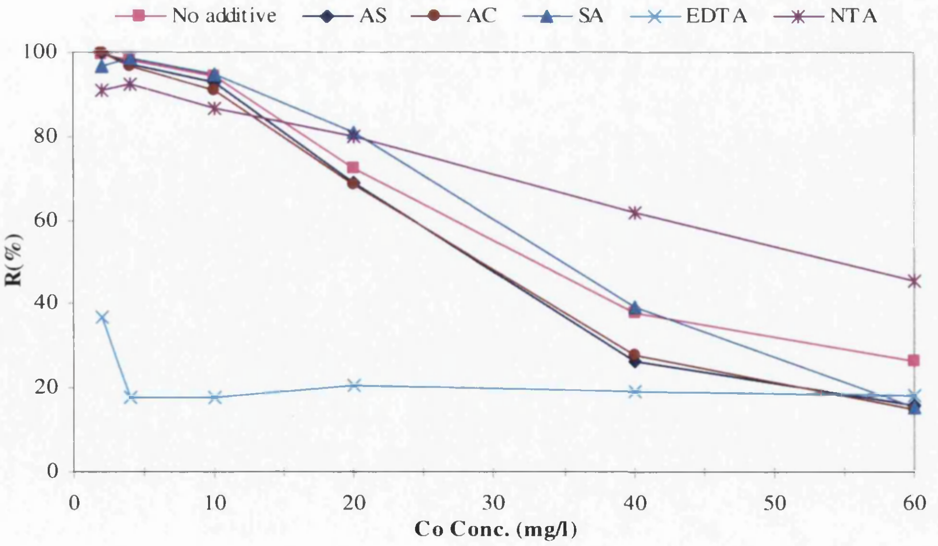


Figure 5.11 Co^{2+} *retention in the presence PEI and various chelating agents as function of mixture feed metal concentrations. (1 g/l PEI, 2 mM chelating agents, pH 5.5).*

In figure (5.12), PEI showed less affinity to complex Cd^{2+} and the lowest retention was observed. In contrast, the presence of various solutes and chelators showed an enhancement to the retention of Cd^{2+} in complex solutions and the extent of enhancement decreases in the following order: AS > EDTA > NTA > SA > AC.

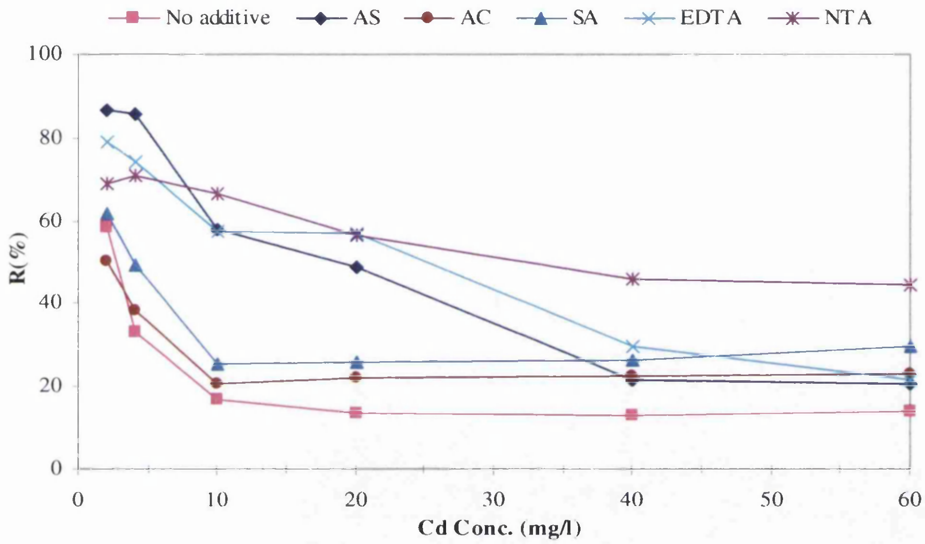


Figure 5.12 *Cd^{2+} retention in the presence PEI and various chelating agents as function of mixture feed metal concentrations. (1 g/l PEI, 2 mM chelating agents, pH 5.5).*

5.3. Effect of EDTA on metal ions retention in the absence of PEI

From the results of previous experiments of chelating agents, EDTA showed a significant effect (as competitive chelating agent) on metal ions retention using polymer enhanced ultrafiltration process. The observed retention values of metal ions using PEI in the presence of EDTA are shown in (figures 5.7- 5.12). It was clear that the addition of EDTA (2 mM) significantly affected the retention and that this was metal ion dependent. However, it is important to evaluate the effect of EDTA on metal ions retention profiles in the absence of PEI, using various feed streams of metal ions (single, binary and mixtures metal solutions) in batch mode of ultrafiltration process. (See section 3.4.3.1 for the details of the experiments procedures).

5.3.1 Effect of EDTA on the retention of metal ions in mixture solution

Figure (5.13) illustrates the typical rejection of metal ions in mixture metals solution in the presence of EDTA as a function of metal feed concentrations. Two types of metal rejection were observed, the positive rejection for (Zn^{2+}, Cd^{2+} Ni^{2+} and Co^{2+}), and the negative rejection was observed for Cu^{2+} and Cr^{6+} suggesting that the permeate has a higher concentrations than the feed for both metals. However, the metals rejection profiles were in the following order: $Zn^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Cr^{6+} > Cu^{2+}$.

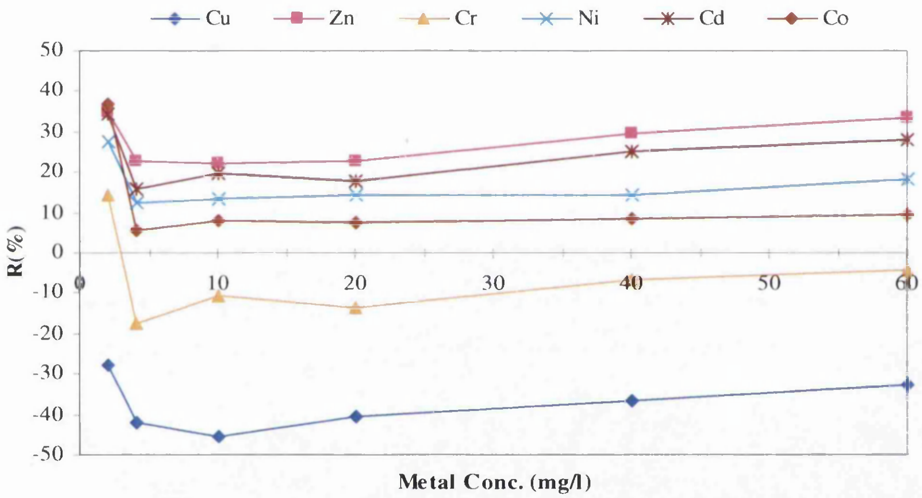


Figure 5.13 *The effect of EDTA on the rejection of metal ions using batch mode ultrafiltration. The experiments were carried out at different feed concentrations of mixture metal solutions; EDTA was 2mM and the pH 5.5.*

5.3.2 Effect of EDTA on the retention of ($Cu^{2+}$and Zn^{2+}) in binary metal solution

The effect of EDTA on the rejection of $Cu^{2+}$and Zn^{2+} in binary metal solution using batch mode ultrafiltration was investigated. The plot of metal ions rejection for $Cu^{2+}$and Zn^{2+} (figure 5.14), showed a similar trend of retention for both metal in comparison to their retention in mixture metal solutions. The positive rejection (~ 40%) was observed for

Zn^{2+} and the negative rejection for Cu^{2+}, indicating a similar influence of EDTA on the metal ions rejection in both solutions (binary and mixture solutions).

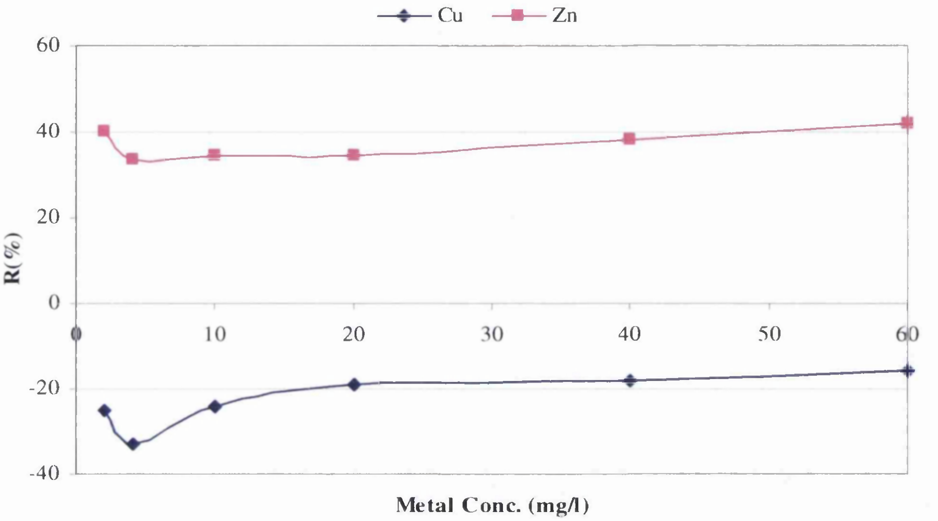


Figure 5.14 *The effect of EDTA on the rejection of* Cu^{2+} and Zn^{2+} *using batch mode ultrafiltration. The experiments were carried out at different feed concentrations of binary metal solutions (*Cu^{2+} and Zn^{2+}*), EDTA was 2mM and the pH 5.5.*

5.3.3 Effect of EDTA on the retention of (Cu^{2+}) in single metal solution

Rejection of Cu^{2+} plotted as a function of metal concentration for aqueous Cu^{2+} solutions in the presence of EDTA (figure 5.15) showed a negative rejection (-30%) of Cu^{2+} at all metal feed concentration, suggesting that the presence of EDTA caused the negative rejection of Cu^{2+} for all different concentrations of feed solutions studied.

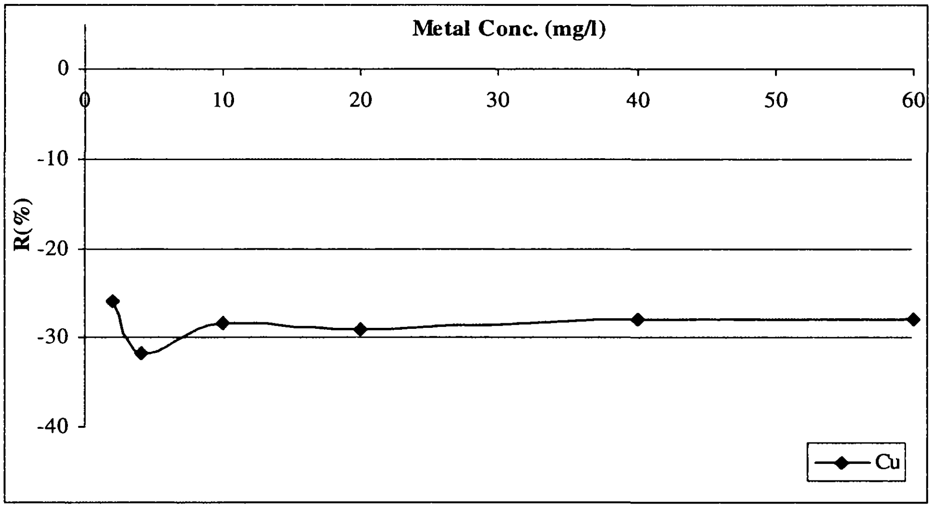


Figure 5.15 The effect of EDTA on the rejection of Cu^{2+} using batch mode ultrafiltration. The experiments were carried out at different feed concentrations of single metal solution (Cu^{2+}); EDTA was 2mM and the pH 5.5.

5.4. Binding studies and analysis of mixture metals with PEI in the presence of different chelators

Also the investigation for binding studies of mixture metals (Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+}, and Cd^{2+}) with PEI in batch mode PEUF were considered in the presence of low molecular weight solutes and chelators. The influences of the chelating agents (Ammonium sulfate, Sodium acetate, Ammonium chloride, NTA and EDTA) on the binding of several kinds of heavy metal ions and their competitions effect were examined in the presence of PEI in more details according to Langmuir isotherms (Appendix 3). The chelating agents were introduced individually to the complex solutions (mixture of metals and polymer) and both concentrations 0.2 mM and 2 mM were used in these investigations. (Details of the experiments methods have been described previously in section 3.4.3).

5.4.1 Investigation of the binding mixture metals to PEI in the presence of 0.2 mM chelating agents

In an effort to further understand for the adsorption process of heavy metal ions to PEI under the influences of various chelating agents, the maximum binding capacity of PEI to the metal ions in the complex solutions was estimated for the plots of metal retention as function of metals concentrations (figures 5.1- 5.6). Therefore, the applicability of the Langmuir isotherm (equation 3.3) to these systems was explored and the experimental data from batch mode polymer enhanced ultrafiltration were correlated using the linearised Langmuir equation (equation 3.5). The Langmuir isotherms allowed estimation of maximum capacity of the polymer for metal ions (Q_{max}), and the equilibrium constant (K_L) in competitive processes (tables 5.1- 5.3). Results acquired from the rearranged Langmuir equation showed that the Langmuir model adequately describes the process. This is evident from the values of R^2. However, the goodness of fit of the data for Cr^{6+} in the presence of NTA or EDTA is quite poor. This is possibly because little retention occurred due to competitive influences of these chelating agents. The experimental values of maximum adsorption capacities (Q_{max}) for mixture metal ions in the absence of chelating agents were: Cu^{2+} 68.03 mg/g (1.07 mmol/g), Cr^{6+} 59.88 mg/g (1.15 mmol/g), Zn^{2+} 25.32 mg/g (0.387 mmol/g), Co^{2+} 14.43 mg/g (0.245 mmol/g), Ni^{2+} 8.75 mg/g (0.149 mmol/g) and Cd^{2+} 4.62 mg/g (0.041 mmol/g). In the competitive systems, the adsorption capacities of Cu^{2+} were observed as follow: EDTA 45.45 mg/g (0.71 mmol/g) > ammonium chloride 44.44 mg/g (0.7 mmol/g) > sodium acetate 38.61 mg/g (0.6 mmol/g) > ammonium sulfate 33.45 mg/g (0.526 mmol/g) > NTA 31.9 mg/g (0.5 mmol/g), for Cr^{6+} they were in the following order: sodium acetate 55.55 mg/g (1.07 mmol/g) > ammonium chloride 53.76 mg/g (1.034 mmol/g) > EDTA 53.19 mg/g (1.023 mmol/g) > ammonium sulfate 50.25 mg/g (0.97 mmol/g) > NTA 43.48 mg/g (0.84 mmol/g), for Zn^{2+} they were in the following order: EDTA 23.92 mg/g (0.366 mmol/g) > NTA 22.93 mg/g (0.35 mmol/g) > sodium acetate 16.45 mg/g (0.252 mmol/g) > ammonium chloride 15.72 mg/g (0.24 mmol/g) > ammonium sulfate 15.22 mg/g (0.233 mmol/g), for Ni^{2+} they were in the following order: NTA 21.46 mg/g (0.36 mmol/g) > ammonium sulfate 9.37 mg/g (0.16 mmol/g) > sodium acetate 7.98 mg/g (0.136 mmol/g)

> EDTA 7.59 mg/g (0.129 mmol/g) > ammonium chloride 7.42 mg/g (0.126 mmol/g) and for Co^{2+} the maximum capacities were: NTA 22.62 mg/g (0.38 mmol/g) > EDTA 13.13 mg/g (0.223 mmol/g) > ammonium sulfate 12.25 mg/g (0.21 mmol/g) > ammonium chloride 12.08 mg/g (0.205 mmol/g) > sodium acetate 10.15 mg/g (0.172 mmol/g). An inverse trend was observed for the Cd^{2+} binding capacity in the presence of chelating agents compared to other metal ions. The enhancement of Cd^{2+} binding decreased in the following order: NTA 17.7 mg/g (0.157 mmol/g) > sodium acetate 10.12 mg/g (0.09 mmol/g) > ammonium sulfate 9.36 mg/g (0.083 mmol/g) > EDTA 7.87 mg/g (0.07 mmol/g) > ammonium chloride 4.85 mg/g (0.043 mmol/g), while that obtained without chelators was 4.62 mg/g (0.041 mmol/g).

It is concluded that the presence of other chelating agents in the complex solution affects the maximum adsorption of a particular ion and metal ions-chelates compete against each other for the available sites of the polymer. On the other hand, the adsorption capacity for metal ion was also changed depending on the coupled chelating agent.

Table 5.1 *Cu^{2+} and Zn^{2+} experimental data from the application of Langmuir isotherms for mixture metal ions with 0.2 mM chelating agents in batch mode PEUF process, the data were fitted to linearised form of these experiments.*

Experiment Metals + (1 g/l PEI) + (0.2 mM add.)	Cu^{2+}					Zn^{2+}				
	Q_{max}		K_L		R^2	Q_{max}		K_L		R^2
	(mg/ g_{PEI})	(mmol/ g_{PEI})	(mg/ l)	(mmol/ l)		(mg/ g_{PEI})	(mmol/ g_{PEI})	(mg/ l)	(mmol/ l)	
PEI	68.03	1.07	14.73	0.232	0.991	25.32	0.387	4.52	0.069	0.981
PEI+ AS	33.45	0.526	7.22	0.114	0.984	15.22	0.233	0.69	0.01	0.931
PEI+ AC	44.44	0.7	7.75	0.122	0.992	15.72	0.24	1.52	0.023	0.942
PEI+ SA	38.61	0.6	10.69	0.168	0.97	16.45	0.252	0.88	0.013	0.924
PEI+EDTA	45.45	0.71	6.31	0.1	0.984	23.92	0.366	6.14	0.094	0.977
PEI+ NTA	31.9	0.5	4.23	0.067	0.989	22.93	0.35	4.46	0.068	0.996

Table 5.2 *Cr^{6+} and Ni^{2+} experimental data from the application of Langmuir isotherms for mixture metal ions with 0.2 mM chelating agents in batch mode PEUF process, the data were fitted to linearised form of these experiments.*

Experiment Metals + (1 g/l PEI) + (0.2 mM add.)	Cr^{6+}					Ni^{2+}				
	Q_{max}		K_L		R^2	Q_{max}		K_L		R^2
	(mg/ g_{PEI})	(mmol/ g_{PEI})	(mg/ l)	(mmol/ l)		(mg/ g_{PEI})	(mmol/ g_{PEI})	(mg/ l)	(mmol/ l)	
PEI	59.88	1.15	2.56	0.049	0.999	8.75	0.149	0.36	0.006	0.996
PEI+ AS	50.25	0.97	2.83	0.054	0.997	9.37	0.16	0.53	0.009	0.952
PEI+ AC	53.76	1.034	2.82	0.054	0.998	7.42	0.126	0.49	0.0083	0.978
PEI+ SA	55.55	1.07	1.93	0.037	0.999	7.98	0.136	0.37	0.0063	0.792
PEI+EDTA	53.19	1.023	6.46	0.124	0.358	7.59	0.129	1.08	0.0184	0.991
PEI+ NTA	43.48	0.84	4.45	0.085	0.323	21.46	0.36	13.47	0.23	0.996

Table 5.3 *Co^{2+} and Cd^{2+} experimental data from the application of Langmuir isotherms for mixture metal ions with 0.2 mM chelating agents in batch mode PEUF process, the data were fitted to linearised form of these experiments.*

Experiment Metals + (1 g/l PEI) + (0.2 mM add.)	Co^{2+}					Cd^{2+}				
	Q_{max}		K_L		R^2	Q_{max}		K_L		R^2
	(mg/ g_{PEI})	(mmol/ g_{PEI})	(mg/ l)	(mmol/ l)		(mg/ g_{PEI})	(mmol/ g_{PEI})	(mg/ l)	(mmol/ l)	
PEI	14.43	0.245	0.19	0.003	0.989	4.62	0.041	7.44	0.066	0.774
PEI+ AS	12.25	0.21	0.28	0.0047	0.98	9.36	0.083	12.1	0.11	0.861
PEI+ AC	12.08	0.205	0.198	0.0033	0.986	4.85	0.043	12.78	0.114	0.695
PEI+ SA	10.15	0.172	0.13	0.0022	0.938	10.12	0.09	22.67	0.2	0.897
PEI+EDTA	13.13	0.223	5.11	0.087	0.915	7.87	0.07	1.74	0.015	0.884
PEI+ NTA	22.62	0.38	1.02	0.017	0.993	17.7	0.157	10.95	0.097	0.923

5.4.2 Competitive binding of metal ions to PEI in the presence of chelating agents

Under competitive conditions of 2 mM chelating agents, the maximum capacity of metal binding to the polymer (see tables 5.4- 5.6) and possible way of competition (see figures 5.16- 5.21) according to Langmuir isotherms model (equations 3.3 and 3.5) were investigated.

The experimental data for mixed metal ions (Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+}, and Cd^{2+}) were correlated by linearised Langmuir equation. The representation of $1/Q$ versus $1/Y$, following Langmuir treatment for the adsorption of metal ions to the PEI in the absence and presence of various chelators, is shown in figures (5.16- 5.21).

Figure (5.16) shows that the binding profile of Cu^{2+} was inhibited by the presence of several solutes and chelators. According to the results obtained when the type of solutes or chelators changed, there appeared to be remarkable difference in Q_{max} with the type of binding curves, such as, for EDTA. The maximum binding amount, in terms of polyethelenimine (PEI) was determined from the intercept and slope of the plots of the binding curves, and these values are summarized in table 5.4. The value of Q_{max} for the standard complex solution of Cu^{2+}/ PEI (no additive) was found to be 68.03 mg/g (1.07 mmol/g) and the value decreased with addition of 2mM of solutes or chelators to the complex in the following order: ammonium chloride 35.97 mg/g (0.566 mmol/g) > sodium acetate 31.85 mg/g (0.5 mmol/g) > ammonium sulfate 24.81 mg/g (0.39 mmol/g) > NTA 18.08 mg/g (0.28 mmol/g). While the equilibrium constant occurs in the same order of maximum binding results, for no additive complex the equilibrium constant was 14.73 mg/l (0.232 mmol/l) > ammonium chloride 7.86 mg/l (0.124 mmol/l) > sodium acetate 5.28 mg/l (0.083 mmol/l) > ammonium sulfate 4.72 mg/l (0.074 mmol/l) > NTA 4.65 mg/l (0.073 mmol/l). In the case of EDTA, the application of Langmuir isotherms presents negative Q_{max} and low R^2 value. This observation of negative sign supports the data exhibited in figure (5.7), and that the observed Cu^{2+} retention is inhibited by the presence of 2 mM EDTA in the metals/ polymer complexes.

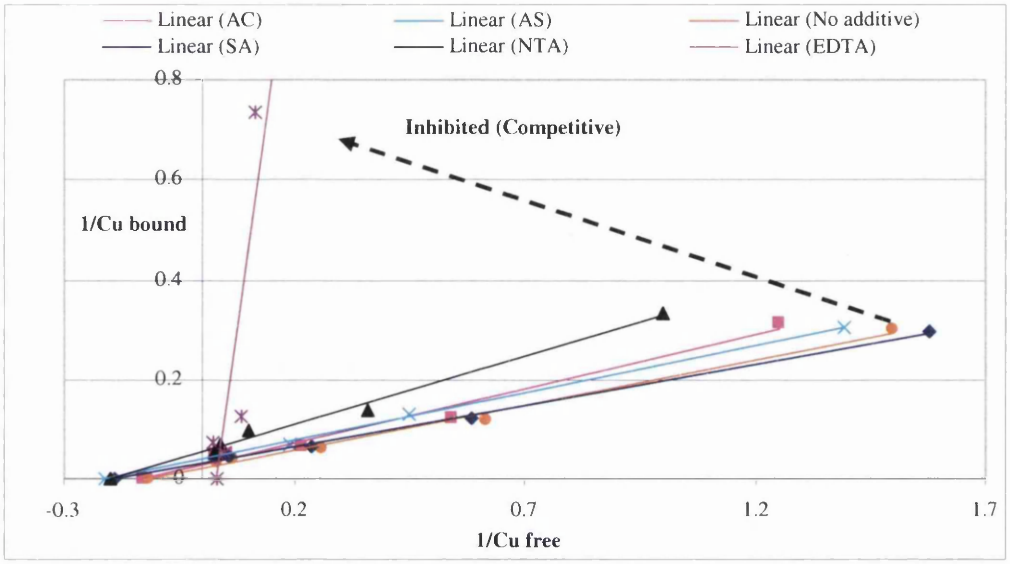


Figure 5.16 *Competitive adsorption of Cu^{2+} in the presence of various chelating agents according to the application of linearised form of langmuir isotherms. (At different concentrations of mixture metal ions, 2 mM chelating agents and 1 g/l PEI)*

Figure (5.17) illustrate the binding of Zn^{2+} to the PEI in the absence and presence of various chelating agents. It was observed that the binding type of Zn^{2+} to PEI in the presence of EDTA or NTA was different from other chelators, and this was caused by the inhibitory effects of the EDTA and NTA which is exhibited by the negative sign of maximum binding capacities (Q_{max}) in table 5.4. On the other hand, the results of Q_{max} obtained under the presence of ammonium sulfate, ammonium chloride and sodium acetate were 16.47 mg/g (0.252 mmol/g), 16.69 mg/g (0.255 mmol/g) and 19.49 mg/g (0.298 mmol/g), respectively, while that obtained without chelators was 25.32 mg/g (0.387 mmol/g). Also, the equilibrium constant occurs in the following order: sodium acetate 0.53 mg/l (0.008 mmol/l), ammonium sulfate 0.76 mg/l (0.012 mmol/l), ammonium chloride 1.08 mg/l (0.016 mmol/l) and 4.52 mg/l (0.069 mmol/l) for mixture of metals/ polymer without chelators.

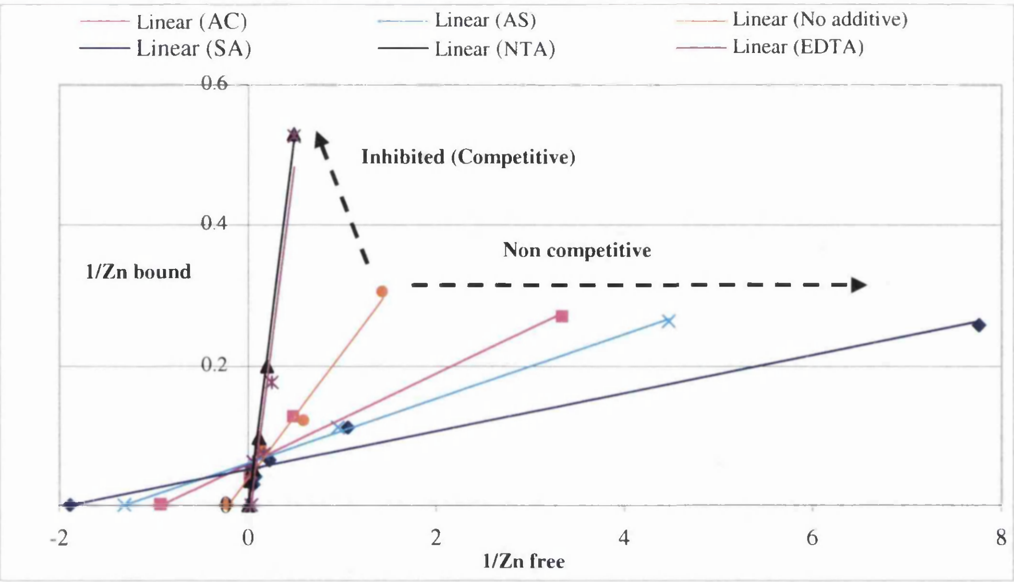


Figure 5.17 *Adsorption type of Zn^{2+} in the presence of various chelating agents according to the application of linearised form of Langmuir isotherms. (At different concentrations of mixture metal ions, 2 mM chelating agents and 1 g/l PEI)*

In order to compare the binding performances of PEI for copper and zinc treatments in a mixed solution of metal ions under the influences of inhibitors, the values of Q_{max}, K_L and R^2 obtained from the application of Langmuir isotherms are summarized in Table 5.4

***Table 5.4** Cu^{2+} and Zn^{2+} experimental data from the application of Langmuir isotherms for mixture metal ions with 2 mM chelating agents in batch mode PEUF process, the data were fitted to linearised form of these experiments.*

Experiment	Cu^{2+}					Zn^{2+}				
Metals + (1 g/l PEI) + (2 mM add.)	Q_{max}		K_L		R^2	Q_{max}		K_L		R^2
	(mg/ g_{PEI})	(mmol/ g_{PEI})	(mg/ l)	(mmol/ l)		(mg/ g_{PEI})	(mmol/ g_{PEI})	(mg/ l)	(mmol/ l)	
PEI	68.03	1.07	14.73	0.232	0.991	25.32	0.387	4.52	0.069	0.981
PEI+ AS	24.81	0.39	4.72	0.074	0.998	16.47	0.252	0.76	0.012	0.993
PEI+ AC	35.97	0.566	7.86	0.124	0.978	16.69	0.255	1.08	0.016	0.94
PEI+ SA	31.85	0.5	5.28	0.083	0.995	19.49	0.298	0.53	0.008	0.953
PEI+EDTA	-5.25	-0.08	-34.4	-0.54	0.951	-45.4	-0.69	-48.2	-0.74	0.919
PEI+ NTA	18.08	0.28	4.65	0.073	0.989	-97.1	-1.48	-109	-1.67	0.997

The treatment of Cr^{6+} in the presence of different chelating agents (figure 5.18), showed a competitive impact for all these agents compared with the polymer/ metals complex solution (no additive). However, the inhibitory effects caused by NTA and EDTA agents was very significant and this was clear from the negative signs of maximum binding capacities (Q_{max}) and the equilibrium constants (K_L) shown in table 5.5. On the other hand, the values of (Q_{max}) obtained in the presence of sodium acetate, ammonium chloride and ammonium sulfate were 55.86 mg/g (1.074 mmol/g), 53.47 mg/g (1.028 mmol/g) and 50 mg/g (0.96 mmol/g), respectively, while that obtained without chelating agent was 59.88 mg/g (1.15 mmol/g). It was found that the sequence of equilibrium constants was in contrast with binding capacity order as follows: ammonium sulfate 4.46 mg/l (0.086 mmol/l), ammonium chloride 3.62 mg/l (0.07 mmol/l), sodium acetate 2.61 mg/l (0.05 mmol/l) and for the complex in the absence of chelators was 2.56 mg/l (0.049 mmol/l).

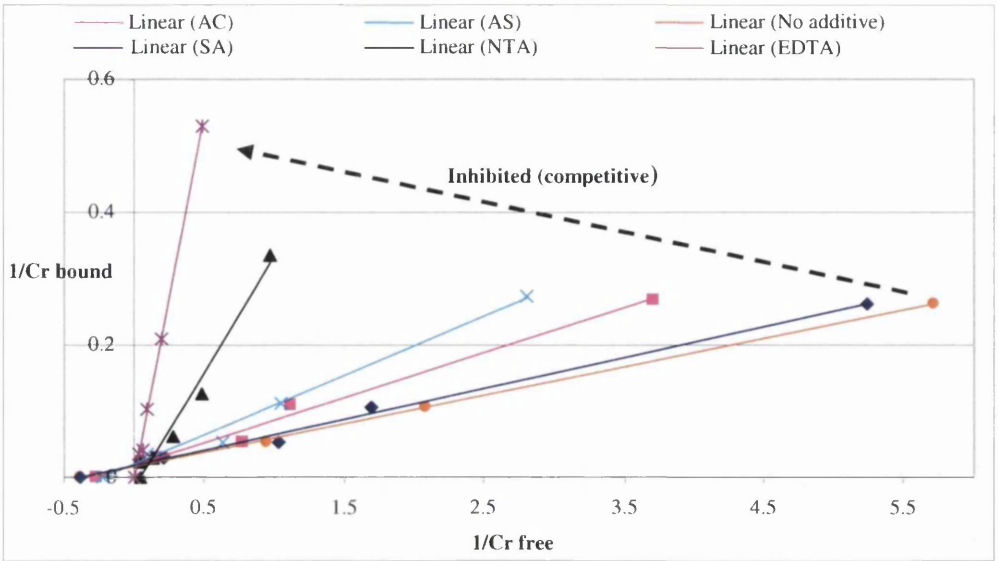


Figure 5.18 *Competitive adsorption of* Cr^{6+} *in the presence of various chelating agents according to the application of linearised form of Langmuir isotherms. (At different concentrations of mixture metal ions, 2 mM chelating agents and 1 g/l PEI)*

Results for Ni^{2+} binding (figure 5.19), could be classified into competitive and non competitive adsorption due to the presence of various solutes and chelators in the mixture of metal/ PEI complex solution. It was observed that, the presence of sodium acetate and ammonium sulfate in the complex showed an enhancement for the Ni^{2+} binding. In contrast, the binding of Ni^{2+} using PEI was inhibited by the presence of other chelating agents and the order of inhibition increased as follow: ammonium chloride < NTA < EDTA. However, these observations were supported by the results of application Langmuir isotherms shown in table 5.5. The binding capacity for Ni^{2+}/ PEI in the complex metals polymer solution was changed depending on the type of chelators. In the cases of sodium acetate and ammonium sulfate in the complex solution, the affinity of PEI to bind Ni^{2+} was increased indicating maximum capacities (Q_{max}) and low equilibrium constants (K_L) as shown in table 5.5. The presence of NTA in the complex showed a high maximum capacity 23.04 mg/g (0.39 mmol/g) and high equilibrium constant 12.9 mg/l (0.22 mmol/l). On the other hand, poor binding of Ni^{2+} was clear from the negative sign of (Q_{max}) in the competitive reaction of EDTA with the complex.

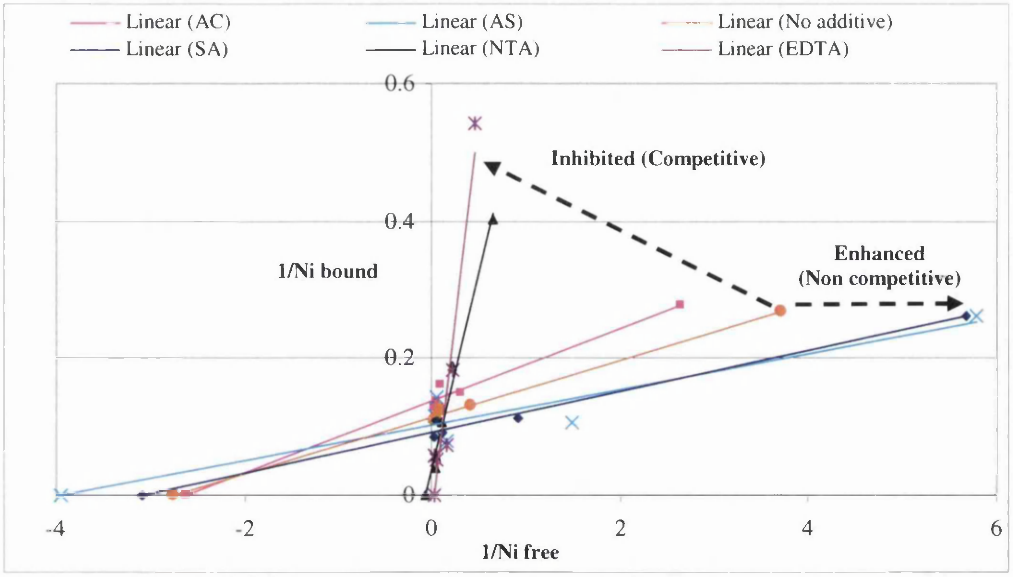


Figure 5.19 *Adsorption type of* Ni^{2+} *in the presence of various chelating agents according to the application of linearised form of Langmuir isotherms. (At different concentrations of mixture metal ions, 2 mM chelating agents and 1 g/l PEI)*

The adsorption isotherm coefficients for Cr^{6+} and Ni^{2+} obtained from the slopes and intercepts of the linear plots of Langmuir adsorption are listed in table 5.5 below.

Table 5.5 Cr^{6+} *and* Ni^{2+} *experimental data from the application of Langmuir isotherms for mixture metal ions with 2 mM chelating agents in batch mode PEUF process, the data were fitted to linearised form of these experiments.*

Experiment	Cr^{6+}					Ni^{2+}				
Metals + (1 g/l PEI) + (2 mM add.)	Q_{max}		K_L		R^2	Q_{max}		K_L		R^2
	(mg/ g_{PEI})	*(mmol/ g_{PEI})*	*(mg/ l)*	*(mmol/ l)*		*(mg/ g_{PEI})*	*(mmol/ g_{PEI})*	*(mg/ l)*	*(mmol/ l)*	
PEI	59.88	1.15	2.56	0.049	0.999	8.75	0.149	0.36	0.006	0.996
PEI+ AS	50	0.96	4.46	0.086	0.984	9.76	0.166	0.25	0.004	0.816
PEI+ AC	53.47	1.028	3.62	0.07	0.986	7.25	0.123	0.38	0.0065	0.965
PEI+ SA	55.86	1.074	2.61	0.05	0.993	10.92	0.186	0.32	0.0054	0.983
PEI+EDTA	-83.3	-1.6	-95.2	-1.83	0.997	-35.8	-0.61	-40.9	-0.697	0.922
PEI+ NTA	-55.5	-1.07	-19.5	-0.37	0.977	23.04	0.39	12.9	0.22	0.985

In figure (5.20), the Co^{2+} binding curves showed the competitive effects of the presence of different chelating agents and the influences of these inhibitions were exhibited in the following order: NTA 23.31 mg/g (0.39 mmol/g) > sodium acetate 12.55 mg/g (0.213 mmol/g) > ammonium sulfate 11.4 mg/g (0.193 mmol/g) > ammonium chloride 11.25 mg/g (0.19 mmol/g) as shown in table 5.6. In fact the presence of chelators in the complex solution exhibited lower adsorption capacity for Co^{2+} ions compared with no additives solution except for NTA. The details of Langmuir adsorption results are shown in tables 5.6 below.

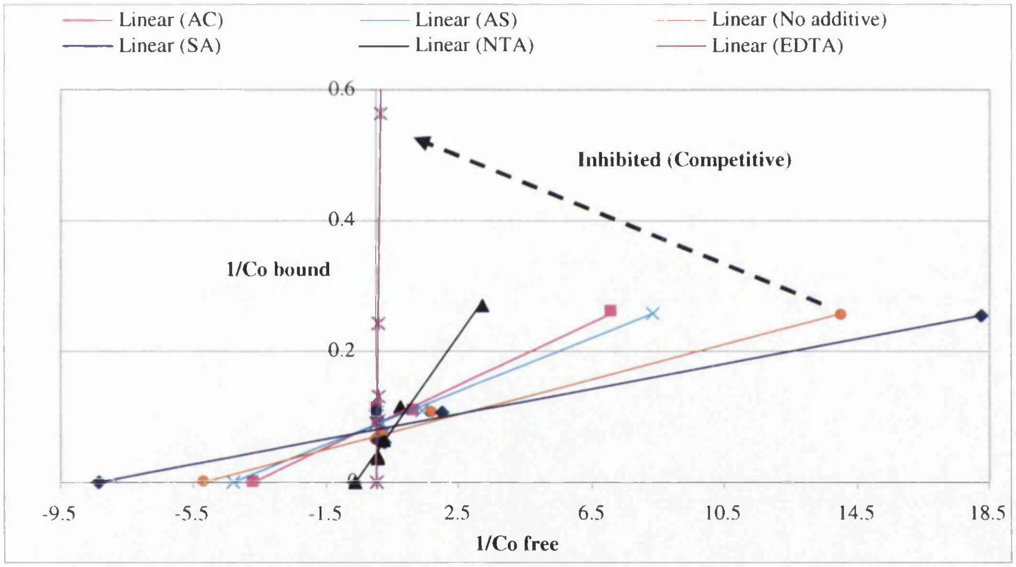


***Figure 5.20** Competitive adsorption of Co^{2+} in the presence of various chelating agents according to the application of linearised form of Langmuir isotherms. (At different concentrations of mixture metal ions, 2 mM chelating agents and 1 g/l PEI)*

Since it was determined that the existence of the chelating agents evidently enhanced the retention of Cd^{2+} ions in the complex solution (figure 5.12), further studies were focused on the binding of Cd^{2+} ions to PEI in the presence of various chelators. For all the chelating agents tested in this study, the non competitive binding curves are illustrated in (figure 5.21). In comparison to a mixed solution without chelators, the enhancement of Cd^{2+} adsorption capacities was influenced by presence of chelators in the complex in the following order: NTA 26.81 mg/g (0.238 mmol/g) > EDTA 18.48 mg/g (0.164 mmol/g) > ammonium sulfate 9.41 mg/g (0.084 mmol/g) > sodium acetate 8.36 mg/g (0.074 mmol/g) > ammonium chloride 7.97 mg/g (0.071 mmol/g). The results of maximum binding capacities (Q_{max}) and equilibrium constants (K_L) can be seen in table 5.6. In fact the evidence of low R^2 can be explained by the low affinity of PEI for binding Cd^{2+} ions, and this is clear from the low retention observed during batch mode polymer enhanced ultrafiltration experiments.

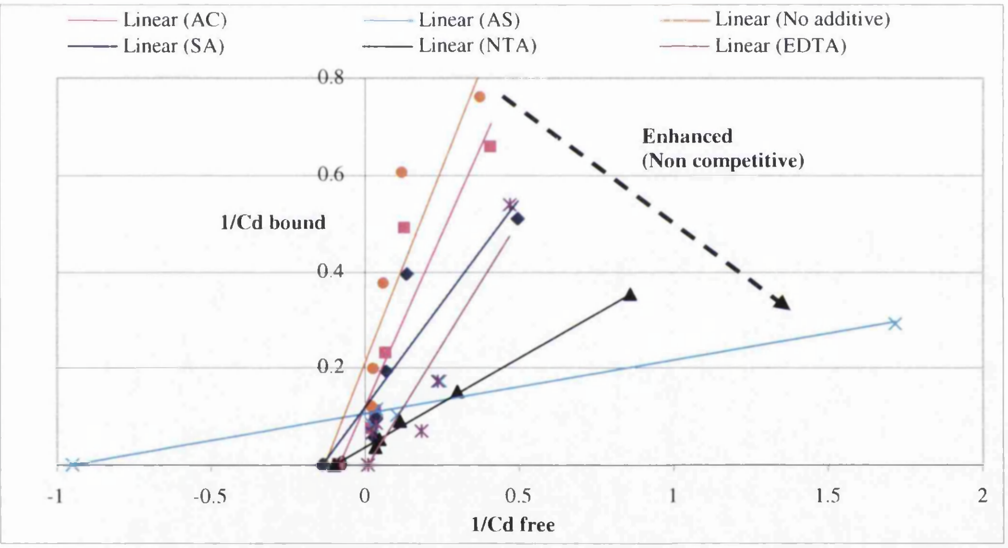


Figure 5.21 *Non competitive adsorption for Cd^{2+} in the presence of various chelating agents according to the application of linearised form of Langmuir isotherms. (At different concentrations of mixture metal ions, 2 mM chelating agents and 1 g/l PEI)*

Table 5.6 summarizes the results of application of Langmuir isotherms adsorption (Q_{max}, K_L and R^2) obtained from a series of batch experiments with various chelating agents for Co^{2+} and Cd^{2+} binding in mixture metal/ polymer solutions.

Table 5.6 *$Co^{2+}$and Cd^{2+} experimental data from the application of Langmuir isotherms for mixture metal ions with 2 mM chelating agents in batch mode PEUF process, the data were fitted to linearised form of these experiments.*

Experiment ***Metals + (1 g/l PEI) + (2 mM add.)***	***Co^{2+}***					***Cd^{2+}***				
	Q_{max}		*K_L*		*R^2*	*Q_{max}*		*K_L*		*R^2*
	(mg/ g_{PEI})	*(mmol/ g_{PEI})*	*(mg/ l)*	*(mmol/ l)*		*(mg/ g_{PEI})*	*(mmol/ g_{PEI})*	*(mg/ l)*	*(mmol/ l)*	
PEI	14.43	0.245	0.19	0.003	0.989	4.62	0.041	7.44	0.066	0.774
PEI+ AS	11.40	0.193	0.23	0.0039	0.965	9.41	0.084	1.05	0.009	0.91
PEI+ AC	11.25	0.19	0.27	0.0046	0.957	7.97	0.071	11.45	0.1	0.814
PEI+ SA	12.55	0.213	0.12	0.002	0.934	8.36	0.074	7.21	0.064	0.756
PEI+EDTA	-46.7	-0.79	-221	-3.75	0.999	18.48	0.164	15.64	0.139	0.673
PEI+ NTA	23.31	0.395	1.67	0.028	0.988	26.81	0.238	9.85	0.087	0.997

5.5. Conclusions

In most of the previous PEUF studies using PEI, the main parameters affecting metal/polymer complexation, such as pH, loading ratio, polymer type and operating conditions were investigated for single and binary metal solutions with different modes of operation (See Chp.2, section 2.4, 6). In this work, an investigation into the batch mode PEUF process using PEI with mixture metal solutions (Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+}) in the presence of various competing solutes and chelators agents have carried out and shown different mechanisms of metals retention. The chelators competitors agents used in these investigations were: Ammonium sulfate, Ammonium chloride, Sodium acetate, Ethylenediaminetetra acetic acid (EDTA) and Nitrilotriacetic acid (NTA). Retention profiles and binding studies of metal ions was affected by the presence of these chelating competitive agents, suggesting that the competition for binding of metal ions on PEI can be seen in four possible ways:

1. The metals bind preferentially to EDTA and other chelators than to PEI.
2. The binding of the metal ions to PEI directly.
3. The binding of both chelators and metals to PEI.
4. The electrostatic binding of negatively or positively charged ions to PEI interfering with the binding of the metals.

These types of interactions would be anticipated in complex waste solutions such a landfill leachate for example. These materials are typical and in quite high concentrations as organic acids and ammonia and are mainly derived from anaerobic digestion for waste organic materials.

