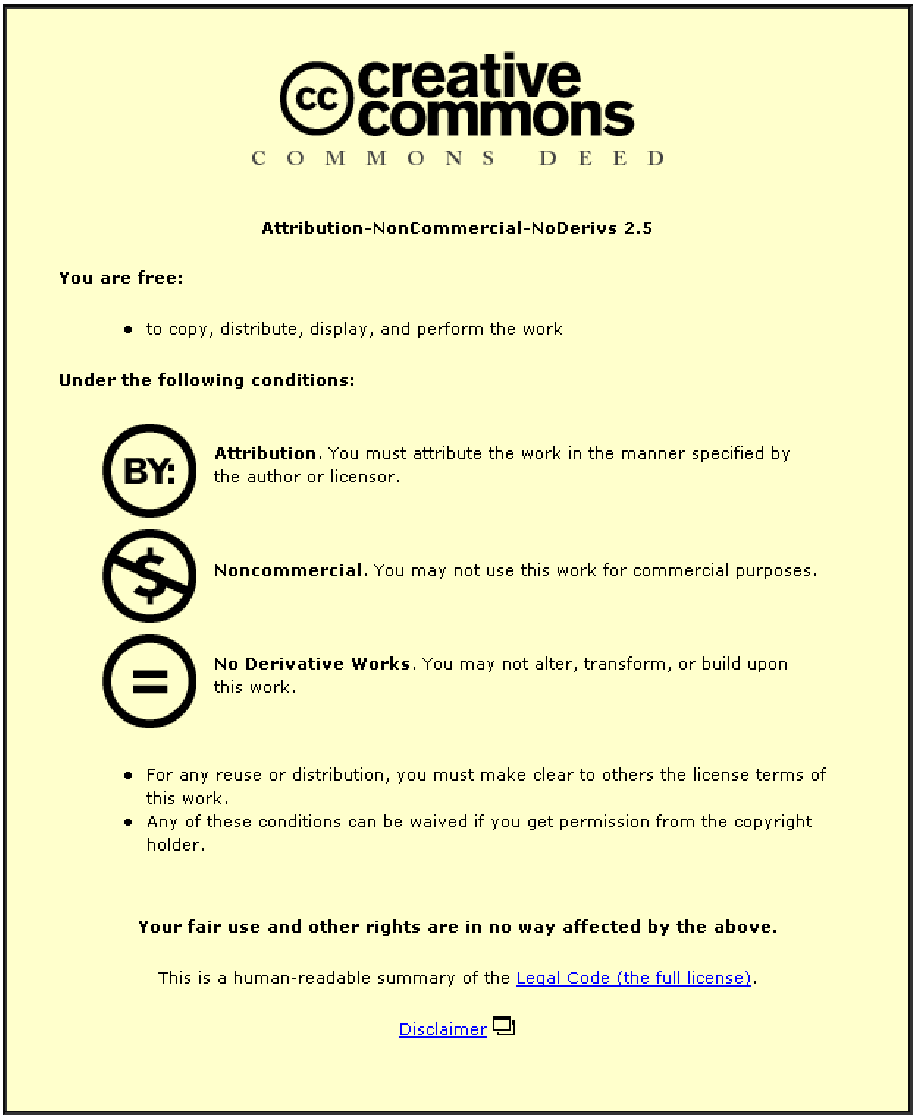

Investigations of the use of natural organic matter as a remediation material

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ABSTRACT

Industrial activities and accidental releases often introduce a large amount of inorganic and organic contaminants to the environment. Humic substances interact strongly with metals and organic pollutants. In this study, this property was exploited in order to establish new remediation materials in two environmental applications and in one pharmaceutical application. The two remediation materials under investigation were sludge and sediment, ST sludge and CE sludge, respectively.

The first application aimed at investigating the use of the remediation materials to remove arsenic, iron, and uranium from the industrial effluents. The main results were the release of iron from ST sludge inhibited its usage as remediation material whereas CE sludge showed excellent performance. The extractions were both rapid and efficient. The second application studied the extraction of organic contaminants. The objective of this study was to find a new remediation material for removal of organic contaminants. The remediation materials showed similar and excellent performance on extraction of chlorinated anilines, phenols and benzenes. The third application investigated the extraction of iodine species from urine. It aimed at determining whether the radioactive iodine can be extracted from the urine and thereby concentrated into a smaller volume of solid. Even though the extraction percentages from urine were not as promising as from deionised water and synthetic urine, scientific interest was raised and further investigations on the effect of the composition of urine and solubility of sludges for the extraction of iodine species were recommended.

The outcome of the presented study was interesting both scientifically and economically. The promising extraction results for arsenic, iron and uranium indicate that the CE sludge is ready to be tested in a field study. The extraction of organic compounds by both remediation materials was also promising. However, further studies on permeability and solubility were recommended.

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INTRODUCTION AND OUTLINE OF THESIS

CHAPTER 1 – INTRODUCTION AND OUTLINE OF THESIS

Heavy metal and organic compound contamination in soils, sediments, surface and groundwaters is a major environmental concern. The rapid increase of industrial activities in recent decades has introduced large amounts of contaminants into the environment. Even though several different approaches to protect the environment, such as regulations on discharged wastes, have been established, the legacy of previous activities is still present. For example, metal contaminants that have been immobilised in soil can be released to groundwater by changes in environmental conditions, such as the amount of rainfall and, its acidity. In addition, some organic contaminants are resistant to degradation and can therefore be found in soils for long time periods. Thus, prevention of contaminant release to the environment and clean-up of contaminants already present in nature is of high importance.

This project investigates the use of two remediation materials (a sludge and a sediment) as sorbents for metals and organic compounds. The sludge is a waste product from drinking water purification (referred as ST sludge), and the sediment originates from a Ukrainian lake (referred as CE sludge). These materials are rich in humic substances which are known to extract several metals and some organic compounds [1,2]. The objective of this study was to investigate the use of these materials in two industrial and one pharmaceutical application as detailed below.

i) Application 1 - Extraction of arsenic, iron and uranium from industrial effluents

Kaolinite which is mined in China Clay plants has a brown colour due to the presence of iron (Fe^{3+}). The commercial value of kaolinite is increased by removing the colour [3,4]. Iron can be removed from the clay by the addition of acid and a reducing agent by which Fe^{3+} is reduced to soluble Fe^{2+}. The addition of acid releases other contaminants such as uranium and arsenic. The objective of this study is to investigate the use of the ST and CE sludges to remove arsenic, iron, and uranium from industrial effluents.

ii) Application 2 - Extraction of organic contaminants

A common method used to remediate contaminants from soil and groundwater is the so called “pump and treat method” in which contaminated groundwater is pumped from the ground and cleaned in a suitable plant. The method is expensive, has high energy requirements, carries the risk of exposure on contamination, and is unable to remove contaminants firmly attached onto the soil. In the early 1990s an innovative *in situ* approach, the so called permeable reactive barrier, was developed for groundwater remediation. As groundwater flows through it, the barrier extracts contaminants, or at least reduces their concentration in the groundwater. One objective of this project was to find a new, cost efficient and environmentally friendly, remediation material for removal of contaminants from groundwater. In previous studies, both the ST sludge and the CE sludge have been shown to be good sorbents for several metals [1,2], and thus this investigation concentrated on extraction of organic compounds. The organic compounds were selected from the Groundwater Regulations 1998 List 1 [5].

iii) Application 3 - Extraction of iodine species from urine

Radioiodine (^{131}I) may be given to patients with thyroid problems for diagnosis or treatment. It has been estimated that 35% to 75% of the administered dose is excreted in the urine, perspiration and saliva within the first 24 hours after dosing [6]. In some parts of Europe, the radioactive urine is collected in tanks in the hospital and stored until the activity of the urine has decayed to below regulation limits. The objective of this investigation is to determine whether the radioactive iodine can be extracted from the urine by the ST and CE sludges and thereby concentrated in a smaller volume of solid. The advantage in having the radioactivity in solid waste compared to liquid waste is its easier handling and storage, i.e. smaller volume and prohibiting leakages of radioactivity.

1.1 Outline of this thesis

This chapter (**Chapter 1**) introduces the sources of soil and groundwater contamination. The remediation materials under investigation (ST and CE sludges) are rich in humic substances and therefore discussion on humic substances and their behaviour as remediation materials is presented.

Chapter 2 presents the origins of the ST and CE sludges and their composition. The experimental investigations included determinations of elemental, organic, and inorganic compositions of the ST and CE sludges and their buffering, cation exchange and proton exchange capacities. In addition, investigations of solubility and leaching of metals from the remediation materials were also carried out.

Chapter 3 discusses the extraction of arsenic, iron and uranium from industrial effluents. The production of waste effluents from the China Clay industry is described along with the current waste treatment methods. The speciation of a metal has a significant effect on its behaviour, thus speciation studies for arsenic, iron and uranium were carried out using the JCHESS programme [7]. Maximum extraction capacities for the metals under investigation were determined using electrolyte and real effluents. In addition, the kinetics of removal of the elements were investigated in batch experiments and in dynamic flow-through systems in packed columns.

Chapter 4 describes the most common configurations of permeable reactive barriers and their reactive processes. The organic compounds under investigation were mainly pesticides and some discussion on their usage is presented. The remediation material has to fulfil at least three basic requirements; it has to effectively extract contaminants, it should not be soluble under environmental conditions, and it has to remain porous under pressure. The solubility studies are presented in **Chapter 2** and the extraction of organic compounds in **Chapter 4**.

Removal of radioactive iodine from urine is described in **Chapter 5**. The extraction studies in deionised water, synthetic urine and actual urine were carried out in batch experiments and in columns. In addition, the effects of the addition of two oxidising agents, Chloramine T and potassium permanganate, were investigated.

Chapter 6 summarises the results from the previous chapters and discusses the suitability of the use of the remediation materials in the applications presented earlier.

1.2 Introduction to soil and groundwater contamination

Pollution in soils, sediments and water bodies by metals and organic compounds, such as pesticides, is a matter of concern. Groundwater is an essential source of drinking water [8] and, therefore, very important for living organisms. If aquifers become contaminated, the contaminants can migrate long distances [8] and cause problems far away from the contaminated site. Because of the hazard to humans, animals and plants, the protection of groundwater is essential.

The major possible sources of land pollutants are diverse [9];

- waste disposal sites
- scrap yards
- ship and vehicle breaking yards
- gas works
- petroleum refineries
- petrol storage and distribution
- petrol service stations
- coal mining and coal storage
- electricity generation
- iron and steel works
- metaliferous mining and smelting
- metal products fabrication and metal finishing
- chemical works
- glass-making and ceramics
- textile plants

- dye works
- leather tanneries
- timber and timber products treatment works
- manufacture of integrated circuits and semi-conductors
- food processing
- water treatment and sewage works
- heavy engineering installations
- radioactive waste processing
- military bases and training areas
- the burial of diseased farm livestock

Also improper waste disposal and accidents involving hazardous substances can be added to the list [8]. These activities have led to situations where contaminants have migrated into groundwater [8]. In many cases the contaminated sites are on rural and scarcely populated areas with low land value [8]. Because of the high price of clean-up and the low land value, the clean-up of sites is not considered to be cost effective [8]. In contrast, in densely populated areas the high cost of the clean-up is not an obstacle because the problem needs to be solved before it affects limited drinking water supplies [8].

1.3 Humic substances

Humic substances are degradation products of plants and animal residues, and they are ubiquitous in nature [10]. Since the source of the humic substance and the stage of the degradation can vary, humic substances cannot be described in terms of unique chemical structures [11]. They have a significant role in nature, because they are essential for holding water and nutrients and releasing it to plants [11]. They also influence the distribution of other organic compounds and chemical species by extracting them [11].

Organic matter can be divided into two classes of compounds, non-humic material and humic substances [12]. The non-humic material consists of protein, polysaccharides, nucleic acids, and small molecules, such as sugars and amino acids [12]. Humic substances can be operationally divided into three groups based on their solubility under acid and alkaline conditions [13] [12]. Humins are the insoluble fraction of the humic substances [13]. Humic acids are the soluble fraction but are insoluble below pH 2 [13]. Fulvic acids are soluble under at all pHs [13]. The highest average molecular weight of fulvic acid is about 5 kDa, the lowest average molecular weight of humic acid is about 12 kDa and the molecular weight of humin is at least 70 kDa [14].

An early “polymer model” concept suggested that humic substances were comprised of randomly coiled macromolecules that had elongated shapes in basic or low-ionic-strength solutions, but became coils in acidic or high-ionic strength solutions [13]. A more recent concept, the supramolecular association, suggests that humic substances are relatively small and chemically diverse organic molecules, which form clusters linked by hydrogen bonds and hydrophobic interactions [13]. In suitable aqueous solutions, these associations are able to form micellar structures i.e. the hydrophobic parts form the interior and the hydrophilic exterior regions of the structure [13]. The high molecular weight and basic hydrophobicity of the humic acids favours formation of micelle-like structures, and the hydrophobic nucleus can give inner sorption sites for organic hydrophobic pollutants [15], such as polyaromatic hydrocarbons (PAH) [16]. Steric hindrance and molecular interactions may play an important role in binding between polyaromatic hydrocarbons and humic substances [16].

Compositional and structural models for humic materials have been reported by several research groups [17]. The experimental models are based on breaking down the material through pyrolysis or thermochemolysis and the determination of components generated [17]. The relative quantity of components generated can be used to rebuild the overall structure [17]. Nevertheless, there are numerous possibilities for re-constructing the structure [17].

Humic substances are classified as amphoteric polyelectrolytes, since they can carry both positive and negative charges [11]. Their charge is predominantly negative due to the dissolution of carboxylic, hydroxyl, and phenolic groups [11]. Other important functional groups are amines, carbonyl groups, and quinines [14]. The negative charge has a great influence on their metal complexation properties [11]. For example, carboxyl groups deprotonate to negatively charged carboxylates around pH 4 and thus can bind cationic species [14]. Kopinke *et al.* suggested that a nitro group causes stronger binding than the hydroxyl group [18]. The common presence of both of these groups leads to stronger interactions with the organic matter [18]. Dunnivant *et al.* suggested that the reactive natural organic matter constituent may be the quinone-type moieties [19].

1.4 Humic substances as reactive materials

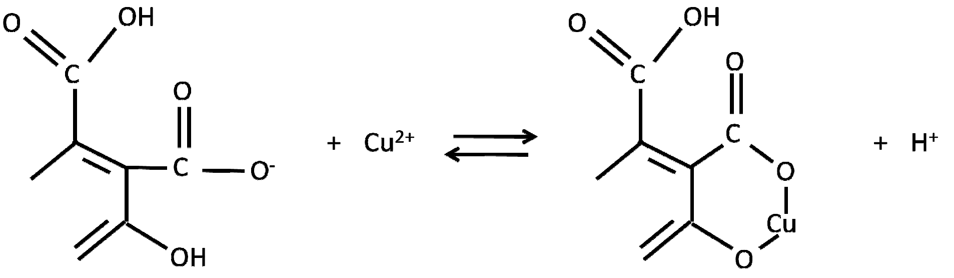
Humic substances are rich in oxygen-containing functional groups such as carboxylic and phenolic groups [20,21]. Owing to the presence of functional groups containing oxygen, and to a lesser extent, nitrogen and sulphur, humic substances are capable of interacting with metals in solution in a number of ways [22]. Humic substances can [22];

1. Form soluble complexes with metal ions
2. Cause precipitation of metal ions via reduction
3. Cause precipitation of metal ions via adsorption, ion exchange or other sorption processes
4. Modify the sorption behaviour of mineral surfaces with respect to metal ions
5. Modify the behaviour of colloidal particles of metals
6. Affect the rates of geological processes.

Humic substances can be envisaged to have a distribution of binding sites consisting of a large number of “weak sites” and smaller number of “stronger sites” [23]. Carboxylic (-COOH) and phenolic (-OH) groups are responsible for the majority of metal binding [22]. The most abundant cation-binding group in humic substances is carboxylate ($-COO^-$) which are the least discriminatory among metals, next are the phenolate groups [23]. Nitrogen-containing groups are less abundant and they favour the softer metals [23]. The most discriminatory, and least abundant, are sulphur containing groups, which strongly favour soft metal cations [23]. Many functional groups of humic substances contain atoms, such as nitrogen and oxygen, which are capable of acting as ligands [24]. Humic substances contain a mixture of ligands, rather than a single well-defined complexing agent due to their different origins [22]. The variety of functional groups and the various ways in which they can interact with metals leads to a near infinite number of metal-humic complexes that can be formed [24].

Humic and fulvic acids are known to interact strongly with both cations [12] and hydrophobic organic pollutants [15]. Humic and fulvic acids have a wide range of free energies for metal complexation due to their polyfunctionality, i.e. each molecule possesses many complexing sites of different chemical nature, and due to their polyelectrolytic nature, i.e. the molecules bear high electric charge densities, due to the presence of a large number of dissociable functional groups per physical entity [11]. Humic and fulvic acids can bind virtually all transition metals, including the lanthanides, actinides, and the alkali earth metals [12]. The binding sites in humic matter for metal cations fall into at least three categories [23]:

1. Non-specific sites, in which the binding occurs due to electrostatic attraction of the cations by negatively, charged humic matter. There is little selectivity in terms of chemical differences among cations, but cations of higher charge are preferentially bound.
2. Abundant weak sites formed by oxygen-containing ligands, such as carboxyl and phenolic groups. Schematic reactions for OH and COOH groups with a metal (Cu^{2+}) are presented below (reactions 1.1 and 1.2) [25]. Reaction involving both phenolic OH and COOH groups are postulated to be the most important [25].
3. Stronger and less abundant sites formed by combinations of oxygen, nitrogen and sulphur.