Comparison between the retention profiles of Cu^{2+} in mixture metals solutions with PEI in the presence of different chelators competitors, showed a significant reduction on the retention of Cu^{2+} with increasing concentrations of chelators competitors from 0.2 mM to 2 mM (figures 5.1 and 5.7), and indicating competitive binding of metal ions to PEI (figure 5.16). However, the retention profiles of Cu^{2+} under different conditions of feed in batch mode experiments at pH 5.5 were concluded and shown in figure 5.22. About 37 ± 5 % of Cu^{2+} rejection was observed with pure Cu^{2+} solution due to the direct interaction with the membrane, and about 87 ± 4 % of Cu^{2+} retention was obtained in the presence of PEI as complexing agent. The retention Cu^{2+} using PEI was relatively low (13 ± 5 %) under competitive conditions with EDTA, suggesting that the metals bind preferentially to EDTA than to PEI. In contrast, a negative rejection of Cu^{2+} (-28 ± 5 %) was observed in the presence of EDTA and indicating different mechanism appeared to have been involved.

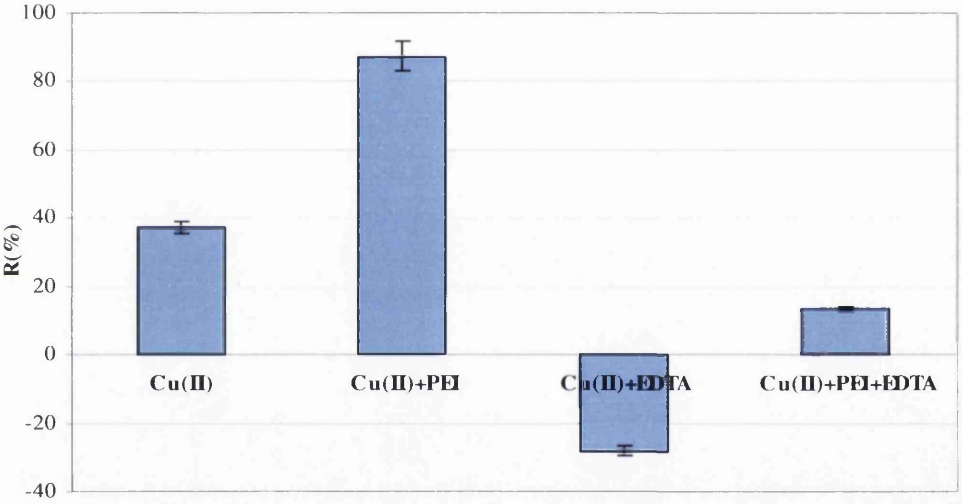


Figure 5.22 *Cu^{2+} retention profiles under different conditions of feed processes, (Solutions of Cu^{2+}, Cu^{2+}+PEI, Cu^{2+} + EDTA and Cu^{2+}+PEI+EDTA were prepared with 10 mg/l Cu^{2+}, 1 g/l PEI, 2 mM EDTA at pH 5.5).*

In the case of Zn^{2+} retention in complex solutions (figures 5.2 and 5.8), the presence of high concentrations of chelators competitors showed a lower reduction of Zn^{2+} retention compared with the presence of low concentrations of these chelators, except for sodium acetate where an enhancement of Zn^{2+} retention was observed. These observations indicate both mechanisms, competitive and non competitive, were involved in Zn^{2+} retention as shown in figure 5.17.

The presence of EDTA in the complex of metals/polymer solution showed a significant reduction of Co^{2+} and Cr^{6+} retention (figures 5.11 and 5.9), and inhibiting their complexation with PEI (figures 5. 20 and 5.18). In contrast, an increase of Co^{2+} and Ni^{2+} retention at high metal feed concentrations (> 20 mg/l) was evident in the presence of NTA (figures 5.10 and 5.11). It produced similar and high results of maximum binding capacity of both metals (tables 5.5 and 5.6) compared with the control solution. However, enhancement of Ni^{2+} retention was also observed in the presence of sodium acetate and ammonium sulfate (figure 5.10), indicating the binding of both competitors and metals to PEI was likely to be responsible. The only instance where an increase in metal retention under competitive condition of all various chelators competitors was for Cd^{2+} (figures 5.6 and 5.12), and an apparent increase in maximum binding capacity (tables 5.3 and 5.6) was expected and suggested some mechanism other than complexation may have contributed to these observations.

The Langmuir isotherm was applied to the data from competitive solutions and provided reasonable fits to the data. Suggesting that for data where complexation (non competitive binding) appears to be the main mechanism causing the observed retention of metal ions, the model provides a reasonable description of the process. For much of the data exhibiting competitive binding the application of Langmuir adsorption isotherms indicates nonsensical results such as negative values of maximum binding capacity (Q_{max}). This observation suggests that other ways of competition for binding of metal ions on PEI were likely to have been responsible, and the observed metal retention is not entirely due to complexation with PEI. Generally, the data of maximum binding capacity (Q_{max}) of metal ions to PEI and the equilibrium constants (K_L) under competitive conditions of various chelating agents competitive are summarized in table 5.7.

Table 5.7 *Summary of experimental data of* Q_{max} and K_L *from applying the Langmuir adsorption isotherm for single and mixed metal ions solutions in the absence and presence of various chelators competitors in batch mode of PEUF process, the data were fitted to linearised form of these experiments.*

Experiment Metals + (1 g/l PEI) + (2 mM add.)		***Mixed metals solutions***						***Single metal solutions***
		PEI	***PEI + AS***	***PEI + AC***	***PEI + SA***	***PEI + EDTA***	***PEI + NTA***	***PEI***
Cu^{2+}	Q_{max} (mg metal/g_{PEI})	68.03	24.81	35.97	31.85	- 5.25	18.08	169.5
	K_L (mg/l)	14.73	4.72	7.86	5.28	- 34.4	4.65	22.3
Zn^{2+}	Q_{max} (mg metal/g_{PEI})	25.32	16.47	16.69	19.49	- 45.4	- 97.08	55.2
	K_L (mg/l)	4.52	0.76	1.08	0.53	- 48.2	- 109	1.56
Cr^{6+}	Q_{max} (mg metal/g_{PEI})	59.88	50	53.47	55.86	- 83.3	- 55.55	60.6
	K_L (mg/l)	2.56	4.46	3.62	2.61	- 95.2	- 19.5	10.2
Ni^{2+}	Q_{max} (mg metal/g_{PEI})	8.75	9.76	7.25	10.92	- 35.8	23.04	19.2
	K_L (mg/l)	0.36	0.25	0.38	0.32	- 40.9	12.9	1.43
Co^{2+}	Q_{max} (mg metal/g_{PEI})	14.43	11.4	11.25	12.55	- 46.7	23.31	16.6
	K_L (mg/l)	0.19	0.23	0.27	0.12	- 221	1.67	0.76
Cd^{2+}	Q_{max} (mg metal/g_{PEI})	4.62	9.41	7.97	8.36	18.48	26.81	10.3
	K_L (mg/l)	7.44	1.05	11.45	7.21	15.64	9.85	2.08

Chapter 6

Studies of PEUF in continuous feed using cross flow ultrafiltration

6.1. Introduction

The next stage of the research was to develop the investigation further by the use of continuous feed rather than batch processes, described in the proceeding chapter. The approach was to confirm the previous measurements and calculations, and to highlight differences between batch and continuous systems.

Experiments of polymer enhanced ultrafiltration in aqueous solutions (section 3.5) were therefore performed in continuous feed processes with a variety of feed compositions. These ranged from single and mixed metal ions solutions to more complex and competitive mixtures of compounds, in continuous ultrafiltration processes using a cross flow rig (Section 3.3.4).

As with the previous study, aqueous solutions of single and mixed metal ions (Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+}) were studied. Ultrafiltration experiments of these metal ions solutions were conducted in the absence and presence of PEI. The retention of metal ions (equation 3.1) during the continuous feed of ultrafiltration experiments was determined as a function of filtration factor (equation 2.5) for a better understanding of the effect of PEI on metal ion retention. In a similar way, an investigation of the influences of different chelator competitors on metal ion retention with PEI in continuous mode operation was also made. The chelating competitors used in these investigations were: Ammonium sulfate (AS), Ammonium chloride (AC), Sodium acetate (SA), Ethylenediaminetetra acetic acid (EDTA) and Nitrilotriacetic acid (NTA). (Details of experimental methods are described in sections 3.5.1-3.5.4). Moreover, the applications of the Langmuir and Freundlich isotherms (equations 3.3 and 3.5) to these systems were investigated using linear forms of both models (equations 3.4 and 3.6) and compared with previous results (Appendix 3).

The main aims of this present work were therefore to investigate the following processes using a continuous feed:

- Retention profiles of metal ions as a function of filtration factor in the absence of both the PEI and the chelating competitive agents.
- Single metal ions retention profiles with PEI in the absence of chelating agents.
- Mixed metal ion retention with PEI in the absence and presence of various competitive chelating agents.
- The applications of the Langmuir and Freundlich isotherms for single and mixture metals solutions in the presence of PEI.
- The ability of the Langmuir isotherm model to describe the binding of mixed metal ions to PEI in the presence of different chelator competitors using a continuous feed.

6.2. Retention profiles of metal ions in continuous mode ultrafiltration

6.2.1 Metal ion retention without PEI in the absence of chelator competitors

Ultrafiltration experiments of mixture metal ions were conducted in the absence of both PEI and chelating competitive agents in a continuous process at pH 5.5 (see section 3.5.1.2). Figure 6.1 shows the concentrations of metal ions free in the permeate as a function of time. It was observed that the metal concentrations increased with increasing process time. The concentrations of Copper and Chromium in the permeate were lower compared with other metals in the solutions. However, the membrane rejection for metal ions as a function of filtration factor was described by the wash in curve of: $R = e^{-F}$ (assumes perfect mixing with no interaction with membrane, see figure 6.2). In figure 6.2, the observed retention for Cadmium, Zinc, Nickel and Cobalt showed a similar trend to the exponential retention curve, and no significant retention of these metal ions was achieved during this experiment. In contrast, the retention profiles of both Copper (Cu^{2+}) and Chromium (Cr^{6+}) were observed to be in a linear relationship with the filtration factor, indicating some degree of retention occurred for both metals ions in aqueous solution of mixture metals. The interaction may involve a complex of these two metals or a more general interaction with membrane.

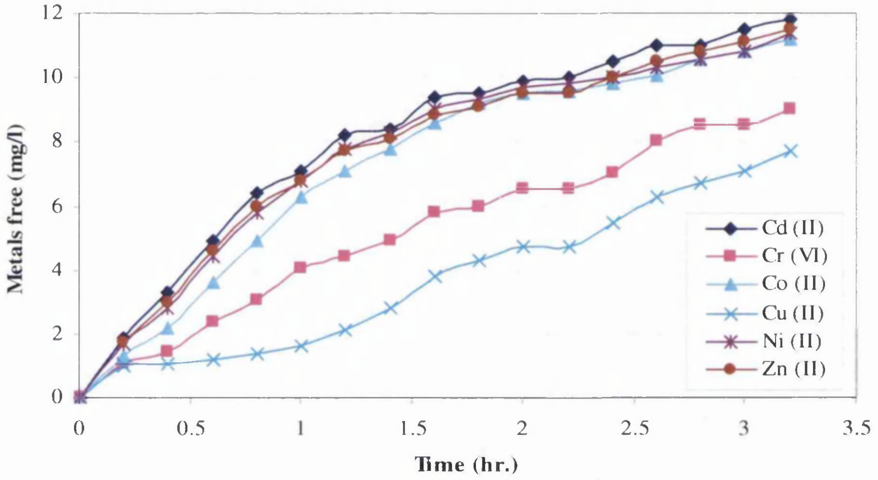


Figure 6.1 *Metal ions concentrations in the permeate as a function of time in the absence of PEI for PM50 ultrafiltration membrane using cross flow UF rig. (Feed concentrations of the metals were 14 mg/l metal ion, 25 °C, flow rate 5 l/hr., pH 5.5).*

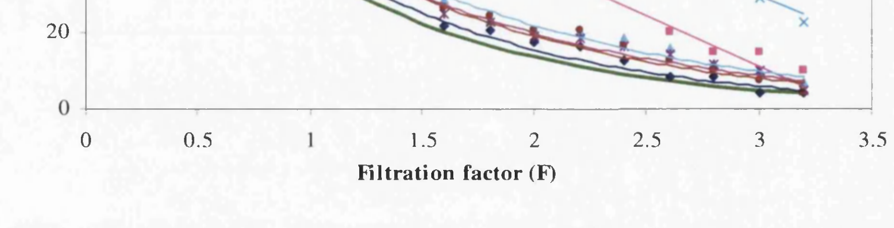


Figure 6.2 *Metal ions retention profiles as function of filtration factor in the absence of PEI for PM50 ultrafiltration membrane using cross flow UF rig. Using the data from Fig. 6.1, the retention and filtration factor were determined to construct the plot. (Calculation presented in Appendix 4)*

6.2.2 Single metal ions retention with PEI in the absence of chelating agents

PEUF experiments of aqueous solution of single metals (Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+}) were investigated in the presence of PEI. A series of experiments were carried out with different single metal ion feed concentration (70 mg/l). The feed was fed to the reservoir containing 1 g/l PEI and run in continuous mode at pH 5.5 (section 3.5.2).

Figure 6.3 presents the results of these experiments and show the measured concentrations of metal ions in the permeate as a function of time. They indicate the different affinities of metal binding to PEI in single metal solutions. This was also indicated by the retention profiles of metal ions with respect to filtration factor as presented in figure 6.4. The exponential "wash in" line (Exp^{-F}) is shown in figure 6.4, integration of the difference between this line and the out put concentration represent the amount of retention of the metal in the system. So as the experiment proceeds, the retention tends towards zero as the capacity of the polymer is saturated. The retention of Co^{2+}, Cd^{2+} and Zn^{2+} showed similar results and indicated low affinity of these metals to the PEI in individual aqueous solutions. However, more retention of Zn^{2+} was observed as indicated by the filtration factor (2.5 to 5) compared with Co^{2+} and Cd^{2+}. The observed retention of Ni^{2+} using PEI decreased in an approximately linear relationship with the filtration factor and indicated a better affinity of this metal to PEI than Co^{2+}, Cd^{2+} and Zn^{2+} but with high capacity (i.e. RF = 5). On the other hand, a similar trend of retention was observed for Cu^{2+} or Cr^{6+} in the presence of PEI, and the affinity was very high for both metals until the filtration factor reach 1.8 and 2.6 for Cu^{2+} and Cr^{6+} respectively, suggesting high capacity as well as good affinity of these metals to PEI. At this stage, metal affinity under these conditions was as follows: $Cr^{6+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+}$.

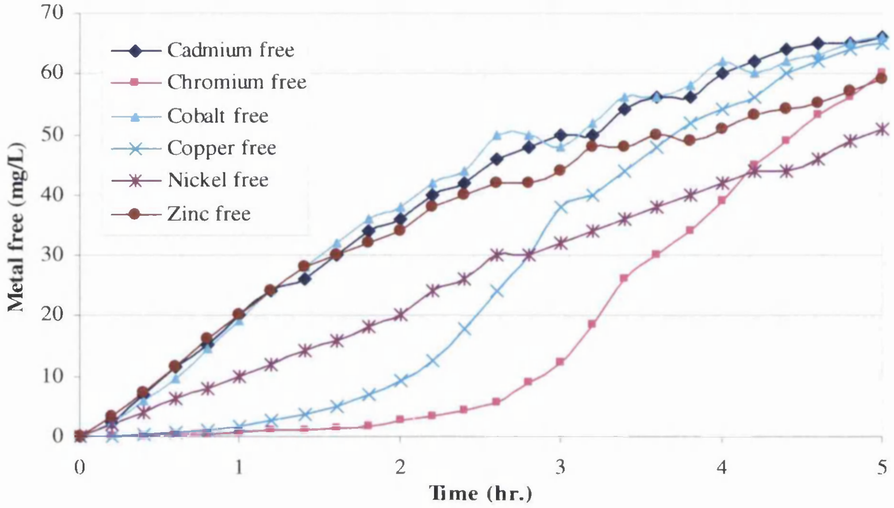


Figure 6.3 *Metal ions concentrations in the permeate as a function of time for single metal solutions in the presence of PEI using cross flow UF rig. (Single metal feed solutions with 70 mg/l concentration, 1 g/l PEI, pH 5.5, 25 ℃, flow rate 5 l/hr.)*

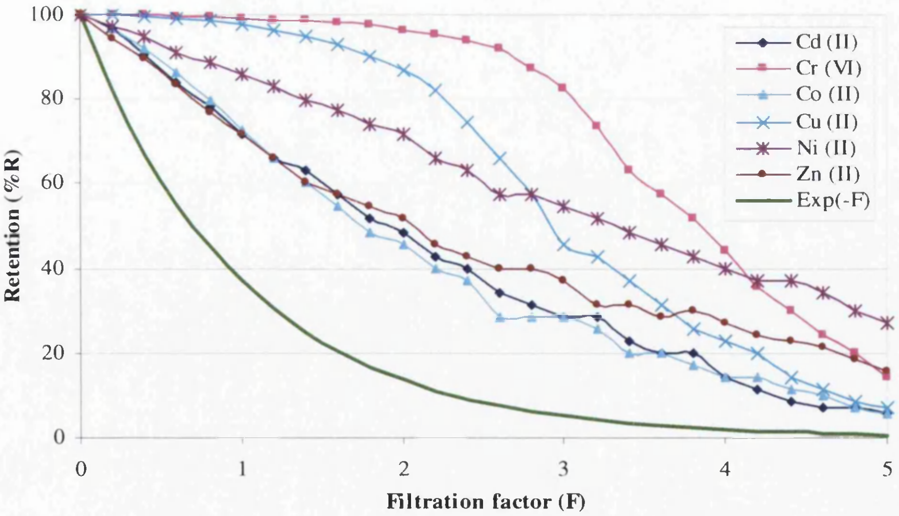


Figure 6.4 *Retention profiles of different single metals as a function of filtration factor using polymer enhanced ultrafiltration with continuous feeding. (Single metal feed solutions with 70 mg/l concentration, 1 g/l PEI, pH 5.5). Refer to data calculation in Appendix 4. [Exp$^{(-F)}$ = wash in curve].*

6.2.3 Mixed metal ion retention with PEI in the absence of chelating agents

The retention profiles of mixtures of metal ions (Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+}) in the presence of PEI was investigated using the continuous feed of polymer enhanced ultrafiltration process (see section 3.5.3). The experimental results in figure 6.5 were obtained by measuring the concentrations of metal ions in the permeate at regular intervals of time. These results show that the concentration profile of metal in mixed solution in the presence (figure 6.5) and absence (figure 6.1) of PEI are substantially different. Up to 2 - 2.5 hours, exit concentrations are lower than in absence of PEI. Also when mixed metal ions are compared with single metal solutions, the concentrations profile are different (figure 6.3 vs. figure 6.5). The mixture gives a great differentiation of out put concentrations than with the individual metal ions, e.g. Copper (Cu^{2+}) and Cobalt (Co^{2+}).

Retention profiles as a function of filtration factor (figure 6.6), indicated high retention of Cu^{2+} and Cr^{6+} among other metals in solution. Thus, the observed retention was believed to have been largely due to complexation with PEI compared with data acquired in the absence of PEI (figure 6.2). A reasonable retention of Co^{2+} was also obtained in competitive conditions with other metals to the available site of PEI, compared with the data presented in figure 6.2. In contrast, the retention profiles of Zn^{2+}, Ni^{2+} and Cd^{2+} showed a little binding affinity or capacity to PEI under competitive conditions of metal ions, and the saturated sorption of the polymer was reached at filtration factor between 4 and 4.5. Under competitive conditions of metal ions to the PEI, Ni^{2+} showed less affinity among other metals at low filtration factor. In general, the metals affinity to the polymer was as follows: $Cu^{2+} > Cr^{6+} > Co^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+}$. When compared with individual metals (figure 6.4) and mixtures of metals (figure 6.6), Cadmium (Cd^{2+}) and Zinc (Zn^{2+}) are a lower concentrations in the mixture, the system become rapidly saturated while Copper (Cu^{2+}) and Chromium (Cr^{6+}) have a greater binding capacity, indeed the system become more selective for Copper.

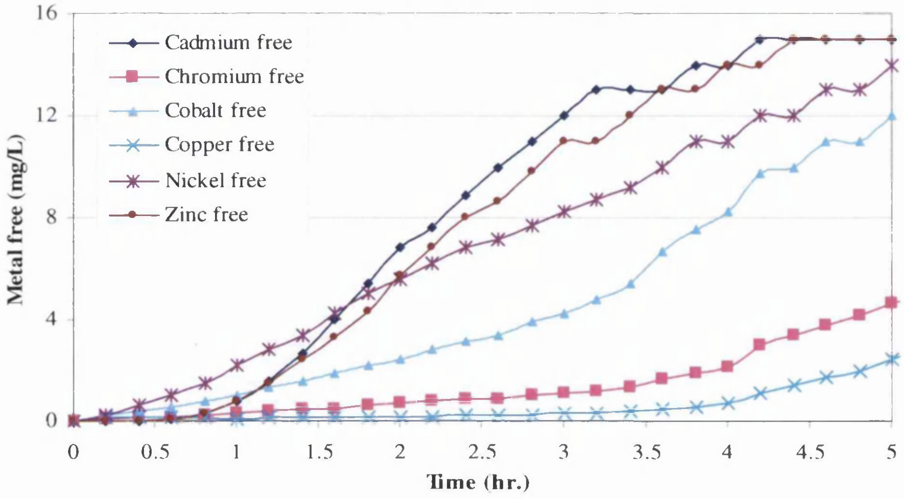


Figure 6.5 *Metal ions concentrations in the permeate as a function of time for mixture metal solution in the presence of PEI using cross flow UF rig. (Metals feed solution with 14 mg/l concentrations of each metal, 1 g/l PEI, pH 5.5, 25 ℃, flow rate 5 l/hr.).*

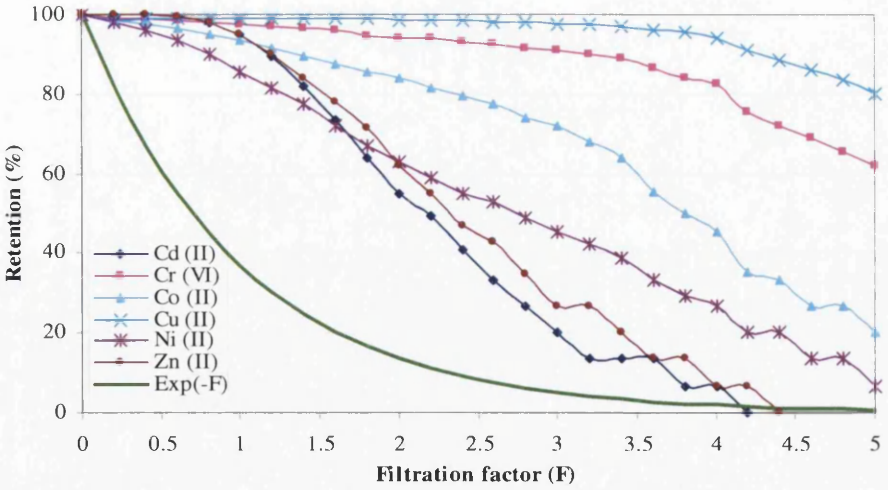


Figure 6.6 *Retention profiles of mixture metals as a function of filtration factor using polymer enhanced ultrafiltration with continuous feeding. (Metals feed solution with 14 mg/l concentrations of each metal, 1 g/l PEI, pH 5.5).*

[Refer to data calculation in Appendix 4].

6.2.4 Relative metal ions enrichment in PEUF

Because the relative retention of individual metal ions is different in a mixture, a system of stage wise purification is possible. Using the data obtained in figure 6.5, it is possible to demonstrate purification/ enrichment of one metal over another in the mixed metal ions solution (see figure 6.7). The purification factor was calculated by the ratio of specific concentration values of metal ions using the following expression:

$PF_i = C_{it}/C_{ip}$ ....(equation 6.1)

Where:

PF_i : Purification Factor of metal *i*

C_{ip} : Concentration of metal *i* in the permeate (mg/l)

C_{it} : Total concentration of metal *i* (mg/l).

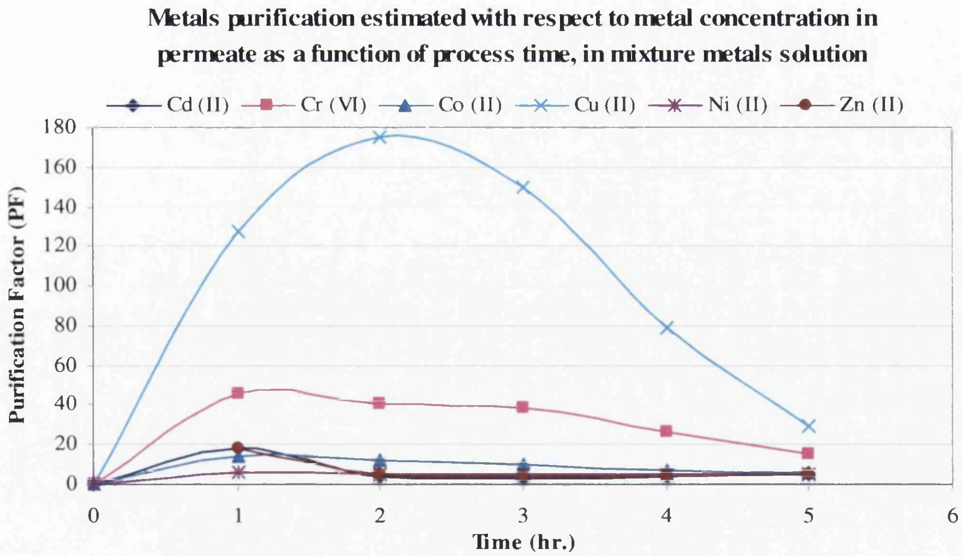


***Figure 6.7** Relative metal ions purification/ enrichment using continuous feed of PEUF involving mixture metal ions solution with PEI. (Metals feed solution with 14 mg/l concentrations of each metal, 1 g/l PEI, pH 5.5, 25 °C, flow rate 5 l/hr.).*

6.2.5 Mixed metal ion retention with PEI in the presence of chelating agents

In order to investigate the effect of various chelating competitive agents on the retention of metal ions in the presence PEI, experiments were conducted using continuous mode ultrafiltration. Aqueous solutions of mixture six metal ions (Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+}) were prepared in the presence of 2 mM concentrations of: Ammonium sulfate, Ammonium chloride, Sodium acetate, Nitrilotriacetic acid and Ethylenediaminetetra acetic acid, respectively. Also, the same concentration of each chelators competitors was added to other solutions of 1 g/l PEI in the reservoir to the purpose of PEUF experiments and all the experimental solutions adjusted at pH 5.5 (Details of the experimental procedures are explained in section 3.5.4).

6.2.5.1 Effect of Ammonium sulfate (AS)

The presence of ammonium sulfate in the complex solution was investigated by measuring the concentrations of metal ions in the permeate with respect to the process time (figure 6.8). Generally, the binding capacity of the system has been reduced (eg. figure 6.5 vs 6.8). Most notable the binding of Chromium (Cr^{6+}) has been significantly effected so that Copper (Cu^{2+}) binding now dominates the system. Then, plotting the retention of metal ions as a function of filtration factor (figure 6.9) showed a significant negative impact of adding ammonium sulfate to the system. The observed retention values of all metal ions in the solution were greatly reduced, in comparison to the results acquired in the absence of ammonium sulfate (figure 6.6). The evident dramatic reduction in retention of these metals was thought to be due to competition between ammonium sulfate and the metal ions to the available site of PEI. With an average retention of 70%, Copper (Cu^{2+}) had the highest affinity to PEI among other metals in the solution.

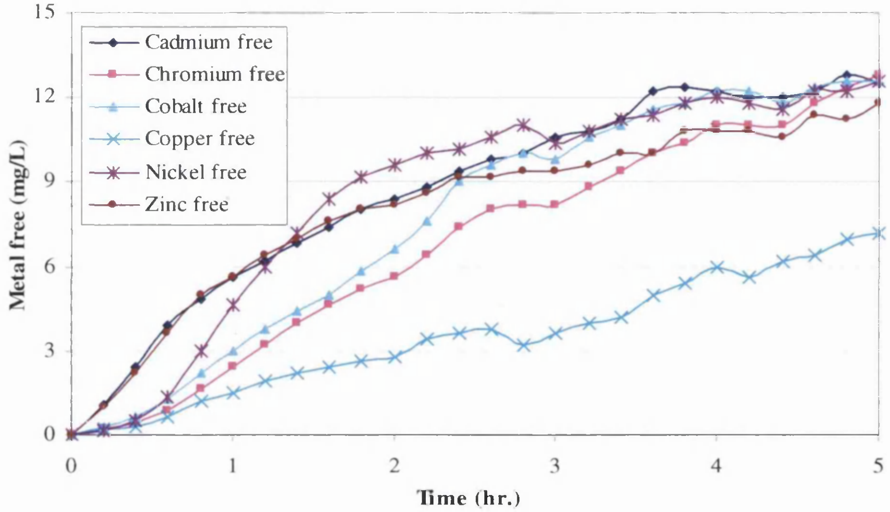


Figure 6.8 *Metal ions concentrations in the permeate as a function of time for mixture metal solution in the presence of PEI and ammonium sulfate using cross flow UF rig. (Metals feed solution with 14 mg/l concentrations of each metal, 2 mM AS, 1 g/l PEI, pH 5.5, 25 °C, flow rate 5 l/hr.).*

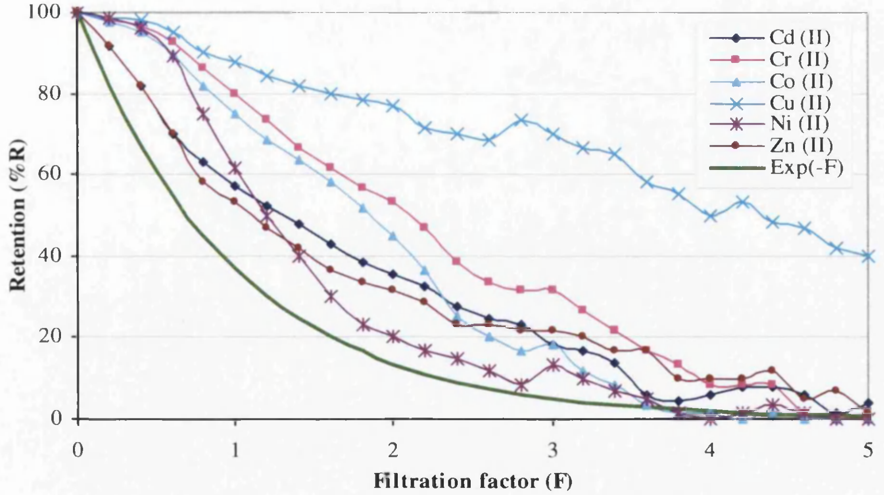


Figure 6.9 *Retention profiles of mixture metals in the presence of Ammonium sulfate as a function of filtration factor using polymer enhanced ultrafiltration with continuous feeding. (Mixture metals feed solution with 14 mg/l concentrations of each metal, 2 mM AS, 1 g/l PEI, pH 5.5). [Refer to data calculation in Appendix 4].*

6.2.5.2 Effect of Ammonium chloride (AC)

The experimental results of binding metal ions to PEI under competitive condition of ammonium chloride are shown in figure 6.10, the concentrations of metal ions in the permeate were plotted as a function of time. The results show reduced binding capacity with Copper (Cu^{2+}) and Chromium (Cr^{6+}) dominating. The retention profiles of Cu^{2+} and Cr^{6+} in mixture metals solution with PEI (figure 6.11) indicated almost similar results of retention for both metal in the presence of ammonium chloride. In this case, the significant decrease in retention of both metals was observed at high filtration factor from 3.5 to 5, compared with their retention in the absence of ammonium chloride (figure 6.6). The retention profile of Co^{2+} followed a similar trend to that of Co^{2+} in the absence of ammonium chloride, while Ni^{2+} retention profiles showed little difference at low filtration factor. However, the retention values for both Zn^{2+} and Cd^{2+} were significantly decreased in comparison with the data obtained in the absence of ammonium chloride (figure 6.6), especially at low filtration factor. This suggests a poor affinity of both metals for PEI, under competitive conditions of mixed metals ions with ammonium chloride.

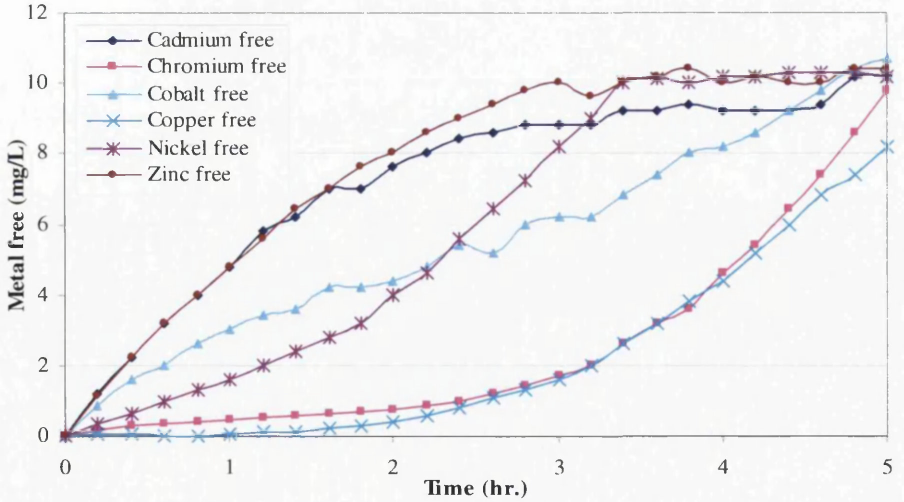


Figure 6.10 *Metal ions concentrations in the permeate as a function of time for mixed metal solution in the presence of PEI and ammonium chloride using cross flow UF rig. (Metals feed solution with 14 mg/l concentrations of each metal, 2 mM AC, 1 g/l PEI, pH 5.5, 25 °C, flow rate 5 l/hr.).*

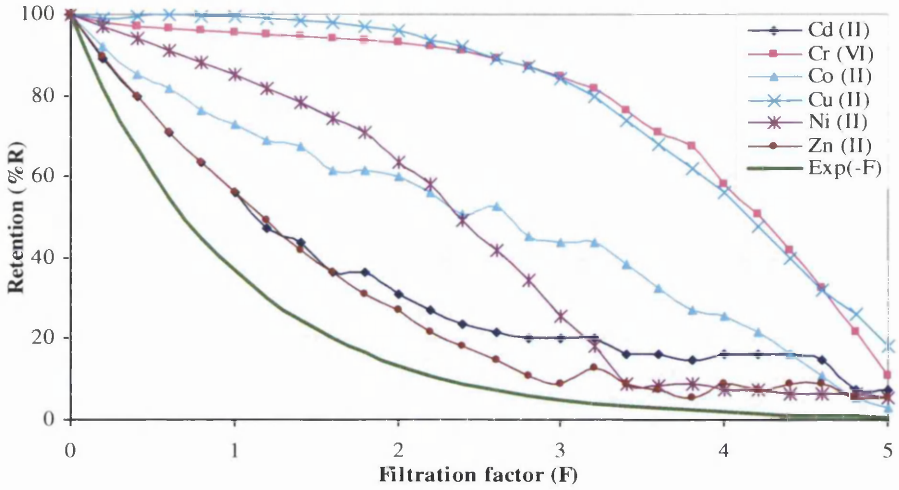


Figure 6.11 *Retention profiles of mixture metals in the presence of ammonium chloride as a function of filtration factor using polymer enhanced ultrafiltration with continuous feeding. (Mixture metals solution with 14 mg/l concentrations of each metal, 2 mM AC, 1 g/l PEI, pH 5.5). [Refer to data calculation in Appendix 4].*

6.2.5.3 Effect of Sodium acetate (SA)

Figure 6.12 illustrated the concentrations of free metal ions as a function of time obtained from the experiment of complex metal/ polymer under competitive condition with sodium acetate. The concentration profiles show that the binding capacity has been reduced. The capacity is also significantly enhanced for Cobalt (Co^{2+}) and Nickel (Ni^{2+}). The retention values for mixed metal ions using PEI in the presence of sodium acetate (figure 6.13), were significantly different from previously discussed data of other chelating competitive agents (figures 6.9 and 6.11). Clearly suggesting that the presence of sodium acetate during PEUF had little effect on the retention of Cu^{2+}, Zn^{2+}, Cr^{6+} and Cd^{2+}, compared with the data obtained in the absence of Sodium acetate (figure 6.6). However, significant enhancement of metals retention was observed for Ni^{2+} and Co^{2+} respectively, and then the affinity of metals to PEI changed to the following order: $Cu^{2+} > Cr^{6+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+}$.

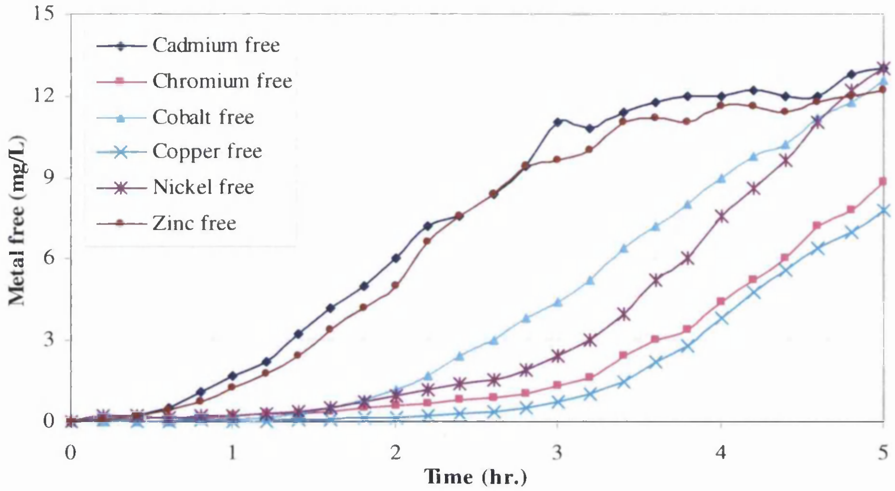


Figure 6.12 *Metal ions concentrations in the permeate as a function of time for mixture metal solution in the presence of PEI and Sodium acetate using cross flow UF rig. (Metals feed solution with 14 mg/l concentrations of each metal, 2 mM SA, 1 g/l PEI, pH 5.5, flow rate 5 l/hr., 25 ℃).*

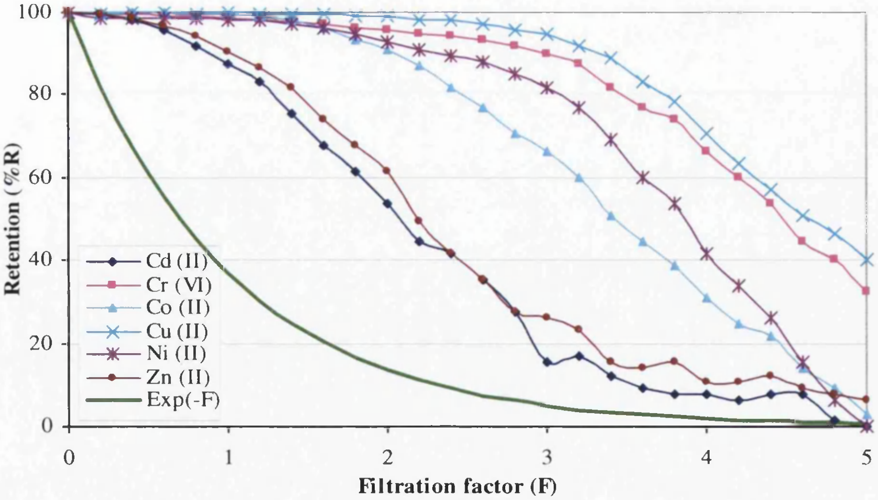


Figure 6.13 *Retention profiles of mixture metals in the presence of Sodium acetate as a function of filtration factor using polymer enhanced ultrafiltration with continuous feed. (Mixture metals feed solution with 14 mg/l concentrations of each metal, 2 mM SA, 1 g/l PEI, pH 5.5). [Refer to data calculation in Appendix 4].*

6.2.5.4 Effect of Nitrilotriacetic acid (NTA)

The influence of presence NTA in complex solution was studied and the concentrations of metal ions free in the permeate were plotted with respect to the process time (figure 6.14). The effect of NTA on the concentration profiles compared with the control (figure 6.5) is that the binding capacity has been reduced generally and most notable is the decrease in Copper (Cu^{2+}) and Chromium (Cr^{6+}) binding. The effect of adding NTA on the retention of metal ions in complex solution with PEI is shown in figure 6.15. Retention values of Cu^{2+}, Cr^{6+} and Co^{2+} under these conditions showed a different trend to those discussed in figure 6.6, a significant reduction of these metals retention appeared to exhibit an approximately linear relationship with the filtration factor. Also, results from figure 6.15 shows lower retention values of Zn^{2+}, Ni^{2+} and Cd^{2+} occurring in the presence of NTA. These differences are clear indications that the competition between metal ions and NTA for binding sites on the PEI would reduce the retention values of these metals. However, the affinity of metal ions to PEI in the presence of NTA decreases in the following orders: $Cr^{6+} > Cu^{2+} > Co^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+}$ compared to $Cu^{2+} > Cr^{6+} > Co^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+}$ in the absence of NTA.

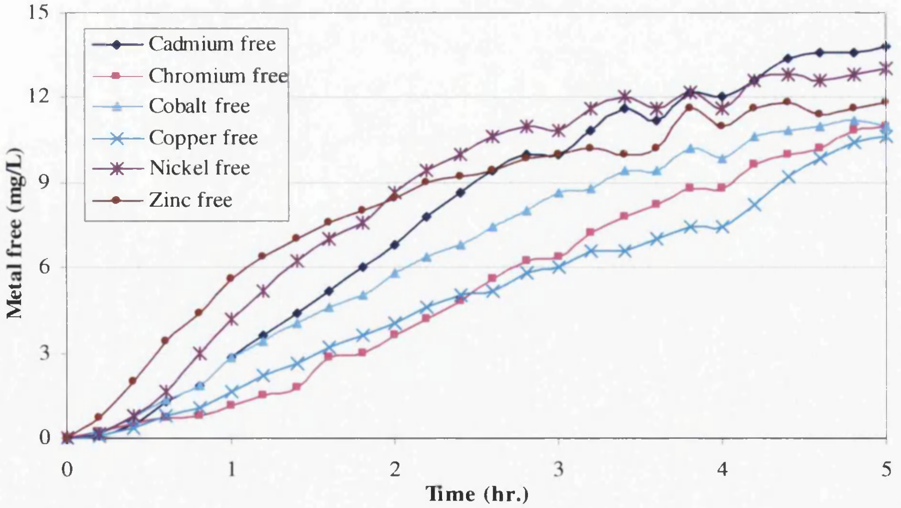


Figure 6.14 *Metal ions concentrations in the permeate as a function of time for mixture metal solution in the presence of PEI and NTA using cross flow UF rig. (Metals feed solution with 14 mg/l concentrations of each metal, 2 mM NTA, 1 g/l PEI, pH 5.5, flow rate 5 l/hr., 25 °C).*

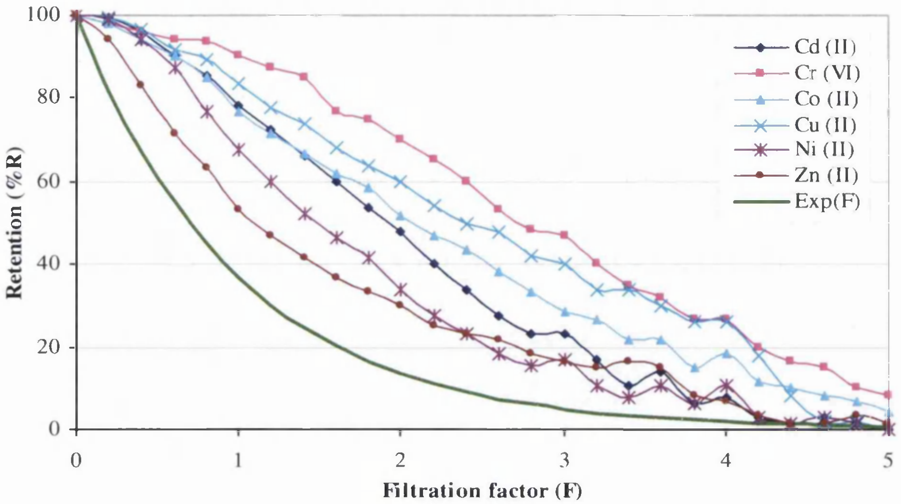


Figure 6.15 *Retention profiles of mixture metals in the presence of NTA as a function of filtration factor using polymer enhanced ultrafiltration with continuous feed. (Mixture metals feed solution with 14 mg/l concentrations of each metal, 2 mM NTA, 1 g/l PEI, pH 5.5, flow rate 5 l/hr., 25 °C). [Refer to data calculation in Appendix 4].*

6.2.5.5 Effect of Ethylenediaminetetra acetic acid (EDTA)

The effect of EDTA addition to the complex of metals/polymer solution was then investigated. The experimental results, shown in figure 6.16, indicate the inhibiting effect of adding EDTA on the binding of metal ions to PEI in the complex solution. EDTA reduces the binding of metal ions to PEI such that both the selectivity and capacity are reduced. However, figure 6.17 illustrated the retention of metal ions with PEI in the presence of EDTA as a function of filtration factor. Thus, the retention values of all metal ions were altered by the addition of EDTA to the complex solution of PEI compared with the data presented in figure 6.6. A significant reduction of metal ions retention in the presence of EDTA was observed, indicating clear competition between metal ions and EDTA for available site on the PEI or competition of PEI and EDTA for metal ions. The only increase in metal ion retention under competitive conditions with EDTA was obtained for Zn^{2+} and Cd^{2+} at filtration factor from 2.5 to 4, where an apparent increase in retention by about 20%. However, the affinity of metal ions to PEI in the presence of EDTA was as follows: $Cu^{2+} > Cr^{6+} > Ni^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+}$.