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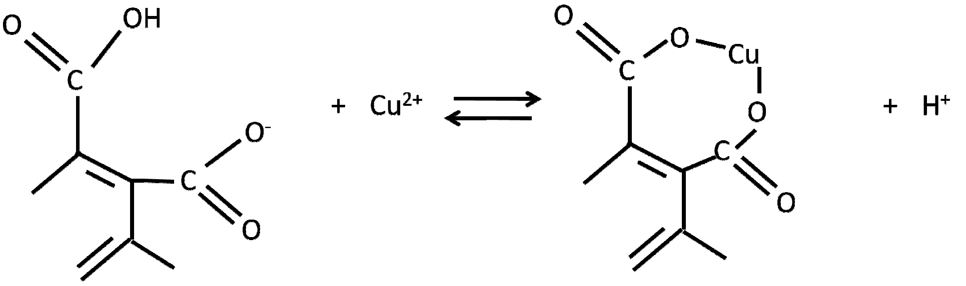

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The strength of the binding depends strongly on the metal ion [12]. Humic substances favour softer metals, such as Pb and Cu, over harder metals, such as Zn or Ca [12]. The softest cations, such as Ag and Cd, are highly polarisable, which means that their electron sheaths are readily deformed by an electric field [23]. Hard cations are not polarisable, and include Na, Mg, Al, and Th, and ligands containing oxygen atoms, and especially fluorine [23]. Hard ions tend to bind preferentially to O-donor sites whereas soft ions prefer N-donor and S-donor sites [22]. In addition, among the O-donor sites, there is likely to be a range in hardness-softness depending on whether the site is predominated by carboxylate or phenolate groups, and on the nature of the immediate chemical environment of the groups [22].

Weak electrostatic attraction of counter ions is the simplest kind of binding of metal cations by humic substances [23]. It is possible that metal ions are first complexed at sites to which they are most suited, then, as these are saturated, enter sites for which they have a lower affinity [24]. Displacement of a complexed metal is possible either if the displacing ion has a greater affinity for the site or is present in much higher concentrations, or both [24]. Hydrogen ions have high affinity for many complexing sites and compete effectively with metal ions [24].

They can also modify complexing functional groups (protonation of amines to form salts at low pH and the carboxylic acid/carboxylate ion reaction) [24]. Therefore, pH plays an important role in metal complexation [24] along with ionic strength [12]. It is hypothesised that at low pH, humic substances occur a tightly coiled, cross-linked (via H-bonding) conformation where metal binding sites are not readily available, but at higher pH they occur as a more open conformation [22]. At any particular binding site, the strength of interaction with the metal ion depends on [24];

1. The affinity of the metal ion for the particular site
2. Position of the site within the humic material, i.e. steric hindrance can play a role in binding
3. The nature of the functional groups around the complexing site. For example, an aliphatic hydroxyl group is much less acidic, and therefore a much weaker ligand than a phenolic hydroxyl group

As a conclusion, it can be said that metal binding by humic substances is complicated due to the complex structure of humic substances, their polyelectrolyte nature, possible changes in structure as a function of pH, ionic strength and metal loading [22].

Bonding mechanisms for the extraction of organic chemicals by humic substances include ion exchange, hydrogen bonding, and coordination through an attached metal ion (ligand exchange) [25]. Organic chemicals that either exist as cations or become positively charged through protonation can be extracted through ion exchange [25]. Also sorption can occur by physical adsorption (van der Waals forces) on a surface or by partitioning into a hydrophobic media, such as natural organic matter, or both [25,26]. For organic molecules containing ionisable COOH groups, a salt linkage through a divalent cation on the organic exchange site is possible [25].

Sorption of organic pollutants depends on their surface charge and aqueous solubility both of which are affected by pH [9]. pH affects both the organic pollutant and the physical and chemical characteristics of humic substances [15]. For example, the low affinity of humic substances for binding pentachlorophenol (PCP) is due to the hydrophilic character of PCP and the binding decreases with increasing pH, because the dissociated form of PCP is more soluble in water [15]. The differences in binding affinities of the samples from different sources are not fully understood, but one explanation is the abundance of key sub-components in the organic material [15]. Also, studies have reported that the aromaticity of the organic matter is a key factor for binding organic contaminants [15].

Generally humic acids have a greater affinity for binding hydrophobic compounds than fulvic acids but fulvic acids have a higher metal complexing capacity [15]. The different behaviour of humic and fulvic acids can be explained by their different molecular weights [15]. Since fulvic acids have a lower molecular weight and a higher percentage of carboxylic groups than humic acids, their hydrophilicity increases [15]. This is the reason why fulvic acids are soluble at low pH [15].

1.5 Conclusions

The objective of this thesis is to investigate the remediation behaviour of the ST and CE sludges in two industrial and one pharmaceutical applications. The remediation materials under investigation are rich in humic substances which are macromolecules that can bind both metals and organic compounds. Therefore, these remediation materials can potentially be used for decontamination of large amount of inorganic and organic compounds from different solutions such as groundwater and industrial effluents.

CHAPTER 2

CHARACTERISATION OF REMEDIATION MATERIALS

CHAPTER 2 – CHARACTERISATION OF REMEDIATION MATERIALS

2.1 Introduction and outline of this chapter

There is a strong relationship between the composition of a material and its extraction behaviour. Therefore, detailed characterisation of the remediation materials (ST and CE sludges) under investigation is important. It is also important to know the origin of the materials (in this case the production process of Severn Trent sludge and the environmental parameters prevailing in the lake from which the Ukrainian sediment originates) because they might give an insight into possible leaching problems of metals and humic substances. In addition to the physical composition of the ST and CE sludges (elemental, organic, inorganic and functional groups), the buffering behaviour and cation exchange capacities were determined. A good remediation material must also be relatively insoluble in aqueous environments thus the solubilities of the sludges were studied by column experiments.

2.2 Origin of the sludge provided by Severn Trent Water

The ST sludge, provided by Severn Trent Water, is generated as a by-product in the production of drinking water. Raw water is collected from Ladybower and Derwent reservoirs in Bamford and it is processed at Bamford Water Works. The process includes adding polymeric ferric sulphate ($Fe_x(SO_4)_y$) [28]) i.e. “Ferripol” to obtain an iron concentration of approximately 7-10 mg dm^{-3}. The addition of Ferripol causes humic substances to coagulate and flocculate. The coagulation and flocculation processes are discussed in detail in section 2.2.1. The flocculated material (sludge) is left to form a sediment and is removed from the water by centrifugation. At Bamford, Severn Trent Water produces a highly organic-rich sludge at a rate of about a tonne per month and until now, the produced sludge has been mainly sent to landfill. The addition of Ferripol suggests high iron content in the sludge but further characterisation was needed. The wet sludge was air dried, ground and sieved through a 1 mm-pore size screen. This remediation material is referred to as ST sludge (Figure 1).

Figure 1. Picture of ST sludge.

2.2.1 Production of sludge

There are a number of treatment processes which can be used to purify water by removing suspended, colloidal and dissolved matter [28]. The process chosen depends on the nature of the raw water, the space available to construct the plant, a consideration of operating and capital costs, and, often, personal or company preferences [28]. Preliminary treatments such as raw-water storage, screening, aeration, straining, preliminary settling, and pre-ozonation can be followed by coagulation and flocculation [28]. Coagulation is a process in which a chemical reagent is added to water to destabilise colloidal particles which rapidly flocculate with other suspended particles to form larger more readily settled particles. Coagulation can be carried out by naturally occurring chemical reagents, such as starch, iron and aluminium salts or by synthetic cationic, anionic and non-ionic polymers [29]. Coagulation occurs quickly whereas flocculation is a longer-term process [28]. Flocculation is caused by Brownian motion, stirring and differential settling [28]. The aim of the coagulation and flocculation processes is to produce particles of a size that can be removed by settlement, flotation, or filtration [28]. The four main methods for destabilising colloidal systems are [28]:

- Double layer compression - an electrolyte is added to increase the concentration of ions. Increased ion concentration decreases the thickness of the electrical double layer that surrounds each colloidal particle. Thus, it allows the particles to move closer to each other and attractive forces have more chance of overcoming the electrical forces that keep them apart.
- Charge neutralisation - ions with opposite charge to that of the colloidal particles are added. The addition can lead to sorption of the ions on to the colloidal material and reduction of surface charge which reduces the electrical forces keeping particles apart.
- Entrapment in a precipitate - when soluble aluminium and iron salts are added at the correct pH value, they will precipitate as hydroxide flocs. If colloids are present in the water, hydroxides tend to precipitate using colloidal particles as nuclei and forming flocs around the particles. Once the hydroxide floc has been formed it can physically entrap other colloidal particles. Carbonate precipitates are often used.
- Particle bridging – large organic molecules such as anionic and cationic polymers with multiple electrical charges are believed to work by bridging between particles.

When ferric or aluminium coagulants are added to water they initially form trivalent ferric or aluminium ions which then hydrate to form complexes with hydroxyl molecules [28]. Depending on pH and concentrations, the iron and aluminium will eventually precipitate as a hydroxide floc [28]. Iron and aluminium salts increase the acidity of the mixture therefore lime ($Ca(OH)_2$) or calcium bicarbonate ($Ca(HCO_3)_2$) can be added as a source of alkalinity [29, [30]. The reactions for ferric sulphate i.e. ferripol with lime and calcium bicarbonate are [29,30]:

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Fe(OH)_3\downarrow + 3CaSO_4 \quad (2.1)$$

$$Fe_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_3\downarrow + 3CaSO_4 + 6CO_2 \quad (2.2)$$

Even though polymerised coagulants are more expensive, they have a number of advantages; they are effective at low temperatures, promote faster floc formation, allow lower dosage rates with saving in pH adjustment chemicals, and are possibly more effective with algae [28].