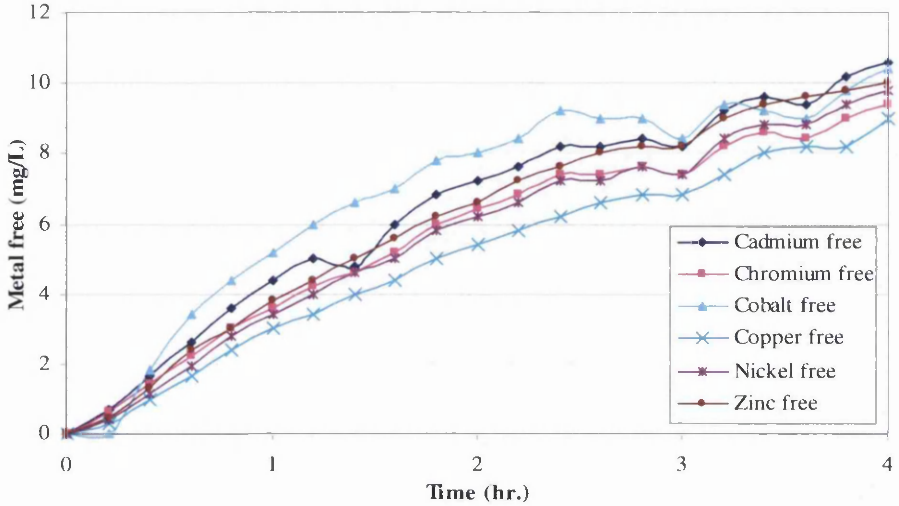


Figure 6.16 *Metal ions concentrations in the permeate as a function of time for mixture metal solution in the presence of PEI and EDTA using cross flow UF rig. (Metals feed solution with 14 mg/l concentrations of each metal, 2 mM EDTA, 1 g/l PEI, pH 5.5, flow rate 5 l/hr., 25 °C).*

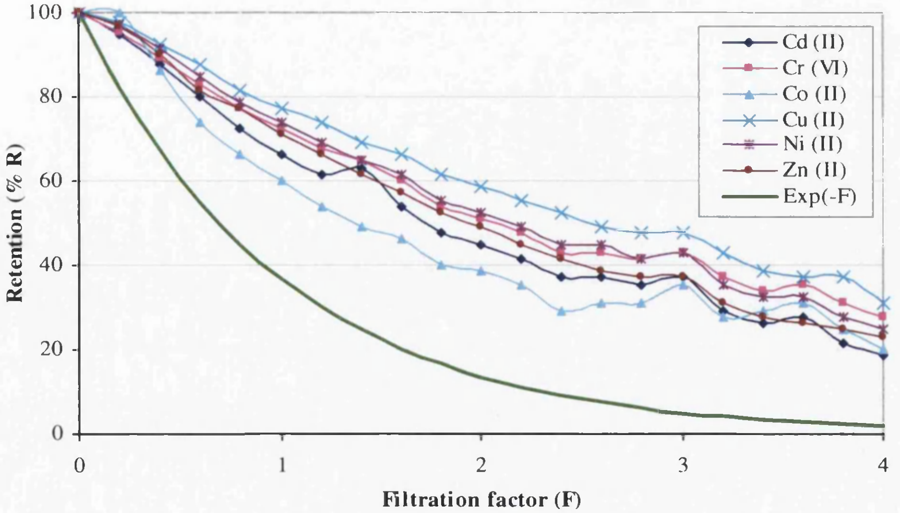


Figure 6.17 *Retention profiles of mixture metals in the presence of EDTA as a function of filtration factor using polymer enhanced ultrafiltration with continuous feed. (Mixture metals feed solution with 14 mg/l concentrations of each metal, 2 mM EDTA, 1 g/l PEI, pH 5.5). [Refer to data calculation in Appendix 4].*

6.3. Metals binding in cross flow PEUF based on adsorption isotherms

6.3.1 Single metal binding with PEI and the adsorption model prediction

Binding studies were carried out for individual aqueous complex solutions of single metal ions and PEI in continuous mode of PEUF using cross flow ultrafiltration rig. Samples from permeate were taken at regular intervals of time and the concentrations of free metal ions were determined. The amount of each metal ions bound to the polymer (PEI) was determined experimentally at pH 5.5. Then, the applicability of the Langmuir and Freundlich isotherm models to describe these systems was explored, using the linear form of the Langmuir isotherm (equation 3.4) and the linear form of the Freundlich isotherm (equation 3.6). (See section 3.5.2 for the details of experimental procedures).

The experimental data of single metal adsorption isotherms for Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+} are shown in figure 6.18. These results showed that a good binding of PEI was observed for Cr^{6+} and Cu^{2+}, respectively. In contrast, PEI showed less affinity to bind Ni^{2+}, Zn^{2+}, Cd^{2+} and Co^{2+}, especially at low metal concentrations. However, the affinity of PEI for these metals followed the order $Cr^{6+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+}$.

The same figure shows the individual metal adsorption represented by the Langmuir isotherm model (equation 3.3). It is seen that the Langmuir model fit the experimental data reasonably well, through all the range of metals concentrations studied.

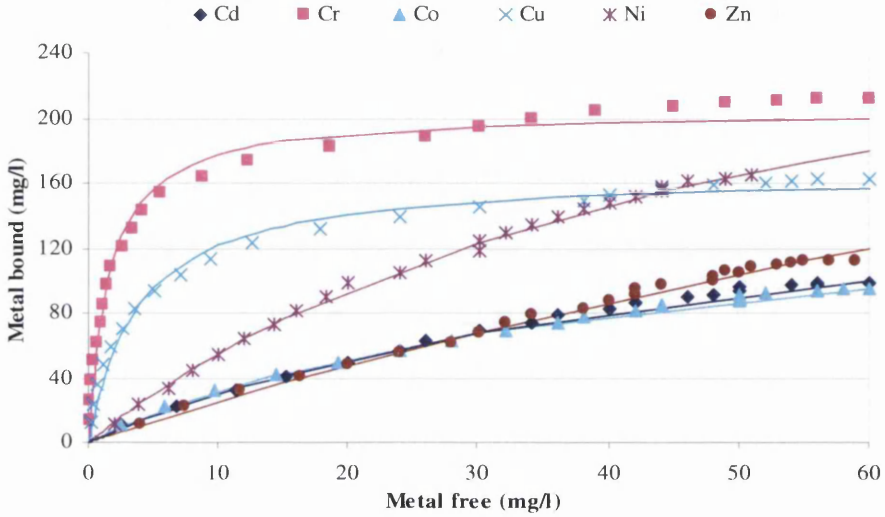


Figure 6.18 *Results of binding of single metal ions to PEI in continuous mode of PEUF process, experiments (points) and using Langmuir model (lines) at pH 5.5, 1 g/l PEI, and single metal feed solutions with 70 mg/l.*

The applications of Freundlich isotherm model (equation 3.5) to predict the same experimental data of single metals (Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+}) are shown in figure 6.19. It is seen that the model showed a good fit for the experimental results except for Cr^{6+} and Cu^{2+}. However, Freundlich isotherm model showed less accuracy of prediction experimental results compared with Langmuir isotherm model. This was clear from the values of square linear regression (R^2) are shown in table 6.1.

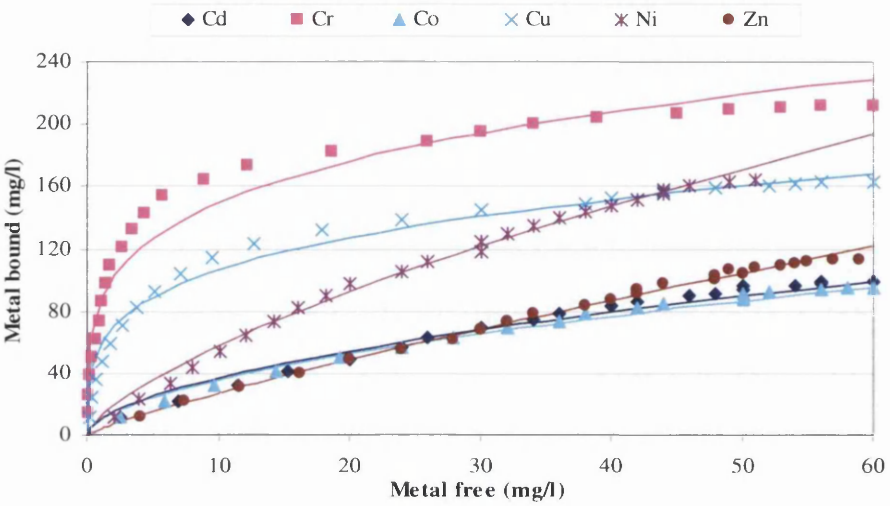


Figure 6.19 *Results of binding of single metal ions to PEI in continuous mode of PEUF process, experiments (points) and using Freundlich model (lines) at pH 5.5, 1 g/l PEI, and 70 mg/l metal concentrations.*

The Langmuir isotherms allowed estimation of maximum capacity of the polymer for metal ions (Q_{max}), and the equilibrium constant (K_L) at pH 5.5 using continuous mode PEUF. In table (6.1), the Langmuir data showed that the Q_{max} for Co^{2+} was 161.3 mg/g_{PEI} (2.74 mmol/g), for Cu^{2+} was 163.9 mg/g (2.58 mmol/g), for Cd^{2+} was 188.68 mg/g (1.68 mmol/g), for Cr^{6+} was 200 mg/g (3.85 mmol/g), for Ni^{2+} was 333.3 mg/g (5.68 mmol/g) and for Zn^{2+} was 500 mg/g (7.65 mmol/g). While the equilibrium constants were in the following order: Cr^{6+} 1.5 mg/l (0.029 mmol/l), Cu^{2+} 3.31 mg/l (0.052 mmol/l), Co^{2+} 42.1 mg/l (0.714 mmol/l), Ni^{2+} 51 mg/l (0.869 mmol/l), Cd^{2+} 54.2 mg/l (0.482 mmol/l) and Zn^{2+} 190.3 mg/l (2.91 mmol/l). Compared with these data the experimental results showed that with an increase of the equilibrium constant (K_L) value, less affinity of PEI to metal ions was observed. However, the values of (R^2) in single metal solutions indicate that the results obtained with Langmuir isotherm appeared to offer the better description of the binding conditions than those obtained with Freundlich isotherm.

***Table 6.1** Data derived from applying Langmuir and Freundlich isotherms model for single metal ions in continuous mode of PEUF process, the data were fitted to linearised form of these experiments.*

Langmuir Isotherm								Freundlich Isotherm			
Exp.	Slope K_L/Q_{max}	Intercept $1/Q_{max}$	Q_{max}		K_L		R^2	Intercept ($Ln\ K_F$)	n	K_F ($mg^{1-n}\ g^{-1}l^n$)	R^2
			(mg/g_{PEI})	($mmol/g_{PEI}$)	(mg/l)	($mmol/l$)					
Cu^{2+}/ PEI	0.020	0.0061	163.9	2.58	3.31	0.052	0.983	4.08	0.255	59.1	0.966
Cr^{6+}/ PEI	0.007	0.005	200	3.85	1.5	0.029	0.991	4.46	0.236	86.8	0.93
Zn^{2}/ PEI	0.381	0.002	500	7.65	190.3	2.91	0.993	1.39	0.833	4.0	0.988
Co^{2}/ PEI	0.261	0.0062	161.3	2.74	42.1	0.714	0.989	2.32	0.546	10.2	0.968
Ni^{2+}/ PEI	0.153	0.003	333.3	5.68	51	0.869	0.997	2.5	0.674	12.2	0.991
Cd^{2}/ PEI	0.287	0.0053	188.7	1.68	54.2	0.482	0.966	2.35	0.548	10.5	0.923

6.3.2 Mixture metal binding with PEI and the adsorption models prediction

As an extension, to the work carried out on the binding studies of single metal solutions (section 6.3.1), the competition within a mixture of metals to PEI in continuous mode PEUF were investigated. Aqueous solutions of six metal ions (Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+}) were prepared in the presence of PEI, and subjected to ultrafiltration process as described in section 3.5.3. The competitive adsorption isotherms results of mixed metal ions on PEI are shown in figure 6.20. It was observed that a significant reduction of metal ions bound to PEI in mixtures solution when compared with their adsorption in single metal adsorption systems. These experimental results indicated a strong competition between the various metal ions for the available sites of PEI. As a result, it was found that the highest affinity of PEI was for Cu^{2+} and Cr^{6+}. In the mean time, Ni^{2+} demonstrated a lower binding to PEI at the initial period of the process. For these metals, the adsorption capacity followed the order of $Cu^{2+} > Cr^{6+} > Co^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+}$, which may be attributed to their different adsorption affinities in competitive for the polymer. In figure 6.20, the experimental data of the mixture metals adsorption isotherms were predicted using Langmuir isotherms model. Plots of the linear form of the Langmuir isotherm showed that much of the data gave a fairly good prediction using the Langmuir model. However, less accuracy was obtained for Cu^{2+} and Cr^{6+} at high metals concentrations and in the case of Zn^{2+} at low metal concentrations.

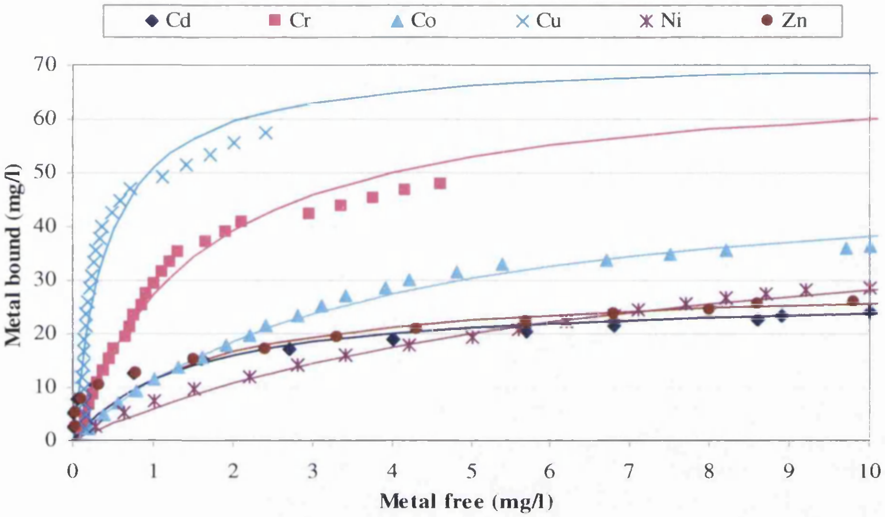


Figure 6.20 *Results of binding of mixture metal ions to PEI in continuous mode of PEUF process, experiments (points) and using Langmuir model (lines) at pH 5.5, 1 g/l PEI, and 14 mg/l metal concentrations of each metal.*

Figure 6.21 compares the predicted data of Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+} and Cd^{2+} using Freundlich isotherms model with the experimental data. It is seen that the Freundlich model failed to predict the experimental data of Cu^{2+}, Cr^{6+} and Co^{2+}, while good prediction was observed for Ni^{2+}, Zn^{2+} and Cd^{2+}. However, it is obvious that the Langmuir isotherms model offered a better prediction for the experimental data compared with the Freundlich model in mixed metal complex solutions. This was supported by the better values of (R^2) obtained in Langmuir isotherms in comparison with the Freundlich models (table 6.2). Also, the Langmuir data showed that the maximum capacity (Q_{max}) of metal bound in mixed metal solution as follow: Cu^{2+} 71.43 mg/g_{PEI} (1.124 mmol/g), Cr^{6+} 68.96 mg/g (1.326 mmol/g), Co^{2+} 52.1 mg/g (0.884 mmol/g), Ni^{2+} 46.73 mg/g (0.796 mmol/g), Zn^{2+} 29.76 mg/g (0.455 mmol/g) and Cd^{2+} 26.74 mg/g (0.238 mmol/g). The equilibrium constants were in the following order: Cu^{2+} 0.4 mg/l (0.006 mmol/l), Cd^{2+} 1.36 mg/l (0.012 mmol/l), Cr^{6+} 1.51 mg/l (0.029 mmol/l), Zn^{2+} 1.6 mg/l (0.024 mmol/l), Co^{2+} 3.59 mg/l (0.061 mmol/l) and Ni^{2+} 6.7 mg/l (0.114 mmol/l).

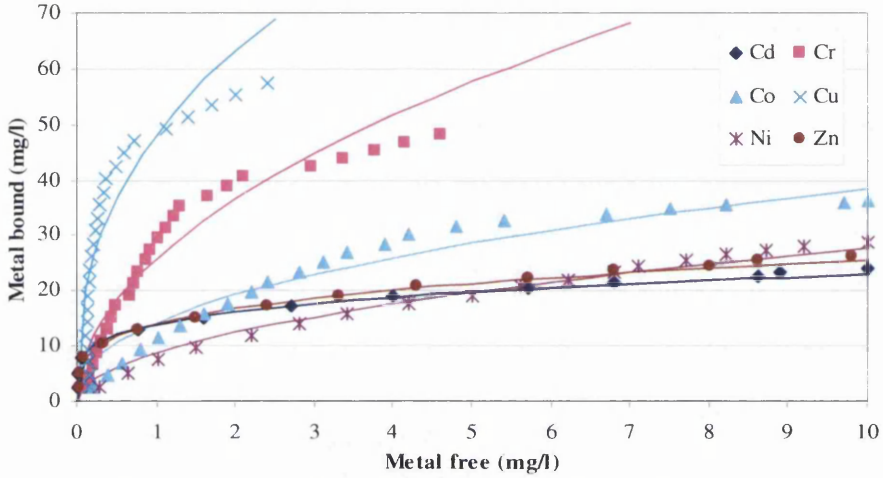


Figure 6.21 *Results of binding of mixture metal ions to PEI in continuous mode of PEUF process, experiments (points) and using Freundlich model (lines) at pH 5.5, 1 g/l PEI, and 14 mg/l metal concentrations of each metal.*

Table 6.2 *Data derived from applying Langmuir and Freundlich isotherms model for mixture metal ions in continuous mode of PEUF process, the data were fitted to linearised form of these experiments.*

Langmuir Isotherm								**Freundlich Isotherm**			
Exp.	**Slope** K_L/Q_{max}	**Intercept** $1/Q_{max}$	Q_{max} (mg/ g_{PEI})	Q_{max} (mmol/ g_{PEI})	K_L (mg/ l)	K_L (mmol/ l)	R^2	**Intercept** (Ln K_F)	n	K_F (mg^{1-n} $g^{-1}l^n$)	R^2
Cu^{2+}/ PEI	0.006	0.014	71.43	1.124	0.4	0.006	0.957	3.88	0.385	48.5	0.84
Cr^{6+} / PEI	0.022	0.0145	68.96	1.326	1.51	0.029	0.978	3.26	0.494	26	0.911
Zn^2 / PEI	0.054	0.0336	29.76	0.455	1.6	0.024	0.974	2.64	0.26	13.9	0.979
Co^2 / PEI	0.069	0.0192	52.1	0.884	3.59	0.061	0.986	2.67	0.426	14.4	0.916
Ni^{2+} / PEI	0.143	0.0214	46.73	0.796	6.7	0.114	0.99	2.17	0.499	8.78	0.966
Cd^2 / PEI	0.051	0.0374	26.74	0.238	1.36	0.012	0.962	2.64	0.215	13.9	0.961

6.4. Effect of the chelating agents on the binding of metal ions to PEI

The investigation of binding conditions of mixed metals (Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+}, and Cd^{2+}) with PEI in continuous mode of PEUF process were considered in the presence of various chelating agents competitors. For this purpose, (Ammonium sulfate (AS), Sodium acetate (SA), Ammonium chloride (AC), NTA and EDTA) were used. However, these chelators competitors were introduced individually to the complex of metal-polymer solutions, details of the experimental methods have been described previously in section 3.4.3). The applicability of the Langmuir isotherm model (equation 3.3) to predict these systems was explored when the experimental data of PEUF were correlated using the linearised Langmuir model (equation 3.5).

6.4.1 Cu^{2+} binding with PEI in the presence of various chelators

The equilibrium adsorption of Cu^{2+} on PEI in the absence and presence of chelating agents is shown in figure 6.22. It was observed that the binding of Cu^{2+} to PEI was significantly inhibited when the chelating agents were present in the solutions compared with the complex of copper-PEI (no additive). Significant drops in the binding capacity of Cu^{2+} was obtained especially with EDTA, NTA and ammonium sulfate due to competition effects. At extremely low copper concentration, PEI reveals a higher affinity to Cu^{2+} in the presence of sodium acetate and ammonium chloride compared with the other chelating agents. When the copper concentration increased, the PEI affinity to Cu^{2+} decreased and the competitive ability followed the order: EDTA > NTA >AS > AC > SA. In the same figure, the experimental data of the mixed metals adsorption isotherms in the presence of chelating agents were predicted using Langmuir isotherms model. Plots of the linear form of the Langmuir isotherm showed that much of the data gave a good prediction; this was confirmed by the high values of R^2 in table 6.3. As can be seen from the table, the Langmuir isotherm allowed estimation the maximum capacity of the polymer for metal ions (Q_{max}), and the equilibrium constant (K_L) in competitive processes. The value of Q_{max} for the complex solution of Cu^{2+}/ PEI (no additive) was found to be 71.43 mg/g (1.124 mmol/g) and the values decreased on addition of 2mM concentration of the chelating agent to the complex solution in the following order: EDTA 51.54 mg/g (0.811 mmol/g) > ammonium sulfate 50.76 mg/g (0.799 mmol/g) > sodium acetate 40.65 mg/g (0.64 mmol/g) > ammonium chloride 39.52 mg/g (0.622 mmol/g) > NTA 39.37 mg/g (0.62 mmol/g). The equilibrium constants were in the following order: EDTA 14.59 mg/l (0.23 mmol/l) > NTA 5.63 mg/l (0.0886 mmol/l) > ammonium sulfate 5.5 mg/l (0.086 mmol/l) > ammonium chloride 0.55 mg/l (0.0086 mmol/l) > no additive 0.4 mg/l (0.006 mmol/l) > sodium acetate 0.29 mg/l (0.0046 mmol/l). These results indicate that the (Q_{max}) values do not reflect the results shown in the figure, and that the lower values of (K_L) mean the strong binding for metal ions by the polymer and less competitive effects. In general, the binding of Cu^{2+} to PEI was inhibited by the presence of different chelating competitive agents in the complex metal-polymer solutions, and that was also observed previously in batch mode PEUF experiments (section 5.4.2).

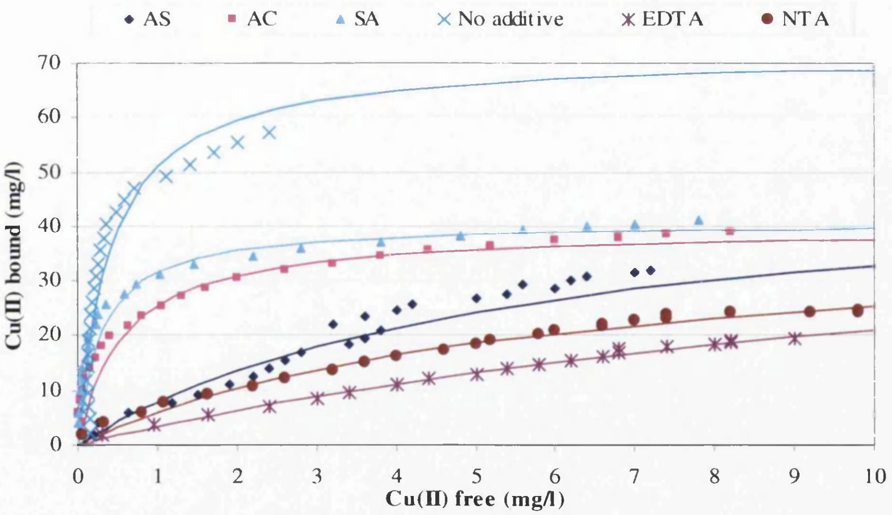


Figure 6.22 *Results of binding of mixture metal ions to PEI in continuous mode of PEUF process , competitive adsorption of Cu^{2+} in the presence of various chelating agents [experiments (points) and using langmuir isotherm model (lines) at pH 5.5, 2 mM chelating agents, 1 g/l PEI and 14 mg/l metal concentrations of each metal]*

6.4.2 Zn^{2+} binding with PEI in the presence of various chelators

Figure (6.23) illustrates the binding of Zn^{2+} to the PEI in the absence and presence of various chelating agents. The experimental data showed that the presence of EDTA, NTA, AS or AC in the complex solutions significantly altered the adsorption of Zn^{2+}; indicating a poor affinity of the PEI to bind the metal ions and exhibiting a linear relationship. In contrast, less inhibitory effect on the adsorption of Zn^{2+} was observed when SA was present in the complex solution and a similar trend of binding curve was obtained. On the other hand, the Langmuir isotherm model was applied to the experimental results and reasonable data prediction were obtained except at low metal concentrations.

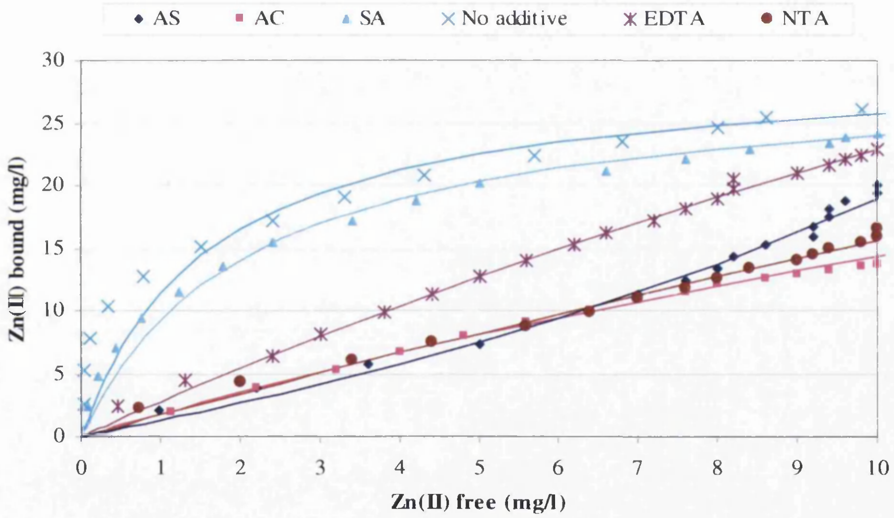


Figure 6.23 *Results of binding of mixture metal ions to PEI in continuous mode of PEUF process , competitive adsorption of Zn^{2+} in the presence of various chelating agents [experiments (points) and using langmuir isotherm model (lines) at pH 5.5, 2 mM chelating agents, 1 g/l PEI and 14 mg/l metal concentrations of each metal]*

However, the Langmuir adsorption isotherm results shown in table (6.3) represented the competition effect of these chelating agents on the adsorption of Zn^{2+} by means of high or negative sign of (Q_{max}). Here, the maximum binding capacities of Zn^{2+} obtained in the presence of chelating agents as follow: NTA 156.25 mg/g (2.39 mmol/g) > EDTA 117.6 mg/g (1.8 mmol/g) > ammonium chloride 63.69 mg/g (0.974 mmol/g) > sodium acetate 28.98 mg/g (0.443 mmol/g) > ammonium sulfate -47.85 mg/g (-0.73 mmol/g); that obtained without chelators was 29.76 mg/g (0.455 mmol/g). Also, the equilibrium constants (K_L) occur in the following order: NTA 90.69 mg/l (1.39 mmol/l), EDTA 41.36 mg/l (0.633 mmol/l), ammonium chloride 34.5 mg/l (0.528 mmol/l), sodium acetate 2.13 mg/l (0.0326 mmol/l), and ammonium sulfate -35.7 mg/l (-0.55 mmol/l). While the equilibrium constant that obtained for the Zn^{2+}/PEI complex in the absence of chelating agent was 1.6 mg/l (0.024 mmol/l).

In order to compare the binding conditions of PEI for copper and zinc treatments in mixed solution of metal ions under the influences of different chelating agents, the values of Q_{max}, K_L and R^2 obtained from the slopes and intercepts of the linear plots of Langmuir adsorption isotherm are listed in table 6.3 below.

Table 6.3 *Cu^{2+} and Zn^{2+} experimental data from the application of Langmuir isotherm model for mixture metal ions with 2 mM chelating agents competitors in continuous mode of PEUF process, the data were fitted to linearised form of these experiments.*

Experiment	Cu^{2+}					Zn^{2+}				
Metals + (1 g/l PEI) + (2 mM add.)	Q_{max}		K_L		R^2	Q_{max}		K_L		R^2
	(mg/ g_{PEI})	(mmol/ g_{PEI})	(mg/ l)	(mmol/ l)		(mg/ g_{PEI})	(mmol/ g_{PEI})	(mg/ l)	(mmol/ l)	
PEI	71.43	1.124	0.4	0.006	0.957	29.76	0.455	1.6	0.024	0.974
PEI+ AS	50.76	0.799	5.5	0.086	0.934	-47.85	-0.73	-35.7	-0.55	0.988
PEI+ AC	39.52	0.622	0.55	0.0086	0.98	63.69	0.974	34.5	0.528	0.972
PEI+ SA	40.65	0.64	0.29	0.0046	0.963	28.98	0.443	2.13	0.0326	0.989
PEI+EDTA	51.54	0.811	14.59	0.23	0.992	117.6	1.8	41.36	0.633	0.998
PEI+ NTA	39.37	0.62	5.63	0.0886	0.99	156.25	2.39	90.69	1.39	0.987

6.4.3 Cr^{6+} binding with PEI in the presence of various chelators

The adsorption of Cr^{6+} in the presence of different chelators competitors (figure 6.24), was affected by all of them compared with the Cr^{6+}- PEI complex solution (no additive). As can be seen, a similar competitive trend of Cr^{6+} binding to PEI was observed in presence of sodium acetate (SA) or ammonium chloride (AC). At low metal concentrations, the amount of Cr^{6+} adsorbed increased rapidly in the presence of SA or AC, indicating that the competitive effects were not pronounced. As the metal concentrations increased further, the amount of Cr^{6+} bound was affected more pronouncedly in these systems compared with the Cr^{6+}-PEI complex system. On the other hand, a significant reduction of the amount of Cr^{6+} bound was observed in the presence of other chelating agents in the complex solution. Suggesting a less affinity of PEI to the Cr^{6+} ions and strong competition by the chelating agents in the following order: EDTA > AS > NTA. However, the application of Langmuir isotherm model to the experimental results showed a quite good prediction and reasonable fit to the experimental data.

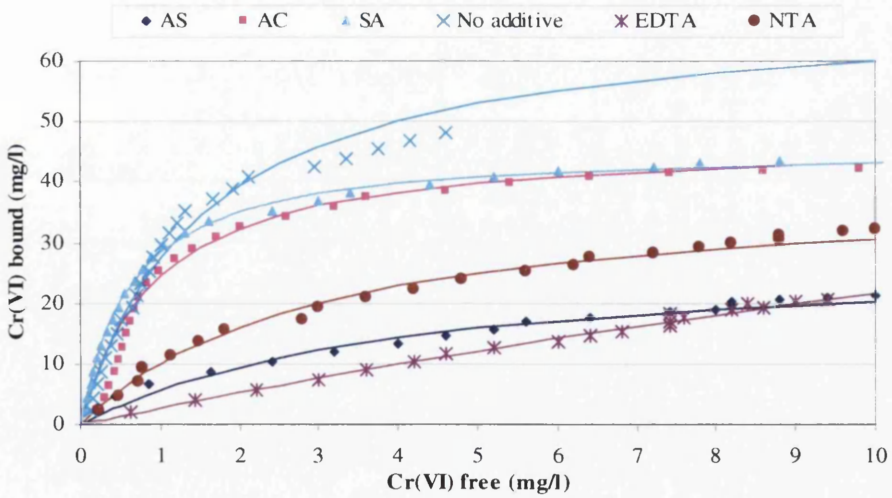


Figure 6.24 *Results of binding of mixture metal ions to PEI in continuous mode of PEUF process , Competitive adsorption of Cr^{6+} in the presence of various chelating agents [experiments (points) and using langmuir isotherm model (lines) at pH 5.5, 2 mM chelating agents, 1 g/l PEI and 14 mg/l metal concentrations of each metal]*

As a result of study of Cr^{6+} binding from mixture metal/polymer solutions in presence and absence of chelation agents, it was found that the the maximum binding capacities (Q_{max}) were inhibited as follow: EDTA > AS > NTA > AC > SA. However, Langmuir isotherms results (table 6.4) showed that (Q_{max}) decreased in the following order: EDTA 108.7 mg/g (2.09 mmol/g) > ammonium chloride 46.95 mg/g (0.9 mmol/g) > sodium acetate 45.66 mg/g (0.878 mmol/g) > NTA 39.68 mg/g (0.76 mmol/g) > ammonium sulfate 28.7 mg/g (0.552 mmol/g). While that obtained without chelators was 68.96 mg/g (1.326 mmol/g). Also, the equilibrium constant (K_L) occurred in the following order: EDTA 40.14 mg/l (0.772 mmol/l), ammonium sulfate 4.12 mg/l (0.079 mmol/l), NTA 2.95 mg/l (0.0567 mmol/l), ammonium chloride 0.91 mg/l (0.0175 mmol/l), sodium acetate 0.61 mg/l (0.012 mmol/l). The equilibrium constant that obtained for Cr^{6+}/PEI complex in the absence of chelating agent was 1.51 mg/l (0.029 mmol/l). However, this inhibition effect due to the presence of different chelating agents was in agreement with the competitive results obtained in batch mode PEUF experiments (section 5.4.2).

6.4.4 Ni^{2+} binding with PEI in the presence of various chelators

The results of binding of Ni^{2+} ions to PEI in the presence and absence of various chelating agents are shown in figure (6.25). It was observed that the existence of sodium acetate (SA) in the aqueous solution of complex metals-PEI evidently enhanced the adsorption of Ni^{2+}. Strongly suggesting PEI formed better complexes with Ni^{2+} and that some mechanism other than complexation contributed to the observed enhancement. This enhancement agrees with the results obtained in batch mode PEUF (section 5.4.2). In contrast, the presence of other chelating agents in the complex solution caused a significant reduction of Ni^{2+} adsorption due to the competition effect in the following order: AC > AS > NTA. Also, a different binding of Ni^{2+} was observed in the presence of EDTA in the complex solution and that was in the form of linear relationship. On the other hand, Langmuir isotherm model successfully predicted the experimental data in figure 6.25, except for the complex of ammonium sulfate and NTA at low concentrations. This is evident from the values of square linear regression (R^2) (table 6.4).

In table (6.4), the maximum binding capacity (Q_{max}) of Ni^{2+} in the absence of the chelating agents was 46.73 mg/g (0.796 mmol/g), and that the (Q_{max}) was decreased in the presence of the chelating agents in the complex solutions in the following order: sodium acetate 44.64 mg/g (0.76 mmol/g) > ammonium chloride 31.75 mg/g (0.54 mmol/g) > NTA 25.25 mg/g (0.43 mmol/g) > ammonium sulfate 22.78 mg/g (0.39 mmol/g). Also, the equilibrium constant (K_L) occurred in the following order: NTA 6.05 mg/l (0.103 mmol/l), ammonium chloride 3.17 mg/l (0.054 mmol/l), ammonium sulfate 3.12 mg/l (0.053 mmol/l), sodium acetate 0.82 mg/l (0.014 mmol/l). While the equilibrium constant obtained for Ni^{2+}/PEI complex in the absence of chelating agent was 6.7 mg/l (0.114 mmol/l). In the case of EDTA, the maximum binding capacity of Ni^{2+} and the equilibrium constant were 91.74 mg/g (1.563 mmol/g) and 26.72 mg/l (0.455 mmol/l), respectively. Indicating different mechanism was responsible for this observation.

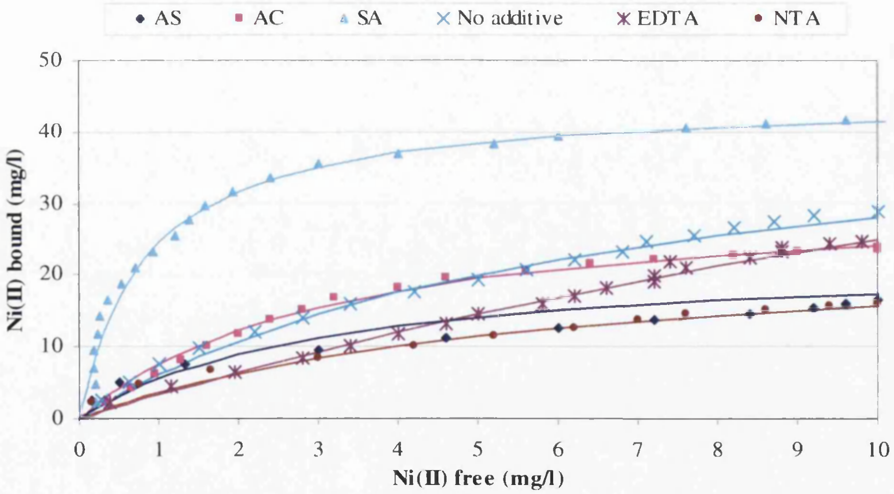


Figure 6.25 *Results of binding of mixture metal ions to PEI in continuous mode of PEUF process , Competitive adsorption of Ni^{2+} in the presence of various chelating agents [experiments (points) and using langmuir isotherm model (lines) at pH 5.5, 2 mM chelating agents, 1 g/l PEI and 14 mg/l metal concentrations of each metal]*

Table (6.4) below summarizes the results of applying the Langmuir adsorption isotherm (i.e. Q_{max}, K_L and R^2) obtained from a series of continuous experiments of PEUF with various chelating agents for Cr^{6+} and Ni^{2+} binding in mixture metals/polymer solutions.

***Table 6.4** Cr^{6+} and Ni^{2+} experimental data from the application of Langmuir isotherm model for mixture metal ions with 2 mM chelating agents competitors in continuous mode of PEUF process, the data were fitted to linearised form of these experiments.*

Experiment	Cr^{6+}					Ni^{2+}				
Metals + (1 g/l PEI) + (2 mM add.)	Q_{max}		K_L		R^2	Q_{max}		K_L		R^2
	(mg/ g_{PEI})	(mmol/ g_{PEI})	(mg/ l)	(mmol/ l)		(mg/ g_{PEI})	(mmol/ g_{PEI})	(mg/ l)	(mmol/ l)	
PEI	68.96	1.326	1.51	0.029	0.978	46.73	0.796	6.7	0.114	0.99
PEI+ AS	28.7	0.552	4.12	0.079	0.983	22.78	0.388	3.12	0.053	0.85
PEI+ AC	46.95	0.9	0.91	0.0175	0.989	31.75	0.54	3.17	0.054	0.989
PEI+ SA	45.66	0.878	0.61	0.012	0.99	44.64	0.76	0.82	0.014	0.994
PEI+EDTA	108.7	2.09	40.14	0.772	0.996	91.74	1.563	26.72	0.455	0.993
PEI+ NTA	39.68	0.76	2.95	0.0567	0.984	25.25	0.43	6.05	0.103	0.987

6.4.5 Co^{2+} binding with PEI in the presence of various chelators

Figure 6.26 shows the amount of Co^{2+} bound to PEI in the absence and presence of different chelating agents. Once again, the presence of sodium acetate in the complex solution enhanced the adsorption of Co^{2+} compared to the adsorption of Co^{2+} in the complex solutions without the addition of chelating agents. Also, a significant reduction of Co^{2+} adsorption was observed in the presence of EDTA, ammonium sulfate, NTA and ammonium chloride. It is deduced that there is a low affinity of PEI to bind Co^{2+} in the presence of these chelators. However, the applications of Langmuir isotherm model to predict the experimental results of Co^{2+} adsorption are shown in figure 6.26. It is seen that the prediction was reasonable, but it failed to predict the experimental data in the case of ammonium chloride where the behavior of the model is linear. In fact, this was confirmed from the values of R^2 in table 6.5. Thus, the maximum binding capacities of Co^{2+}/PEI in the complex solutions were dependent on the type of chelating agents competitors used. In the case of sodium acetate, NTA or ammonium sulfate in the complex solutions, the maximum capacities (Q_{max}) were 39.52 mg/g (0.67 mmol/g), 35.71 mg/g (0.6 mmol/g) and 27.78 mg/g (0.47 mmol/g), respectively; indicating a lower affinity of PEI to bind Co^{2+} in the presence of these chelators compared with the complex solution without additives 52.1 mg/g (0.884 mmol/g). Also, the equilibrium constants in the presence of various chelating competitive agents were in the following order: NTA 5.31 mg/l (0.09 mmol/l) > ammonium sulfate 4.24 mg/l (0.072 mmol/l) > sodium acetate 0.85 mg/l (0.014 mmol/l) and that for no additive complex solution was 3.59 mg/l (0.061 mmol/l). However, the presence of ammonium chloride in the complex solution showed a high maximum capacity 175.4 mg/g (2.98 mmol/g) and high equilibrium constant 47.6 mg/l (0.81 mmol/l) which was reflected the linear relationship obtained by the Langmuir model. On the other hand, poor binding of Co^{2+} was clear from the negative sign of (Q_{max}) in the competitive reaction of EDTA with the complex.

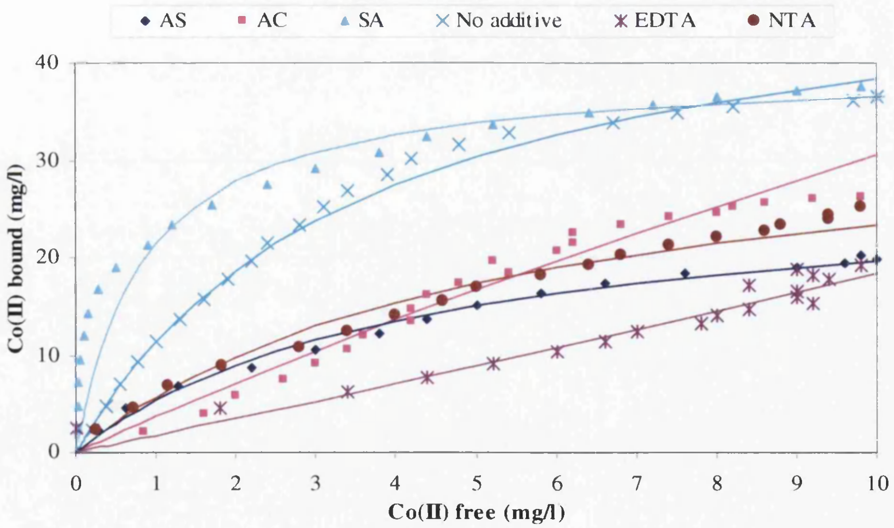


Figure 6.26 *Results of binding of mixture metal ions to PEI in continuous mode of PEUF process , Competitive adsorption of Co^{2+} in the presence of various chelating agents [experiments (points) and using langmuir isotherm model (lines) at pH 5.5, 2 mM chelating agents, 1 g/l PEI and 14 mg/l metal concentrations of each metal]*

6.4.6 Cd^{2+} binding with PEI in the presence of various chelators

In figure 6.27, it was observed that the presence of chelating competitive agents in the complex solution influenced the binding of Cd^{2+}/PEI. Under comparable conditions, it seems that the extent of the drop in adsorption ability decreases in the order: ammonium chloride ~ ammonium sulfate > EDTA > NTA > sodium acetate. This is due to the different chelating ability of Cd^{2+} with these ligands in competition to the available site of PEI. In fact, the effect of aqueous-phase chelation is comparatively weak in the case of sodium acetate, especially at high metals concentrations. On the other hand, the application of Langmuir isotherms model showed an approximate linear relationship for the complexes with ammonium chloride, ammonium sulfate and EDTA. At extremely low metals concentrations, low accuracy of prediction was observed for the complexes of NTA, sodium acetate and for the complex of Cd^{2+}/PEI without chelators competitors (no additive).

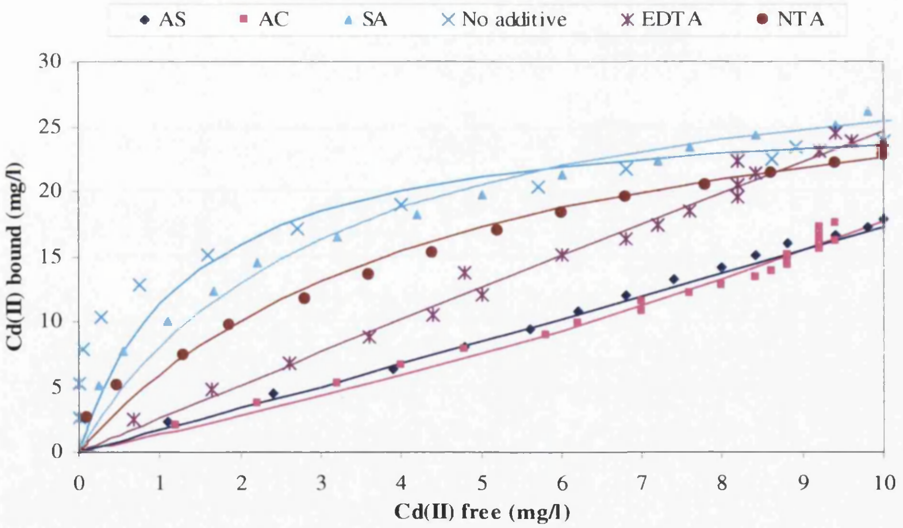


Figure 6.27 *Results of binding of mixture metal ions to PEI in continuous mode of PEUF process , Competitive adsorption of Cd^{2+} in the presence of various chelating agents [experiments (points) and using langmuir isotherm model (lines) at pH 5.5, 2 mM chelating agents, 1 g/l PEI and 14 mg/l metal concentrations of each metal]*

However, the inhibitory effects caused by ammonium sulfate and ammonium chloride agents was very significant on the binding conditions and this was clear from the negative signs of maximum binding capacities (Q_{max}) and the equilibrium constants (K_L) shown in table (6.5). Also, the values of (Q_{max}) which obtained in the presence of sodium acetate and NTA were 33.44 mg/g (0.297 mmol/g) and 32.89 mg/g (0.292 mmol/g) respectively, while that obtained without chelating agent was 26.74 mg/g (0.238 mmol/g). It was found that the sequence of equilibrium constants were in the following order: NTA 4.56 mg/l (0.04 mmol/l), sodium acetate 3.15 mg/l (0.028 mmol/l) and for the complex in the absence of chelators was 1.36 mg/l (0.012 mmol/l). It should be noted that the presence of EDTA in the complex solution showed that the maximum binding capacity of Cd^{2+} and the equilibrium constant were 500 mg/g (4.45 mmol/g) and 193.6 mg/l (1.72 mmol/l), respectively. In fact, a different mechanism was expected to be responsible for this observation.