The flocs are separated from the water in settlement basins or clarifiers with multiple different designs and subsequently by passing through a granular bed of sand or other suitable medium at low speed [28]. A 1998 survey of waterworks' sludge production in the UK revealed that 44.8% of dry solid waste comes from alum coagulation and 32.9% from iron coagulation out of which 51.1% and 56.9%, respectively, were disposed to landfill [28].

2.3 Source of sediment

The second remediation material (CE sludge) under investigation was a sediment material taken from post-glacial Ukrainian lakes which are shallow, anoxic and contain peat type organic matter. Enterpris Ltd has carried out characterisation of a similar sediment which had a high volatile content of 67.7% owing to the predominance of organic substances [31]. The dominant inorganic phases were quartz and calcite [31]. Also minor amounts of potassium feldspar (microcline) and plagioclase (albite) were detected [31]. Detailed composition of similar sediment materials has been provided by Enterpris Ltd, however further characterisation of the investigated sediment was carried out in the concept of this project. In this work, this remediation material is referred as CE sludge which is an abbreviation of its commercial name Clear Earth (Figure 2).

Figure 2. Picture of CE sludge.

2.4 Reagents and instrumentation

2.4.1 Reagents

All reagents that have been used in the work described in this chapter are listed along with their purities and suppliers in Table 1. A Millipore Corporation^{TM} cartridge purification system was used to produce deionised water (18 MΩ) for the preparation of solutions.

Humic acid, purified twice, was used as a standard in UV measurements. Purification was carried out by dissolving ST and CE sludges in deionised water, and the pH was adjusted to above 10 by addition of sodium hydroxide pellets. Humic acid dissolves above pH 2 and it was separated from insoluble matter (0.45 µm filter). The filtrate, which included both fulvic acid and humic acid, was separated into fulvic and humic acids by adjusting the pH to below 2 using hydrochloric acid and filtering off the precipitated humic acid. The final product, called twice-purified humic acid, was dried in a desiccator.

Table 1. Reagents, their purities and suppliers used in Chapter 2

Reagent	***Purity***	***Supplier***
KSCN	99%	Sigma Aldrich
Methyl isobutyl ketone	≥ 99.5%	Sigma Aldrich
$NH_4Fe(SO_4)_2$•12(H_2O)	99%	Sigma Aldrich
$FeCl_3$•6H_2O	>99%	BDH Laboratory supplies
NaOH	Extra pure grade	Acros
KOH	≥ 85%	Fisons
HCl	Laboratory reagent	Fisher Scientific
$NaNO_3$	99+%	Acros
Cobalt hexamine	99.999%	Acros
28 element standard	Standard	Fisher

2.4.2 Instrumentation

Elemental analyses of solutions were carried out using a Thermo Fisher iCAP 6000 Series ICP-OES with ASX-520 autosampler. Argon was used as a carrier gas. The UV-readings were carried out using a Varian 50 Bio UV-visible spectrophotometer at room temperature using a 1 cm quartz cells. The pH was measured at room temperature using either a Jenway or a Orion pH meter. Organic contents of the sludges were measured by heating in a Carbolite furnace. The mineralogy and elemental compositions were determined using powder diffraction (D8 Advice by Bruker) and X-ray fluorescence spectrometry (XRF) analysis were provided by British Geological Survey. Functional groups were determined using a Shimadzu FTIR-8400S Fourier transform infrared spectrophotometer.

2.5 Organic and inorganic contents of the ST and CE sludges

Humic substances are considered to have a major role in extraction and immobilisation of contaminants in the environment, thus characterisation of the extraction materials was commenced by determining their organic and inorganic content. The experiments were carried out by loss on ignition method (LOI) [32] in which the organic matter content is considered to be equal to the loss of mass on ignition even though some weight loss can also occur due to dehydroxylation of clay minerals during heating. The porcelain crucibles (triplicates) were first dried in furnace at 400 ˚C for 2 hours after which they were left to cool. 2 grams of sludges (diameter <0.5 mm) were placed in the crucible and excess water was removed by heating the samples at 80 ˚C for 24 hours. The samples were cooled in a desiccator, weighted and then the organic matter was destroyed in a furnace at 400 ˚C for 16 hours. The LOI was calculated using equation 2.3.

$$\text{LOI} = \frac{weight(80) - weight(400)}{weight(80)} \times 100\% \qquad (2.3)$$

Weight(80) = weight (g) of the sample after heating at 80˚C
Weight(400) = weight (g) of the sample after heating at 400˚C

Figure 3. Ashes from ST (A) and CE (B) sludges (17 h at 400 ˚C).

The cooled ash samples (Figure 3) were weighed and the organic and inorganic percentages of the sludges were calculated by mass loss. The results were averaged and they show (Figure 4) that almost half of the ST sludge (49.7%) is organic whereas 82.7% of the CE sludge is organic.

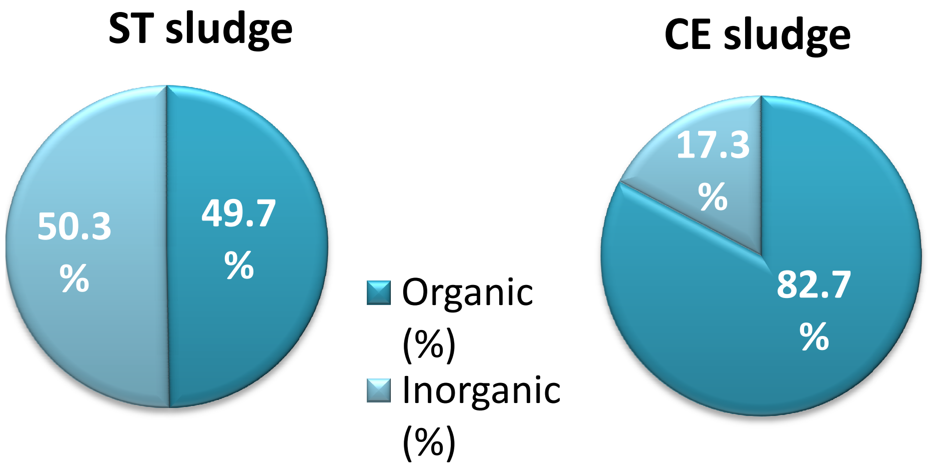


Figure 4. Organic and inorganic contents of the ST and CE sludges.

2.6 Humic acid and fulvic acid content in the organic fractions

After the determination of total organic content of the sludges, the individual organic fractions which mainly contain humin (insoluble organic matter), humic acid and fulvic acid were quantified. The characteristics of humic acid and fulvic acid have been discussed in detail in Chapter 1.

The humic acid and fulvic acid contents were determined according to a modified method by van Zomeren *et al.* [33]. The scheme of the method used is given in Figure 5. The procedure involved acidification of 20 g of sludge (triplicate) with 1 mol dm^{-3} HCl solution to pH 1-2, the volume was adjusted to 200 cm^{3} with 0.1 mol dm^{-3} HCl. This suspension was equilibrated by continuous stirring on an orbital shaker for 1 hour and then centrifuged (3000 rpm, 10 min). The supernatant containing fulvic acid (FA fraction 1) was separated from the solid matter by filtration. Humic acid was dissolved from the solid matter by adjusting the solution to pH 7 by addition of 1 mol dm^{-3} NaOH solution and thereafter 0.1 mol dm^{-3} NaOH solution was added to a final volume of 200 cm^{3}. The final pH of the solution was above pH 12 to ensure humic acid solubility. The suspension was stirred overnight with nitrogen bubbling, then centrifuged

(3000 rpm, 10 min) and the insoluble matter and supernatant were separated by decantation. The humic acid in the supernatant was precipitated by addition of 6 mol dm^{-3} HCl under constant stirring until pH 1 was reached. The suspension was left to stand overnight after which it was centrifuged (3000 g, 10 min) and the supernatant (HA fraction 1) was separated from the fulvic acid fraction (FA fraction 2) by decantation. FA fraction 2 was then combined with FA fraction 1. Known volumes of HA and FA fractions were bench dried and the solids were weighed. Humic and fulvic acid percentages were calculated from the results.