Table 6.5 summarizes the results of applying the Langmuir adsorption isotherm (i.e. Q_{max}, K_L and R^2) obtained from a series of continuous PEUF experiments with various chelating agents for Co^{2+} and Cd^{2+} binding in mixture metals/ PEI solutions.

Table 6.5 *Co^{2+} and Cd^{2+} experimental data from the application of Langmuir isotherms model for mixture metal ions with 2 mM chelating agents competitors in continuous mode of PEUF process, the data were fitted to linearised form of these experiments.*

Experiment *Metals + (1 g/l PEI) + (2 mM add.)*	Co^{2+}					Cd^{2+}				
	Q_{max}		K_L		R^2	Q_{max}		K_L		R^2
	(mg/ g_{PEI})	*(mmol/ g_{PEI})*	*(mg/ l)*	*(mmol/ l)*		*(mg/ g_{PEI})*	*(mmol/ g_{PEI})*	*(mg/ l)*	*(mmol/ l)*	
PEI	52.1	0.884	3.59	0.061	0.986	26.74	0.238	1.36	0.012	0.962
PEI+ AS	27.78	0.47	4.24	0.072	0.979	-333.3	-2.96	-203	-1.8	0.989
PEI+ AC	175.4	2.98	47.6	0.81	0.934	-49.5	-0.44	-37.9	-0.34	0.968
PEI+ SA	39.52	0.67	0.85	0.014	0.965	33.44	0.297	3.15	0.028	0.974
PEI+EDTA	-263.1	-4.46	-153	-2.6	0.98	500	4.45	193.6	1.72	0.984
PEI+ NTA	35.71	0.6	5.31	0.09	0.97	32.89	0.292	4.56	0.04	0.99

6.5. Conclusions

The aim of this chapter was to investigate the ability of continuous feed of PEUF process for the separation of metal ions from various feed streams of aqueous solutions. There is no work published on the PEUF separation of complex mixture of metals using a continuous contacting process, similarly the competition between metals/ PEI/ chelators and competitors has not been studied.

In an attempt to identify the effect of metal ion competition on the retention and binding conditions in PEUF, experiments in the presence of PEI have been carried out for three different systems: single metal solutions, mixed metals solutions and complex solutions in the presence of various chelators competitors. Aqueous solutions of six metal ions (Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+}, and Cd^{2+}) were investigated in continuous mode PEUF using cross flow ultrafiltration rig. Application of Langmuir and Freundlich isotherms models to predict the experimental data of single and mixture metal ions solutions allowed investigation of the feasibility of determining maximum binding capacities of metal ions and the equilibrium constants.

The experiment carried out in this chapter gave some interesting and informative results and illustrated some of differences between batch and continuous systems. It also illustrated some of the complexities. The experimental approach and the analysis gave good reliable data on which conclusion about the results could be made. These are discussed under the following headings:

6.5.1 Filtration performance

Results of the retention profiles with respect to the filtration factor from aqueous solution of single metals were different from the retention results obtained from experiments of mixture metals. The affinity of PEI to bind single metals (figures 6.3 and 6.4) was in the following order: $Cr^{6+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+}$, while the affinity of PEI for the metals in mixture solution (figures 6.5 and 6.6) was: $Cu^{2+} > Cr^{6+} > Co^{2+} > Ni^{2+} > Zn^{2+}$

> Cd^{2+}. In fact, the competition of metal ions on the polymer binding sites may was responsible for this observation. This was evident from observed reduction of maximum binding capacities of mixtures metals solution compared to those obtained from the single metal solutions (tables 6.1 and 6.2).

Further studies were focused on the effect of chelating competitive agents [Ammonium sulfate, Ammonium chloride, Sodium acetate, Ethylenediaminetetra acetic acid (EDTA) and Nitrilotriacetic acid (NTA)] on the retention and binding conditions of PEI to the metal ions in mixed solutions. In the presence of ammonium sulfate (figure 6.9), it was found that the retention of metal ions was significantly altered and that the reduction was observed for all the metal ions in the solution. This suggests inhibitory effects of ammonium sulfate were evident for this reduction in metal retention. In the case of ammonium chloride (figure 6.11), the retention profile was metal ions dependent, indicating that the retention of Cd^{2+} and Zn^{2+} was inhibited while other metals in the solution showed a similar trend of retention compared with those in the absence of a chelator (figure 6.6). However, the presence of sodium acetate in the complex showed no effect on the retention of Cu^{2+}, Zn^{2+}, Cr^{6+} and Cd^{2+}, while an enhancement of retention was observed for Co^{2+} and Ni^{2+} (figure 6.13) and produced similar effects to those gained previously from studies using batch of PEUF (section 5.22). On the other hand, inhibition effect of the presence of NTA and EDTA in the complex solution caused a significant reduction in metal ions retention (figures 6.15 and 6.17). Indicate poor affinity of PEI to bind the metal ions under competitive conditions with NTA and EDTA.

The affinity of PEI to bind the metal ions using a continuous feed process can be concluded as follow:

- Single metal solutions: $Cr^{6+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+}$.
- Mixed metals solution: $Cu^{2+} > Cr^{6+} > Co^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+}$.
- Mixture of metal ions solutions with various chelators competitors:
  - Sodium acetate: $Cu^{2+} > Cr^{6+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+}$.
  - Ammonium sulfate: $Cu^{2+} > Cr^{6+} > Co^{2+} > Ni^{2+} > Zn^{2+} \sim Cd^{2+}$.
  - Ammonium chloride: $Cu^{2+} \sim Cr^{6+} > Ni^{2+} > Co^{2+} > Zn^{2+} \sim Cd^{2+}$.

- NTA: $Cr^{6+} > Cu^{2+} > Co^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+}$
- EDTA: $Cu^{2+} > Cr^{6+} \sim Ni^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+}$.

The presence of PEI had little effect on the retention of Cd^{2+} and Zn^{2+} from PEUF experiments in continuous feed system. In general, the average retention of metal ions under competitive conditions of the chelators competitors was compared with the average retention of control metal solution with PEI (no additive) and summarized in figure 6.28.

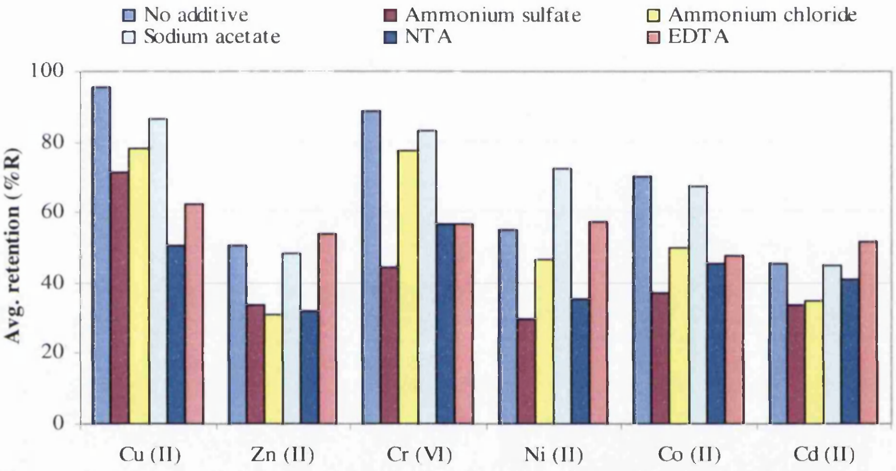


Figure 6.28 *Average retention profiles of mixture metals ions in the presence and absence of chelating competitive agents using continuous feed of PEUF.*

6.5.2 Adsorption isotherms

Application of Langmuir model to predict the experimental results of mixture metal ions with PEI under competitive condition with chelating competitors provided a reasonable prediction of the data (tables 6.3-6.5). However, Langmuir isotherms also provided the maximum binding capacities for these systems, indicating some nonsensical results such as negative or large values of (Q_{max}). These observations were confirmed in two cases, at poor metal ion retention with some chelating competitors or with the linear form of model prediction. In fact, the effect of aqueous-phase chelation is comparatively weak in the case of sodium acetate, due to the small equilibrium constants, suggesting enhancement or no significant effect on the metal adsorption to PEI. It should be noted that for strong chelating agents such as EDTA or other competitors (AS, AC), the negative or large values of (Q_{max}) are combined to a negative or large equilibrium constants and resulting a poor adsorption of metal ions to PEI (tables 6.3-6.5). Under similar competitive conditions, maximum capacities of metal ions bind to PEI resulting from the application of Langmuir isotherm in continuous feed of PEUF were far greater than those obtained from batch system (tables 5.7 and 6.6) and they were almost similar for Cu^{2+}-PEI complex in single and mixed metals solutions of both systems.

***Table 6.6** Summary of experimental data of* Q_{max} and K_L *from applying the Langmuir adsorption isotherm for single and mixed metal ions solutions in the absence and presence of various chelators competitors in continuous mode of PEUF process, the data were fitted to linearised form of these experiments.*

Experiment *Metals + (1 g/l PEI) + (2 mM add.)*		*Mixed metals solutions*						*Single metal solutions*
		PEI	*PEI + AS*	*PEI + AC*	*PEI + SA*	*PEI + EDTA*	*PEI + NTA*	*PEI*
Cu^{2+}	Q_{max} (mg metal/g_{PEI})	71.43	50.76	39.52	40.65	51.54	39.37	163.9
	K_L (mg/l)	0.4	5.5	0.55	0.29	14.59	5.63	3.31
Zn^{2+}	Q_{max} (mg metal/g_{PEI})	29.76	- 47.85	63.69	28.98	117.6	156.25	500
	K_L (mg/l)	1.6	- 35.7	34.5	2.13	41.36	90.69	190.3
Cr^{6+}	Q_{max} (mg metal/g_{PEI})	68.96	28.7	46.95	45.66	108.69	39.68	200
	K_L (mg/l)	1.51	4.12	0.91	0.61	40.14	2.95	1.5
Ni^{2+}	Q_{max} (mg metal/g_{PEI})	46.73	22.78	31.75	44.64	91.74	25.25	333.3
	K_L (mg/l)	6.7	3.12	3.17	0.82	26.72	6.05	51
Co^{2+}	Q_{max} (mg metal/g_{PEI})	52.1	27.78	175.44	39.52	- 263.1	35.71	161.3
	K_L (mg/l)	3.59	4.24	47.6	0.85	- 153.4	5.31	42.1
Cd^{2+}	Q_{max} (mg metal/g_{PEI})	26.74	- 333.3	- 49.5	33.44	500	32.89	188.68
	K_L (mg/l)	1.36	- 203	- 37.9	3.15	193.6	4.56	54.2

6.5.3 Metal purification from mixtures using PEI and other additives (competitors/ chelators)

The data presented (section 6.2) shows that differential separation and thus purification is possible using these systems. Separation using PEI to preferentially bind a metal from mixture gave an enriched retentate and a depleted permeate, e.g. Copper (Cu^{2+}) and Zinc (Zn^{2+}) in figure 6.5. Addition of chelators or competitors also changes the relative retention of metals in these systems, giving even more scope to purify metals.

Because the Langmuir equation fit the data very well, this will provides the basis of an analytical tool to optimize the separation of metals using the PEUF method. It can be envisaged that high resolution multistage system could be developed. This is a novel and exciting finding that may have relevance in metal recovery and purification from wastes.

Chapter 7

Mathematical modeling of Continuous feed PEUF

7.1. Introduction

The mathematical modeling for continuous feed PEUF process was developed from the fundamental principle of mass balance based on the application of Langmuir isotherms process. Three types of complex metal-polymer solutions were investigated. They were: complex solutions of single metal, complex solutions of mixture metals and complex solutions of mixture metals in the presence of chelating agents. However, the continuous mode of process was assumed to behave as a continuous stirred tank reactor (CSTR). In this mode, the feed solution enters the tank continuously at a flow rate Φ_0 and a constant concentration $[M]_0$. The tank initially contains polymer solution which is able to form a complex of metal ions (Q) varies with time. Solution of free metal ions flows steadily out of the tank, but its concentration $[M]_p$ varies with time. However, the feed flow rate was adjusted to equal the outlet feed flow rate while maintaining a constant fluid volume (V).

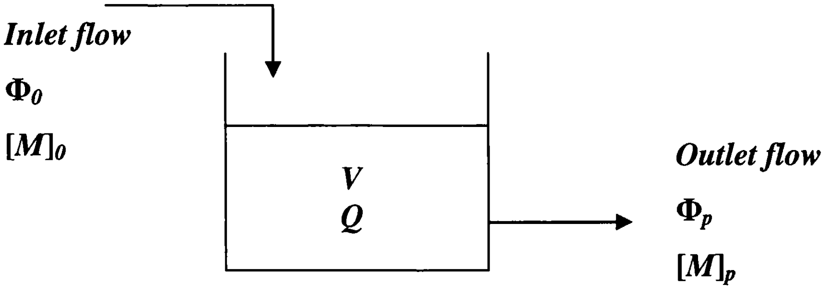


***Figure 7.1** The schematic of a continuous PEUF process*

Where:

Φ_0 = Feed flow rate (l/hr.)

Φ_p = Permeate flow rate (l/hr.)

$[M]_0$ = Concentration of metal ion in the feed (mg/l)

$[M]_p$ = Concentration of metal ion in the permeate (mg/l)

V = Volume of the fluid in the reservoir tank (l)

Q = The amount of metal bound (mg metal/g polymer).

Overall mass balance of metal ions concentrations can be written as follows:

Rate of accumulation = Input – output – rate of generation ....*(equation 7.1)*

Mathematically, equation 7.1 above can be written as follows:

$$V\frac{\partial Q}{\partial t} = \Phi_0[M]_0 - \Phi_p[M]_p - V\frac{\partial[M]_p}{\partial t} \quad \text{.......................................}\textit{(equation 7.2)}$$

At constant fluid volume where the flow rate is constant ($\Phi_0 = \Phi_p = \Phi$), the metal ion concentrations in the permeate stream as a function of time can be written as follow:

$$V\frac{\partial[M]_p}{\partial t} = \Phi\left([M]_0 - [M]_p\right) - V\frac{\partial Q}{\partial t} \quad \text{...}\textit{(equation 7.3)}$$

The Langmuir isotherms equation is,

$$Q = \frac{Q_{\max}[M]_p}{K_L + [M]_p} \quad \text{......................... ....}\textit{(equation 7.4)}$$

The differential equation of Langmuir isotherms can be determined as follows:

$$Q' = \frac{\partial Q}{\partial t} = \frac{\left\{\left(K_L + [M]_p\right)\left(Q_{\max} \times [M]'_p\right)\right\} - \left\{\left(Q_{\max} \times [M]_p\right)\left([M]'_p\right)\right\}}{\left\{K_L + [M]_p\right\}^2} \text{........}\textit{(equation 7.5)}$$

Rearranging equation 7.5,

$$Q' = \frac{\partial Q}{\partial t} = \frac{\{(K_L \times Q_{\max} \times [M]'_p)\}}{\{K_L + [M]_p\}^2} \quad \text{...(equation 7.6)}$$

Introducing equation 7.6 into equation 7.3, metal concentration in the permeate stream as a function of time can be considered as follow:

$$[M]'_p = \frac{\partial [M]_p}{\partial t} = \left\{ (\Phi/V)\left([M]_0 - [M]_p\right) - \left(\frac{K_L \times Q_{\max} \times [M]'_p}{(K_L + [M]_p)^2} \right) \right\} \quad \text{.............(equation 7.7)}$$

Equation 7.7 can be rearranged,

$$[M]'_p = \frac{\Phi\left([M]_0 - [M]_p\right)}{V\left\{1 + \frac{K_L \times Q_{\max}}{(K_L + [M]_p)^2}\right\}} \quad \text{...(equation 7.8)}$$

Furthermore, the changing of metal ion concentration with time in permeate stream can be calculated by simultaneously solving the differential equation (7.8), and this has been solved by applying a numerical method (Euler's method) using a excel spreadsheet program (Appendix 4). As a result, the following expression is obtained:

$$[M]_{p,t+\Delta t} = [M]_{p,t} + \frac{\Delta t\, \Phi_t \left([M]_0 - [M]_{p,t}\right)}{V\left\{1 + \frac{K_L\, Q_{\max}}{(K_L + [M]_{p,t})^2}\right\}} \quad \text{...(equation 7.9)}$$

Once we considered the equations of mass balance in conjunction with the Langmuir isotherms for the system in the form of differential equation, the following expression of metal retention coefficient as a function of filtration factor ($R_{iF+\Delta F}$) can be obtained:

$$R_{iF+\Delta F} = \left\{ 1 - \left(\frac{ \left\{ [M]_{p,t} + \Delta F \, \Phi_t \left([M]_0 - [M]_{p,t} \right) / \, V \left\{ 1 + \left(K_L \, Q_{\max} \right) / \left(K_L + [M]_{p,t} \right)^2 \right\} \right\} }{ [M]_0 } \right) \right\} \times 100$$

……………………………*(equation 7.10)*

Equations 7.9 and 7.10 allow prediction the experimental data of metal concentrations in the permeate stream besides the metal retention coefficients in continuous mode of PEUF processes, providing we know:

- Feed flow rate (Φ)
- Filtration factor (F)
- Initial metal concentration ($[M]_0$)
- The fluid volume in the reservoir tank (V)
- Maximum binding capacities (Q_m) and equilibrium constants (K_L) of metal ions.

The equations above describe an individual metal interaction, for multicomponent metal systems several sets of equations were required to solve the problem. The constants (Q_m , K_L) for each metal were obtained from previous data in Chapter 6.

However, in order to simplify the calculations, the following assumptions were made:

(1) The formation of metal-hydroxy complexes is neglected.
(2) Equilibrium between the polymer and metal ions is reached instantaneously.
(3) The complex of metal-polymer is completely retained by the ultrafiltration membrane.
(4) There is no interaction between the ultrafiltration membrane and free metal ions, which means that the value of coefficient of membrane retardation equals one.
(5) All metal ions in the solution, in the tank, are assumed to be bound to the polymer or free in the solution.
(6) Because the tank is well stirred, it is considered that the metal concentrations free in the tank equal that in the outlet flow.

7.2. Modeling of Single metal ions in continuous mode PEUF

The mathematical modeling in section 7.1 was constructed to predict the experimental data of free single metal ions concentrations observed in continuous feed of PEUF process. The solutions of single metal ions (Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+}) were investigated in the presence of PEI as complexing agent. The constants for the calculations are given in table 6.6. However, the experimental results of metal concentrations in the permeate stream and the predicted values by model as a function of process time are shown in figure (7.2). It was observed that the model provided good values in comparison with the experimental data for all metals investigated.

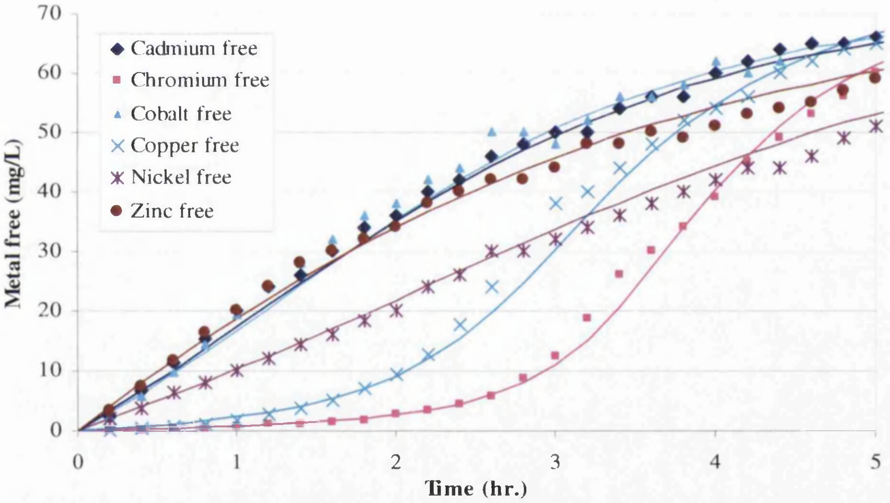


Figure 7.2 *Comparison of single metal ions concentrations in the permeate stream as a function of process time between experimental data and the model using a continuous feed PEUF. The experimental data were performed as symbols and the results from model were drawn as lines. [The concentrations of single metal ions in the feed solutions were 70 mg/l and the PEI concentration was 1g/l. The feed flow rate was controlled at 5 l/hr while maintaining a constant fluid volume and the solutions pH was adjusted at 5.5. (Experimental details are described in sections 3.5.2)].*

7.3. Modeling of mixture metal ions in continuous mode PEUF

The model also was investigated to predict the experimental data of mixed metal ion concentrations in the permeate stream as a function of time using continuous feed of PEUF. The experimentally derived constants for the Langmuir isotherm are given in table 6.6. At constant feed flow rate, the concentrations of metal ions in the permeate stream were measured experimentally (symbols). Then, these results were predicted using the proposed model in section 7.1 (lines). As a result, figure 7.3 presents the concentrations of metal ions in the permeate stream obtained from experimental data and simulated model as a function of process time. It was observed that the model predictions correlated well with the results from the experiments. Co^{2+} gave the worst prediction especially at intermediate time (2 – 3.5 hr.).

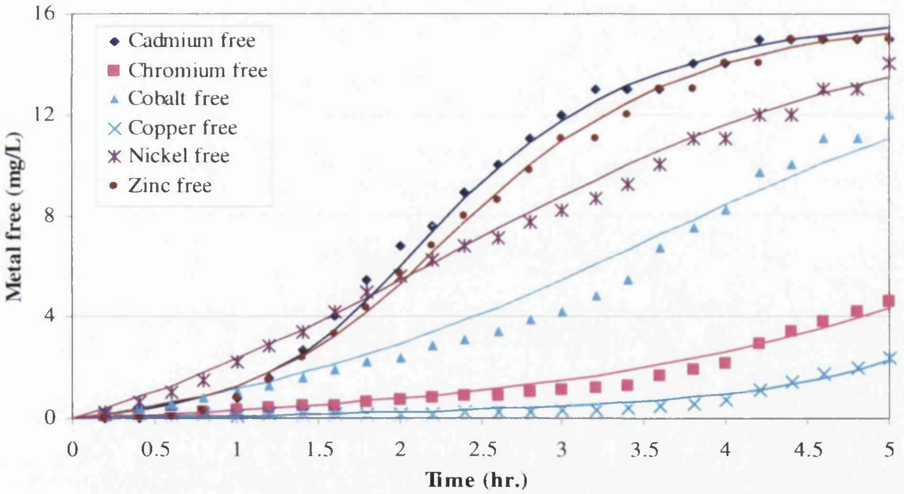


Figure 7.3 *Comparison of mixture metal ions concentrations in the permeate stream as a function of process time between experimental data and the model using a continuous feed PEUF. The experimental data were performed as symbols and the results from model were drawn as lines.[The feed solution of mixture metal ions (Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+}) was prepared with 14 mg/l metal concentrations. 1g/l of PEI was used as complexing agent. (Experimental details can be found in sections 3.5.3)].*

7.4. Modeling of mixture metal ions-chelates in continuous feed PEUF

Under competitive conditions of various chelating agents, the results of metal concentrations in the permeate streams as a function of time were determined experimentally in the presence of PEI. Solutions of six mixture metals (Cu^{2+}, Zn^{2+}, Cr^{6+}, Ni^{2+}, Co^{2+}, and Cd^{2+}) were prepared at fixed feed concentrations (14 mg/l). Different chelating agents with 2 mM concentrations of (Ammonium sulfate, Ammonium chloride, Sodium acetate, Ethylenediaminetetra acetic acid (EDTA) and Nitrilotriacetic acid (NTA) were introduced to the complex solutions. (See section 3.5.4 for the details of experimental procedures). The experimental constants results in the presence of chelators/competitors used in the calculation are given in table 6.6. Then, the experimental data were predicted using the model proposed in section 7.1. As results, the experimental data were compared with the values predicted from the model under competitive conditions (figures 7.4 – 7.8). The symbols represented the experimental data whereas the simulated results from models were drawn as lines.

7.4.1 Model prediction results in the presence of Sodium acetate

Figure (7.4) illustrates the results of free metal ions as a function of time in using a continuous feed PEUF, under competitive condition of sodium acetate. It was observed that the model more successfully fits the experimental data of Cu^{2+}, Cr^{6+}, Ni^{2+} and Co^{2+} than for Zn^{2+} and Cd^{2+}. Indicating less affinity of PEI to complex the metal ions of Zn^{2+} and Cd^{2+} in the presence of sodium acetate caused these deviations.

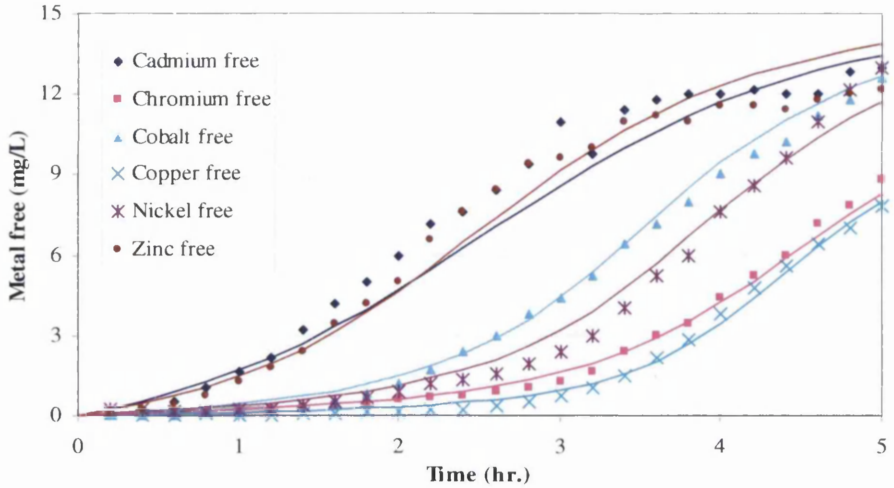


***Figure 7.4** Comparison of mixture metal ions concentrations in the permeate stream as a function of process time between experimental data and the model using a continuous feed PEUF in the presence of sodium acetate (SA). The experimental data were performed as symbols and the results from model were drawn as lines.[Metals feed solution with 14 mg/l concentrations of each metal, 2 mM SA, 1 g/l PEI, pH 5.5, 25 ℃, flow rate 5 l/hr.].*

7.4.2 Model prediction results in the presence of Ammonium sulfate

The experimental results of complex solution of metal-PEI in the presence of ammonium sulfate were compared with the data from the proposed model as performed in figure 7.5. Generally, the prediction of concentrations of free metal ions as a function of time significantly affected by the presence of ammonium sulfate and that this was metal ion dependent. However, the model does not show a good fit with experimental data except for Cu^{2+} as well as for Cr^{6+} and Co^{2+} at time less than 3 hr. Ni^{2+} model does not predict the wash out curve, the model predicting more retention than was observed.

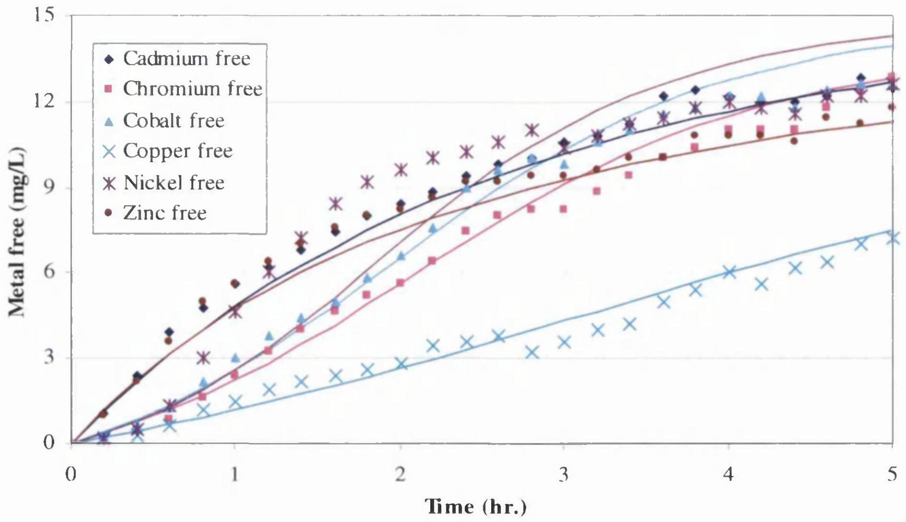


***Figure** 7.5 Comparison of mixture metal ions concentrations in the permeate stream as a function of process time between experimental data and the model using using a continuous feed PEUF in the presence of ammonium sulfate (AS). The experimental data were performed as symbols and the results from model were drawn as lines.[Metals feed solution with 14 mg/l concentrations of each metal, 2 mM AS, 1 g/l PEI, pH 5.5, 25 ℃, flow rate 5 l/hr.].*

7.4.3 Model prediction results in the presence of Ammonium chloride

The experimental data of the complexation of metal ions with PEI in the presence of ammonium chloride were predicted using the proposed model as shown in figure 7.6. The model provided a good prediction for the experimental results of Cu^{2+}. In the case of Cr^{6+}, Ni^{2+}, Co^{2+} and Cd^{2+}, the model correlated well with the experimental data at the beginning of the process (time < 2 hr.). However, the model did not fit well the experimental data of Zn^{2+}. The observed Cr^{6+} and Co^{2+} concentrations in the model were slightly higher than that obtained by experiments at time > 2 hr. Suggesting a significant impact of adding ammonium chloride to the complex solution on the prediction of free metal ions in the permeate stream.

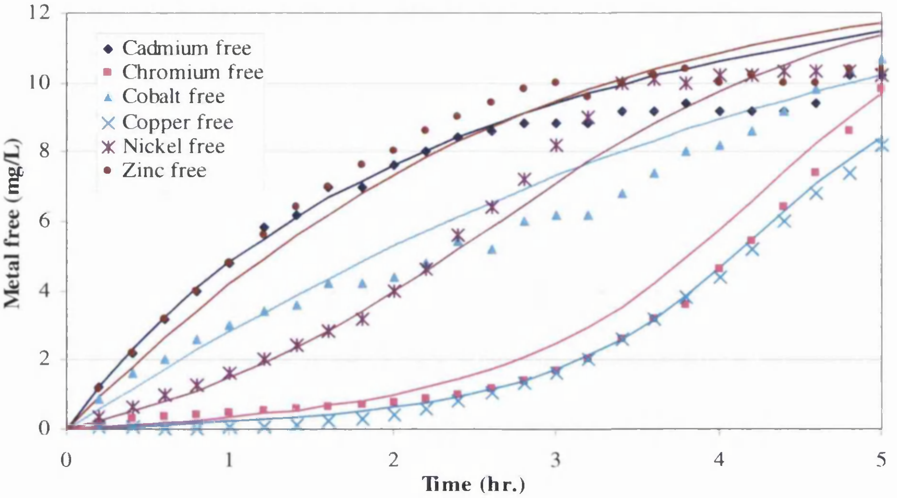


Figure 7.6 *Comparison of mixture metal ions concentrations in the permeate stream as a function of process time between experimental data and the model using using a continuous feed PEUF in the presence of ammonium chloride (AC). The experimental data were performed as symbols and the results from model were drawn as lines. .[Metals feed solution with 14 mg/l concentrations of each metal, 2 mM AC, 1 g/l PEI, pH 5.5, 25 °C, flow rate 5 l/hr.].*

7.4.4 Model prediction results in the presence of NTA

Figure 7.7 shows the concentrations of metal ions in the permeate stream as a function of process time from the experimental data and the predicted values under competitive condition with NTA. The model produced a good fits to the experimental data, but low accuracy was obtained for the metal concentrations at high operating time (t > 4) especially for Zn^{2+}.

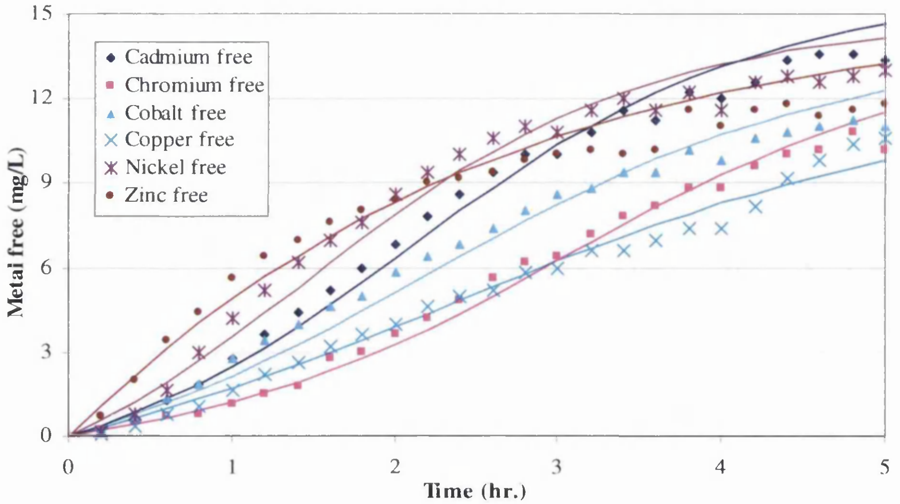


***Figure** 7.7 Comparison of mixture metal ions concentrations in the permeate stream as a function of process time between experimental data and the model using a continuous feed PEUF in the presence of NTA. The experimental data were performed as symbols and the results from model were drawn as lines. .[Metals feed solution with 14 mg/l concentrations of each metal, 2 mM NTA, 1 g/l PEI, pH 5.5, 25 °C, flow rate 5 l/hr.].*

7.4.5 Model prediction results in the presence of EDTA

The experimental results of the presence of EDTA in the complex solution were compared with the data from the proposed model. The results of different metal concentrations appeared in the permeate stream as functions of time are shown in figure 7.8. Reasonable agreement between the model prediction and the experimental data were obtained, but a significant deviation from the data was evident for Co^{2+} indicating the worse fit especially during intermediate time (0.5 hr. to 2.5 hr.).

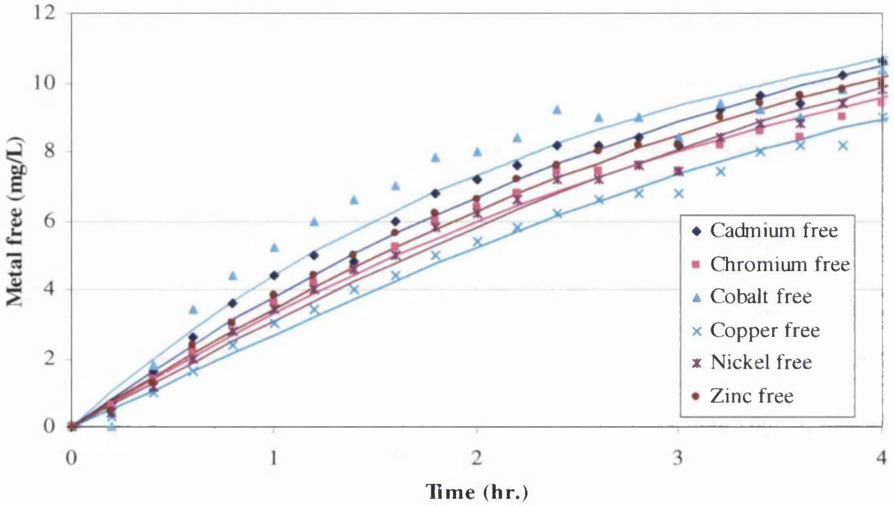


Figure 7.8 *Comparison of mixture metal ions concentrations in the permeate stream as a function of process time between experimental data and the model using a continuous feed PEUF in the presence of EDTA. The experimental data were performed as symbols and the results from model were drawn as lines. .[Metals feed solution with 14 mg/l concentrations of each metal, 2 mM EDTA, 1 g/l PEI, pH 5.5, 25 °C, flow rate 5 l/hr.].*

7.5 Modeling of the retention profiles of metals in continuous feed PEUF

The proposed model in this study (section 7.1) was applied to predict the experimental results of the retention values obtained in Chapter 6 section 6.2. Three different systems of aqueous solutions were investigated: solutions of single metal with PEI, solutions of mixture metal ions with PEI and solutions of mixture metal ions with PEI in the presence of different chelating agents. The retention profiles are shown in (figures 7.9 – 7.15), where the symbols represented the experimental data and the simulated results from model were drawn as lines.

7.5.1 Modeling of the retention of Single metals

Experimental results of single metal ions retention in the presence of PEI (section 6.2.2) were represented with the simulated data from the proposed model as shown in figure 7.9. Good agreement between the model predictions and the experimental data for all metal ions were obtained.

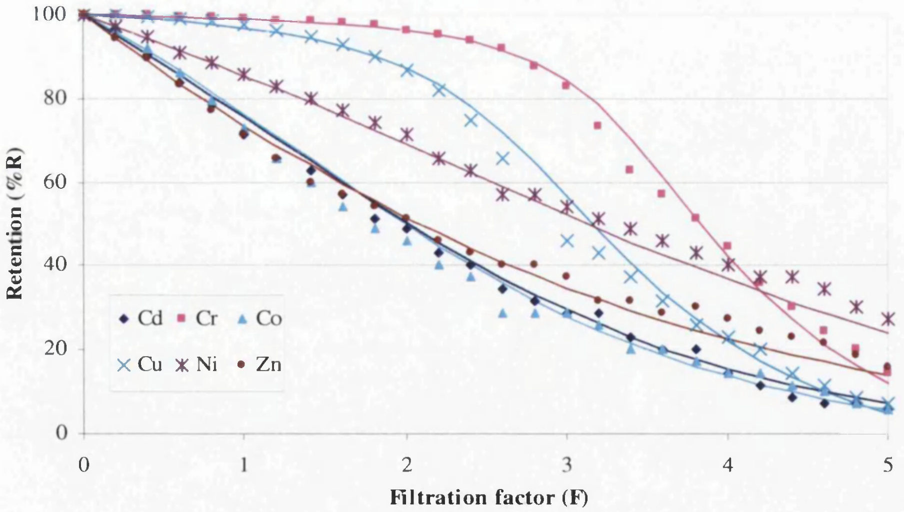


Figure 7.9 *Comparison of single metal ions retention profiles as a function of filtration factor between experimental data and the model using a continuous feed PEUF. The experimental data were performed as symbols and the results from model were drawn as lines, [70 mg/l metal concentrations and 1 g/l PEI at pH 5.5].*

7.5.2 Modeling of the retention of mixture metals

Experimental results of mixture metal ions retention in the presence of PEI (section 6.2.3) were represented with the simulated data from the proposed model as shown in figure 7.10. Good agreement between the model predictions and the experimental data for all metal ions were obtained except for Co^{2+} at the intermediate filtration process (F= 2~2.5).

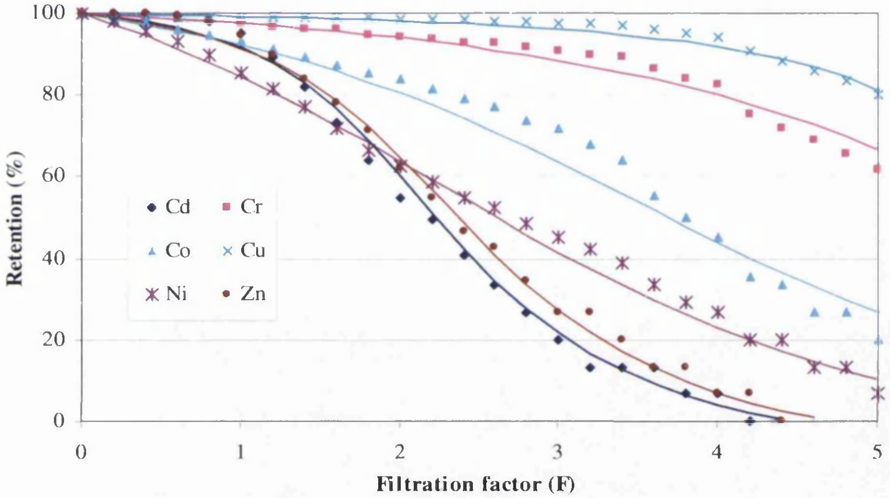


__Figure 7.10__ Comparison of mixture metal ions retention profiles as a function of filtration factor between experimental data and the model using a continuous feed PEUF. The experimental data were performed as symbols and the results from model were drawn as lines [14 mg/l metal concentrations and 1 g/l PEI at pH 5.5].

7.5.3 Modeling of the retention of mixture metal ions-chelates

7.5.3.1 Modeling of the retention profiles of metals-chelates ammonium sulfate

Experimental results of the metals retention with PEI in the presence of ammonium sulfate (section 6.2.4.1) were represented with the simulated data from the proposed model as shown in figure 7.11. A competitive affect of chelating agent caused disagreement between the model predictions and the experimental data for the most of metal ions retention. However, poor prediction was observed for Ni^{2+} and Co^{2+} compared to other metals in the solution.

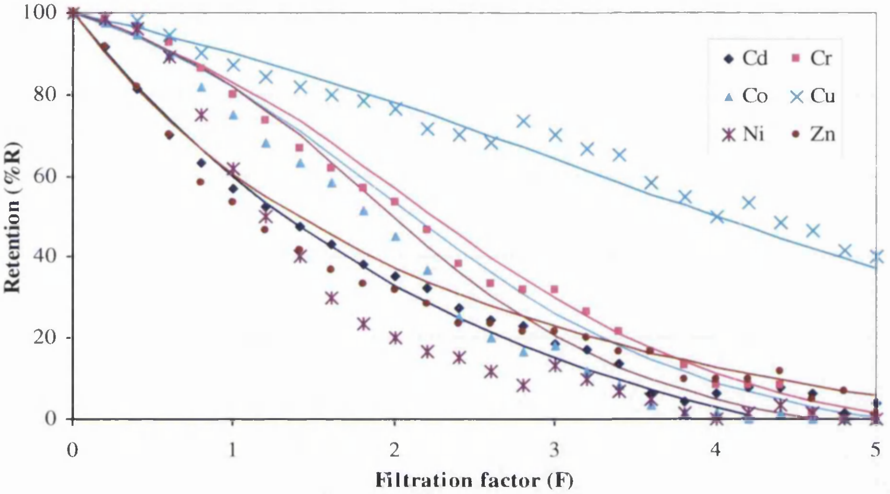


Figure 7.11 *Comparison of mixture metal ions retention profiles as a function of filtration factor between experimental data and the model using a continuous feed PEUF in the presence of ammonium sulfate. The experimental data were performed as symbols and the results from model were drawn as lines [14 mg/l metal concentrations, 2mM ammonium sulfate and 1 g/l PEI].*

7.5.3.2 Modeling of the retention profiles of metals-chelates ammonium chloride

Experimental results of the metals retention with PEI in the presence of ammonium chloride (section 6.2.4.2) were represented with the simulated data from the proposed model as shown in figure 7.12. A competitive affect of chelating agent caused slight differences between the model predictions and the experimental data for metal ions retention except for Cu^{2+}. This is due to the higher affinity of PEI towards Copper under competitive condition with ammonium chloride.

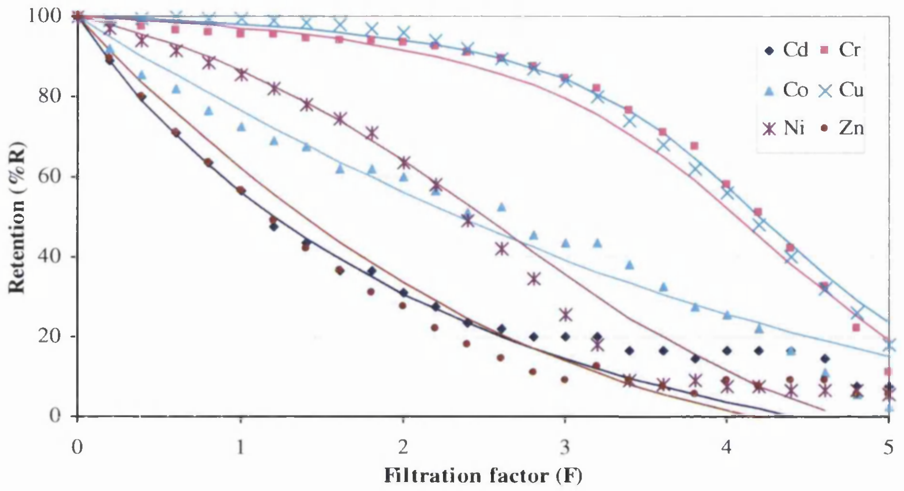


Figure 7.12 *Comparison of mixture metal ions retention profiles as a function of filtration factor between experimental data and the model using a continuous feed PEUF in the presence of ammonium chloride. The experimental data were performed as symbols and the results from model were drawn as lines [14 mg/l metal concentrations, 2mM ammonium chloride and 1 g/l PEI].*

7.5.3.3 Modeling of the retention profiles of metals-chelates sodium acetate

Experimental results of the metals retention with PEI in the presence of sodium acetate (section 6.2.4.3) were represented with the simulated data from the proposed model as shown in figure 7.13. Good agreement between the model predictions and the experimental data were obtained for the retention of Cu^{2+}, Cr^{6+}, Ni^{2+} and Co^{2+}. In contrast, a significant deviation between the experimental data and the model was observed for Cd^{2+} and Zn^{2+}, where both metals exhibited less degree of complexation compared with the other metal ions in the solution.

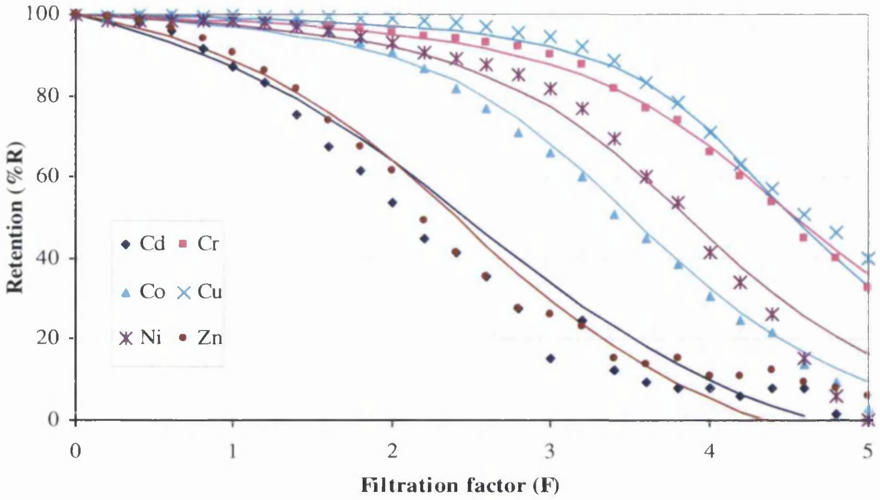


Figure 7.13 *Comparison of mixture metal ions retention profiles as a function of filtration factor between experimental data and the model using a continuous feed PEUF in the presence of sodium acetate. The experimental data were performed as symbols and the results from model were drawn as lines [14 mg/l metal concentrations, 2mM sodium acetate and 1 g/l PEI].*

7.5.3.4 Modeling of the retention profiles of metals-chelates NTA

Experimental results of the metals retention with PEI in the presence of NTA (section 6.2.4.4) were represented with the simulated data from the proposed model as shown in figure 7.14. The model produced good predictions for the experimental data of the retention of Cr^{6+}, Cu^{2+} and Co^{2+}, compared with Cd^{2+}, Ni^{2+} and Zn^{2+}. Suggesting competitive impact of NTA caused different complexation affinities of metal ions to the polymer and that this metal ions dependent.

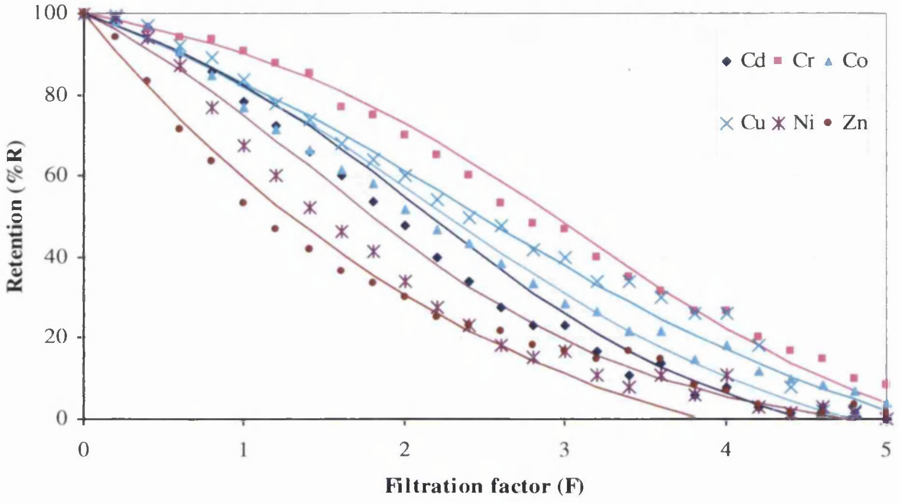


***Figure 7.14** Comparison of mixture metal ions retention profiles as a function of filtration factor between experimental data and the model using a continuous feed PEUF in the presence of NTA. The experimental data were performed as symbols and the results from model were drawn as lines [14 mg/l metal concentrations, 2mM NTA and 1 g/l PEI].*

7.5.3.5 Modeling of the retention profiles of metals-chelates EDTA

Experimental results of the metals retention with PEI in the presence of EDTA (section 6.2.4.5) were represented with the simulated data from the proposed model as shown in figure 7.15. A competitive affect of EDTA for some metal ions caused slightly disagreement between the model predictions and the experimental data of the metal ions retention. However, good agreement between the experimental data and the model was obtained for Cu^{2+} and Cr^{6+}. In the cases of other metal ions in the solutions, significant differences between the experimental results and the predicted data were observed for Co^{2+} and Cd^{2+} during high filtration process (filtration factor > 2.5), Indicating no evidence of complexation due to a strong competitive impact of EDTA for both metal ions in the solution.

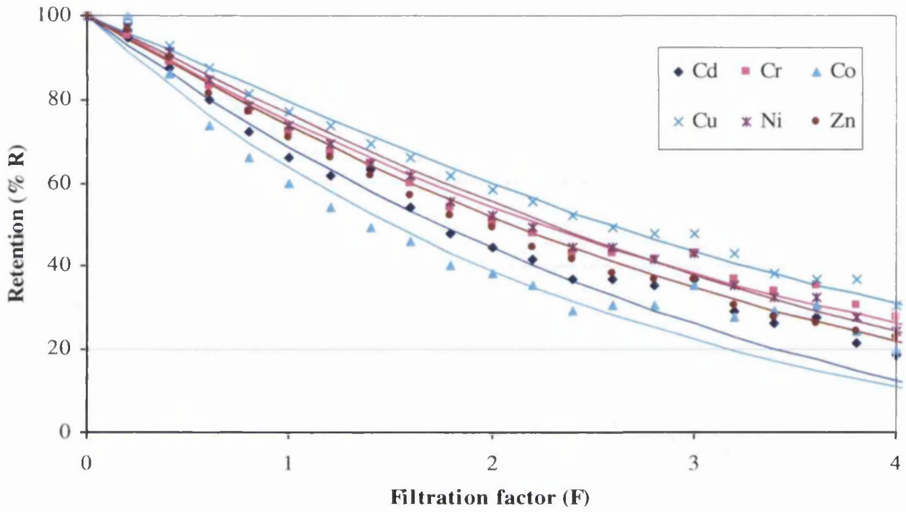


Figure 7.15 *Comparison of mixture metal ions retention profiles as a function of filtration factor between experimental data and the model using a continuous feed PEUF in the presence of EDTA. The experimental data were performed as symbols and the results from model were drawn as lines [14 mg/l metal concentrations, 2mM EDTA and 1 g/l PEI].*

7.6. Conclusions

A mathematical modeling was employed to describe and investigate various complex solutions characteristics using a continuous feed PEUF process. The model was developed using the basic principles of mass balance in continuous feed system combined with the Langmuir adsorption isotherm equation using an Excel spreadsheet. The model was tested using experimental data from a systems operating with solutions of single metal with PEI, mixture metals with PEI and complex solutions with various chelating agents or competitors. The use of model allowed prediction of the concentrations of metal ions in the permeate as well as the retention values of metal ions for these systems. Good agreement between the model predictions and the experimental results were obtained with minor exception in the case of competitive situations where competitors and chelators affect the complex processes (see figures 7.5 and 7.6). However, it is possible to use this model to predict performance and purification of mixture metal ions (Chapter 6 section 6.2.4 gives methodology for further investigations in multistage purification processes). Some further improvements are possible especially competition with chelators competitors for metal ions in complex solutions should be taken into account.

Chapter 8

Overall conclusions and recommendations

The removal and purification of metal ions from solution containing low concentration of metals has important implications in a number of fields associated with waste treatment, environmental clean up and recovery of valuable resources. In the initial literature survey many process options are possible; however, PEUF seemed to be potentially the most suitable to investigate for the removal and recovery of metals at low concentrations (see introduction). PEI has been identified as a very promising chelating polymer that can be used in PEUF process (section 2.3). It has been widely studied and it is relatively environmentally friendly. PEUF processes have been investigated for several years but none have been applied on a large scale. The reason for this is that only relatively simple laboratory systems have been investigated and studies involving complex real system have not been carried out (section 2.2). This project aimed to investigate some of the potential problems associated with competition from other substances found in real systems and their relative importance in applied situations. The work reported here does show that competition for ions from other chelators or competitors is possible and change the performance compared to ideal simple systems. It also showed some potential advantages of this approach by changing capacity and selectivity of the separation based on PEUF processes.

8.1. Binding studies by adsorption isotherms

At the heart of the processes is a polymer with the ability to bind metals by chelation and this utilizes metal properties for high selectivity. Adsorption isotherms describe the way in which metal bind to the polymer. The ability of adsorption isotherms to describe different binding systems of PEUF can be used as indication for the effectiveness of this process under competitive conditions, influencing both capacity and selectivity of these systems. It is well established that the metal binding is pH dependent with good binding at > pH 5 and no binding at < pH 3 (section 4.3). The binding is also selective and can take place in higher ionic strength (not the case with ion exchange).

An investigation and comparison of the binding of single metal ions and mixtures of metal ions with polyethylenimine (PEI) using batch and continuous PEUF process were reported (sections 4.4, 6.3.1 and 6.3.2) as well as effect of the presence of various chelators competitors in mixtures of metal/polymer solutions (sections 5.4 and 6.4). The linear regression fits of the Langmuir and Freundlich isotherms to the data obtained for single metal and mixtures of metal ions in solutions with PEI at pH 5.5 showed that the Langmuir isotherm fitted the experimental data very well, offering a better description of the binding of metal ions to the polymer than the Freundlich isotherm. However, fitting the Langmuir isotherm to the batch experimental data also allowed evaluation of the maximum binding capacity, Q_{max}, of the polymer for each metal ion in both systems at the given solution conditions. The following trends for the Q_{max} values were found in batch mode:

$Cu^{2+} > Cr^{6+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+}$ (Single metal ions)
$Cu^{2+} > Cr^{6+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Cd^{2+}$ (Under competitive conditions of metal ions)

These values can be useful when considering the retention of the metal ions in the ultrafiltration process.

Comparing the values of maximum binding capacity in both systems showed that the Q_{max} values for Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} decrease substantially (by 50% or greater) under competitive conditions whereas the Q_{max} values for Cr^{6+} and Co^{2+} remain very similar to the values for the single metal ion polymer solutions. This suggests that Cr^{6+} and Co^{2+} have different binding mechanisms or bind to different sites than the other metal ions and so are not affected by the presence of these ions. However, Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} all seem to be competing for the same binding sites on the polymer and are affected by the presence of other ions (Tables 4.1 and 4.2).

In the presence of various chelators competitors in the complex solutions using batch system (section 5.4.2), a significant reduction of Q_{max} was observed for all metal ions in the mixture solutions except for Cd^{2+} and indicating nonsensical results such as negative values of Q_{max} due to a poor binding and a strong competition of some chelators (see Table 5.7). However, the affinity of PEI to bind these metal ions in mixture solutions of batch adsorption was influenced as follow:
In the presence of sodium acetate: $Cr^{6+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Cd^{2+}$.
In the presence of ammonium sulfate: $Cr^{6+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Cd^{2+}$.
In the presence of ammonium chloride: $Cr^{6+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+} > Ni^{2+}$.
In the presence of NTA: $Cd^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+} > Cr^{6+} > Zn^{2+}$.
In the presence of EDTA: $Cd^{2+} > Co^{2+} \sim Ni^{2+} \sim Cu^{2+} \sim Cr^{6+} \sim Zn^{2+}$.

Under similar competitive processes in continuous feed, maximum capacities (Q_{max}) of metal ions bind to PEI using Langmuir isotherm (sections 6.3 and 6.4) were far greater than those obtained from batch system (tables 5.7 and 6.6) and they were almost similar for Cu^{2+}-PEI complex in single and mixed metals solutions in both systems. Again, some negative values of Q_{max} were evident and suggesting a lack of metal binding to PEI would be responsible for this observation. However, the affinity of PEI to bind metal ions in continuous process was different from batch system and the order as follow:

$Zn^{2+} > Ni^{2+} > Cr^{6+} > Cd^{2+} > Cu^{2+} > Co^{2+}$ (Single metal ions)
$Cu^{2+} > Cr^{6+} > Co^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+}$ (Under competitive conditions of metal ions)
Similarly with the addition of competitors and chelators, the following orders were noted:
In the presence of sodium acetate: $Cr^{6+} > Ni^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+}$.
In the presence of ammonium sulfate: $Cu^{2+} > Cr^{6+} > Co^{2+} > Ni^{2+} > Cd^{2+} \sim Zn^{2+}$.
In the presence of ammonium chloride: $Co^{2+} > Zn^{2+} > Cr^{6+} > Cu^{2+} > Ni^{2+} > Cd^{2+}$.
In the presence of NTA: $Zn^{2+} > Cu^{2+} \sim Cr^{6+} > Co^{2+} > Cd^{2+} > Ni^{2+}$.
In the presence of EDTA: $Cd^{2+} > Zn^{2+} > Cr^{6+} > Ni^{2+} > Cu^{2+} > Co^{2+}$.

Clearly the additions change the bind affinity and binding capacity of these systems.

Because the Langmuir equation fit the data very well, this will provides the bases of an analytical tool to optimize the separation of metals using the PEUF method. It can be envisaged that high resolution multistage system could be developed exploiting these differences. This is a novel and exciting finding that may have relevance in metal recovery and purification from wastes. However, the model was developed in this work using the fundamental principles of mass balance in continuous feed system combined with Langmuir adsorption isotherm equation, allowed to predict the experimental results very well with minor exception in the case of competitive situations where competitors and chelators can significantly affect the complex processes (see Chapter 7).

8.2. PEUF process performance for metal ions retention

8.2.1 Process capability of PEUF

The polymer enhanced ultrafiltration process (PEUF) has several major advantages over solid phase equivalent systems because the system is dissolved in water and there are no significant mass transfer limitations. This enhances not only the kinetics but also the affinity of these systems to bind metal at very low concentrations. Using the complex binding mechanisms also allow for high selectivity. In instances where complexation was thought to be responsible for the observed retention of single and mixture metals in batch and continuous PEUF process (sections 4.3, 6.2.2 and 6.3), other mechanisms also were evident in the presence of various chelators and competitors (sections 5. 2, 5.3 and 6.2). These mechanisms appeared to include:

- The binding of the metal ions to PEI directly.
- Metal interaction with the membrane
- The metals bind preferentially to EDTA and other chelators than to PEI.
- The binding of both chelators and metals to PEI.
- The electrostatic binding of negatively or positively charged ions to PEI interfering with the binding of the metals.
- Precipitation.

The effectiveness of the PEUF process using a batch system is heavily dependent on the solution pH, membrane surface charge and the concentrations of metal ions in the feed (sections 4.2 and 4.3). In the absence of the polymer all the metal ions showed similar retention characteristics. At low pH values (pH < 5) the retention of the metal ions was low (< 20%) for all the metal ions considered. For higher pH values (pH > 5) the retention of ions climbed although this still remained low for most of the metal ions. The highest retention values were seen for Cu^{2+}, Zn^{2+} and Cd^{2+} where the values reached about 55% at pH values greater than pH 6. The higher retention of these ions at higher pH values is due to the precipitation of the appropriate metal hydroxide. Hence as solution pH increases the formation of insoluble hydroxides is likely to become the major mechanism responsible for metal ion retention.

When the polymer is present the retention of the metal ions increases in comparison with the retention of the metal ions when no polymer is present. For high pH values (pH > 5) the retention of metal ions in the presence of the polymer is greater than 90%. This indicates that the polychelatogen, PEI, had a good affinity for binding to the metal ions especially at higher pH values. Significant increases in the retention of Cu^{2+} and Cr^{6+} is due to strong complexation of these metals with the PEI polymer, and this was in agreement with the results obtained when using a continuous PEUF process (section 6.2.2). However, PEI showed less affinity to form a complex with Ni^{2+}, Co^{2+}, and Cd^{2+} metals especially at low pH where the increasing H^+ concentration favours protonation of the binding sites on the polymer which prevents these metal ions binding at that site. As pH increases, the retention of metal ions increases due to the greater availability of binding sites on the polymer together with the precipitation of metal hydroxides on the membrane surface at pH ≥ 6.

Membrane surface charge is also a factor which is critical to the process performance (section 4.2). The membrane material and pore size are two parameters which can substantially affect membrane surface charge and consequently the process. It was observed that at the isoelectric point of the membrane (~pH 3.9) the retention of the metal ions is extremely low when no polymer is added. The retention of metal ions then increased with increasing pH value as the membrane becomes negatively charged and the precipitation of hydroxy-complexes is established. In most cases, the highest retention was observed when the membrane had its highest negative charge i.e. at $pH > 6$. A similar trend was observed when the polymer was added to the solutions. With polymer added, the lowest retention of the metal ions was observed when the membrane was positively charged ($pH < 3.9$).

8.2.2 Other interesting retention phenomena

In batch PEUF, the effect of metal concentrations in the feed on the retention profiles of single metal ion/polymer solutions (section 4.4.1) showed that at the lowest concentration of metal ions (i.e. 2 mg/l) all the metal ions showed high retention (> 80%). As the concentration of metal ions increased, differing retention profiles were found. For Cu^{2+} and Cr^{6+} ions, the retention profile remains level for all concentrations of metal ions used. This is because the Q_{max} value for each of these metal ions is relatively high (169.5 mg metal/ g_{PEI} for Cu^{2+} ions and 60.6 mg metal / g_{PEI} for Cr^{6+}) in comparison to the maximum concentration of metal ions used i.e. 60 mg/l. For the other ions used as the Q_{max} value is approached the retention of the metal ions starts to drop as the polymer becomes saturated with metal ions so no more ions can be bound. This results in more free metal ions in the solution which will pass through the membrane into the permeate.

However, the retention values with the metal concentrations under competitive conditions of metals (section 4.4.2) showed that the retention profiles for Cr^{6+} and Co^{2+} were similar to those obtained for the single metal ion/polymer solutions of these ions, showing no significant impact of metals competition on the retention of these ions. For the other metal ions, the highest retention was observed at low metal concentrations, with a dramatic drop in retention being observed as the concentration of the metal ions increases. Again, the retention profiles of metal ions using a continuous feed PEUF indicated high retention of Cu^{2+} and Cr^{6+} among other metals in the solution. Thus, the observed retention was believed to have been largely due to complexation with PEI compared to data acquired in the absence of PEI (sections 6.2.1-3).

Retention profiles of metal ions in batch mode PEUF (section 5.2) indicate that the presence of high concentrations of chelators competitors in complex solutions caused a lower reduction of metal ions retention compared to the presence of low concentrations, except for Cd^{2+} which showed an enhancement in the retention in the presence of these chelating competitors. Indicating different mechanisms other than complexation with the polymer were responsible. Indeed, a significant inhibitions effect of these chelators competitors on metal ions retention with PEI was extended when the continuous mode of PEUF is used with exceptional for the presence of sodium acetate (section 6.2) where a significant enhancement of retention was observed for Ni^{2+} and Co^{2+}, respectively. This observation was in agreement with the results of metal ions retention in batch mode PEUF experiments (section 5.2), indicating a non competitive mechanism was involved as shown in section 5.4.2. Of the metal ions studied, a strong affinity was observed for the formation of complexes between Cu^{2+} and PEI, lack of complexation was evident as EDTA and NTA were present in the solutions (sections 5.2.2 and 6.2.4).

In both systems – batch and continuous – the presence of EDTA in complex solutions significantly affected the retention profiles of metal ions and indicating a poor affinity of PEI to bind metal ions. This phenomenon was probably due to formation of metal-EDTA complexes observed to be preferential to the formation of metal-PEI complexes (sections 5.2.2 and 6.2.4.5). However, applying EDTA to metal ions solutions in the absence of PEI showed a negative rejection for Cu^{2+} and Cr^{6+}, allowing other potential mechanisms to be responsible for this observation (section 5.3), and further investigations would be necessary to verify this observation. On the other hand, the retention of metal ions with PEI in the presence of ammonium sulfate and ammonium chloride (sections 5.2.1, 2 and 6.2.4.1, 2) was significantly altered and that the reduction was observed for all the metal ions in the solution. Suggesting inhibitory effects of both competitors was evident and an electrostatic interaction was thought to be involved, interfering with the binding of the metals to PEI.

The data presented (section 6.2) shows that differential separation and thus purification is possible using these systems. Separation using PEI to preferentially bind a metal from mixture gave an enriched retentate and a depleted permeate, e.g. Copper (Cu^{2+}) and Zinc (Zn^{2+}) in section 6.2.3. Addition of chelators or competitors also changes the relative retention of metals in these systems, giving even more scope to purify metals. Thus, the idea of purification valuable metals using multistage systems is also useful in the case of selective separation of mixture metal ions using PEI.

8.3. Applications and operating conditions for PEUF processes

Batch mode PEUF using stirred cell ultrafiltration unit (dead-end) and continuous feeding of PEUF using cross flow ultrafiltration rig were used in this present work (sections 3.3.3 and 3.3.4). The performance of these systems for metal ions filtration under different conditions of feed solutions was compared. Selection of membranes suitable for PEUF is a critical factor effecting separation process. Two types of membrane used in this work were: Intersep-Nadir polysulphone with a (MWCO) of 30 kDa was used in batch mode experiment and the hollow fiber cartridge membrane of 50 kDa (MWCO) was used in continuous experiments. Branched chain PEI with an average molecular weight of 750,000 was used, the polymer has primary secondary tertiary amine groups.

PEUF experiments in batch mode were investigated using a 50 ml stirred cell ultrafiltration unit under fixed operating conditions (pressure 3 bar, temperature 25°C and the ultrafiltration procedure was then stopped when a 50 % of the solution volume was filtered). This allowed investigating and comparing the filtration characteristics of metal ions under similar operating conditions. In this system, the mixed complex solutions were placed into the cell and then an overpressure applied. In contrary, the continuous feeding of PEUF using a cross flow ultrafiltration rig the metal and polymer solutions were placed separately in feed tank and reservoir, respectively. However, using batch mode of PEUF allowed choosing the suitable pH for metal ions filtration and then this was applied to a continuous feed process of PEUF. It was observed in batch system that at pH 5.5 the maximum retention and binding of metal ions to PEI were obtained. The continuous mode of PEUF was then operated at constant feed flow rate, constant temperature (25°C) and the solutions pH was adjusted at pH 5.5.

In continuous process using cross flow ultrafiltration rig, the feed solution is parallel or tangential to the membrane surface and the permeate pass through the membrane due to a difference in pressure while the retentate is recycled to the system. In contrast, the feed solution of batch mode PEUF flows perpendicularly through the membrane resulting a retentate with high metal content will stay behind the membrane (inside the cell) while a free metal ions flow through the membrane as permeate. However, the concentration polarization phenomena in cross flow ultrafiltration system is lower than in batch mode. This was evident from the flux measurements studies of aqueous solutions of heavy metals using batch mode ultrafiltration (section 4.3). These experiments have shown that the addition of the polymer significantly reduces the flux of the process (by approximately 50%) for equivalent solution conditions. This is due to the metal ion and polymer forming a complex which cannot pass through the membrane resulting in concentration polarization at the membrane surface which reduces the flux. Although reduction of flux was anticipated by the addition of 1 g/l PEI, the addition of small quantities of metals also significantly affected the flux when comparing these values to the reference solutions. Flux was enhanced by up to 40% by the addition of 10 mg/l of Co^{2+} and Ni^{2+} to buffer solutions. Cr^{6+} and Cd^{2+} had little effect on the flux whilst Zn^{2+} and Cu^{2+} reduced the flux. This shows that some of the metals studied significantly interact with the membrane and membrane pores. Membrane flux in the presence and absence of PEI, metals and other additives are summarized in table 8.1 (Data from chapters 4&5).

Table 8.1 *Flux rate as a function of PEI, metals and other additives*

Individual metal solutions				**Mixed metal solutions**	
Without PEI		**With PEI**		**Exp. type**	**Flux (m^3m^2/hr.)**
Exp. type	**Flux (m^3m^2/hr.)**	**Exp. type**	**Flux (m^3m^2/hr.)**		
Pure water	0.096	-	-	-	-
Buffer solution	0.078	PEI solution	0.045	PEI	0.064
Cu^{2+}	0.031	Cu^{2+}	0.034	PEI + AS	0.083
Cr^{6+}	0.087	Cr^{6+}	0.044	PEI + AC	0.059
Zn^{2+}	0.04	Zn^{2+}	0.033	PEI + SA	0.052
Ni^{2+}	0.12	Ni^{2+}	0.056	PEI + NTA	0.077
Co^{2+}	0.137	Co^{2+}	0.068	PEI + EDTA	0.053
Cd^{2+}	0.086	Cd^{2+}	0.05		

Note: (1) averaged data of 2 or 3 repetitions.
(2) NADIR polysulphone membrane 30 kDa MWCO, at 25°C and 3 bar.
(3) 5 % error.

However, this work suggests that PEUF should be applied for recovery of valuable metals (e.g. Ag, Au and Pt) due to their financial importance, or for separation of toxic metals from discharge streams or decommissioning processes (e.g. Cd, Cr and Hg) due to their impact for the health and to the environment as well. Batch mode PEUF can be used for heavy metal removal from system involving solids (leaching) and poor dissolution kinetics while the continuous feed can be applied for recovery and purification of metal ions from aqueous metal solutions. PEI with molecular weight of 750,000 showed lower ability for metal ion retention compared to other molecular weight PEI reported from the available literature. However, high affinity of PEI to bind Cu^{2+} and Cr^{6+} was evident, and maximum binding capacity was obtained for both metals using batch or continuous PEUF.

8.4. Recommendations for future work

Based on the work in this study, a lot of interesting and exciting concepts need to be tested:

1. Large scale operation with real systems applications are required to estimate cost and efficiency (e.g. polymer loss in which economic and environmental risk).

2. The application PEUF to specific problems:

(i). Metal removal and decontamination:

There is a growing market for decommissioning, decontamination and detoxification of land and facilities. One interesting area is the use of this process to decontaminate biological sludges that naturally accumulate metals to dangerous concentrations. The recovery of metals from waste is also possible, so reducing the demand for mining and the exploitation for virgin resources.

(ii) Investigation of mining of low grade ores:

There are massive amount of metal remaining in tailing ponds in many mining operations around the world with the high value of metal. PEUF process could be used to recover and purify metals from these systems. This hydrometallurgy approach is environmentally friendly with low energy consumption and with little or no pollution.

(iii). Metal purification systems:

Because of the selectivity of these systems, purification to high level is possible without the use of large amount of energy or the significant consumption of other materials (chemicals).

3. New polymers and polymer/chelator hybrids for specific binding should be considered. The potential for improving these processes by the use of new polymer or polymer/ chelator hybrids is considerable and should be considered carefully. Highly specific metal recovery systems will have considerable value.

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Nomenclature

a : Represents the free metal fraction of the total metal concentration in the cell solution.

C : Solute concentrations in the boundary layer (Kmol/m^3)

C_m : The concentration at the membrane surface (Kmol/m^3)

C_G : Solute concentration in gel layer (Kmol/m^3)

C_{it} : Total concentration of metal i (mg/l).

C_{fi} : The concentration of metal ion *i* in the feed (mg/l)

C_{pi} : The concentration of metal *i* in the permeate (mg/l)

$C_Z^{filtrate}$: The metal ion concentration of the filtrate solution at a given instant (mol l^{-1}).

C_Z^{free} : The value of the molarity of metal ions not bound to the polymer chains (mol l^{-1}).

C_Z^{init} : The initial metal ion concentration (mol l^{-1})

C_1^{ia} : The initial metal ion concentration in experiments 'a'

C_1^{ib} : The initial metal ion concentration in experiments 'b'

c^P : Polymer concentration (mol of monomeric unit l^{-1})

D : The diffusion coefficient

E : The enrichment factor can be expressed as a ratio of metal concentrations in feed and in retentate.

F : The filtration factor, expressed as filtrate volume to the volume of washing fluid.

[H] : The proton concentration

[HL] : Non-dissociated polymer form

$i = 1,\ldots m$: Number of a metal in a multicomponent solution

J : The flux (volumetric rate per unit area (m^3m^2/hr.))

$j = 1,\ldots n$: Number of ligand groups coordinated with a metal ion in a macromolecular complex

K_a : The polymer dissociation constant

K_F : The Freundlich equilibrium constant ($mg^{1-n}\ g^{-1}l^n$)

K_i : Non-stepwise complex formation constant of the i^{th} metal

K_{ij} : Stepwise complex formation constant of the i^{th} metal

K_L : The Langmuir equilibrium constant (mg/l).

K_m : The complex formation constants

K_P : Protonation constant for a polymer

K_p : The complex formation constants

$K_{ik}^{(h)}$: Stability constant of the hydroxyl complexes of the i^{th} metal

K_Z^L : Apparent thermodynamic constant derived from Langmuir isotherm ($mol^{-1}l$)

$k = 1,\ldots p$: Number of OH groups coordinated with a metal ion in a soluble hydroxyl complex.

k_s : The overall mass transfer coefficient

k_z : Retention parameter (equation 2.21)

k_Z^m : The coefficient of membrane retardation

$k_1^{'}, k_2^{'}$: The dissociation constants

[L] : Concentrations of free polymer (mol/L)

$[L]_t$: Total concentrations polymer (mol/L)

$[M]$: The molar concentration of the ith ion,

$[M]_0$: The initial metal concentration.

$[M]_O$: Concentration of metal ion in the feed (mg/l)

$[M]_P$: Concentration of metal ion in the permeate (mg/l)

$[M_i]$: Concentrations of free metal ions (mol/L)

$[M_i]_t$: Total concentrations of a metal (mol/L)

$[M_iL_j]$: Concentration of a macromolecular complex of the i^{th} metal containing j groups per metal ion (mol/L)

$[M_i(OH)_k]$: Concentration of a hydroxy complex of the i^{th} metal containing k OH groups

m : The number of hydroxides ions in one soluble metal hydroxyl complex.

n : is a constant.

$[P]$: The polymer concentration (g/l)

P-X : Polymer ligand,

P-X:Y : Polymer-metal complex

PF_i : Purification Factor of metal i

Q : The amount of metal bound (mg metal/g polymer).

Q_{max} : The maximum capacity of polymer (mg metal/g polymer).

$Q_Z^{\max}$: Maximum amount of metal ions that may condense on the polymer surface per monomeric unit.

R_i : Retention of the i^{th} metal by a membrane

R_L : Retention of a polymer by a membrane

Rm : The membrane resistance (m^{-1})

R_Z : Retention of metal ions of valence Z

$R_i^{(h)}$: Retention of a metal hydroxide by a membrane

R_1 : Retention value for the metal

R_2 : Retention value for the metal polymer complex

T : The time necessary for a washing fluid volume to pass through the cell (hr.).

u_z : Retention parameter (equation 2.21)

V : Volume of the fluid in the reservoir tank (L)

V_f : The volume of the feed solution

V_0 : The initial volume

V_p : The permeate volume

V_r : The volume of the retentate

V_f^{sat} : The total volume of the filtrate when the saturation of the polymer is achieved

v_z : Retention parameter (equation 2.21)

X : Functional molecule or group

Y_i : The metal free in solution (mg/l)

z : The subscript z always refers the valence of the metal ion

Greek symbols

β : The initial concentration ratio of polymer to metal ions

Δt : The time difference (hr.)

ΔF : The filtration factor difference (L)

Δp : The transmembrane pressure difference (bar)

δ : The boundary layer thickness (m)

Σ : The summation extends over all the ions in the solution

μ : The solvent viscosity (Ns/m^2)

Φ_0 : Feed flow rate (l/hr.)

Φ_p : Permeate flow rate (l/hr.)

ψ : The ionic strength

Abbreviations used

AC : Ammonium chloride

AS : Ammonium sulfate

CP : Concentration Polarization

CSTR : continuous stirred tank reactor

EDTA : Ethylenediaminetetra acetic acid

ICP-OES : Inductively Coupled Plasma-Optical Emission Spectrometry

LPR : Liquid-phase polymer-based retention

MWCO : Molecular weight cut off

NTA : Nitrilotriacetic acid

P : Polymer

PAUF : Polymer-assisted ultrafiltration

PEI : polyethylenimine

PEUF : Polymer Enhanced Ultrafiltration

PSU : Polymer-supported ultrafiltration

SA : Sodium acetate

UF : Ultrafiltration

Y : Target metal ion

Z : Non-target metal ion

Appendices

Appendix 1 UK and EU Environmental Legislation

A.1.1 Introduction

Environmental legislation of the United Kingdom (UK) and the European Union (EU) are closely linked. This applies also to matters related to water pollution and industrial waste. The EU Parliament has significant input into the development of environmental policy and legislation to be adopted and incorporated by its Member States including the UK. The EU commission initiates policy, mostly done by the Directorate General XI (DGXI), and the EU council (group of relevant ministers of each Member State) transforms such policy into legislation. As *EU Regulation* it becomes binding for all the Member States, as *EU Directive* any legislation has to be transferred into national, in this case, UK law before being applied by UK operators [104].

The UK Government, on the other hand, is the most relevant legislator concerning national law affecting industry and commerce and the main producer of national legislation. Policy making is initiated by the Department of Environment, Transport and the Region (DETR) with help from the Department of Trade and Industry (DTI) and other relevant industrial and business entities. Form of EU and UK legislation:

EU Regulations: Binding on all Member States in their entirety and directly applicable in law. Normally used for detailed and specific issues.

EU Directives: These must be transferred into the national law of each Member State.

EU Decisions: Binding in their entirety, they may be addressed to a government, a private enterprise or an individual.

UK Acts of Parliament: Laws generated by the UK. They will include laws derived from EC Directives.

UK Regulations: Enabled by Acts of Parliament and made by Ministers. These are made by government ministers under rights, powers and duties which stem from Acts.

UK Orders: Give the force of law to enabling actions of Ministers [105].

A.1.2 European Environment Agency (EEA)

The EEA is based in Copenhagen and started its activities in November 1994 (being fully operational in 1996). It is an independent legal entity run by a management board which elects its own chair with one representative from each EU Member State, two members designated by the European Commission (one from DGXI) and two designated by the European Parliament.

The mission of the EEA is to deliver timely, targeted, relevant and reliable information to policy making agents and the public to support the development and implementation of environmental policies in the Community and in the Member States [106]. Its primary objective is ‘to set up and manage a network for European information and observation and to ensure the dissemination of comparable information’. In its 1997 work programme it defines its goal as ‘to be an independent source of environmental information, efficient and demand driven’. The EEA does not seek to create more data but to make more effective use of existing data by collating and standardizing it. This way it can provide ‘knowledge in a nutshell’ that is ready for use by policy-makers.

A.1.2.1 European Legislation in Water Pollution

Pollution is defined in EU environmental policy as follows: the direct or indirect introduction of substances, vibrations, heat or noise into air, water and land as a result of human activity. This may be harmful to human health or the quality of the environment, result in damage to material property, or impair or interfere with amenities and other legitimate uses of the environment. The EU also sub-divides pollution as being either *point source* or *diffuse source. Point source pollution* refers to pollutants originating from individual, usually identifiable points of discharge. These can include discharge of industrial, domestic or municipal waste water, urban run-off as well as leakage from storage tanks, industrial installations, farmyards and landfill sites. *Diffuse source pollution*, on the other hand, describes a number of widely scattered sources that are difficult to identify and control. A typical example is that which results from agricultural practices, including the use of pesticides and nitrates to increase crop yield. It may also result from acidification, namely the emission of air-borne pollutants, particularly sulphur dioxide, nitrogen oxide and ammonia from large combustion plants such as coal-fired power generation stations or industrial manufacturing sites. These air-borne pollutants can be carried for thousands of miles before being deposited in rivers and lakes through rainfall. In either case, the environmental damage caused will depend on the nature of the pollution, but may involve potential hazards to human health, detrimental impacts on the ecosystem or disrupting the environmental balance.

Water, in EU policy terms, is divided into various categories. These include fresh water, marine water, groundwater and surface water. Water is also distinguished by its socioeconomic uses, such as drinking water supplies, water used by agriculture and industry [106]. European environmental legislation designed to limit the pollution of both fresh water and sea water generally aims to prevent pollution at source. Two main categories of measure can be distinguished:

- Directives setting out quality objectives. These establish minimum quality levels for fresh water and sea water, based on the different potential uses of water.
- Directives relating to the protection of the aquatic environment against pollution by dangerous substances.

As early as 1976 the Council adopted a directive to prevent pollution by products which, in view of their toxicity, persistence and bioaccumulation, constitute a particular and permanent threat to the environment and public health. Black (I) and Gray (II) lists of dangerous substances were drawn up for this purpose [27].

A.1.2.2 Directive 76/464/EEC- Water pollution by discharges of certain dangerous substances.

One of the first water related directives to be adopted was the Directive 76/464/EEC of 4 May 1976. It dealt with pollution caused by certain dangerous substances discharged into the aquatic environment of the community and aimed at regulating potential aquatic pollution by thousands of chemicals already produced in Europe at that time. The Directive covered discharges to inland surface waters, territorial waters, inland coastal waters and groundwater, which was taken out in 1980 and was regulated separately under the Council Directive 80/68/EEC. The new Directive introduced the concept of list I and list II substances and its purpose was to eliminate pollution from list I substances and to reduce the effect of list II pollutants.

List I and 'Candidate List I'

List I included a number of groups and families of pollutants from which certain individual substances were to be selected on the basis of their:

- Persistence
- Toxicity
- Bioaccumulation

In 1982, the commission expanded the list by adding 129 'Candidate List I substances' and subsequently another three substances were added bringing the total up to 132.

Up to now, 18 individual substances of the "Candidate List I" have been regulated in five specific Directives (also called 'daughter' directives) setting emission limit values and quality objectives on a community level. The regulations of other "Candidate List I Substances" was suspended in the beginning of the 1990's due to the preparation of a more comprehensive and integrated permitting system for industrial installations. In 1996, the Directive on Integrated Pollution Prevention and Control, the IPPC Directive (96/61/EC) was adopted. The Directive includes the emission limit values for the 18 list I substances of the specific directives as minimum requirements for large installations.

List I of families and groups of substances

List I contains certain individual substances which belong to the following families and groups of substances, selected mainly on the basis of their toxicity, persistence and bioaccumulation, with the exception of those which are biologically harmless or which are rapidly converted into substances which are biologically harmless:

1. Organohalogen compounds and substances which may form such compounds in the aquatic environment,
2. Organophosphorus compounds,
3. Organotion compounds,
4. Substances in respect of which it has been proved that possess carcinogenic properties in or via the aquatic environment,
5. Mercury and its compounds,
6. Cadmium and its compounds,
7. Persistent mineral oils and hydrocarbons of petroleum origin,
8. Persistent synthetic substances which may float, remain in suspension or sink and which may interfere with any use of the waters [107].

List of substances which could belong to list I (Candidate List I Substances).

List I substances	Specific Directives
Aldrin	Council Directive 88/347/EEC amending 86/280/EEC
Cadmium and its compounds	Council Directive 83/513/EEC
Carbon tetrachloride	Council Directive 86/280/EEC
Chloroform	Council Directive 88/347/EEC amending 86/280/EEC
DDT (including metabolites DDD and DDE)	Council Directive 86/280/EEC
1,2-Dichloroethane	Council Directive 90/415/EEC amending 86/280/EEC
Dieldrin	Council Directive 88/347/EEC amending 86/280/EEC
Endrin	Council Directive 88/347/EEC amending 86/280/EEC

Hexachlorobenzene	Council Directive 88/347/EEC amending 86/280/EEC
Hexachlorobutadiene	Council Directive 88/347/EEC amending 86/280/EEC
Hexachlorocyclohexane (including all isomers and lindane)	Council Directive 84/491/EEC
Mercury and its compounds	Council Directive 82/176/EEC and Council Directive 84/156/EEC
Pentachlorophenol	Council Directive 86/280/EEC
Tetrachloroethylene	Council Directive 90/415/EEC amending 86/280/EEC
Trichlorobenzene (technical mixture)	Council Directive 90/415/EEC amending 86/280/EEC
1,2,4-Trichlorobenzene	Council Directive 90/415/EEC amending 86/280/EEC
Trichloroethylene	Council Directive 90/415/EEC amending 86/280/EEC
Isodrine	Council Directive 88/347/EEC amending 86/280/EEC

Specific Directive Regulating List I Substance

Based on Article 6 of Council Directive 76/464/EEC, the council set specific emission limit values and quality objective for 18 list I substances in five specific directives, also called 'daughter' directives:

- Council Directive of 22 March 1982 on limit values and quality objectives for mercury discharges by the chlor-alkali electrolysis industry (82/176/EEC).
- Council Directive of 26 September 1987 on limit values and quality objectives for cadmium discharge (85/513/EEC).

- Council Directive of 08 March 1984 on limit values and quality objectives for mercury discharges by sectors other than the chlor-alkali electrolysis industry (84/156/EEC).
- Council Directive of 09 October 1984 on limit values and quality objectives for the discharges of hexachlorocyclohexan (84/491/EEC).
- Council Directive of 12 June 1986 on limit values and quality objectives for discharges of certain dangerous substances in list I of Annex to Directive 74/464/EEC (86/280/EEC) as amended by 88/347/EEC and 90/415/EEC [108].

List II – Pollution reduction programmes

List II includes groups and families of substances that have a deleterious effect on the aquatic environment. It also consists of all the individual list I substances that have not been regulated on community level yet. As there are only 18 'real' list I substances, all the other 114 substances listed under list I must be considered as list II substances. For the relevant pollutants of list II, the commission has recently accessed the pollution reduction programmes under Article 7 of Directive 76/464/EEC in all member states [108].

List II of Families and Groups of Substances

- Substances belonging to the families and groups of substances in list I for which the limit values referred to Article 6 of the Directive have not been determined.
- Certain individual substances and categories of substances belonging to the families and groups of substances listed below, and which have a deleterious effect on the aquatic environment, which can, however, be confined to a given area and which depend on the characteristics and location of the water into which they are discharged.

1. The following metalloids and metals and their compounds:

    1. Zinc
    2. Copper
    3. Nickel
    4. Chromium
    5. Lead
    6. Selenium
    7. Arsenic
    8. Antimony
    9. Molybdenum
    10. Titanium
    11. Tin
    12. Barium
    13. Beryllium
    14. Boron
    15. Uranium
    16. Vanadium
    17. Cobalt
    18. Thallium
    19. Tellurium
    20. Silver

2. Biocides and their derivatives not appearing in List I.
3. Substances which have a deleterious effect on the taste and/or smell of the products for human consumption derived from the aquatic environments and compounds liable to give rise to such substances in water.
4. Toxic or persistent organic compounds of silicon, and substances which may give rise to such compounds in water, excluding those which are biologically harmless or are rapidly converted in water into harmless substances.
5. Inorganic compounds of phosphorus and elemental phosphorus.
6. Non persistent mineral oils and hydrocarbons of petroleum origin.
7. Cyanides, fluorides.
8. Substances which have an adverse effect on the oxygen balance, particularly: ammonia, nitrites [107].

A.1.2.3 Transition to the Water Framework Directive

As part of the ongoing restructuring of the community water policy, the Directive 76/464/EEC (water pollution by discharges of certain dangerous substances) is now integrated in the Water Framework Directive (2000/60/EC) which was adopted in September 2000, and Directive 76/464/EEC will be fully repeated in 2013.

Article 22 together with Article 16 of the Water Framework Directive (2000/60/EC) set out the transitional provisions for the existing Directive on discharges of certain dangerous substances (76/464/EEC). In summary, the provisions are as following:

- Article 6 (List I substances) was repeated with the entry into force of Directive 2000/60EC;
- List of priority substances has replaced the 'candidate list I' of 1982;
- 'Rest' of 76/464/EEC including the emission reduction programmes will be still in place until 2013 (transition period).
- Review of 'Specific Directives' within 2 years after entry into force of Directive 2000/60/EC [108].

The Water Framework Directive (2000/60/EC) came into force on 22 December 2000 and member states had until December 2003 to transpose it into national law. The purpose of the Directive is to establish a framework for the protection of inland surface water, transitional waters, coastal waters and groundwater [109].

A.1.2.4 Chemical Pollution of Surface Waters and the Water Framework Directive

The major part on community strategy against pollution of surface waters control policy is set out in Article 16 of the water framework Directive (2000/60/EC) which lays down new procedures for the identification of substances and development of control measures. As a first step, the European Parliament and Council adopted Decision No. 2455/2001/EC establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC. The decision identifies a list of substances of concern (priority substances) that present a significant risk to or via the aquatic environment. The commission is currently preparing community-wide emission controls and quality standards for the priority substances. The aim is to establish the environmental quality of surface waters as regards chemical status which needs to be reached by 2015. The aim is also to establish measures at community level to help reaching this quality status and other environmental objectives for the Water Framework Directive (Article 4, Directive 2000/60/EC). Progressive reduction of emissions, losses and discharges of all priority substances – and in addition to achieve phase-out or cessation of emissions, losses and discharges of priority hazardous substances [108].

Priority Substance List

The Water Framework Directive requires a list of "priority substances selected amongst those which present a significant risk to, or via, the aquatic environment". This list is based on the toxicity, persistence, bioaccumulation potential, human health risk and the monitored and modeled concentration of each substance in the aquatic environment. The substances on the 'Priority List' are to be subject to one of two general targets:

- A progressive reduction of pollution or inputs, or
- A cessation or phasing out of discharges, emission and losses.

Within the priority list there are three categories of substance. *Priority Hazardous Substances (PHS)* are considered such that there must be cessation or phasing out of discharges, emissions and losses of these substances within twenty years of the adoption of measures for that purpose. *Priority Substances under Review (PSR)* may, if further investigation justifies it, be proposed as PHS. The third category is *Priority Substances (PS)* which must undergo progressive reduction of discharges, emissions and loses to the environment.