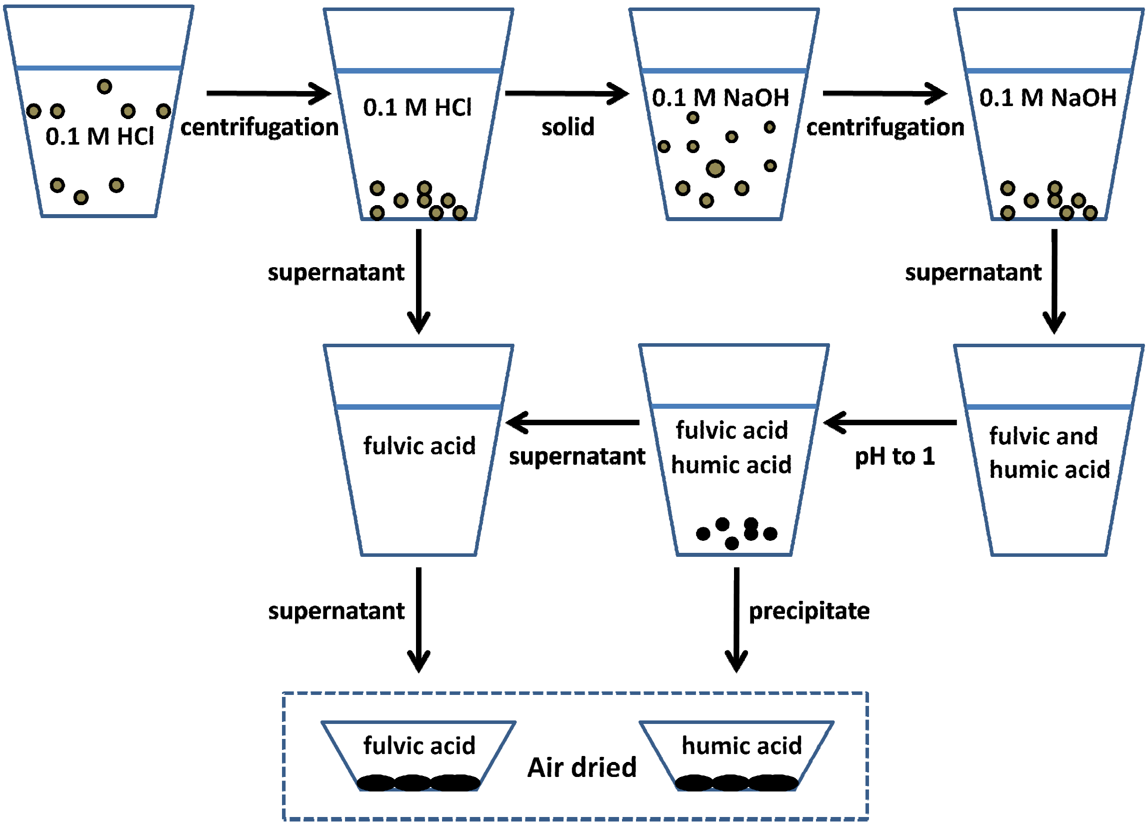


Figure 5. Schematic representation of the batch procedure for determining humic anc fulvic contents of the sludges.

The averaged results of the measurements of the humic and fulvic acid contents of the ST and CE sludges, together with the results of their organic and inorganic contents are shown in Figure 6. The organic fraction of ST sludge contains 19% humic acid, 28% fulvic acid and 3% insoluble organic matter whereas the organic fraction of CE sludge contains 2% humic acid, 27% fulvic acid and 54% insoluble organic matter. The insoluble organic fraction represents the fraction of humin and possible residues of plant degradation especially in the CE sludge. In addition, the fractions of insoluble organic matter may contain humic acid that has been immobilised by clays or other minerals.

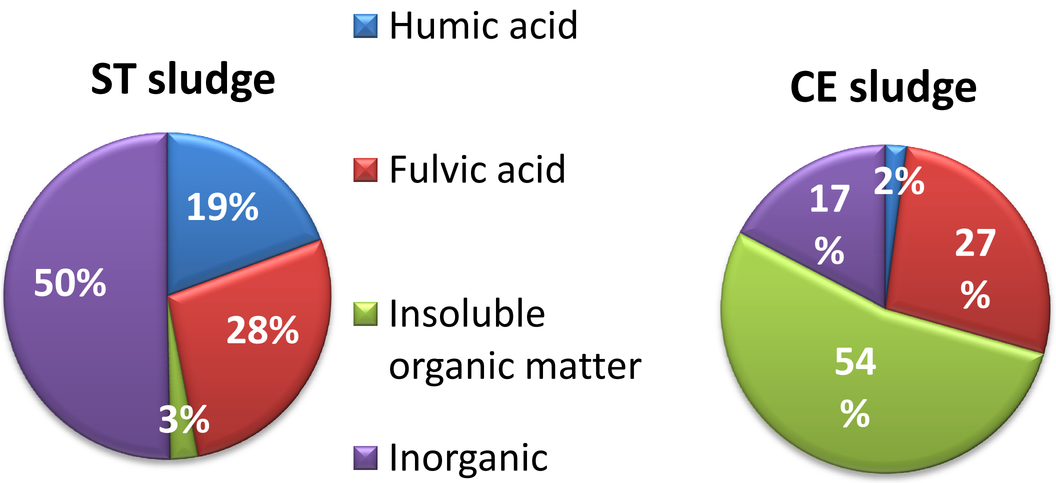


Figure 6. Humic acid, fulvic acid, insoluble organic matter and inorganic matter contents of ST and CE sludges.

2.7 Functional groups in ST and CE sludges

Characterisation of the organic fractions was continued by determining functional groups in the ST and CE sludges. The functional groups of the extracting materials have a significant effect on extraction capacities due to their binding properties. Solid phase FT-IR provides information on the nature, reactivity and structural arrangement of oxygen containing functional groups (mainly COOH, OH and C=O in humic substances [34]) and the relative proportions of aromatic versus aliphatic moieties [35]. The ST and CE sludges were dried in a vacuum oven at 40 ℃ for four hours to remove water prior to measurements. The spectra were measured as absorbance against wavelength and they contained 30 scans (averaged) at range of 400 to 4000 cm^{-1}. Five replicate measurements were collected. Quantitative data on the abundance of the functional groups cannot be given without standards, however the absorbance values can be compared between the ST and CE sludges.

The full scans of the IR-spectra of ST and CE sludges (Figures 7 and 8) exhibit good reproducibility for 5 independent measurements which all show similar structural functional groups. In addition, drying of the materials was efficient because the –OH region (3000 – 3500 cm^{-1}) does not exhibit high absorbance.

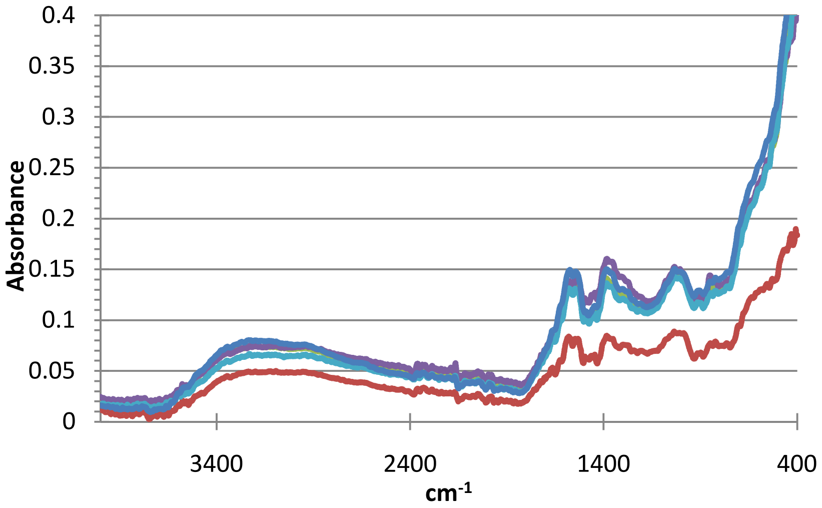


Figure 7. Five replicate FT-IR scans of ST sludge.

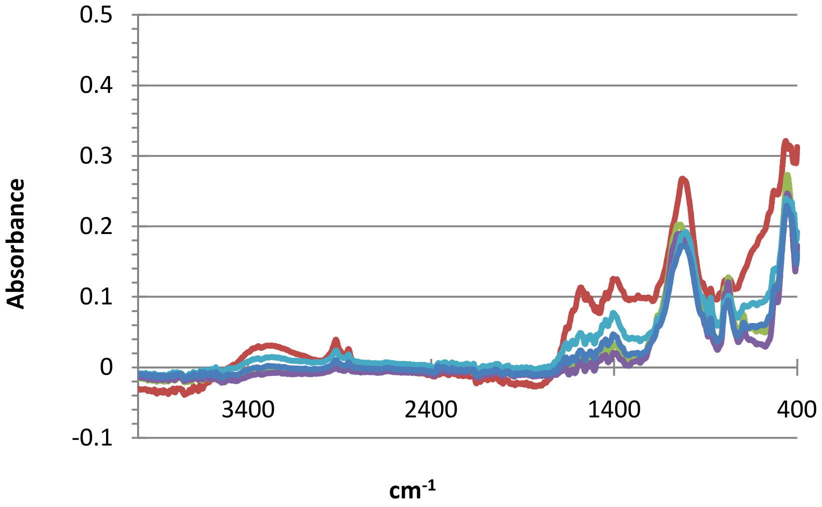


Figure 8. Five replicate FT-IR scans of CE sludge.

The FT-IR scans of the sludges were averaged and divided into three regions (1900-4000 cm^{-1}, 1500-1900 cm^{-1} and 400-1500 cm^{-1}). The divided regions of the spectra are discussed in detail. The interpretations of the absorbance bands of humic substances were carried out as described in the literature [34-45].

The first region from 1900 to 4000 cm^{-1} of the ST and CE spectra are shown in Figure 9. The broad band at 2500 – 3700 cm^{-1} in the ST sample is attributed to OH groups possibly resulting from a combined band of OH (alcohol, phenol), NH (amine and amide), carboxylic acids or water. Because of the broadness of the band, the fine structure of this region may be masked. Nevertheless, the CE sludge sample exhibits more detailed information with a broad band at 3000 – 3500 cm^{-1} which can be attributed similarly to OH groups from alcohols and phenols and NH groups from amine and amide. The twin peaks at 2910 and 2845 cm^{-1} can be identified as stretching of aliphatic C-H groups in CH_2 and CH_3.