The principal benefits expected to result from the priority list measures are improvements in water quality and protection and enhancement of the aquatic and marine ecosystems, wildlife and predators further up the food chain. As of May 2003, the priority list contains 33 substances:

- ***Priority Hazardous Substances (PHS):*** brominated diphenylether (Pentabromo diphenylether only), C10-13-chloroalkanes, cadmium and compounds, hexachlorobenzene, hexachlorocyclohexane (HCH), hexa-chlorobutadiene, mercury and compounds, nonylphenols, polyaromatic hydrocarbons (PAH), pentachlorobenzene, tributyltin compounds;
- ***Priority Substances under Review:*** Anthracene (PAH), atrazine, chlorpyrifos, di(2-ethylhexyl)phthalate (DEPH), diuron, endosulfan, isoproturn, lead and compounds, naphthalene (PAH), octylphenols, pentachlorophenol, simazine, trichlorobenzenes, (1,2,4-trichloro-benzene), trifluralin;

- ***Priority Substances:*** Alachor, benzene, brominated diphenylether (apart from penta), chlorofenvinphos, 1-2-dichloroethane, dichlorometahane, fluoranthene (PAH), nickel and compounds, trichloromethane (chloroform). The substances on the list are already controlled, to varying degrees, by EC and national legislation. Further controls, independent of the Water Framework Directive, are expected for a number of substances as a result of European and other international regulations.

It is anticipated that the following main sectors will be affected by the priority list:

- Chemical industry, in particular organo-chlorine processes;
- Metal and mining industries (including aluminium, stainless steel, plating and ore processes);
- Textiles;
- Wood treatment and forestry;
- PVC manufacture;
- Pesticides production and use in farming;
- Processes relying on the burning of fossil, fuels;
- Iron, steel and coke production.

There could also be impacts on the offshore gas and oil industries, and the waste disposal and incineration sectors [109].

A.1.2.5 The Groundwater Directive

The preamble to Directive 76/464 had already referred to the adoption of specific community rules on discharge into groundwater. This directive requires member states to take the necessary measures to prevent the discharge into groundwater of certain substances (contained in List I in the Annex to the Directive) and to limit the discharge into groundwater of other substances (contained in List II in the Annex) (Article 3). For the purpose of the Directive, 'direct discharge' means the introduction into groundwater of substances without percolation through the ground or subsoil (Article I(2) (b)), while 'indirect discharge' means the introduction into groundwater of substances after percolation through the ground or subsoil (Article I(2) (c)). Member states must prohibit all direct discharge of substances in List I (Article 4). Any disposal or tipping for the purpose of disposal of these substances which might lead to indirect discharge shall be subject to prior investigation, and depending on the results of that investigation be prohibited or require authorization. The investigation shall include examination of the hydrogeological conditions of the area concerned, the possible purifying powers of the soil and subsoil and the risk of pollution and alteration of the quality of the groundwater from the discharge (Article 7). It must, therefore, establish whether the discharge into groundwater is a satisfactory solution from the point of view of the environment. Authorization may be granted only if all technical precautions have been taken to prevent indirect discharges (Article 4). Article 13 requires Member states to monitor compliance with the conditions laid down in each authorization and the effects of discharges on groundwater [27].

A.1.2.6 The Urban Waste Water Directive

Directive 91/271/EEC concerns the collection, treatment and discharge of urban waste water and the treatment and discharge of waste water from certain industrial sectors. Article 3 requires member states to ensure that all agglomerations are provided with collecting systems for waste water, and lays down requirements such a system must meet. Article 4 sets criteria which the treatment of waste water must meet before it may be discharged into the collecting systems. Discharges from urban waste water treatment plants must satisfy certain requirements. Article 11 provides that the discharge of industrial wastewater into collecting systems and treatment plants is subject to prior regulations and/or specific authorization. Article 13 similarly states that biodegradable industrial wastewater from certain industrial sectors which is discharged directly into surface waters is subject to prior regulations and/or specific authorizations. Article 14 is designed to ensure that sludge arising from waste water treatment is re-used wherever possible [27].

Directive 91/676/EEC on the protection of waters against pollution caused by nitrate from agricultural sources contributes to the protection of waterways vulnerable to nitrate pollution arising from fertilizer run-off from agricultural land [110].

A.1.2.7 European Legislation on Waste

Waste management issues played a role in community environmental polices from its very beginnings. The commission's communication of 1972 mentioned the necessity of preventing waste generation and to promote waste recovery.

In September 1989 the Commission set out a community strategy for waste management. It established a number of general strategic considerations and priorities for the waste management in the medium and long term of all waste, whether intended for recycling and reuse or for disposal. Five priorities were listed:

- Prevention or reduction of waste source as the highest priority.
- Promotion of recycling and reuse.
- Waste disposal by dumping or incineration, to be ensure by harmonization of standards on the basis of a high level of environmental protection.
- Tightening up of the existing rules on the transport of waste.
- Cleaning up of sites that have been polluted by waste [27].

Waste has been defined by an EC Directive 75/442/EC as any substance or object that the holder disposes of or is required to dispose of pursuant to the provisions of legislation. Whether waste is dangerous or not, depends upon several criteria: activities from which the wastes come (e.g. medical wastes, companies producing pharmaceuticals and herbicides); substances contained in the wastes (e.g., arsenic, mercury, cadmium, lead, and their compounds); and characteristics of the wastes (inflammability, toxicity, corrosiveness, etc.). In 1994 a comprehensive list of all wastes, hazardous or otherwise, was produced pursuant to Council Directive 75/442/EC (as amended by 91/156/EEC). This list is known as the European Waste Catalogue (EWC 1994, Commission Decision 94/3/EC).

The Commission stated the objective that "as far as possible waste is disposed of in the nearest suitable centers", but that the situation was "different with waste to be recycled". Furthermore, it confirmed that "waste arising within the community which cannot be recycled should be treated within the community where possible, these statements constituted the basis in Article 5 of the amended Directive 75/442. The waste management strategy did not include radioactives waste, which were handled completely separately at community level and monitored under the Euratom Treaty. In 1994, the commission submitted a new communication for a strategy on radioactive waste management, which the council endorsed in the form of a Resolution [111].

All European regulations, those of the community as well as those of national legislation, establish especially strict treatment for toxic and dangerous wastes. According to a community directive of March 20, 1978, replaced in December 1991, these wastes should be stocked, treated and/or disposed of, only be installation, establishments, or enterprises having obtained a special authorization [112].

For products that contain heavy metals, a number of other community directives or regulations limit the content of heavy metals in products. For example, Directive 91/157[55] prohibits the use of certain batteries, where the mercury levels fixed in the Directive are exceeded; an amendment, enlarging this ban, is in preparation. Lead carbons and lead sulphates may not be used in points, cadmium and its compounds are banned from use as colourants or stabilizers for different products. Finally, nickel is prohibited for use in products which come in contact with the human skin [111].

A.1.2.8 Hazardous Waste Directive (91/689/EC)

European Council Directive 91/689/EC (the Hazardous Waste Directive, or HWD) sets the framework within member states of the European community for provisions to control the movement of arisings of hazardous wastes. The aim of the HWD is to provide a precise and uniform European-wide definition of hazardous waste and to ensure its correct management and regulation. Article 1(4) of the HWD defines hazardous waste as wastes featuring on a list drawn up by the European Commission, because they possess one or more of the hazardous properties set out in the HWD.

The EC then identified which of the wastes from the *European Waste Catalogue or EWC 1994*, the comprehensive list of all wastes produced in 1994, were deemed to be hazardous, based on the properties set out in Article 1(4) of the HWD. The resulting list of wastes was called the *Hazardous Waste List (HWL).* The EWC 1994 and HWL have been subsequently updated resulting in a revised *European Waste Catalogue (EWC 2002)* according to the criteria set out in the HWD [113].

A.1.2.9 The IPPC Directive

Directive 96/61/EC concerning integrated Pollution Prevention and Control, the so called "IPPC" Directive, represents an important steps towards as more integrated and horizontal approach. As stated in its preamble, different approaches to controlling emissions into the air, water or soil separately may encourage the shifting of pollution between the various environmental media rather than protecting the environment as a whole. In its general framework for integrated pollution prevention and control the integrated approach is clearly demonstrated by the general obligations of Article 3 of the Directive. Member states are required to ensure that installations are operated in such a way that:

- All the appropriate preventive measures are taken against pollution, in particular through application of the best available techniques.
- No significant pollution is caused.
- Waste production is avoided in accordance with Directive 75/442 on waste; where waste is produced, it is recovered or, where that it technically and economically impossible, it is disposed of while avoiding or reducing any impact on the environment.
- Energy is used efficiently.
- The necessary measures are taken to prevent accidents and limit their consequences.

The Directive contains detailed obligations on the granting of permits (Article 6 and 7) including emission limit values for pollutants likely to be emitted from the installations (Article 9).

Finally, the directive contains various transitional provisions, particularly relevant in respect of Directive 76/464 on pollution caused by certain dangerous substances discharged into the aquatic environment of the community and Directive 84/360 on the combating of air pollution from industrial plants [27].

A.1.3 Characteristics of EU Environmental Legislation

Environmental protection has to take account of complex interrelationships between air, oil and water and biodiversity. The implementation and enforcement of legislation remains the weakest link in EU Environmental Policy for a number of reasons that relate to the particular character of environmental problems. The effective implementation and enforcement of environmental law is often a more immediate priority than some other EU policy areas where it may be easier to rectify the damage caused.

Implementation, which is the process of giving effect to EU environmental policy at national level, is achieved when EU legislation is enacted into national statute and administrative practice. Directives are the most common means of enacting environmental policy, the council and commission are also both empowered to issue regulations which, once adopted, automatically become part of the national legal framework in each member state without the necessity for legislative or administrative implementation. Directives impose obligations of the result to be achieved by a choice of means, while regulations impose obligations of form, in the sense that a regulation automatically becomes an integral part of the national legal system.

The enforcement mechanisms used will depend on the administrative structures in place in the member state concerned. In the UK, responsibility for enforcement is divided between the competent authorities in England and Wales, Scotland and Northern Ireland. Decentralisation of the enforcement process ads to the complexity of ensuring the effectiveness of EU environmental law since it increases the possibility of incomplete or incorrect implementation and enforcement, even within different regions of the same member state. This raises important issues because, in a decentralised system, the national government is not necessarily the body responsible for enforcement and may not be in a strong position to ensure high standards of enforcement in all parts of that Member State [106].

A.1.4 Impact of EC Environmental Legislations in the UK

A large amount of EC legislation had been issued concerning the environment. The directives, which have had the most direct impact on UK land use planning, have been enacted either under Articles 100 or 235 or a combination of these two Articles. The most important directives are the *Environmental Assessment Directive (85/337/EEC),* the *Birds Directive (79/409/EEC), the Habitats Directive (92/43/EEC)*, and the *Waste Framework Directive (75/442/EEC)* as amended in 1992. The Directive on *Freedom of Access to Information (90/313/EEC)* has also imposed obligations to make available environmental information to the public.

Until the implementation of *the Environmental Assessment Directive (85/337/EEC)* directive there existed no legal guarantee that environmental implications would be considered, there was however no obligation on either the developer or the local planning authority to research or analyze the environmental implications of a particular development.

The significance of the *Birds and Habitats Directive (92/43/EEC)* is that the designation of land as a Special Protection Area (SPA) under Article 4 of the Birds Directive or as a Special Area of Conservation (SAC) under Article 3 of the Habitats Directive substantially limits the powers of planning authorities to grant permission for developments which have been assessed as adversely affecting the integrity of the site concerned.

The main importance of *Directive (90/313/EEC)* on freedom of access to environmental information to planning practice is to ensure that there are no legal gaps in the public's right to access environmental information to planning practice. However, under Directive

90/313/EEC the acting body only needs to demonstrate that it has public responsibilities for the environment and is under the control of a public body with such responsibilities. In the case of the newly privatized utilities such as the water companies, it is certainly arguable that they are subject to the Directive. Section 3 of the Water Industry Act 1991 imposes general environmental duties on the water companies and as the Griffn case made clear they are subject to important control powers exercisable by the government.
In case of the *Waste Framework Directive*, Articles 3 to 5 impose certain duties on the member states. These duties are referred in Article 7 as 'objectives' and they have been reproduced in the Waste Management Licensing Regulations 1994 as the 'Relevant Objectives'. The objectives in Article 3 of the Directive deal with the need to minimize waste so far as possible, and to encourage materials recycling and energy recovery. The objectives in Article 4 deal with the need to protect the environment and should be considered in the context of the impact of potentially polluting developments on land use and the amenity of the area. Finally the objective in Article 5 is concerned with establishing an integrated network of disposal installations which will enable self-sufficiency at both the national level and EC level, and disposal in accordance with the proximity principle.

The Waste Management Licensing Regulations 1994 implement the Directive by dividing up the responsibilities for drawing up both the waste plans and for issuing the permits between the local planning authorities and the other pollution control authorities (mainly the waste regulatory authorities in England and Wales) [114].

A.1.5 An Overview of the Pre-Act Framework in UK

Before describing the various options for the Environment Agency (EA) which the government identified in 1991, and the eventual choices made, it is necessary to describe in outline the nature and responsibilities of the various bodies and authorities with responsibility for environmental matters, as they were before the establishment of the EA.

- **Department of Environment**

The department of environment has general, overall responsibility for environmental matters, including the formulation of policies for protecting the environment. Besides acting on the domestic front, Department of Environment is required to participate in EC and other international fora on matters concerned with environmental protection.

- **Her Majesty's Inspectorate of Pollution (HMIP)**

HMIP was created in 1987 from the Industrial Air Pollution Inspectorate of the Health and Safety Executive and the Radiochemical, Hazardous Waste and Water Inspectorates of the Department of Environment. HMIP was responsible for regulating those industrial processes or plant with the greatest potential for pollution and, in particular, had the task of commencing the implementation of the system of integrated pollution control (IPC) which was introduced by the Environmental Protection Act 1990 and which will eventually cover approximately 5,000 major industrial installations. Through its IPC function, HMIP thus had a crucial role in controlling major pollution of air, land and water. Further functions of HMIP included regulating the disposal of radioactive waste under the Radioactive Substances Act 1993, and overseeing the performance of local authorities waste disposal functions.

- **Drinking Water Inspectorate**

The Drinking Water Inspectorate was established following the Water Act 1989. Operating as part of the Department of Environment's Water Directorate, its primary function is to monitor the quality of drinking water supplied by water companies. Besides this monitoring function, the Inspectorate advises Ministers on enforcement and provides them with scientific and technical advice on issues relating to water quality.

- **National Rivers Authority**

Established by the Water Act 1989, the responsibilities of the National Rivers Authority (NRA) covered the protection and improvement of the water environment. The NRA lead the following main functions:

  - Control of pollution of watercourses;
  - Regulation of water obstruction;
  - Flood and coastal defence
  - Independently monitoring river, water quality and discharges from sewage treatment plants.

- **Waste Regulation Authorities**

Waste Regulation Authorities (WRAs) were established by the Environmental Protection Act 1990. WRAs were responsible for the system of licensing and supervision of waste disposal facilities, the enforcement of that system and the control of hazardous waste movements [115].

A.1.6 UK Enforcement Authorities

The main authorities responsible for enforcing environmental legislation are:

- Environment Agency (for England & Wales)
- Scottish Environment Protection Agency (for Scotland).
- Environment and Heritage Service (for Northern Ireland)

They are responsible for enforcing:

  - Waste and Special Waste Legislation
  - Integrated Pollution Control (IPC)
  - Integrated Pollution Prevention and Control (IPPC)
  - Water Resources Act
  - Groundwater Regulations
  - Contaminated Land

Other enforcing authorities include local authorities, sewage undertakers (usually the same as the water supply companies) and the Health & Safety Executive (HSE) has responsibilities relating to hazardous substance legislation [104].

A.1.7 UK Environment Agency (EA)

The Environment Agency (EA) was established under the Environment Act 1995. On 1 April 1996 it took over all the functions of the former National Rivers Authority, Her Majesty's Inspectorate of Pollution and 83 local waste regulations authorities. Its main functions are to manage and regulate the water environment, and control industrial pollution and wastes. The Agency also makes available environmental information, promotes understanding, advises on policy development and implementation, and reports on the state of the environment. It covers England and Wales [116].

The main responsibilities for EA are:

- Applying standards by giving authorization, licenses and consents for emissions, discharges and disposals to air, water and land;
- Monitoring compliance and enforcement;
- Regulating the import, export and movement of waste;
- Assessing national waste disposal needs and priorities'
- Monitoring environmental conditions, publishing statistics and commissioning research;
- Provide authoritative and independent advice to government and advice and guidance to industry on best environmental practice [115].

A.1.8 Pollution Control in the UK

Before April 1991, pollution in the UK was regulated by reference to the environmental media into which it was released– air, land or water – and subjected to three distinct control regimes. Over time, it became apparent that pollution in one medium can have implications in another, for example, burning fossil fuels emits gases which can return to earth in acid rain, harming fresh-water life and reducing soil fertility. Heavy metals, such as cadmium or lead, which are emitted into the air through combustion processes, can similarly return to the sea or land and find their way into our food chain.

With the *Environmental Protection Act 1990 (EPA)*, a new type of statute was created. The EPA, concerned exclusively with pollution, attempts to monitor all environmental media through Integrated Pollution Control (IPC). IPC looks at the effect of a polluting process on the environment as a whole, and attempts to organize pollution control from that standpoint. Together with the Water Resources Act 1991 (WRA 1991), the Environmental Protection Act 1990 contains measures to strengthen the powers and resources of the various inspectorates.

The objectives of the legislation are to:

- Make the air cleaner and safer
- Achieve further improvements in the quality of water
- Establish the levels of emissions that air and waters can safely tolerate, and set up control mechanisms based on them;
- Regulate and rationalize the management of waste;
- Maintain, and strengthen where necessary, controls over pollution from industry and agriculture and dangerous chemical, and other substances; and,
- Provide and necessary incentives to industry to improve its environmental standards and develop clean technologies [117].

A.1.8.1 Framework of the Environmental Protection Act 1990

The Environmental Protection Act 1990 marks the beginning of a new generation of environmental legislation in the United Kingdom. It seeks to provide an integrated approach to pollution control, under which systems are looked at as a whole when applying environment regulations.

Under Part I of the EPA, there are two separate pollution control regimes: *Integrated Pollution Control (IPC)* and *Local Authority Air Pollution Control (LAAPC).* Each establishes similar system requiring authorization for prescribed processes capable of causing harm to the environment. They also share similar regulations for enforcement, publicity and offenses. The distinction between them lies in their responsibilities and their personnel – IPC controls releases into all environment media of air, land and water, whereas local authority air pollution control only regulates releases into air. IPC is enforced by HMIP in England and Wales. LAAPC is enforced by the local authorities.

Integrated Pollution Control (IPC) regulates the most polluting industrial processes and it seeks to achieve the following goals:

- To prevent pollution at source and
- Minimize the risk of harm to human health and the environment using the best available techniques not entailing excessive cost (BATNEEC).
- To encourage and apply the most advanced technical solutions, while recognizing the integrated nature of the environment and the need to achieve the "Best Practicable Option" (BPO) for the environment as a whole given discharges and emissions to more than one medium.
- To ensure that the polluter pays for the necessary controls.
- To apply a "critical loads" approach by assessing the levels of pollutants which local environments can tolerate without significant damage, in order to focus protection on the most vulnerable environment [117].

Pollution Prevention and Control Act 1999, this implements the requirements of EU Directive on *Integrated Pollution Prevention and Control (IPPC).* Sectors will move across according to a phased time table from the EPA 90 IPC/APC schemes to IPPC [62]. Part II of the EPA 1990 deals with waste on land, waste can be defined as (a) any substance which constitutes a scrap material or an effluent or other unwanted surplus substance arising from the application of any process; and (b) any substance or article which requires to be disposed of as being broken, worn out, contaminated or otherwise spoiled. However, this does not include a substance, which is an explosive.

Waste is categorized broadly into controlled waste and non-controlled waste, according to Section 75(4) of the EPA 1990, "controlled waste," means household, industrial and commercial wastes, or any such waste. Other waste called "non control waste" this include agriculture, mines and quarries waste. Wastes, which have properties that render them dangerous, are termed "Hazardous wastes". The UK legislation uses the term "special waste" to present "hazardous waste" [109]. Currently the term "special waste" applies to any controlled waste which either:

(a) consists of or contains any of a number of substances list at schedule of the regulations, namely:

1. Acids and alkalis;
2. Antimony and antimony compounds;
3. Arsenic compounds;
4. Asbestos (all chemical forms);
5. Barium compound;
6. Beryllium and Beryllium compounds;
7. Biocides and phytopharmaceutical substances;
8. Boron compounds;
9. Cadmium and cadmium compounds;
10. Copper compounds
11. Heterocyclic organic compounds containing oxygen, nitrogen or sulphur;
12. Hexavalent chromium compounds;
13. Hydrocarbons and their oxygen, nitrogen and sulphur compounds;
14. Inorganic sulphur-containing compounds;
15. Inorganic cyanides;
16. Inorganic halogen-containing compounds;
17. Laboratory chemicals
18. Lead compounds;
19. Mercury compounds;
20. Nickel and its compounds;
21. Organic halogen compounds, excluding inert polymeric materials;
22. Peroxides, chlorates and perchlorates;
23. Pharmaceutical and veterinary products;
24. Phosphorus and its compounds;
25. Selenium and selenium compounds;
26. Silver compounds;

27. Tarry materials from refining and tar residues from distilling;
28. Tellurium and tellurium compounds;
29. Thallium and thallium compounds;
30. Vanadium compounds;
31. Zinc compounds;

(b) is a medicinal product, as defined in section 130 of the Medicines Act 1965 (substances or articles manufactured for treatment of human beings or animals).

Whilst radioactive waste is generally excluded from the definition of controlled waste, the regulation on special waste may apply to radioactive waste [118].

A number of legislation controls the management of special waste. The key legislation is the Special Waste Regulations, 1996 (as amended). This implement the European Council Directive (91/689/EC) referred to as the Hazardous Waste Directive or HWD for the purpose of identifying and managing such wastes. In addition, Environmental Act 1995 deals with waste and there are a specific regulations which controls the production / disposal of such waste, these are Pollution Prevention and Control Regulations 2000 and Waste Incineration Regulations 2002 [109].

A.1.8.2 Water Resources Act 1991 (WRA 1991)

The Water Resources Act (WRA) came into effect in 1991 replacing the corresponding sections of the Water Act 1989 in order to regulate water pollution. The WRA does not offer a specific definition of water pollution. In practical terms, pollution can be broadly defined as a discernible deterioration in water quality. What is regarded as pollution will vary with the amount and type of the potential pollutant and the receiving waters in question. Substances are considered harmful when their concentration reaches a certain level, which could be minimal for the most dangerous substances. Water pollution can be generated in a variety of sources, including sewage, chemical and agricultural accidents, waste sites, and in particular agricultural and industrial discharges. The WRA, more specifically, regulates discharges to 'Controlled Waters' such as rivers, estuaries, coastal and inland waters. The definition of 'Controlled Waters' can be found in Section 104 of the WRA. The Act also establishes that it is the responsibility of the Environment Agency to deal with water pollution, resource management, flood defense, fisheries, and in some areas, navigation. Among these it is the Agency's responsibility to protect and regulate any discharge to controlled waters with the aim to ensure that any potential polluter needs to seek the permission of the Environment Agency and that the polluter pays the cost of the consequences to their discharge [105].

The Water Resource Act 1991 aims, through regulations, to create environmental standards by empowering the Environmental Agency to monitor and ensure the protection of controlled waters. It, furthermore, establishes that it is a legal offence to pollute controlled waters and to discharge effluent in violation of notices or regulations. In order to prevent pollution, the WRA 1991 authorizes the Secretary of State to make regulations prohibiting persons from having control of polluting matter unless steps have been taken to prevent the entry of the matter into controlled waters.

Under the Water Resources Act 1991 it is an offence to cause or knowingly permit any poisonous, noxious or polluting mater or any solid waste matter to enter any controlled water or to breach the conditions of consent. Penalties are a fine not exceeding £20,000 and/or three months imprisonment if convicted is a Magistrates Court, or an unlimited fine and/or two years imprisonment if convicted in the Crown Court. To make discharges of trade or sewage effluent into controlled waters, the discharger has to apply for consent. Sewage effluent is usually discharged by the sewerage undertaker into controlled waters after it has been treated in accordance with the consent. Schedule 10 of the Water Resources Act 1991 sets out the procedure for obtaining a discharge consent. For industrial discharges, conditions for specific substances will usually be given in absolute numerical limits. Any amount discharged in excess of the limit will be a breach of the consent [117].

A.1.8.3 Water Industry Act 1991

The Water Industry Act came into force in 1991 and consolidates various enactments relating to the appointment of water and sewerage undertakers, conditions of appointment, supply of water and the provision of sewerage services. The sections of the Act which are of particular importance to industry, concern the criteria for discharging effluent into the sewerage system. Sections 118-134 of the Water Industry Act contain the criteria for discharging trade effluent in the sewers. Trade effluent is any liquid waste, in any quantity, that is produced from an organization's operations. Trade effluent can include liquid process wastes, wash water, cooling water, condensate water from compressed air installations, and waste chemicals. No effluent can be discharged into the sewer which may damage the sewer, injure the people working in it or interfere with the working of the sewage treatment works. Processes which are regulated under Environment Protection Act 1990 require a trade effluent consent from the sewerage undertaker [105].

Discharge of trade waste without a consent is a strict liability offence, enforcement of which may involve the sewerage undertaker. There are set procedures for applications to discharge a trade effluent to the sewers which are made to the sewerage undertaker, and a statutory framework is contained in Section 121(4) (a) and 142 of the 1991 Act. Section 94 of the Act provides a statutory duty on the sewage undertakes to supply a sewage system for the discharge and disposal of domestic and industrial liquid waste with standards set for effluent discharged to sewers from trade (industrial) sources through trade effluent consents [110].

A.1.8.4 Environment Act 1995

The Environment Act 1995 is a landmark in the development of environmental law in the United Kingdom. The creation of powerful, wide-ranging new environmental agencies is a central feature of the new legislation. The Act also contains important new law on contaminated land, air quality and waste strategy. Section 57 of the Environment Act

1995 makes provision as regards contaminated land by inserting a new Part IIA into the Environmental Protection Act 1990. The new EPA 1990, Pt. IIA imposes on local authorities a duty to identify any contaminated land in their area. Contaminated land is defined in the Act by reference to 'significant harm' or the 'significant possibility' of such harm being caused to human health or property or the health of other living organisms or the pollution of controlled waters. Where the harm or pollution concerned is or is likely to b 'serious' the contaminated land is to be designated as a special site and comes under the jurisdiction of the Environment Agency (EA) instead of the jurisdiction of the local authority [115].

Identifying special site, and licensing contractors to carry out remediation schemes, will provide much additional work. The system of remediation is complex and expensive. Remedial treatment may take several forms and involves the removal or treatment of the contaminated land and eventual restoration and reclamation of the land. There are standards applicable to the process of remediation, which includes the following recognized techniques:

a) The removal of the contaminating substances from the site for subsequent disposal elsewhere under appropriate containment conditions;
b) On-site retention and isolation of the material, e.g., by encapsulation systems or the use of appropriate barriers, etc;
c) Dilution of the contaminating substances with clean material;
d) The elimination or immobilization of contaminants through biological, chemical and/or physical treatments [110].

Appendix 2

A2.1Calibration standard curves

The calibration curves were produced using Certified solutions of 1000 ppm Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+}, Cd^{2+}, Pb^{2+}, and Sn^{2+} in (1M HNO_3) supplied by Fisher chemicals. The calibration curves were achieved using ICP-OES and measuring the amount of emission (response) at different metal concentrations (figures A.2.1-A.2.6).

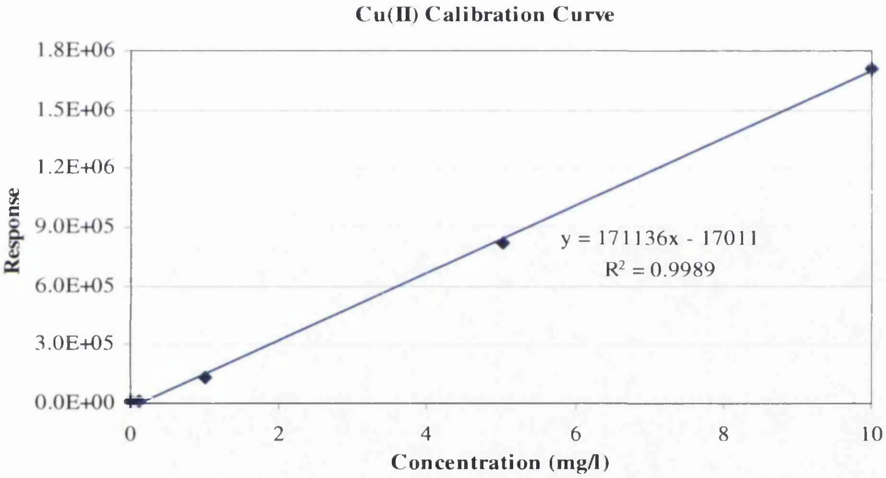

Figure A.2.1 *Calibration standard curve for* Cu^{2+}

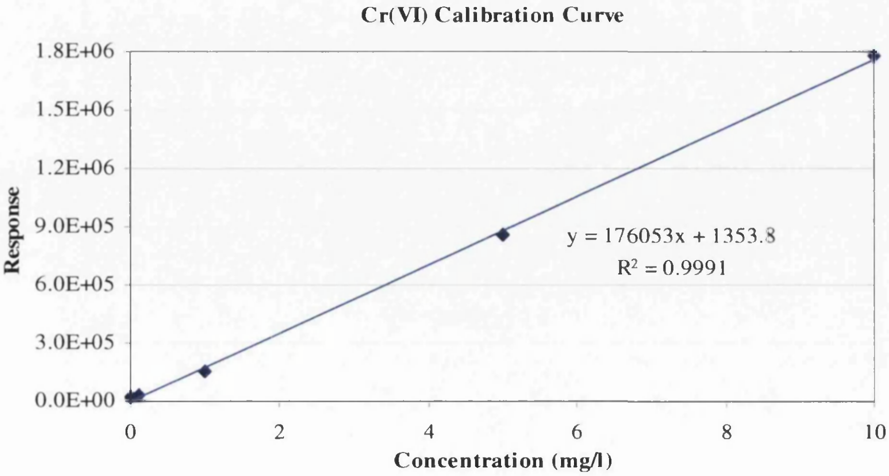

Figure A.2.2 *Calibration standard curve for* Cr^{6+}

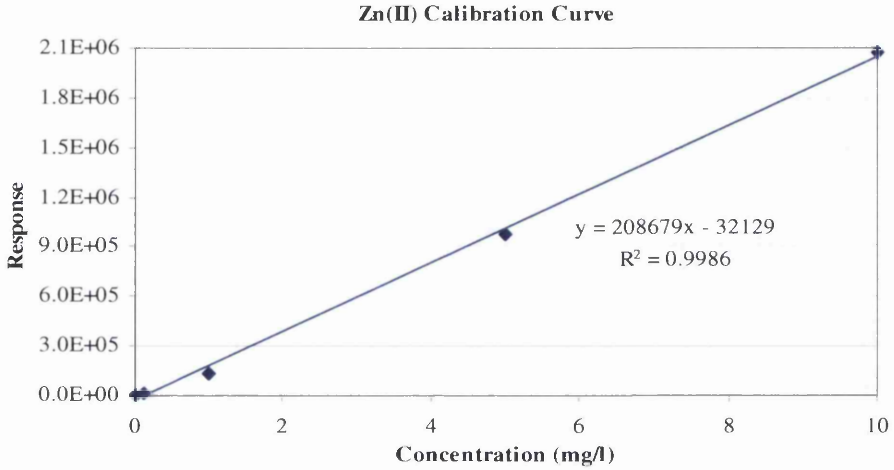

Figure A.2.3 *Calibration standard curve for* Zn^{2+}

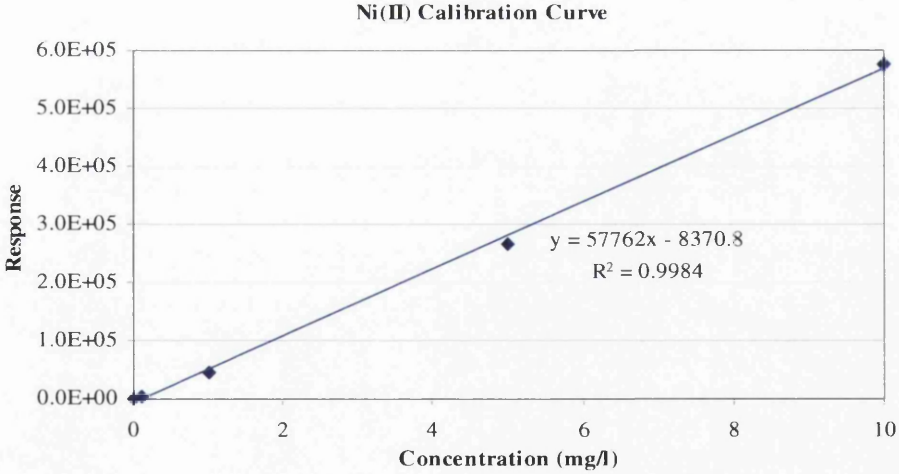

Figure A.2.4 *Calibration standard curve for* Ni^{2+}

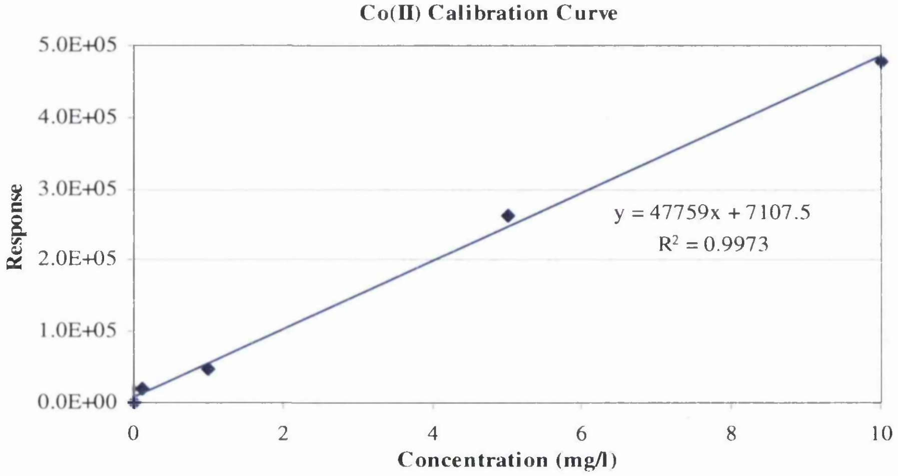

Figure A.2.5 *Calibration standard curve for* Co^{2+}

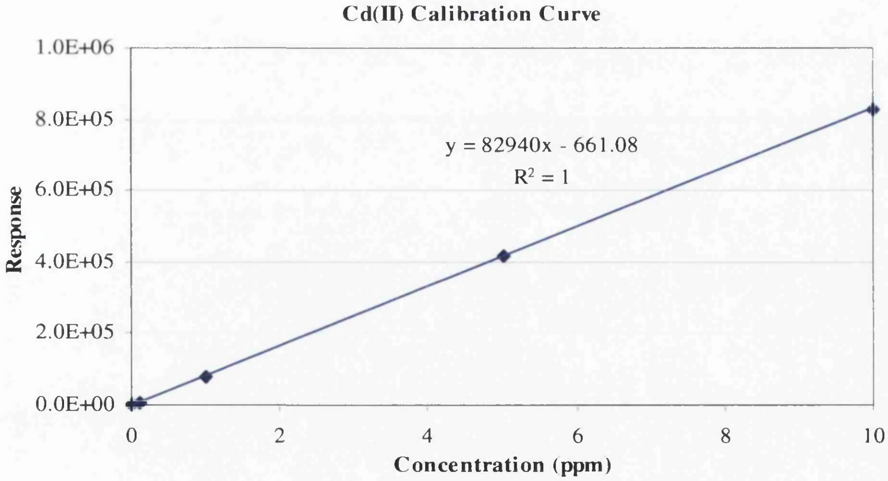

Figure A.2.6 *Calibration standard curve for* Cd^{2+}

Appendix 3

A.3 Results of Langmuir and Freundlich isotherms

A.3.1 Binding results of single metal ions in batch mode PEUF

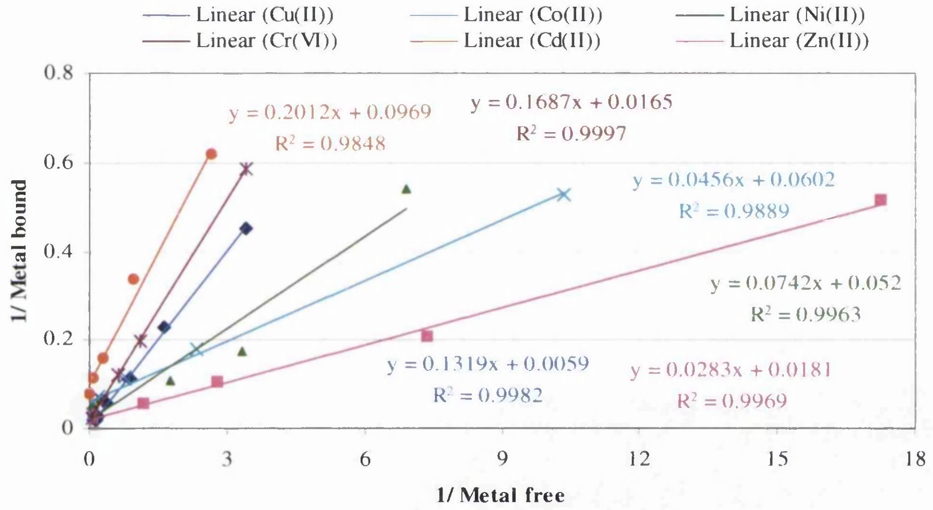

Figure A.3.1 *Linear form of Langmuir isotherms for single metal ions and PEI in batch mode PEUF process.*

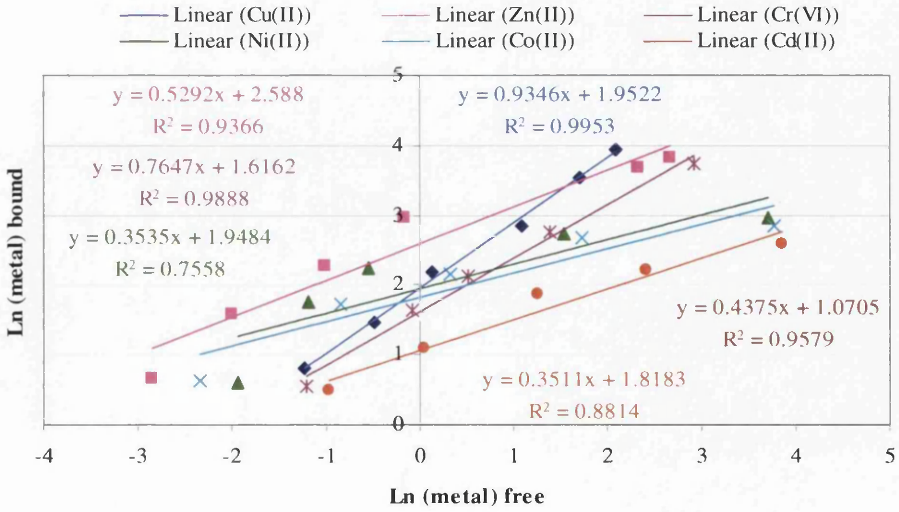

Figure A.3.2 *Linear form of Freundlich isotherms for single metal ions and PEI in batch mode PEUF process.*

A.3.2 Binding results of mixture metal ions in batch mode PEUF

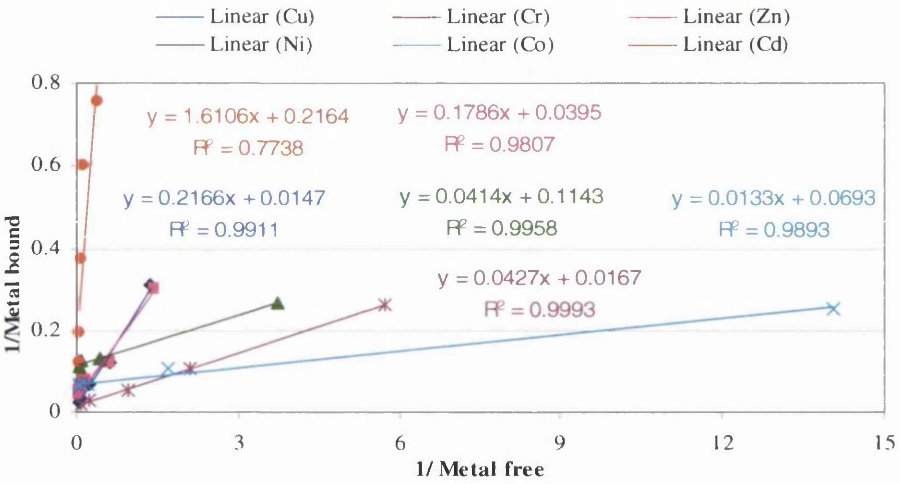

Figure A.3.3 *Linear form of Langmuir isotherms for mixture metal ions and PEI in batch mode PEUF process.*

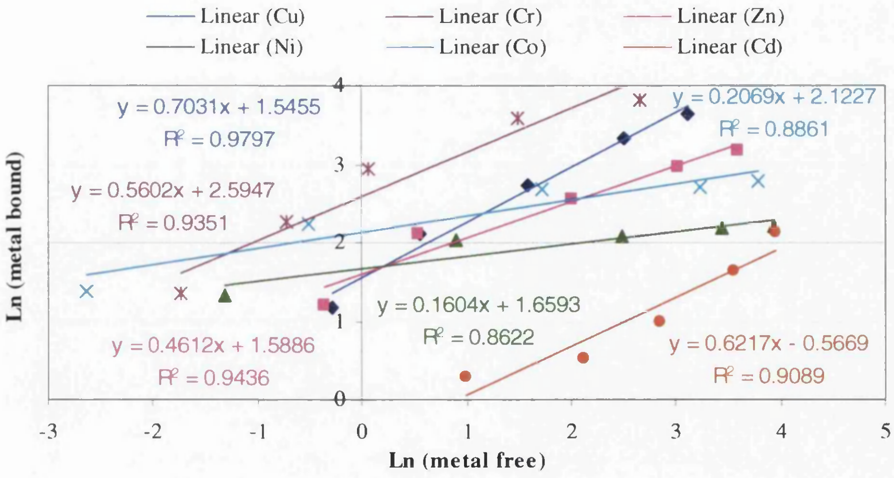

Figure A.3.4 *Linear form of Freundlich isotherms for mixture metal ions and PEI in batch mode PEUF process.*

A.3.3 Competitive results of metal-chelate in batch mode PEUF

A.3.3.1 Langmuir isotherms

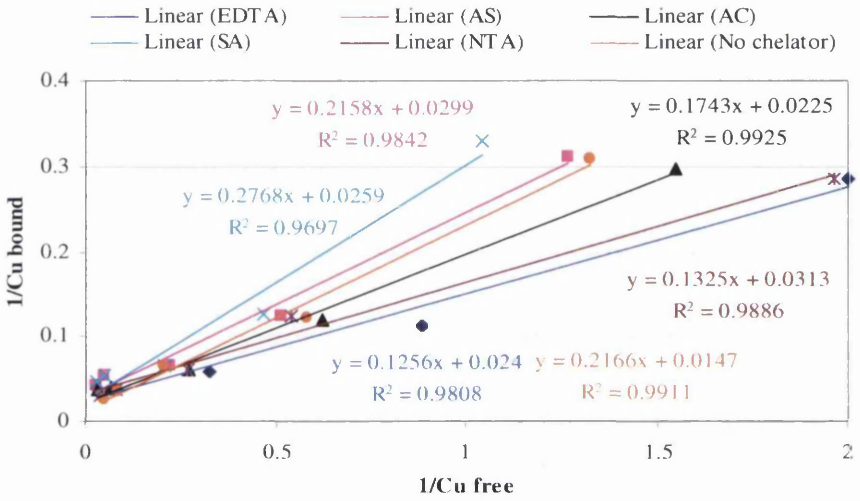

Figure A.3.5 *Linear form of Langmuir isotherms for* Cu^{2+} *, produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 0.2 mM of various chelating agents using batch mode PEUF.*

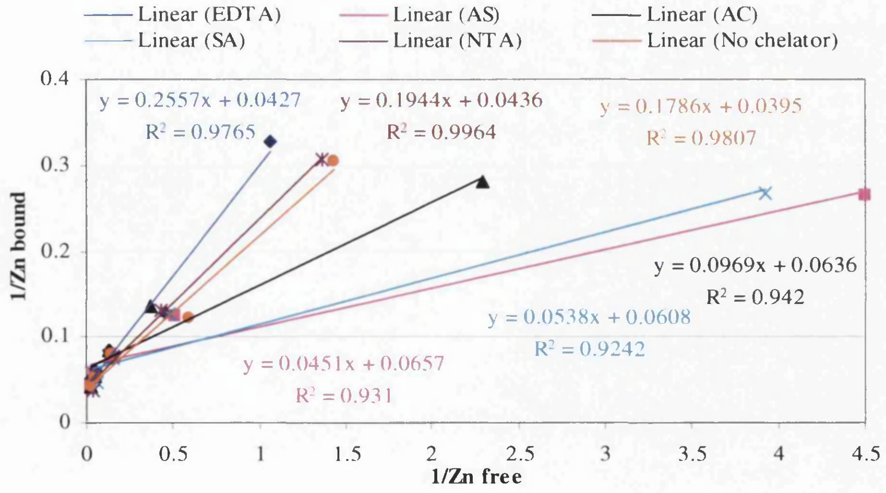

Figure A.3.6 *Linear form of Langmuir isotherms for* Zn^{2+} *, produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 0.2 mM of various chelating agents using batch mode PEUF.*