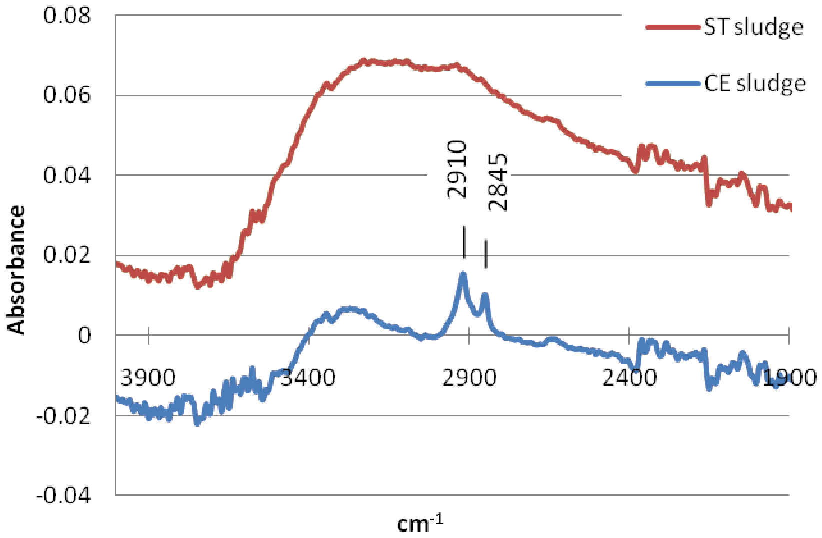


Figure 9. FT-IR region 1900-4000 of ST and CE sludges.

The strong bands of ST and CE sludges in the second region of 1900 – 1500 cm^{-1} can be assigned to C=O and C=C bonds (Figure 10);

- 1660 cm^{-1} band as aromatic ketones, aromatic C=C, hydrogen bonded C=O, double bond conjugated with carbonyl and COO^{-} vibrations and COO^{-} symmetrical stretch
- 1620 cm^{-1} band as aromatic C=C and conjugated carbonyl C=O stretches
- 1570 cm^{-1}, 1540 cm^{-1}, and 1530 cm^{-1} bands as benzene ring

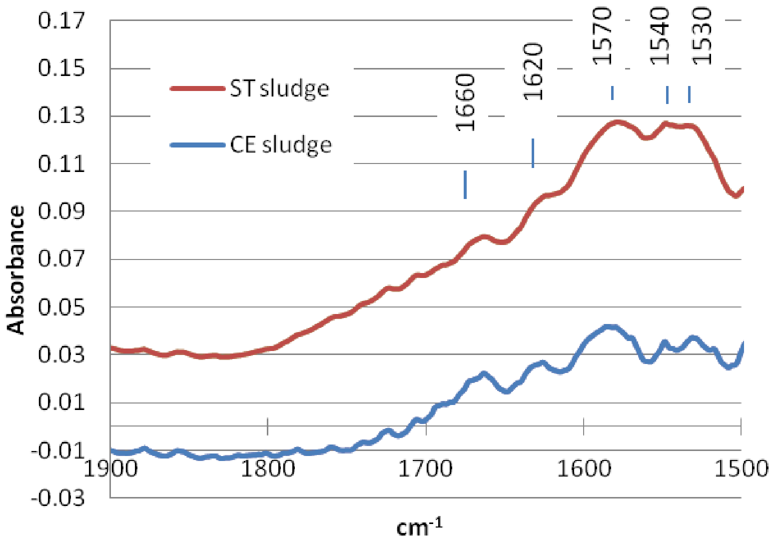


Figure 10. FT-IR region 1500-1900 of ST and CE sludges.

The third region is from 400 to 1500 cm^{-1} (Figure 11). Carboxylate groups exhibit two bands at 1550 cm^{-1} and 1400 cm^{-1} which can be seen in the fingerprint region as the 1380 cm^{-1} band and in Figure 10 as the 1570 cm^{-1} band. The band at 1010 cm^{-1} can be attributed to polysaccharides or Si-O. CE sludge also exhibits a band at 770 cm^{-1} which is caused by Si-O stretching vibrations of quartz and silica. The band at 870 cm^{-1} in the CE sludge is caused by aromatic C-H vibrations.

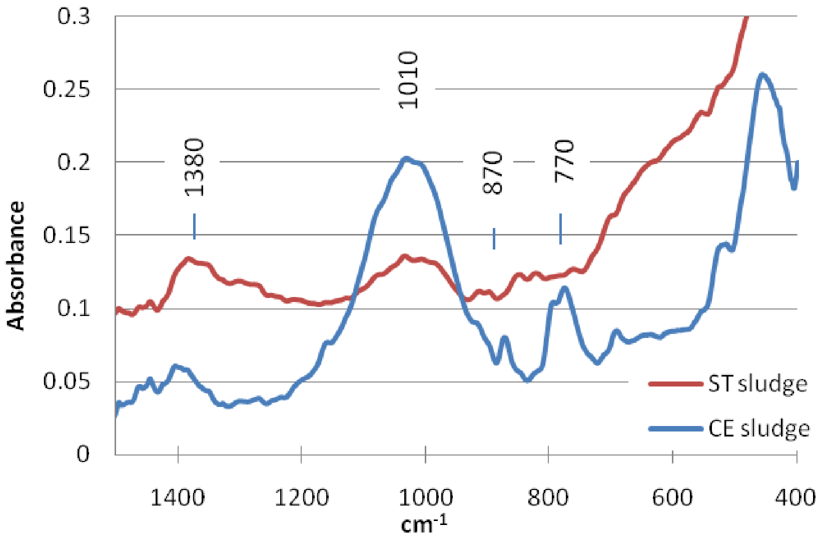


Figure 11. FT-IR region 600-1500 of ST and CE sludges.

The contributions of the inorganic matter in the FT-IR spectra were determined by destroying the organic content of the ST and CE sludges in a furnace overnight at 550 ˚C. The FT-IR pattern of the ST sludge ash (Figure 12) show a band in the 2500 – 3500 cm^{-1} region possibly due to the OH group in iron hydroxide (see 2.9 Mineral and elemental analysis by XRD and XRF analysers) and a sharp quartz band at 1080 cm^{-1}. When this result is compared with the spectra of the original ST sludge (Figure 13, spectra were set to the same level) it can be seen that the band in the 2500 – 3500 cm^{-1} region and the sharp band at 1080 cm^{-1} originate from the inorganic fraction of the material. Thus, the main functional groups in ST sludge are detected in the 1540 cm^{-1} and 1380 cm^{-1} bands attributed to aromaticity and carboxylate groups.

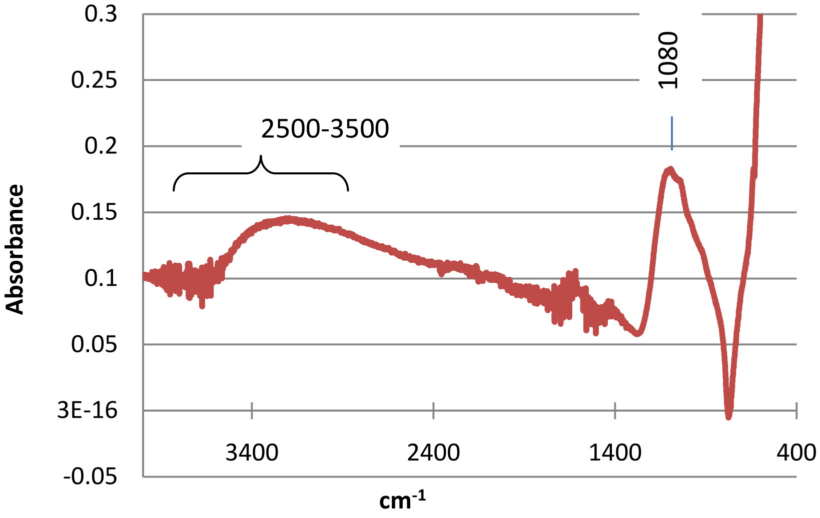


Figure 12. FT-IR region 400-4000 cm^{-1} of the ST sludge ash.

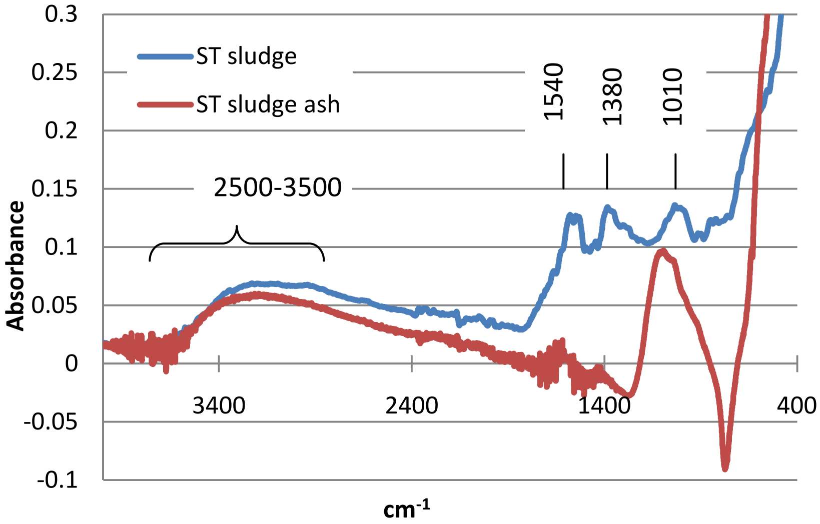


Figure 13. FT-IR region 400-4000 cm^{-1} of original and the ST sludge ash samples. The spectra have been set to same level.

The FT-IR spectra of the CE sludge ash (Figure 14) show bands in the only 400- 1500 cm^{-1} region with two distinctive peaks at 1400 cm^{-1} and 1010 cm^{-1}, two sharp peaks at 870 cm^{-1} and 790 cm^{-1}, two smaller peaks at 680 cm^{-1} and 580 cm^{-1} and a sharp peak at 440 cm^{-1}. When these results are compared with the spectra of the original CE sludge (Figure 15) it can be seen that the majority of the peaks in the fingerprint region originate from the inorganic fraction of the CE sludge. CE sludge does however contain OH groups from alcohols and phenols and/or NH groups from amines and amides (3000-3500 cm^{-1}), aliphatic CH$_2$ and CH$_3$ groups (2845 and 2910 cm^{-1}), and aromatics (1540 cm^{-1}).

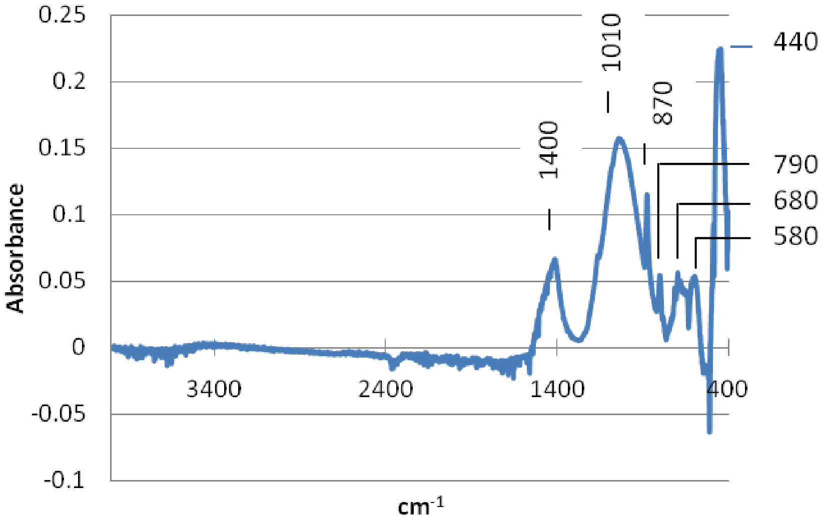


Figure 14. FT-IR region 400-4000 cm^{-1} of ash of CE sludge.

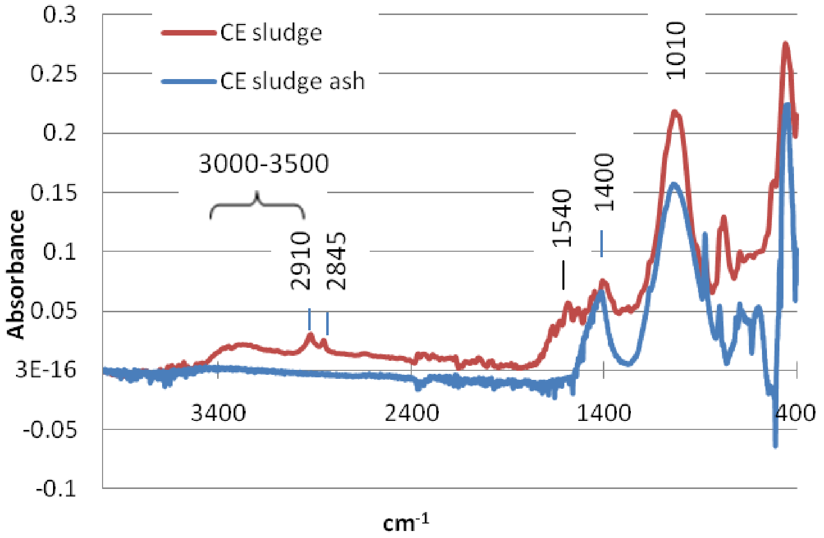


Figure 15. FT-IR region 400-4000 cm^{-1} of original and ash of CE sludge samples.

Interpretation of the bands in the ST and CE sludges are combined in Figure 16. The inorganic matter of ST sludge inhibits reliable interpretation of the 2500-3500 cm^{-1} region but the results suggest the absence of alcohols, phenols, amines, amides and aliphatic CH groups. The absence of aliphatic groups CH_2 and CH_3 indicates that the ST sludge can contain only a small amount of aliphatic hydrocarbons. However, CE sludge contains OH and/or NH functionalities and aliphatic CH_2 and CH_3 groups. Both of the sludges have C=C and C=O functionalities corresponding to aromatic ketones, aromaticity, and carboxylic groups. The ST sludge exhibits higher absorbance in the aromaticity region whereas the CE sludge exhibits higher absorbance at 1010 cm^{-1} due to the presence of quartz. It can be concluded that both ST and CE sludges are aromatic with carboxylate groups as the most abundant functional groups. In general, carboxylic functional groups are considered to dominate the metal ion complexation behaviour of humic substances [43]. For low pH systems (< 2), the ion exchange sites of carboxylic functional groups are mainly protonated and are less available for ion exchange [46]. Within the pH range 2 to 5, the carboxylic acid sites can be appreciably deprotonated and therefore, the metal ion removal is increased by increased pH [46]. Within this pH range, the ion exchange process is the major mechanism for removal of metals from solutions [46].

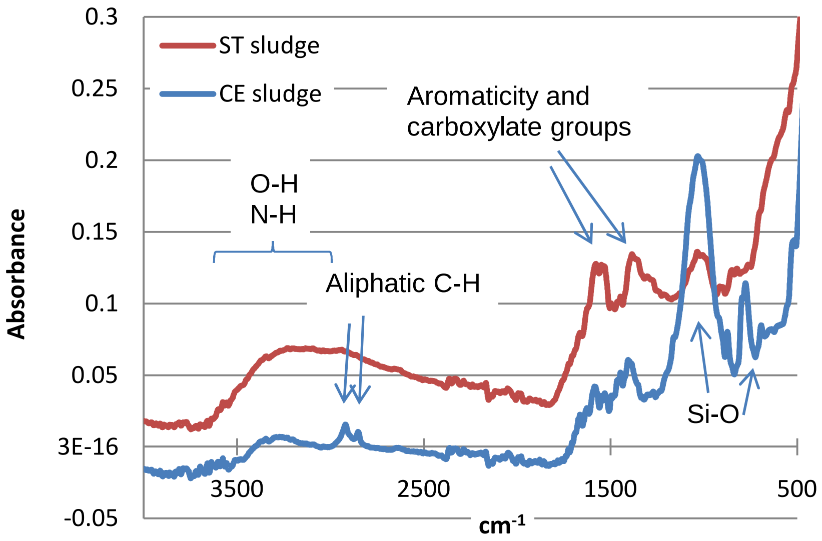


Figure 16. FT-IR spectra of ST and CE sludge with identified bands.

2.8 Iron contents of the ST and CE sludges

After detailed information on the organic fractions of the sludges was obtained, further investigation was carried out on the inorganic fractions. The addition of polymeric ferric sulphate in the production of ST sludge suggested that a significant amount of iron will be present and thus, the iron content of the ST and CE sludges was measured using the thiocyanate method [47].

In the method reported by Marczenko [47], the iron was dissolved from the ash samples (~1 mg, triplicate) produced at 550 ˚C overnight using 12 cm^3 concentrated hydrochloric acid and 8 cm^3 deionised water. The solution was heated to ~ 60 ˚C and iron was precipitated using drops of concentrated ammonia until a red precipitate was formed. The precipitate was separated using a 0.45 µm filter and then dissolved in the minimum amount of hot 2 mol dm^{-3} HCl. The pH was adjusted to pH ~ 1 and the volume to 50 cm^3 using water and NaOH and HCl solutions. 1 cm^3 of iron solution was added to 10 cm^3 of freshly prepared 20% potassium thiocyanate solution. The red coloured $Fe(SCN)^{2+}$ complex was extracted from the aqueous solution into organic solution using 2 cm^3 of methyl isobutyl ketone (MIBK). The extraction was repeated again, and the volume of the MIBK sample solution was adjusted to 25 cm^3. The UV absorbance of the MIBK solution was measured at 495 nm and iron concentrations were calculated using a standard curve prepared from iron(III) chloride in MIBK. The original data are shown in Appendix 1.

The averaged iron contents of the ST and CE sludges are shown in Table 2. The errors were calculated as standard deviation. The high iron content in the ST sludge (ST 22.7 ± 3.3%) was expected as a result of the production process. ST sludge consequently can be a possible source for iron release. The iron content of CE sludge was significantly lower (CE 1.0 ± 0.2%) compared to ST sludge.

Table 2. Iron contents of ST and CE sludges

Material	*Iron (%)*
ST sludge	22.7 ± 3.3
CE sludge	1.0 ± 0.2

2.9 Mineral and elemental analysis by XRD and XRF

It has been established that humic substances have the most significant effect on the extraction of metals and organic compounds. The inorganic fraction of the sludges can also contribute to remediation depending on the reactivity of the components. Thus, further investigations on the inorganic fractions of the sludges were carried out. The mineral compositions of the crystalline materials were determined using XRD and trace metal levels using XRF. The XRD measurements were carried out on dry ST and CE sludges and their ash samples (overnight 550 ºC) and XRF measurements on dry and pulverised (<500 microns) ST and CE sludge ashes.

The XRD results showed that the original ST sample was not crystalline enough for the XRD measurements but the ash sample showed a pattern of iron hydroxide. The result is consistent with the production scheme of the sludge. The XRD results of the original and the ash of the CE sample showed patterns for quartz and calcite. As quartz is relatively inert, the only reactive mineral in the inorganic phase is calcite.

In the XRF measurements, the organic content of the ST sludge was destroyed at 450 ℃, but volatilisation of the organic content of the CE sludge required higher temperature (1050 ℃). These results suggest completely different characteristics of the organic matter in the ST and CE sludges and may explain if the solubility and/or binding properties vary. The XRF results of the ST and CE sludge ashes are presented in Table 3. Majority of the ST ash (90.8%) consists of iron, but some other metals (e.g. Si, Ti, Al, Mn, Ca etc.) are also present in significantly lower abundances. The CE ash consists mainly of silica (87.2%) and calcium (5.2%), but several other metals are also present (Ti, Al, Fe, Mn, Mg, K etc.). These results are in good agreement with the XRD results which showed patterns of iron hydroxide in ST sludge and quartz (contains silica) and calcite (contains calcium) in CE sludge.

Table 3. Results of elemental analysis of ST and CE sludge ashes by XRF.

Element	***Abundance in ST ash (%)***	***Abundance in CE ash (%)***
SiO_2	3.4	87.6
TiO_2	1.6	0.2
Al_2O_3	1.7	2.1
Fe_2O_3	90.8	2.4
Mn_3O_4	1.0	0.2
MgO	0.1	0.3
CaO	0.6	5.2
Na_2O	<0.05	0.2
K_2O	0.05	0.6
P_2O_5	0.2	0.3
SO_3	0.2	0.4
Cr_2O_3	<0.01	<0.01
Sro	<0.01	<0.01
ZrO_2	<0.02	<0.02
BaO	0.02	0.02
NiO	0.02	<0.01
CuO	0.04	<0.01
ZnO	0.05	<0.01
PbO	0.02	<0.01
V_2O_5	<0.01	<0.01
HfO_2	<0.01	<0.01
F	0.3	<0.02
Cl	<0.01	<0.01
Total	100.03	99.33

2.10 Cation exchange capacity (CEC) and exchangeable cations from the ST and CE sludges

Both inorganic and organic fractions of the sludges can contribute to the cation exchange capacity (CEC). The contribution of humic and fulvic acids on CEC is due largely to the ionisation of COOH groups, although some contribution from phenolic OH and NH groups is expected [25]. CEC is a physicochemical characteristic of the material which gives an insight into its ability to bind and release cations. CEC can be quantified by placing a known quantity of material in contact with a known volume of solution that contains an index cation (such as cobalt hexamine or barium chloride) in excess so as to saturate all the exchangeable sites. The CEC can be calculated by measuring the difference between initial and remaining index cation concentrations in the sample after contact with the material. Alternatively, the added analyte adsorbed can be removed and subsequently quantified or the released cations from the exchange sites can be measured.

The cobalt hexamine method [48] was used to determine the cation exchange capacities of ST and CE sludges by placing 2 g of solid (triplicate) in contact with 40 cm^3 of 0.0167 mol dm^{-3} cobalt hexamine chloride solution. The cobalt hexamine ions in solution have a maximum absorbance at 475 nm and a minimum at 380 nm [49] and in this method the absorbance is measured at 472 nm. The samples were shaken on an orbital shaker for one hour and then filtered (0.22 µm). After separation, pH and absorbance at 472 nm were immediately measured. CEC was calculated from the absorbance of the original solution and sample supernatant as:

$$\mathrm{CEC}_{A472} = \left[\frac{(A(orig) - A(sample))}{A(orig)}\right] \times 50 \times \frac{V}{m} \times 100 \qquad (2.4)$$

A(orig) = Absorbance in the original solution at 472 nm (absorbance unit)

A(sample) = Absorbance in the sample supernatant at 472 nm (absorbance unit)

V = volume of original solution (dm^3)
m = dry mass of the sample (g)

A problem of specificity may occur owing to dissolution of organic matter which absorbs in the same region as the cobalt hexamine ion [49]. To determine the effect of dissolved organic matter on the CEC calculations, cobalt concentrations in the original solution and sample supernatants were also measured using ICP-OES. The solutions were acidified (0.5% HNO_3) after spectrophotometry measurements and the cobalt and exchangeable cation (Al^{3+}, Ca^{2+}, Fe^{3+}, K^+, Mg^{2+}, Mn^{2+}, and Na^+) concentrations were determined. The CEC was calculated from the cobalt results using equation 2.5. The results are expressed as $cmol^+ kg^{-1}$.

$$CEC_{Co} = [[Co]_{orig} - [Co]_s] \times \frac{3}{58.93} \times \frac{V}{m} \times 10^3 \times 100 \qquad (2.5)$$

$[Co]_{orig}$ = cobalt concentration of the original solution ($g\ dm^{-3}$)
$[Co]_s$ = cobalt concentration of the sample supernatant ($g\ dm^{-3}$)
V = volume of the sample (dm^3)
m = mass of the sample (g)

Averaged CECs of the ST and CE sludges from UV-Vis and ICP-OES measurements are shown in Table 4. The errors were calculated as standard deviation. The CE sludge has a CEC which is more than twice that of the ST sludge. The higher CEC of the CE sludge can be caused by higher pH (see Table 5) since the CEC of organic matter increases with increasing pH [25]. Dissolved humic substances have not contributed significantly to the UV-Vis measurements since there is only a small difference in the results when measured using UV-Vis and ICP-OES. The difference in the results obtained by the two different methods can be caused by errors introduced in dilutions of sample solutions prior the ICP-OES measurements. The original data are shown in Appendix 1.

Table 4. CECs of ST and CE sludges calculated from UV and ICP-OES measurements

CEC	***ST (cmol$^+$ kg^{-1})***	***CE (cmol$^+$ kg^{-1})***
UV at 472 nm	10.1 ± 1.5	20.6 ± 0.3
Co using ICP-OES	8.9 ± 2.4	24.2 ± 0.6

Table 5 illustrates the concentrations of exchangeable cations from the sludges and the pH of the solutions. The errors were calculated as standard deviation. The pH of the stock cobalt hexamine solution was 5.07. The three major released cations from the ST sludge were potassium (13.7 ± 2.2 mg dm^{-3}), calcium (11.1 ± 1.3 mg dm^{-3}) and manganese (10.6 ± 1.4 mg dm^{-3}) whereas the three major cations released from the CE sludge were magnesium (6.7 ± 0.7 mg dm^{-3}), potassium (3.5 ± 1.2 mg dm^{-3}) and calcium (1.5 ± 0.3 mg dm^{-3}). However, part of the measured calcium in CE sludge samples can originate from dissolved calcite and not from exchangeable sites.

Table 5. Exchangeable cations in ST and CE sludges and the pHs of the solutions

Cation	***ST sludge Concentration (mg dm^{-3})***	***CE sludge Concentration (mg dm^{-3})***
pH	4.6 ± 0.3	7.74 ± 0.03
Al^{3+}	0.13 ± 0.04	< LOQ*
Ca^{2+}	11.1 ± 1.3	1.5 ± 0.3
Fe^{3+}	1.7 ± 0.3	< LOQ*
K^+	13.7 ± 2.2	3.5 ± 1.2
Mg^{2+}	1.7 ± 0.1	6.7 ± 0.7
Mn^{2+}	10.6± 1.4	< LOQ*
Na^+	1.6 ± 0.3	0.58 ± 0.04

*Limit of quantification (LOQ): Al 4 µg dm^{-3}, Fe 41 µg dm^{-3}, and Mn 13 µg dm^{-3}.

2.11 Potentiometric titrations of the ST and CE sludges

Humic substances are weak acids [50] and therefore they buffer pH [23]. They are able to buffer over a wide pH range, since they possess proton-dissociating groups with pK values ranging from 2 to 12 [23]. The acidity of an ionisable functional group depends on its electrostatic environment i.e. the spatial distribution of proximate dipolar groups and formally charged groups in the molecule [25]. The potentiometric titrations give an indication of the amount of acid or base that can be added before the buffer loses its ability to resist pH changes, which is dependent on the amount of conjugated acid and base available in the system [51]. Determination of the pH dependence of the extent of proton dissociation or binding gives useful information and enables discussion of the complexation of humic substances with heavy metals and their binding abilities with organic pollutants [23,50].

Acid-base properties of the ST and CE sludges were investigated by acid-base