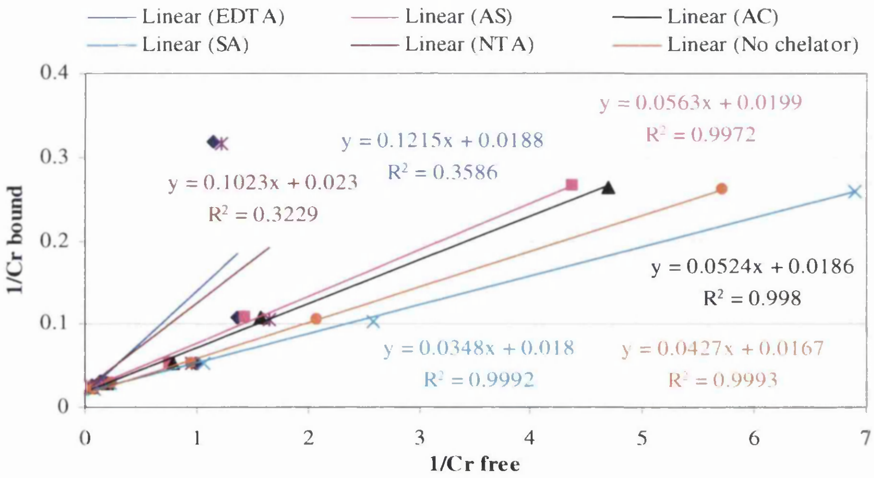

Figure A.3.7 *Linear form of Langmuir isotherms for* Cr^{6+} *, produced from data acquired from PEI solutions containing* Cu^{2+}*,* Zn^{2+}*,* Ni^{2+}*,* Cr^{6+}*,* Co^{2+} *and* Cd^{2+} *in the presence of 0.2 mM of various chelating agents using batch mode PEUF.*

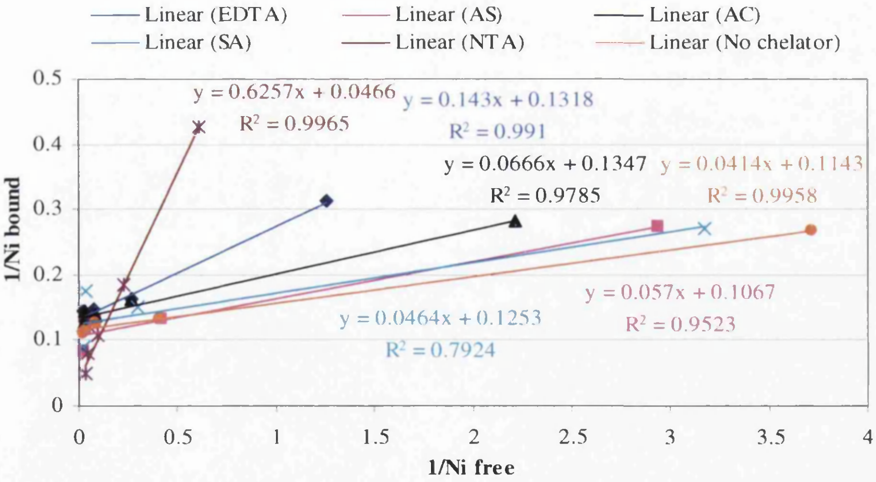

Figure A.3.8 *Linear form of Langmuir isotherms for* Ni^{2+} *, produced from data acquired from PEI solutions containing* Cu^{2+}*,* Zn^{2+}*,* Ni^{2+}*,* Cr^{6+}*,* Co^{2+} *and* Cd^{2+} *in the presence of 0.2 mM of various chelating agents using batch mode PEUF.*

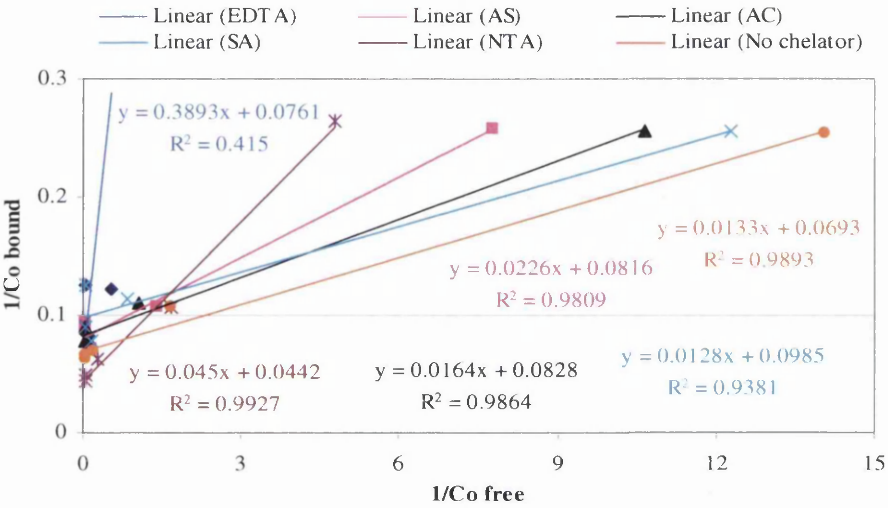

Figure A.3.9 *Linear form of Langmuir isotherms for* Co^{2+} *, produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 0.2 mM of various chelating agents using batch mode PEUF.*

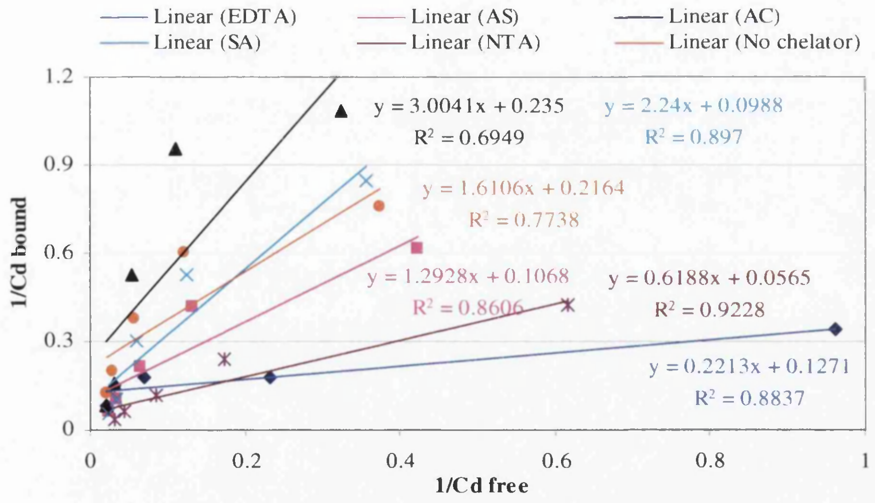

Figure A.3.10 *Linear form of Langmuir isotherms for* Cd^{2+} *, produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 0.2 mM of various chelating agents using batch mode PEUF.*

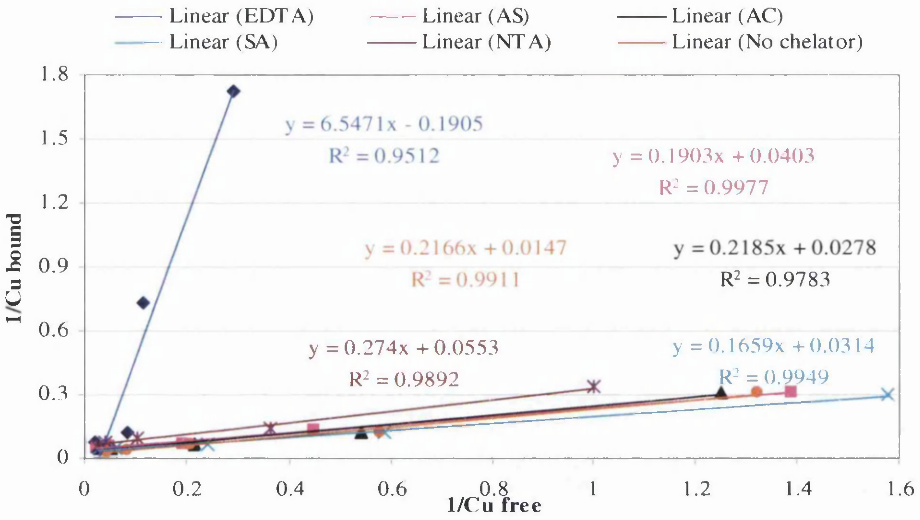

Figure A.3.11 *Linear form of Langmuir isotherms for* Cu^{2+} *, produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 2 mM of various chelating agents using batch mode PEUF.*

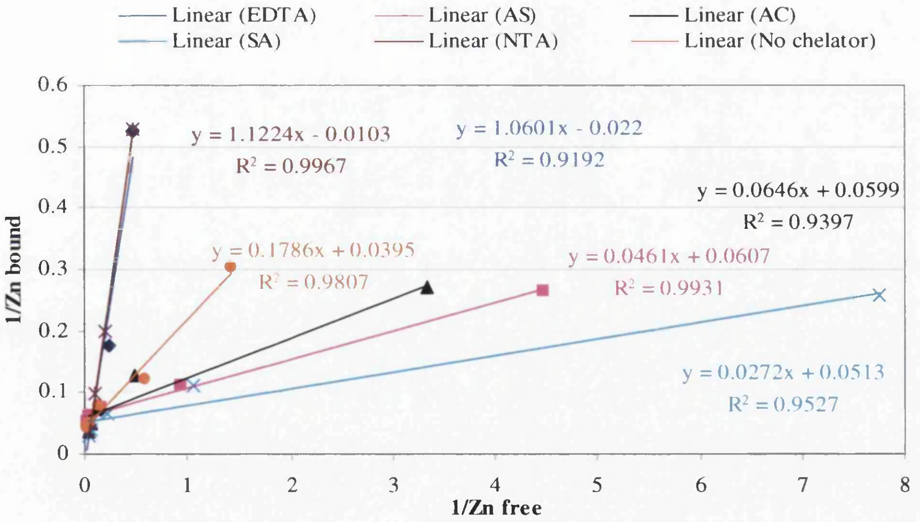

Figure A.3.12 *Linear form of Langmuir isotherms for* Zn^{2+} *, produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 2 mM of various chelating agents using batch mode PEUF.*

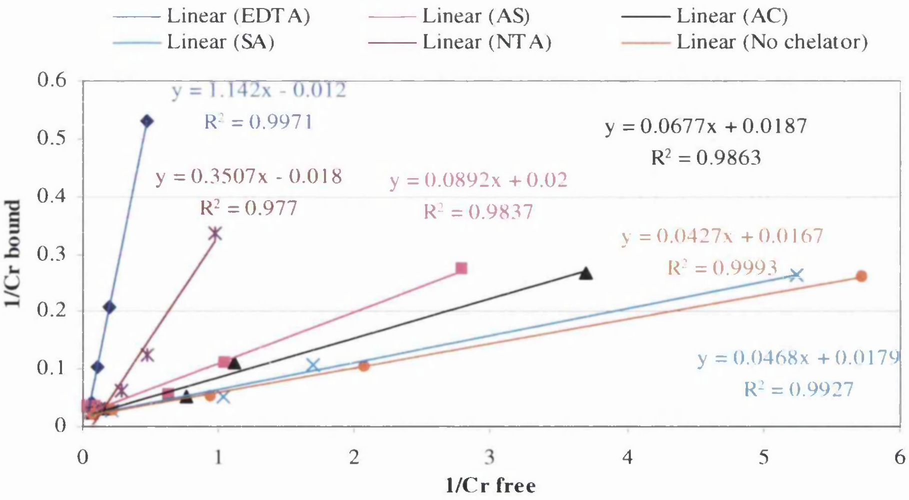

Figure A.3.13 *Linear form of Langmuir isotherms for* Cr^{6+} *, produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 2 mM of various chelating agents using batch mode PEUF.*

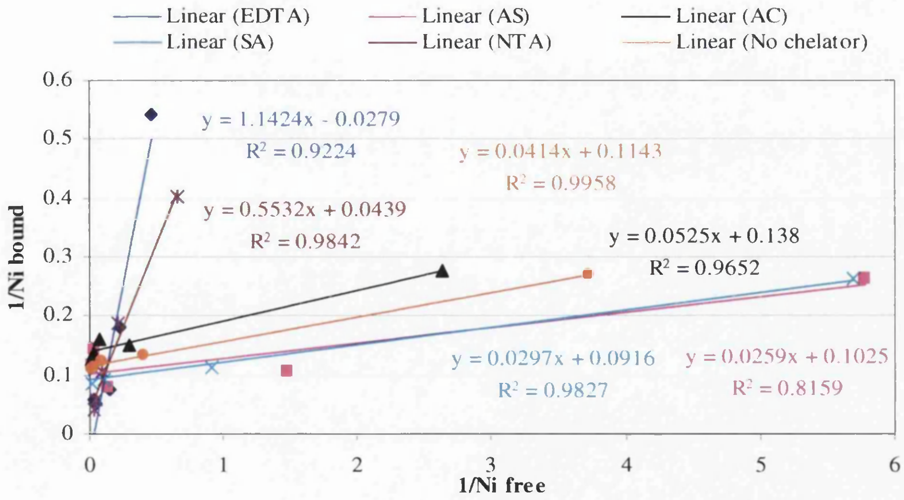

Figure A.3.14 *Linear form of Langmuir isotherms for* Ni^{2+} *, produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 2 mM of various chelating agents using batch mode PEUF.*

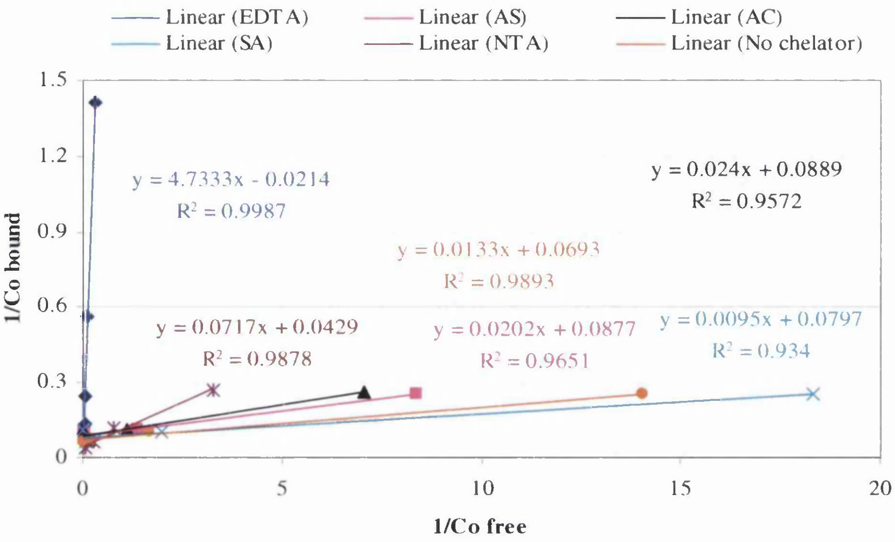

Figure A.3.15 *Linear form of Langmuir isotherms for Co^{2+}, produced from data acquired from PEI solutions containing Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+} in the presence of 2 mM of various chelating agents using batch mode PEUF.*

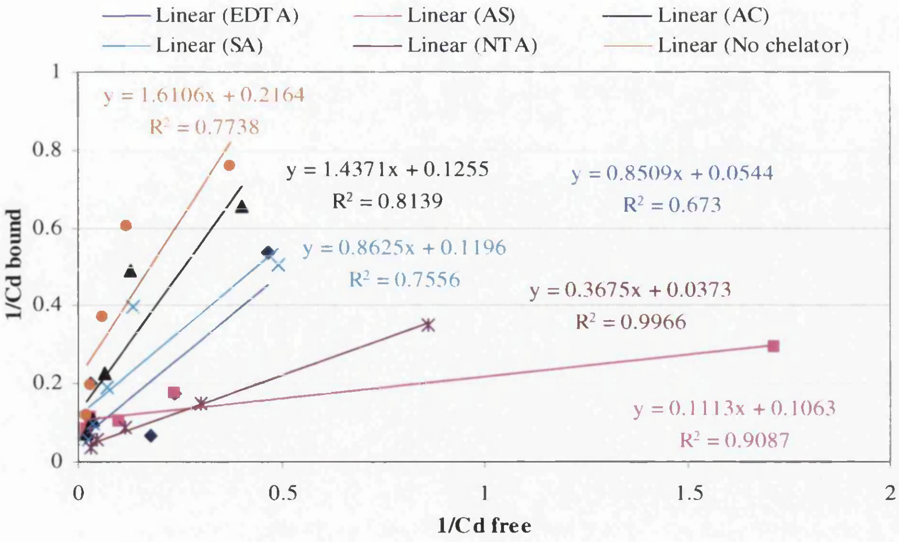

Figure A.3.16 *Linear form of Langmuir isotherms for Cd^{2+}, produced from data acquired from PEI solutions containing Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+} in the presence of 2 mM of various chelating agents using batch mode PEUF.*

A.3.3.2 Freundlich isotherms

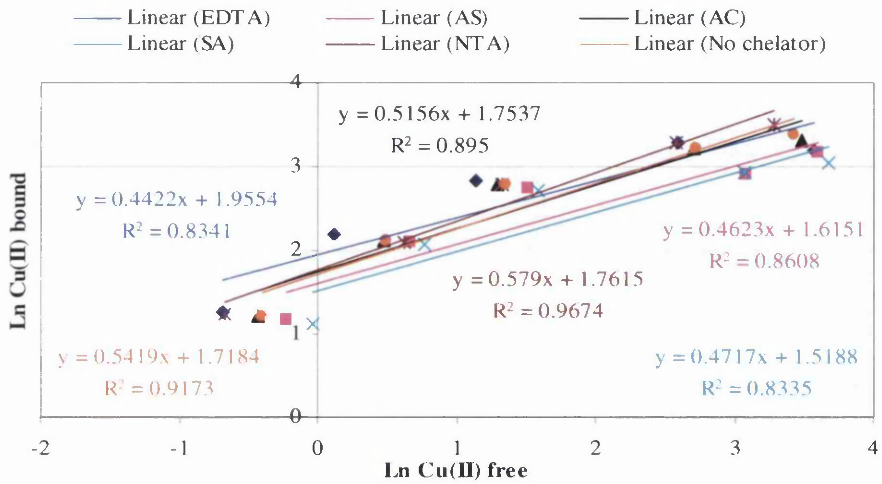

Figure A.3.17 *Linear form of Freundlich isotherms for Cu^{2+}, produced from data acquired from PEI solutions containing Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+} in the presence of 0.2 mM of various chelating agents using batch mode PEUF.*

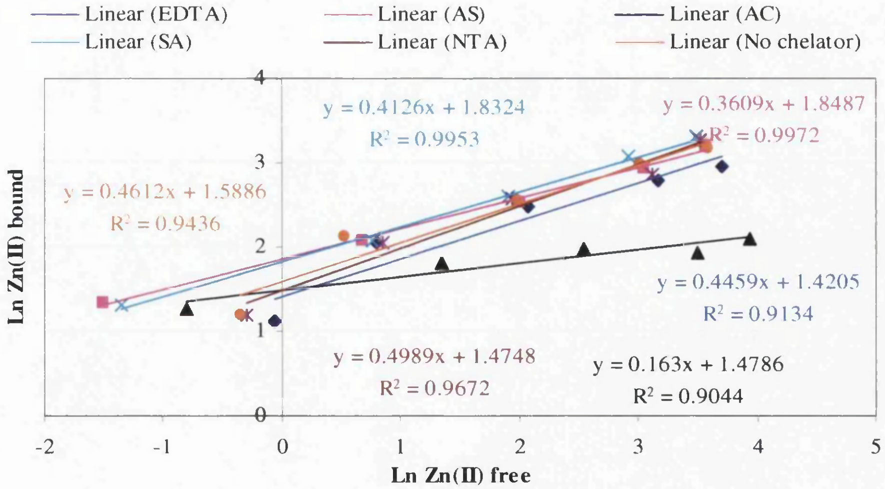

Figure A.3.18 *Linear form of Freundlich isotherms for Zn^{2+}, produced from data acquired from PEI solutions containing Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+} in the presence of 0.2 mM of various chelating agents using batch mode PEUF.*

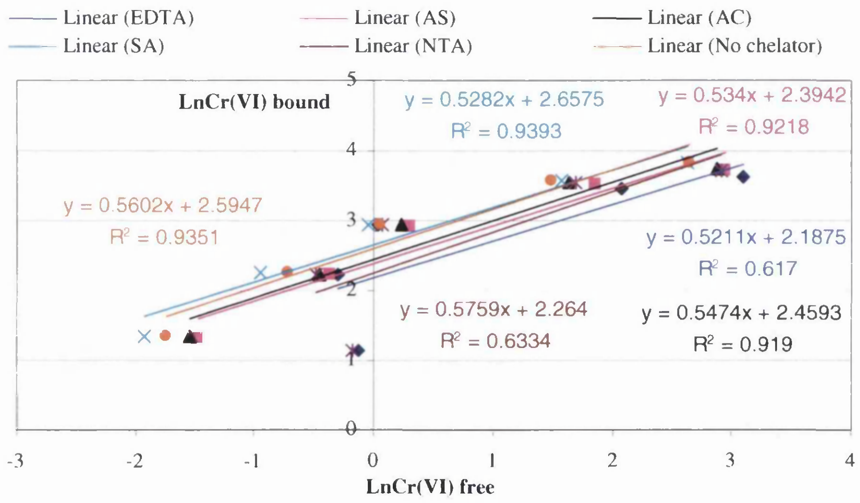

Figure A.3.19 *Linear form of Freundlich isotherms for Cr^{6+}, produced from data acquired from PEI solutions containing Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+} in the presence of 0.2 mM of various chelating agents using batch mode PEUF.*

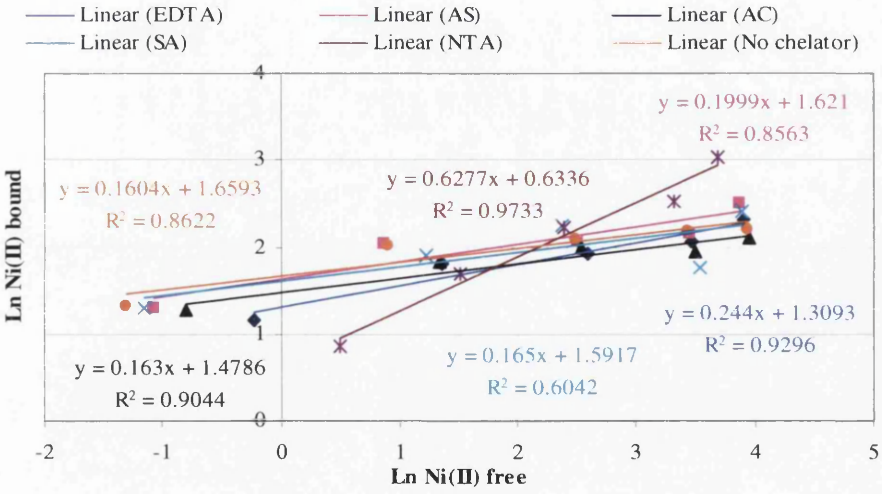

Figure A.3.20 *Linear form of Freundlich isotherms for Ni^{2+}, produced from data acquired from PEI solutions containing Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+} in the presence of 0.2 mM of various chelating agents using batch mode PEUF.*

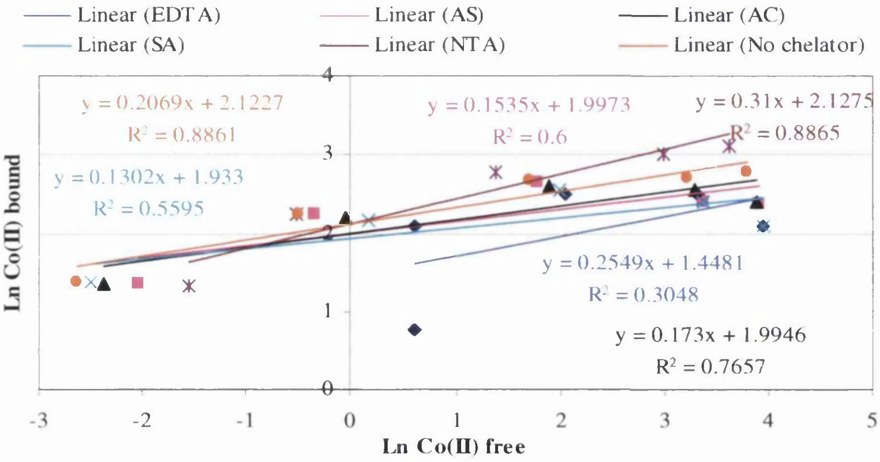

Figure A.3.21 *Linear form of Freundlich isotherms for* Co^{2+} *, produced from data acquired from PEI solutions containing* Cu^{2+}*,* Zn^{2+}*,* Ni^{2+}*,* Cr^{6+}*,* Co^{2+} *and* Cd^{2+} *in the presence of 0.2 mM of various chelating agents using batch mode PEUF.*

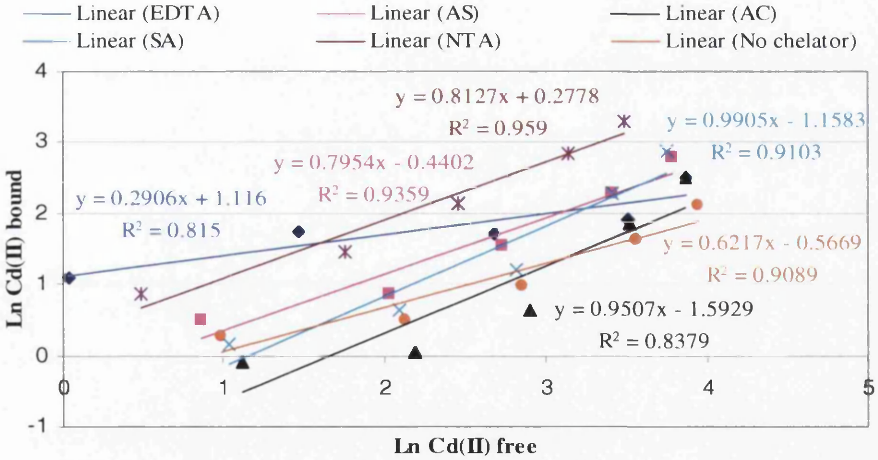

Figure A.3.22 *Linear form of Freundlich isotherms for* Cd^{2+} *, produced from data acquired from PEI solutions containing* Cu^{2+}*,* Zn^{2+}*,* Ni^{2+}*,* Cr^{6+}*,* Co^{2+} *and* Cd^{2+} *in the presence of 0.2 mM of various chelating agents using batch mode PEUF.*

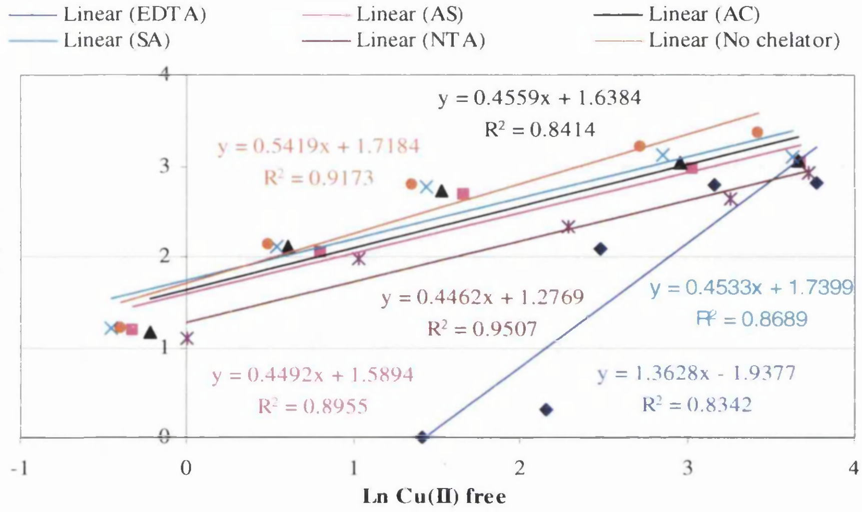

Figure A.3.23 *Linear form of Freundlich isotherms for* Cu^{2+} *, produced from data acquired from PEI solutions containing* Cu^{2+}*,* Zn^{2+}*,* Ni^{2+}*,* Cr^{6+}*,* Co^{2+} *and* Cd^{2+} *in the presence of 2 mM of various chelating agents using batch mode PEUF.*

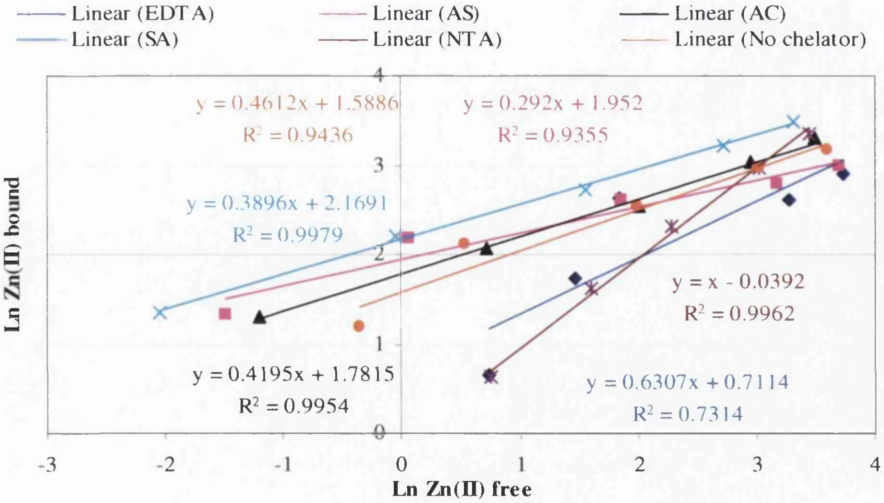

Figure A.3.24 *Linear form of Freundlich isotherms for* Zn^{2+} *, produced from data acquired from PEI solutions containing* Cu^{2+}*,* Zn^{2+}*,* Ni^{2+}*,* Cr^{6+}*,* Co^{2+} *and* Cd^{2+} *in the presence of 2 mM of various chelating agents using batch mode PEUF.*

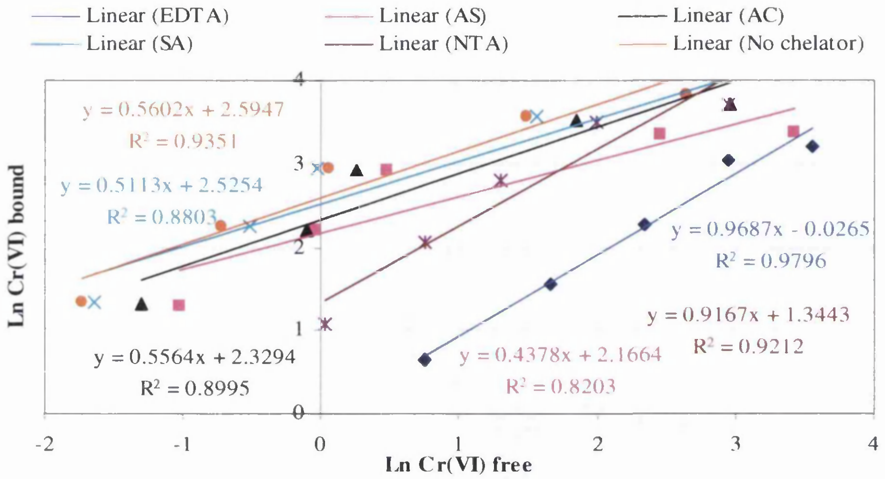

Figure A.3.25 *Linear form of Freundlich isotherms for* Cr^{6+} *, produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 2 mM of various chelating agents using batch mode PEUF.*

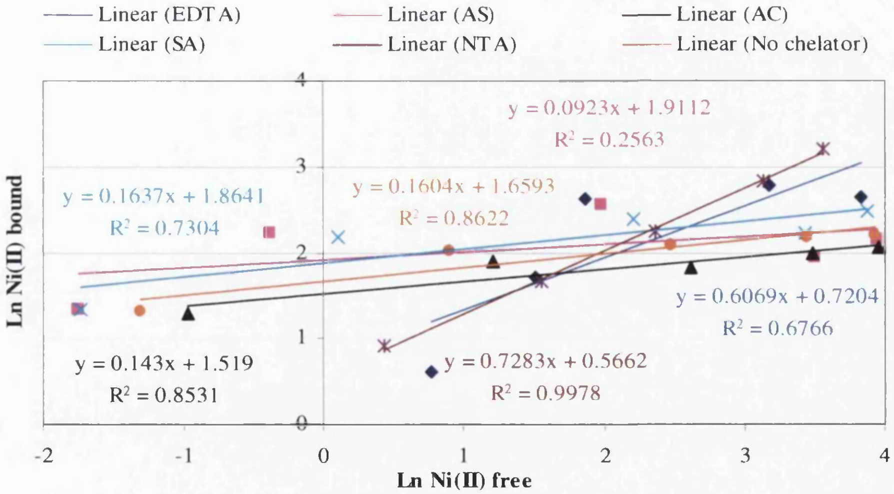

Figure A.3.26 *Linear form of Freundlich isotherms for* Ni^{2+} *, produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 2 mM of various chelating agents using batch mode PEUF.*

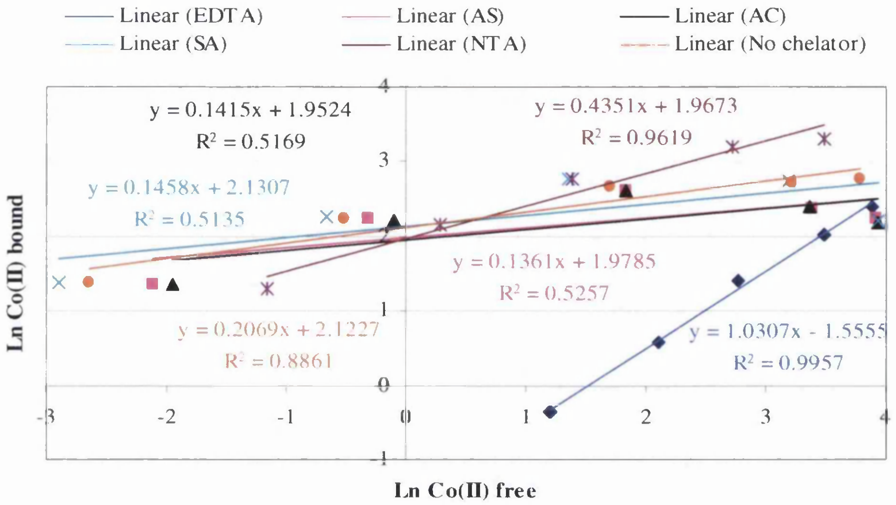

***Figure A.3.27** Linear form of Freundlich isotherms for Co^{2+}, produced from data acquired from PEI solutions containing Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+} in the presence of 2 mM of various chelating agents using batch mode PEUF.*

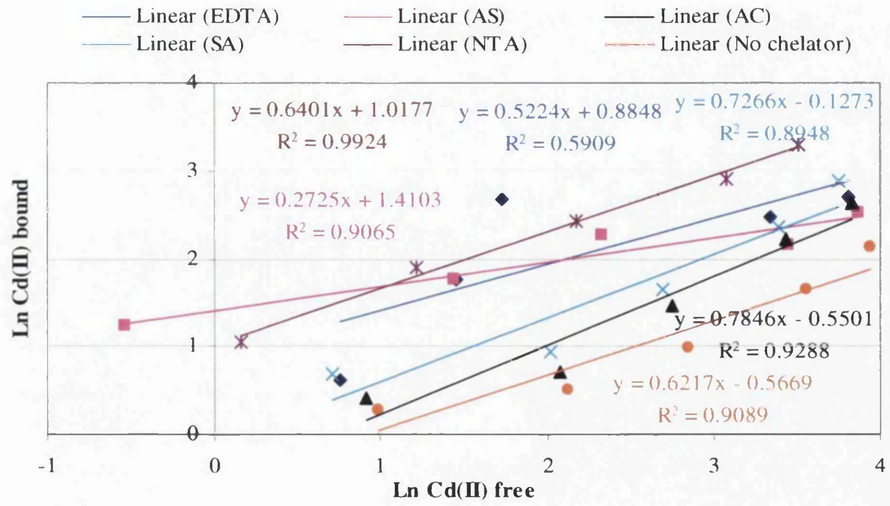

***Figure A.3.28** Linear form of Freundlich isotherms for Cd^{2+}, produced from data acquired from PEI solutions containing Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+} in the presence of 2 mM of various chelating agents using batch mode PEUF.*

A.3.4 Binding results of single metal ions in continuous feed PEUF

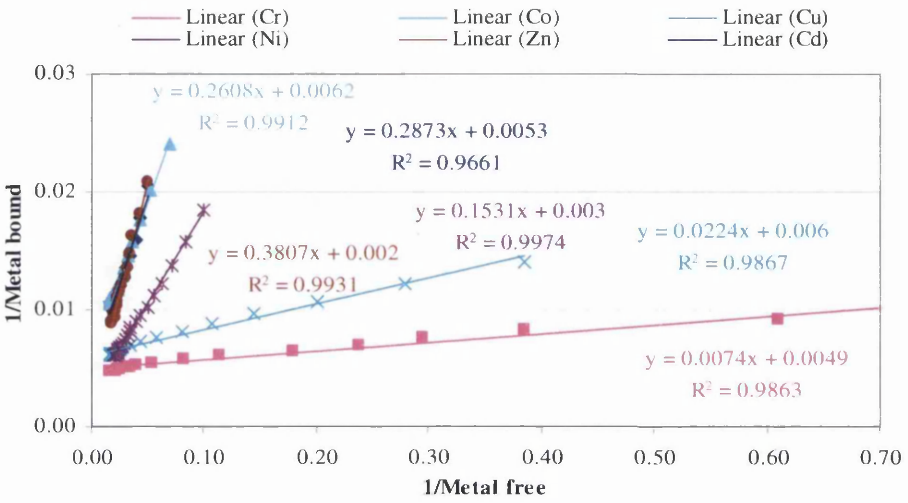

Figure A.3.29 *Linear form of Langmuir isotherms for single metal ions, produced from data acquired from PEI solutions containing single metals in continuous PEUF process.*

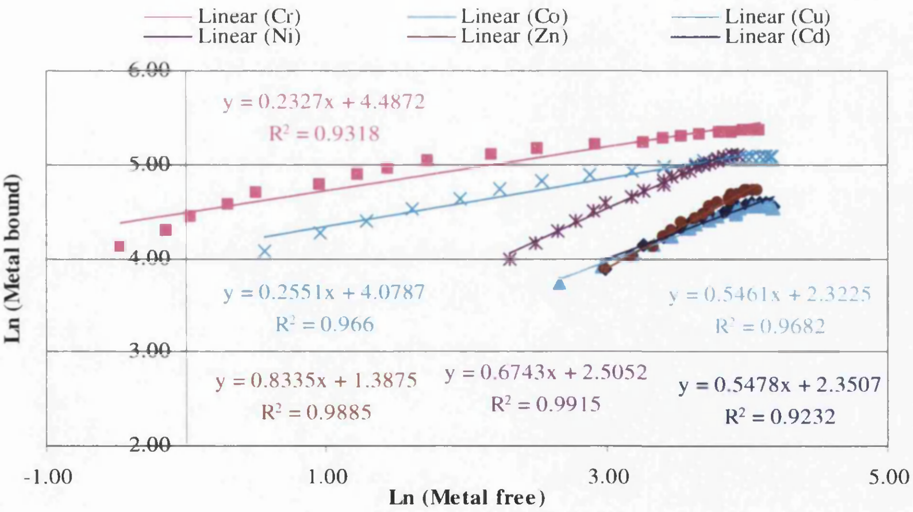

Figure A.3.30 *Linear form of Freundlich isotherms for single metal ions, produced from data acquired from PEI solutions containing single metals in continuous PEUF process.*

A.3.5 Binding results of mixture metal ions in continuous feed PEUF

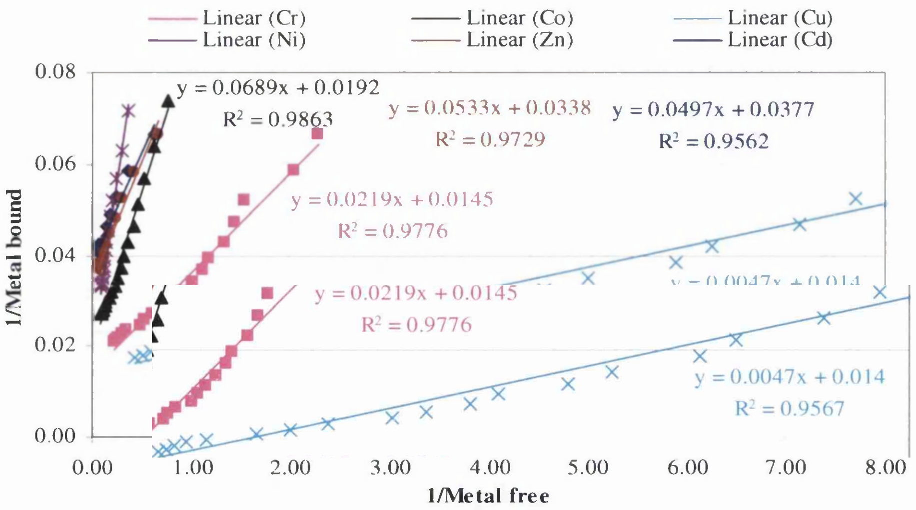

Figure A.3.31 Linear form of Langmuir isotherms for mixture metal ions, produced from data acquired from PEI solution containing Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+} in equal concentrations using continuous feed PEUF process.

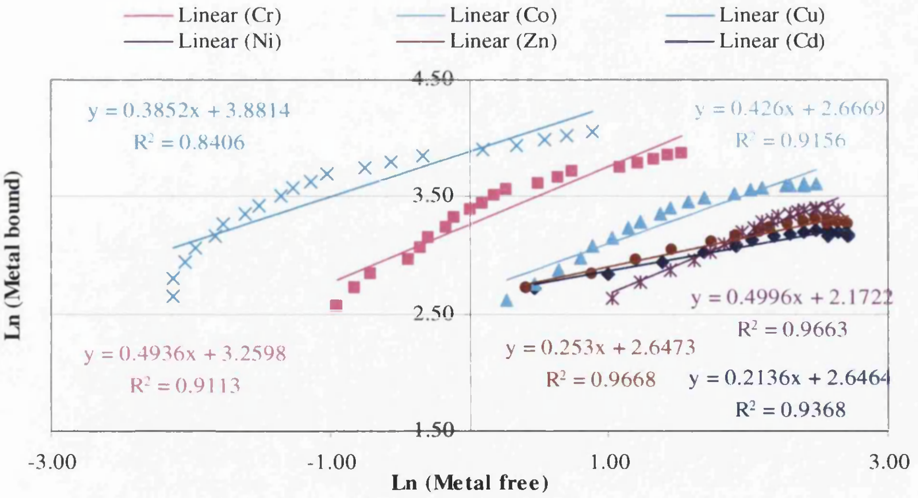

Figure A.3.32 Linear form of Freundlich isotherms for mixture metal ions, produced from data acquired from PEI solution containing Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+} in equal concentrations using continuous feed PEUF process.

A.3.6 Competitive results of metal-chelate in continuous feed PEUF

A.3.6.1 Langmuir isotherms

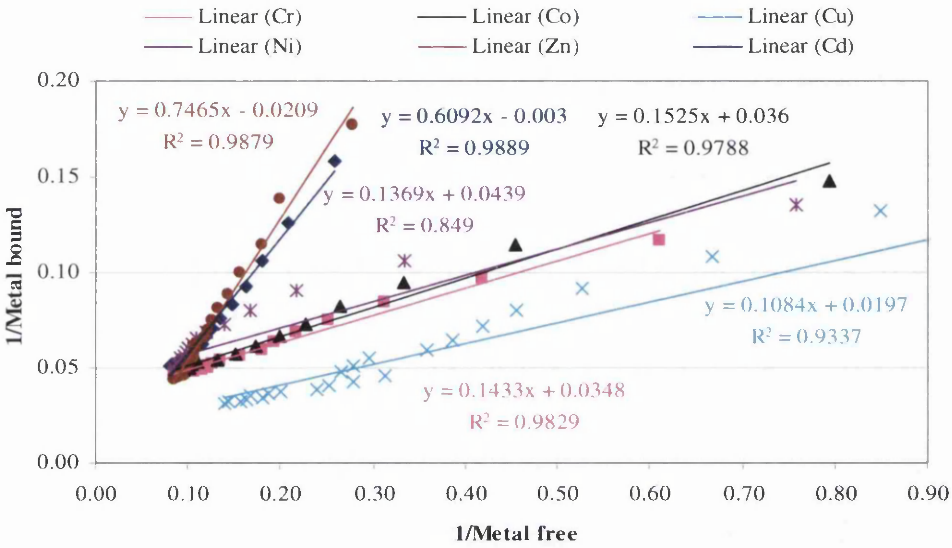

Figure A.3.33 *Linear form of Langmuir isotherms for metal ions , produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 2 mM of Ammonium sulfate using continuous feed PEUF.*

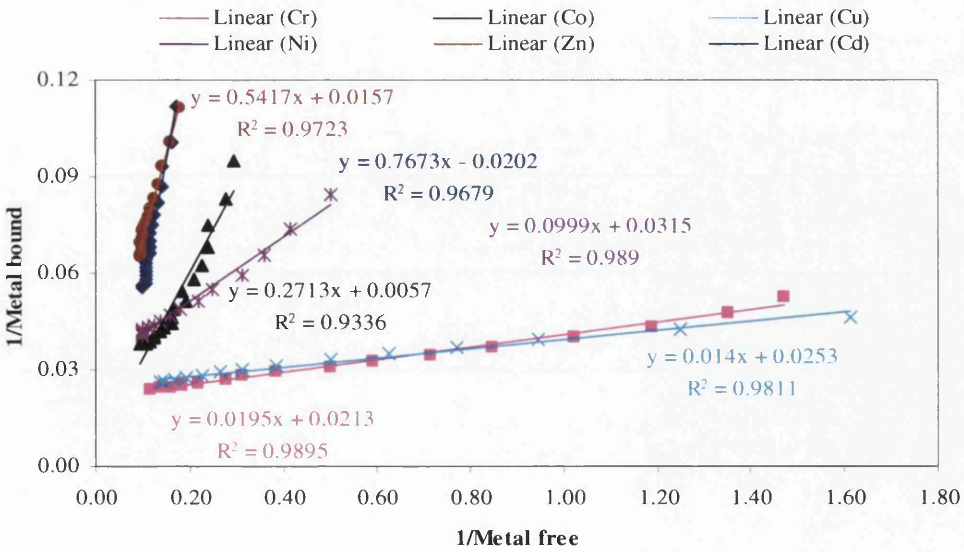

Figure A.3.34 *Linear form of Langmuir isotherms for metal ions , produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 2 mM of Ammonium chloride using continuous feed PEUF.*

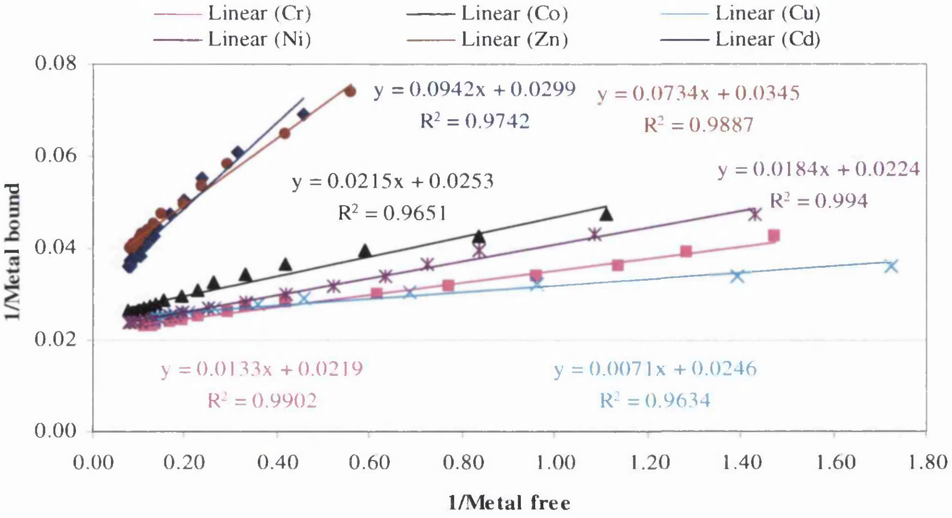

Figure A.3.35 *Linear form of Langmuir isotherms for metal ions , produced from data acquired from PEI solutions containing Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+} in the presence of 2 mM of Sodium acetate using continuous feed PEUF.*

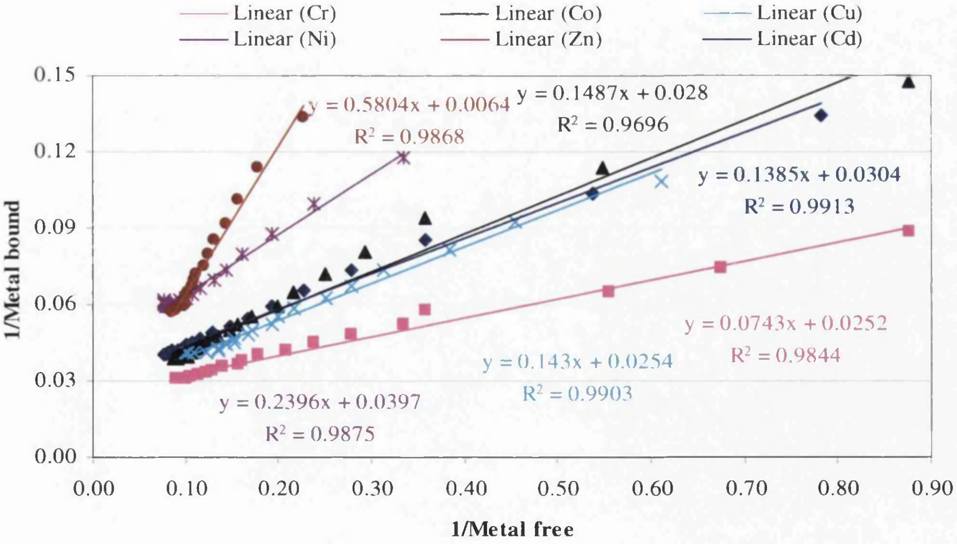

Figure A.3.36 *Linear form of Langmuir isotherms for metal ions , produced from data acquired from PEI solutions containing Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+} in the presence of 2 mM of NTA using continuous feed PEUF.*

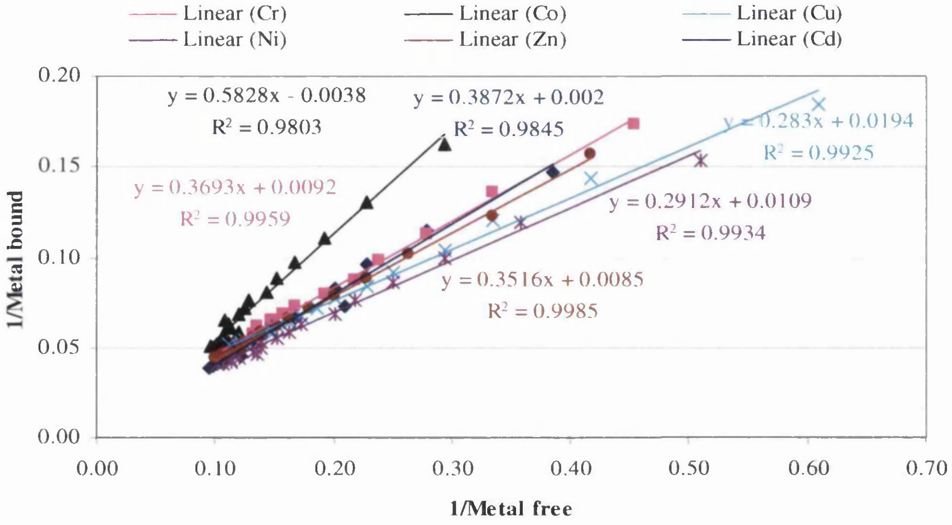

Figure A.3.37 *Linear form of Langmuir isotherms for metal ions , produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 2 mM of EDTA using continuous feed PEUF.*

A.3.6.2 Freundlich isotherms

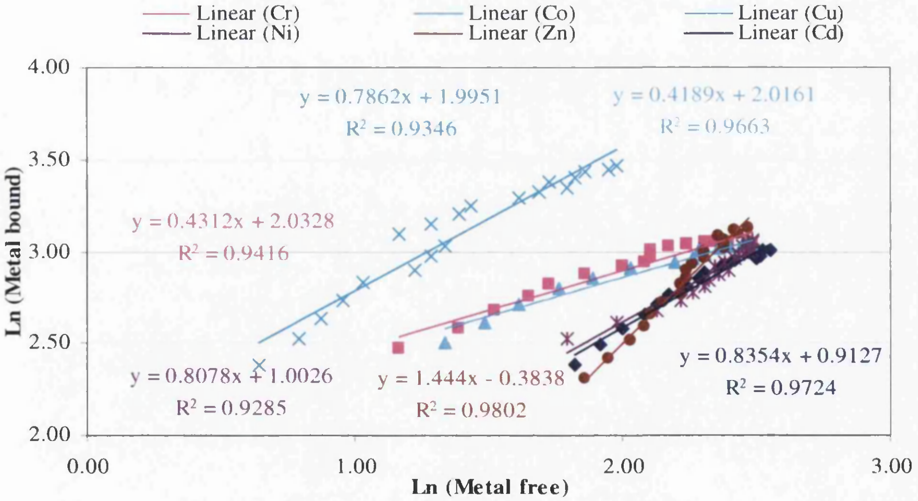

Figure A.3.38 *Linear form of Freundlich isotherms for metal ions , produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 2 mM of Ammonium sulfate using continuous feed PEUF.*

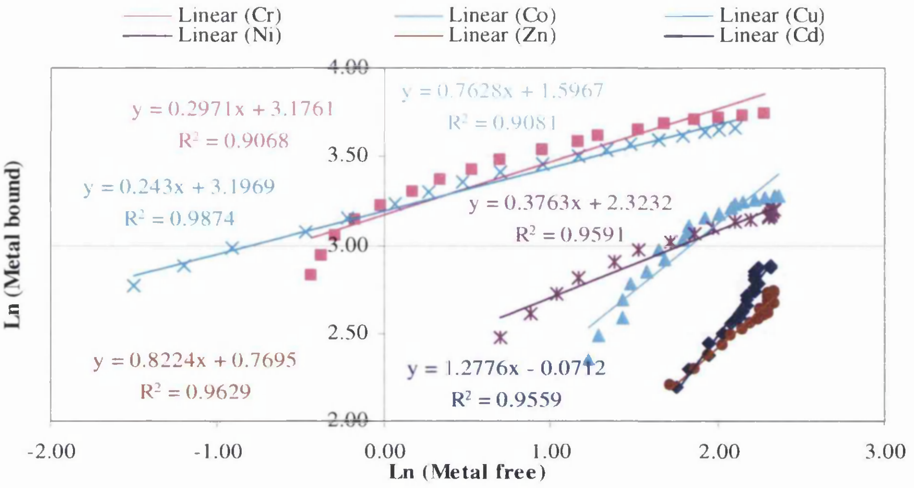

Figure A.3.39 *Linear form of Freundlich isotherms for metal ions , produced from data acquired from PEI solutions containing Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+} in the presence of 2 mM of Ammonium chloride using continuous feed PEUF.*

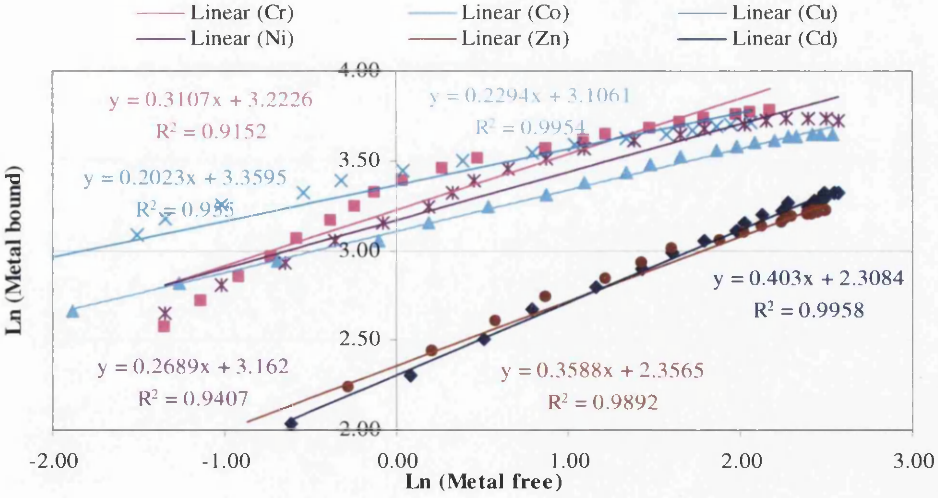

Figure A.3.40 *Linear form of Freundlich isotherms for metal ions , produced from data acquired from PEI solutions containing Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} and Cd^{2+} in the presence of 2 mM of Sodium acetate using continuous feed PEUF.*

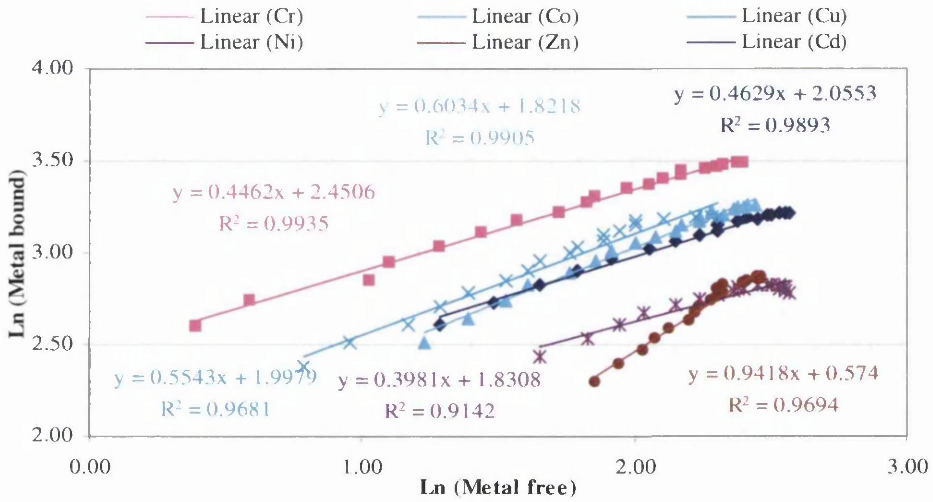

Figure A.3.41 *Linear form of Freundlich isotherms for metal ions , produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 2 mM of NTA using continuous feed PEUF.*

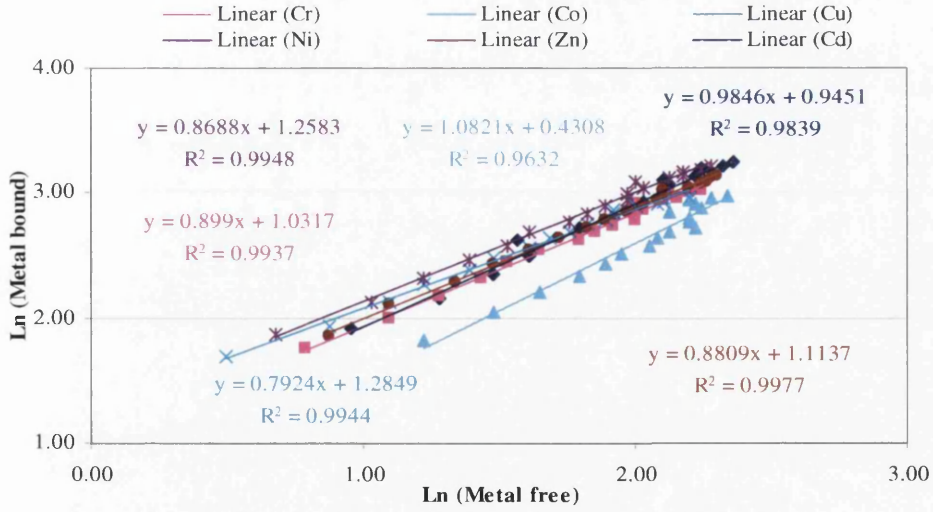

Figure A.3.42 *Linear form of Freundlich isotherms for metal ions , produced from data acquired from PEI solutions containing* Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}, Co^{2+} *and* Cd^{2+} *in the presence of 2 mM of EDTA using continuous feed PEUF.*

Appendix 4

Retention results in continuous feed PEUF

A4.1 Membrane Retention

Initial volume (V_0) = 5 l

Feed concentration (C_f) = 14 mg/l

Flow rate = 5 l/hr

Filtration factor $F = V_p / V_0$ ....*equation 2.5*

Retention $R_i = \left(1 - \frac{C_{pi}}{C_{fi}}\right) \times 100$ ....*equation 3.1*

Where V_p is the permeate volume and C_{pi} is the concentration of metal *i* in the permeate.

Vol. (L)	F -	Cd (II) R (%)	Cr (VI) R (%)	Co (II) R (%)	Cu (II) R (%)	Ni (II) R (%)	Zn (II) R (%)	Exp(-F) R (%)
0	0	100	100	100	100	100	100	100
1	0.2	84.25	89.40	89.25	89.88	86.25	85.50	81.87
2	0.4	72.50	85.95	81.67	89.47	76.67	75.00	67.03
3	0.6	59.17	76.50	70.00	88.00	63.33	61.67	54.88
4	0.8	46.67	69.50	59.17	86.10	51.67	50.00	44.93
5	1	40.83	59.50	47.50	83.70	43.33	43.33	36.78
6	1.2	31.67	56.00	40.83	79.00	35.00	35.83	30.11
7	1.4	30.00	51.00	35.00	72.00	30.83	32.50	24.65
8	1.6	21.67	42.00	28.33	62.00	25.00	26.67	20.19
9	1.8	20.83	40.00	23.33	57.00	22.50	24.17	16.53
10	2	17.50	35.00	20.83	53.00	19.17	20.83	13.53
11	2.2	16.67	35.00	20.00	53.00	18.33	20.83	11.08
12	2.4	12.50	30.00	18.33	45.00	16.67	16.67	9.07
13	2.6	8.33	20.00	15.83	37.00	14.17	12.50	7.43
14	2.8	8.33	15.00	11.67	33.00	11.67	10.00	6.08
15	3	4.17	15.00	10.00	29.00	10.00	7.50	4.98
16	3.2	4.00	10.00	6.67	23.00	5.00	4.17	4.08

A4.2 Retention of single metal

Vol. (L)	F -	Cd (II) R (%)	Cr (VI) R (%)	Co (II) R (%)	Cu (II) R (%)	Ni (II) R (%)	Zn (II) R (%)	Exp(-F) R (%)
0	0	100	100	100	100	100	100	100
1	0.2	96.57	99.99	96.57	99.81	97.23	94.29	81.87
2	0.4	90.29	99.91	91.71	99.46	94.57	89.43	67.03
3	0.6	83.71	99.74	86.29	99.03	91.14	83.43	54.88
4	0.8	78.29	99.46	79.43	98.40	88.57	76.86	44.93
5	1	71.43	99.11	72.57	97.51	85.71	71.43	36.78
6	1.2	65.71	98.77	65.71	96.29	82.86	65.71	30.11
7	1.4	62.86	98.54	60.00	94.86	79.71	60.00	24.65
8	1.6	57.14	98.09	54.29	92.86	77.14	57.14	20.19
9	1.8	51.43	97.66	48.57	90.00	74.00	54.29	16.53
10	2	48.57	96.29	45.71	86.57	71.43	51.43	13.53
11	2.2	42.86	95.14	40.00	82.00	65.71	45.71	11.08
12	2.4	40.00	94.00	37.14	74.57	62.86	42.86	9.07
13	2.6	34.29	92.00	28.57	65.71	57.14	40.00	7.43
14	2.8	31.43	87.43	28.57	57.14	57.14	40.00	6.08
15	3	28.57	82.57	28.57	45.71	54.29	37.14	4.98
16	3.2	28.57	73.43	25.71	42.86	51.43	31.43	4.08
17	3.4	22.86	62.86	20.00	37.14	48.57	31.43	24.65
18	3.6	20.00	57.14	20.00	31.43	45.71	28.57	20.19
19	3.8	20.00	51.43	17.14	25.71	42.86	30.00	16.53
20	4	14.29	44.29	14.29	22.86	40.00	27.14	13.53
21	4.2	11.43	35.71	14.29	20.00	37.14	24.29	11.08
22	4.4	8.57	30.00	11.43	14.29	37.14	22.86	9.07
23	4.6	7.14	24.29	10.00	11.43	34.29	21.43	7.43
24	4.8	7.14	20.00	7.14	8.57	30.00	18.57	6.08
25	5	5.71	14.29	5.71	7.14	27.14	15.71	4.98

A4.3 Retention of mixture metals

Vol. (L)	F -	Cd (II) R (%)	Cr (VI) R (%)	Co (II) R (%)	Cu (II) R (%)	Ni (II) R (%)	Zn (II) R (%)	Exp(-F) R (%)
0	0	100	100	100	100	100	100	100
1	0.2	99.93	99.04	98.60	98.67	98.20	99.89	81.87
2	0.4	99.92	98.79	97.53	98.83	95.87	99.85	67.03
3	0.6	99.59	98.38	96.33	99.00	93.33	99.41	54.88
4	0.8	98.13	97.83	94.80	99.00	90.00	97.87	44.93
5	1	95.00	97.42	93.33	99.08	85.33	94.87	36.78
6	1.2	89.33	96.79	91.33	99.00	81.33	90.00	30.11
7	1.4	82.00	96.33	89.33	99.00	77.33	84.00	24.65
8	1.6	73.33	95.92	87.33	98.92	72.00	78.00	20.19
9	1.8	64.00	94.58	85.33	98.83	66.67	71.33	16.53
10	2	54.67	94.17	84.00	98.67	62.67	62.00	13.53
11	2.2	49.33	93.75	81.33	98.58	58.67	54.67	11.08
12	2.4	40.67	92.92	79.33	98.33	54.67	46.67	9.07
13	2.6	33.33	92.50	77.33	98.17	52.67	42.67	7.43
14	2.8	26.67	91.67	74.00	97.83	48.67	34.67	6.08
15	3	20.00	90.83	72.00	97.67	45.33	26.67	4.98
16	3.2	13.33	90.00	68.00	97.33	42.00	26.67	4.08
17	3.4	13.33	89.17	64.00	97.00	38.67	20.00	24.65
18	3.6	13.33	86.25	55.33	96.08	33.33	13.33	20.19
19	3.8	6.67	84.17	50.00	95.25	29.33	13.33	16.53
20	4	6.67	82.50	45.33	94.08	26.67	6.67	13.53
21	4.2	0.00	75.42	35.33	90.83	20.00	6.67	11.08
22	4.4	0.00	72.08	33.33	88.33	20.00	0.00	9.07
23	4.6	0.00	68.75	26.67	85.83	13.33	0.00	7.43
24	4.8	0.00	65.42	26.67	83.33	13.33	0.00	6.08
25	5	0.00	61.67	20.00	80.00	6.67	0.00	4.98

A4.3.1 Retention of mixture metals in the presence of ammonium sulfate

Vol. (L)	F -	Cd (II) R (%)	Cr (VI) R (%)	Co (II) R (%)	Cu (II) R (%)	Ni (II) R (%)	Zn (II) R (%)	Exp(-F) R (%)
0	0	100	100	100	100	100	100	100
1	0.2	91.69	98.17	97.67	98.33	98.73	91.83	81.87
2	0.4	81.54	96.50	94.83	97.83	95.83	81.67	67.03
3	0.6	70.00	92.83	89.50	94.83	89.00	70.00	54.88
4	0.8	63.08	86.33	81.67	90.17	75.00	58.33	44.93
5	1	56.92	80.00	75.00	87.50	61.67	53.33	36.78
6	1.2	52.31	73.33	68.33	84.17	50.00	46.67	30.11
7	1.4	47.69	66.67	63.33	81.67	40.00	41.67	24.65
8	1.6	43.08	61.67	58.33	80.00	30.00	36.67	20.19
9	1.8	38.46	56.67	51.67	78.33	23.33	33.33	16.53
10	2	35.38	53.33	45.00	76.67	20.00	31.67	13.53
11	2.2	32.31	46.67	36.67	71.67	16.67	28.33	11.08
12	2.4	27.69	38.33	25.00	70.00	15.00	23.33	9.07
13	2.6	24.62	33.33	20.00	68.33	11.67	23.33	7.43
14	2.8	23.08	31.67	16.67	73.33	8.33	21.67	6.08
15	3	18.46	31.67	18.33	70.00	13.33	21.67	4.98
16	3.2	16.92	26.67	11.67	66.67	10.00	20.00	4.08
17	3.4	13.85	21.67	8.33	65.00	6.67	16.67	24.65
18	3.6	6.15	16.67	3.33	58.33	5.00	16.67	20.19
19	3.8	4.62	13.33	1.67	55.00	1.67	10.00	16.53
20	4	6.15	8.33	1.67	50.00	0.00	10.00	13.53
21	4.2	7.69	8.33	0.00	53.33	1.67	10.00	11.08
22	4.4	7.69	8.33	1.67	48.33	3.33	11.67	9.07
23	4.6	6.15	1.67	0.00	46.67	1.67	5.00	7.43
24	4.8	1.54	0.00	0.00	41.67	0.00	6.67	6.08
25	5	3.85	0.00	0.00	40.00	0.00	1.67	4.98

A4.3.2 Retention of mixture metals in the presence of ammonium chloride

Vol. (L)	F -	Cd (II) R (%)	Cr (VI) R (%)	Co (II) R (%)	Cu (II) R (%)	Ni (II) R (%)	Zn (II) R (%)	Exp(-F) R (%)
0	0	100	100	100	100	100	100	100
1	0.2	89.09	98.27	92.18	99.24	97.09	89.64	81.87
2	0.4	80.00	97.27	85.45	99.52	94.18	80.00	67.03
3	0.6	70.91	96.73	81.82	99.90	91.27	70.91	54.88
4	0.8	63.64	96.18	76.36	99.72	88.36	63.64	44.93
5	1	56.36	95.64	72.73	99.44	85.45	56.36	36.78
6	1.2	47.27	95.27	69.09	99.14	81.82	49.09	30.11
7	1.4	43.64	94.73	67.27	98.58	78.18	41.82	24.65
8	1.6	36.36	94.18	61.82	97.80	74.55	36.36	20.19
9	1.8	36.36	93.82	61.82	97.00	70.91	30.91	16.53
10	2	30.91	93.27	60.00	96.00	63.64	27.27	13.53
11	2.2	27.27	92.36	56.36	93.80	58.18	21.82	11.08
12	2.4	23.64	91.09	50.91	92.00	49.09	18.18	9.07
13	2.6	21.82	89.27	52.73	89.40	41.82	14.55	7.43
14	2.8	20.00	87.27	45.45	87.00	34.55	10.91	6.08
15	3	20.00	84.55	43.64	84.00	25.45	9.09	4.98
16	3.2	20.00	81.82	43.64	80.00	18.18	12.73	4.08
17	3.4	16.36	76.36	38.18	74.00	9.09	9.09	24.65
18	3.6	16.36	70.91	32.73	68.00	8.18	7.27	20.19
19	3.8	14.55	67.27	27.27	62.00	9.09	5.45	16.53
20	4	16.36	58.18	25.45	56.00	7.27	9.09	13.53
21	4.2	16.36	50.91	21.82	48.00	7.27	7.27	11.08
22	4.4	16.36	41.82	16.36	40.00	6.36	9.09	9.07
23	4.6	14.55	32.73	10.91	32.00	6.36	9.09	7.43
24	4.8	7.27	21.82	5.45	26.00	6.36	5.45	6.08
25	5	7.27	10.91	2.73	18.00	5.45	5.45	4.98

A4.3.3 Retention of mixture metals in the presence of sodium acetate

Vol. (L)	F -	Cd (II) R (%)	Cr (VI) R (%)	Co (II) R (%)	Cu (II) R (%)	Ni (II) R (%)	Zn (II) R (%)	Exp(-F) R (%)
0	0	100	100	100	100	100	100	100
1	0.2	99.42	99.51	99.85	99.68	98.46	99.38	81.87
2	0.4	98.15	99.34	99.83	99.92	98.46	98.46	67.03
3	0.6	95.85	99.08	99.77	99.92	98.60	96.77	54.88
4	0.8	91.69	98.82	99.62	99.71	98.58	94.15	44.93
5	1	87.23	98.46	99.31	99.83	98.31	90.46	36.78
6	1.2	83.08	98.00	98.83	99.72	98.00	86.31	30.11
7	1.4	75.38	97.54	97.85	99.54	97.23	81.54	24.65
8	1.6	67.69	96.92	96.15	99.29	96.00	73.85	20.19
9	1.8	61.54	96.31	93.08	99.02	94.62	67.69	16.53
10	2	53.85	95.69	90.77	98.98	92.92	61.54	13.53
11	2.2	44.62	94.77	86.92	98.31	90.77	49.23	11.08
12	2.4	41.54	94.00	81.54	98.00	89.38	41.54	9.07
13	2.6	35.38	93.23	76.92	97.23	87.85	35.38	7.43
14	2.8	27.69	92.00	70.77	95.54	85.23	27.69	6.08
15	3	15.38	90.00	66.15	94.46	81.54	26.15	4.98
16	3.2	16.92	87.54	60.00	92.00	76.92	23.08	4.08
17	3.4	12.31	81.54	50.77	88.77	69.23	15.38	24.65
18	3.6	9.23	76.92	44.62	83.08	60.00	13.85	20.19
19	3.8	7.69	73.85	38.46	78.46	53.85	15.38	16.53
20	4	7.69	66.15	30.77	70.77	41.54	10.77	13.53
21	4.2	6.15	60.00	24.62	63.08	33.85	10.77	11.08
22	4.4	7.69	53.85	21.54	56.92	26.15	12.31	9.07
23	4.6	7.69	44.62	13.85	50.77	15.38	9.23	7.43
24	4.8	1.54	40.00	9.23	46.15	6.15	7.69	6.08
25	5	0.00	32.31	3.08	40.00	0.00	6.15	4.98

A4.3.4 Retention of mixture metals in the presence of NTA

Vol. (L)	F -	Cd (II) R (%)	Cr (VI) R (%)	Co (II) R (%)	Cu (II) R (%)	Ni (II) R (%)	Zn (II) R (%)	Exp(-F) R (%)
0	0	100	100	100	100	100	100	100
1	0.2	99.32	98.17	98.00	99.56	98.82	94.00	81.87
2	0.4	96.31	96.00	94.00	96.80	94.15	83.33	67.03
3	0.6	90.15	94.00	90.50	92.00	87.38	71.67	54.88
4	0.8	85.69	93.50	84.83	89.20	76.92	63.33	44.93
5	1	78.46	90.50	76.67	83.60	67.69	53.33	36.78
6	1.2	72.31	87.67	71.67	78.00	60.00	46.67	30.11
7	1.4	66.15	85.00	66.67	74.00	52.31	41.67	24.65
8	1.6	60.00	76.67	61.67	68.00	46.15	36.67	20.19
9	1.8	53.85	75.00	58.33	64.00	41.54	33.33	16.53
10	2	47.69	70.00	51.67	60.00	33.85	30.00	13.53
11	2.2	40.00	65.00	46.67	54.00	27.69	25.00	11.08
12	2.4	33.85	60.00	43.33	50.00	23.08	23.33	9.07
13	2.6	27.69	53.33	38.33	48.00	18.46	21.67	7.43
14	2.8	23.08	48.33	33.33	42.00	15.38	18.33	6.08
15	3	23.08	46.67	28.33	40.00	16.92	16.67	4.98
16	3.2	16.92	40.00	26.67	34.00	10.77	15.00	4.08
17	3.4	10.77	35.00	21.67	34.00	7.69	16.67	24.65
18	3.6	13.85	31.67	21.67	30.00	10.77	15.00	20.19
19	3.8	6.15	26.67	15.00	26.00	6.15	8.33	16.53
20	4	7.69	26.67	18.33	26.00	10.77	6.67	13.53
21	4.2	3.08	20.00	11.67	18.00	3.08	3.33	11.08
22	4.4	1.54	16.67	10.00	8.00	1.54	1.67	9.07
23	4.6	3.08	15.00	8.33	2.00	3.08	1.67	7.43
24	4.8	1.54	10.00	6.67	2.00	1.54	3.33	6.08
25	5	0.00	8.33	4.17	0.00	0.00	1.67	4.98

A4.3.5 Retention of mixture metals in the presence of EDTA

Vol. (L)	F -	Cd (II) R (%)	Cr (VI) R (%)	Co (II) R (%)	Cu (II) R (%)	Ni (II) R (%)	Zn (II) R (%)	Exp(-F) R (%)
0	0	100	100	100	100	100	100	100
1	0.2	94.77	95.23	99.92	97.69	97.08	96.62	81.87
2	0.4	87.38	89.08	86.15	92.62	91.23	90.00	67.03
3	0.6	80.00	83.08	73.85	87.38	84.92	81.54	54.88
4	0.8	72.31	76.92	66.15	81.54	78.46	76.92	44.93
5	1	66.15	72.31	60.00	76.92	73.85	70.77	36.78
6	1.2	61.54	67.69	53.85	73.85	69.23	66.15	30.11
7	1.4	63.08	64.62	49.23	69.23	64.62	61.54	24.65
8	1.6	53.85	60.00	46.15	66.15	61.54	56.92	20.19
9	1.8	47.69	53.85	40.00	61.54	55.38	52.31	16.53
10	2	44.62	50.77	38.46	58.46	52.31	49.23	13.53
11	2.2	41.54	47.69	35.38	55.38	49.23	44.62	11.08
12	2.4	36.92	43.08	29.23	52.31	44.62	41.54	9.07
13	2.6	36.92	43.08	30.77	49.23	44.62	38.46	7.43
14	2.8	35.38	41.54	30.77	47.69	41.54	36.92	6.08
15	3	36.92	43.08	35.38	47.69	43.08	36.92	4.98
16	3.2	29.23	36.92	27.69	43.08	35.38	30.77	4.08
17	3.4	26.15	33.85	29.23	38.46	32.31	27.69	24.65
18	3.6	27.69	35.38	30.77	36.92	32.31	26.15	20.19
19	3.8	21.54	30.77	24.62	36.92	27.69	24.62	16.53
20	4	18.46	27.69	20.00	30.77	24.62	23.08	13.53

A4.4 An example for the model prediction calculations

The model was developed to predict the concentrations of metal ions in the permeate stream and then to determine the retention values of metals in continuous feed PEUF. An example for the model calculations was reported and the first three steps of prediction results were shown for the mixture of metal ions filtration as follow:

In the case of predicting Cu^{2+} concentrations in the permeate:

The Langmuir isotherm constants used were (Q_m = 71.43 mg/g, K_L = 0.4 mg/l)

Cu^{2+} concentration in the feed ($[M]_0$) = 14 mg/l

Flow rate (Φ) = 5 l/hr

Initial volume (V) = 5 l,

At time t + Δt hr., the concentration of cu in the permeate was predicted using the following equation:

$$[M]_{p,t+\Delta t} = [M]_{p,t} + \frac{\Delta t\, \Phi_t \left([M]_0 - [M]_{p,t} \right)}{V\left\{1 + \dfrac{K_L\, Q_{\max}}{\left(K_L + [M]_{p,t}\right)^2}\right\}} \quad \text{...}(equation\ 7.9)$$

At t = 0.2 hr.

$$Cu^{2+}\text{ concentration} = [M]_{0.2} = 0 + \frac{(0.2-0)*5\,(14-0)}{5\left\{1 + \dfrac{0.4*71.43}{(0.4+0)^2}\right\}} = 0.0156\, mg/l$$

Then, Cu^{2+} retention (%) can be calculated as a function of filtration factor (F) using the following equation:

$$R_{iF+\Delta F} = \left\{1 - \left(\frac{\left\{[M]_{p,t} + \Delta F\, \Phi_t \left([M]_0 - [M]_{p,t}\right) / V \left\{1 + (K_L\, Q_{\max}) / \left(K_L + [M]_{p,t}\right)^2\right\}\right\}}{[M]_0} \right)\right\} \times 100$$

$$\text{.................................}(equation\ 7.10)$$

$$R_{0.2}=\left\{1-\left(\frac{\{0+0.2*5(14-0)/\,5\{1+(0.4*71.43)/\,(0.4+0)^2\}\}}{14}\right)\right\}\times 100=99.88$$

At t = 0.4 hr.

Cu^{2+} concentration = $$[M]_{0.4}=0.0156+\frac{(0.4-0.2)*5\,(14-0.0156)}{5\left\{1+\dfrac{0.4*71.43}{(0.4+0.0156)^2}\right\}}=0.0324\ mg/l$$

Cu^{2+} retention =

$$R_{0.4}=\left\{1-\left(\frac{\{0.0156+0.2*5(14-0.0156)/\,5\{1+(0.4*71.43)/\,(0.4+0.0156)^2\}\}}{14}\right)\right\}\times 100=99.76$$

At t = 0.6 hr.

Cu^{2+} concentration = $$[M]_{0.6}=0.0324+\frac{(0.6-0.4)*5\,(14-0.0324)}{5\left\{1+\dfrac{0.4*71.43}{(0.4+0.0324)^2}\right\}}=0.05\ mg/l$$

Cu^{2+} retention =

$$R_{0.6}=\left\{1-\left(\frac{\{0.0324+0.2*5(14-0.0324)/\,5\{1+(0.4*71.43)/\,(0.4+0.0324)^2\}\}}{14}\right)\right\}\times 100=99.64$$

In the case of predicting Cr^{6+} concentrations in the permeate:

The Langmuir isotherm constants used were (Q_m = 68.96 mg/g, K_L = 1.51 mg/l)

Cr^{6+} concentration in the feed ($[M]_0$) = 14 mg/l

Flow rate (Φ) = 5 l/hr

Initial volume (V) = 5 l,

At t = 0.2 hr.

Cr^{6+} Concentration = $$[M]_{0.2}=0+\frac{(0.2-0)*5\,(14-0)}{5\left\{1+\dfrac{1.51*68.96}{(1.51+0)^2}\right\}}=0.0557\ mg/l$$

Cr^{6+} retention =

$$R_{0.2}=\left\{1-\left(\frac{\{0+0.2*5(14-0)/\,5\{1+(1.51*68.96)/\,(1.51+0)^2\}\}}{14}\right)\right\}\times 100=99.6$$

At t = 0.4 hr.

Cr^{6+} Concentration = $[M]_{0.4}=0.0557+\dfrac{(0.4-0.2)*5\,(14-0.0557)}{5\left\{1+\dfrac{1.51*68.96}{(1.51+0.0557)^2}\right\}}=0.115\ mg/l$

Cr^{6+} retention =

$$R_{0.4}=\left\{1-\left(\frac{\{0.0557+0.2*5(14-0.0557)/\,5\{1+(1.51*68.96)/\,(1.51+0.0557)^2\}\}}{14}\right)\right\}\times 100=99.18$$

At t = 0.6 hr.

Cr^{6+} Concentration = $[M]_{0.6}=0.115+\dfrac{(0.6-0.4)*5\,(14-0.115)}{5\left\{1+\dfrac{1.51*68.96}{(1.51+0.115)^2}\right\}}=0.179\ mg/l$

Cr^{6+} retention =

$$R_{0.6}=\left\{1-\left(\frac{\{0.115+0.2*5(14-0.115)/\,5\{1+(1.51*68.96)/\,(1.51+0.115)^2\}\}}{14}\right)\right\}\times 100=98.7$$

In the case of predicting Co^{2+} concentrations in the permeate:

The Langmuir isotherm constants used were (Q_m = 52.1 mg/g, K_L = 3.59 mg/l)

Co^{2+} concentration in the feed ($[M]_0$) = 14 mg/l

Flow rate (Φ) = 5 l/hr

Initial volume (V) = 5 l,

At t = 0.2 hr.

Co^{2+} Concentration = $[M]_{0.2}=0+\dfrac{(0.2-0)*5\,(14-0)}{5\left\{1+\dfrac{3.59*52.1}{(3.59+0)^2}\right\}}=0.193\ mg/l$

Co^{2+} retention =

$$R_{0.2} = \left\{1 - \left(\frac{\{0 + 0.2 * 5(14 - 0)/\ 5\{1 + (3.59 * 52.1)/\ (3.59 + 0)^2\}\}}{14} \right)\right\} \times 100 = 98.62$$

At t = 0.4 hr.

$$\text{Co}^{2+}\ \text{Concentration} = \ [M]_{0.4} = 0.193 + \frac{(0.4 - 0.2) * 5\,(14 - 0.193)}{5\left\{1 + \dfrac{3.59 * 52.1}{(3.59 + 0.193)^2}\right\}} = 0.4\ mg/l$$

Co^{2+} retention =

$$R_{0.4} = \left\{1 - \left(\frac{\{0.193 + 0.2 * 5(14 - 0.193)/\ 5\{1 + (3.59 * 52.1)/\ (3.59 + 0.193)^2\}\}}{14} \right)\right\} \times 100 = 97.1$$

At t = 0.6 hr.

$$\text{Co}^{2+}\ \text{Concentration} = \ [M]_{0.6} = 0.4 + \frac{(0.6 - 0.4) * 5\,(14 - 0.4)}{5\left\{1 + \dfrac{3.59 * 52.1}{(3.59 + 0.4)^2}\right\}} = 0.633\ mg/l$$

Co^{2+} retention =

$$R_{0.6} = \left\{1 - \left(\frac{\{0.4 + 0.2 * 5(14 - 0.4)/\ 5\{1 + (3.59 * 52.1)/\ (3.59 + 0.4)^2\}\}}{14} \right)\right\} \times 100 = 95.47$$

In the case of predicting Ni^{2+} concentrations in the permeate:

The Langmuir isotherm constants used were (Q_m = 46.73 mg/g, K_L = 6.7 mg/l)

Ni^{2+} concentration in the feed ($[M]_0$) = 14 mg/l

Flow rate (Φ) = 5 l/hr

Initial volume (V) = 5 l,

At t = 0.2 hr.

$$\text{Ni}^{2+}\ \text{Concentration} = \ [M]_{0.2} = 0 + \frac{(0.2 - 0) * 5\,(14 - 0)}{5\left\{1 + \dfrac{6.7 * 46.73}{(6.7 + 0)^2}\right\}} = 0.4\ mg/l$$

Ni^{2+} retention =

$$R_{0.2} = \left\{1 - \left(\frac{\left\{0 + 0.2 * 5(14 - 0)/\ 5\left\{1 + (6.7 * 46.73)/\ (6.7 + 0)^2\right\}\right\}}{14}\right)\right\} \times 100 = 97.1$$

At t = 0.4 hr.

$$\mathrm{Ni}^{2+}\ \text{Concentration} = \ [M]_{0.4} = 0.4 + \frac{(0.4 - 0.2) * 5\,(14 - 0.4)}{5\left\{1 + \frac{6.7 * 46.73}{(6.7 + 0.4)^2}\right\}} = 0.834\ mg/l$$

Ni^{2+} retention =

$$R_{0.4} = \left\{1 - \left(\frac{\left\{0.4 + 0.2 * 5(14 - 0.4)/\ 5\left\{1 + (6.7 * 46.73)/\ (6.7 + 0.4)^2\right\}\right\}}{14}\right)\right\} \times 100 = 94$$

At t = 0.6 hr.

$$\mathrm{Ni}^{2+}\ \text{Concentration} = \ [M]_{0.6} = 0.834 + \frac{(0.6 - 0.4) * 5\,(14 - 0.834)}{5\left\{1 + \frac{6.7 * 46.73}{(6.7 + 0.834)^2}\right\}} = 1.3\ mg/l$$

Ni^{2+} retention =

$$R_{0.6} = \left\{1 - \left(\frac{\left\{0.834 + 0.2 * 5(14 - 0.834)/\ 5\left\{1 + (6.7 * 46.73)/\ (6.7 + 0.834)^2\right\}\right\}}{14}\right)\right\} \times 100 = 90.7$$

In the case of predicting Cd^{2+} concentrations in the permeate:

The Langmuir isotherm constants used were (Q_m = 26.74 mg/g, K_L = 1.36 mg/l)

Cd^{2+} concentration in the feed ($[M]_0$) = 14 mg/l

Flow rate (Φ) = 5 l/hr

Initial volume (V) = 5 l,

At t = 0.2 hr.

$$\mathrm{Cd}^{2+}\ \text{Concentration} = \ [M]_{0.2} = 0 + \frac{(0.2 - 0) * 5\,(14 - 0)}{5\left\{1 + \frac{1.36 * 26.74}{(1.36 + 0)^2}\right\}} = 0.155\ mg/l$$

Cd^{2+} retention =

$$R_{0.2}=\left\{1-\left(\frac{\{0+0.2*5(14-0)/5\{1+(1.36*26.74)/(1.36+0)^{2}\}\}}{14}\right)\right\}\times 100=98.89$$

At t = 0.4 hr.

Cd^{2+} Concentration = $[M]_{0.4}=0.155+\dfrac{(0.4-0.2)*5\,(14-0.155)}{5\left\{1+\dfrac{1.36*26.74}{(1.36+0.155)^{2}}\right\}}=0.343\ mg/l$

Cd^{2+} retention =

$$R_{0.4}=\left\{1-\left(\frac{\{0.155+0.2*5(14-0.155)/5\{1+(1.36*26.74)/(1.36+0.155)^{2}\}\}}{14}\right)\right\}\times 100=97.55$$

At t = 0.6 hr.

Cd^{2+} Concentration = $[M]_{0.6}=0.343+\dfrac{(0.6-0.4)*5\,(14-0.343)}{5\left\{1+\dfrac{1.36*26.74}{(1.36+0.343)^{2}}\right\}}=0.574\ mg/l$

Cd^{2+} retention =

$$R_{0.6}=\left\{1-\left(\frac{\{0.343+0.2*5(14-0.343)/5\{1+(1.36*26.74)/(1.36+0.343)^{2}\}\}}{14}\right)\right\}\times 100=95.9$$

In the case of predicting Zn^{2+} concentrations in the permeate:

The Langmuir isotherm constants used were (Q_m = 29.76 mg/g, K_L = 1.6 mg/l)

Zn^{2+} concentration in the feed ($[M]_0$) = 14 mg/l

Flow rate (Φ) = 5 l/hr

Initial volume (V) = 5 l,

At t = 0.2 hr.

Zn^{2+} Concentration = $[M]_{0.2}=0+\dfrac{(0.2-0)*5\,(14-0)}{5\left\{1+\dfrac{1.6*29.76}{(1.6+0)^{2}}\right\}}=0.163\ mg/l$

Zn^{2+} retention =

$$R_{0.2} = \left\{ 1 - \left(\frac{\{0 + 0.2 * 5(14 - 0)/\ 5\{1 + (1.6 * 29.76)/\ (1.6 + 0)^2\}\}}{14} \right) \right\} \times 100 = 98.8$$

At t = 0.4 hr.

Zn^{2+} Concentration = $[M]_{0.4} = 0.163 + \dfrac{(0.4 - 0.2) * 5\,(14 - 0.163)}{5\left\{1 + \dfrac{1.6 * 29.76}{(1.6 + 0.163)^2}\right\}} = 0.357\ mg/l$

Zn^{2+} retention =

$$R_{0.4} = \left\{ 1 - \left(\frac{\{0.163 + 0.2 * 5(14 - 0.163)/\ 5\{1 + (1.6 * 29.76)/\ (1.6 + 0.163)^2\}\}}{14} \right) \right\} \times 100 = 97.45$$

At t = 0.6 hr.

Zn^{2+} Concentration = $[M]_{0.6} = 0.357 + \dfrac{(0.6 - 0.4) * 5\,(14 - 0.357)}{5\left\{1 + \dfrac{1.6 * 29.76}{(1.6 + 0.357)^2}\right\}} = 0.59\ mg/l$

Zn^{2+} retention =

$$R_{0.6} = \left\{ 1 - \left(\frac{\{0.357 + 0.2 * 5(14 - 0.357)/\ 5\{1 + (1.6 * 29.76)/\ (1.6 + 0.357)^2\}\}}{14} \right) \right\} \times 100 = 95.78$$

However, these calculations can be simplified and concluded in the following diagram: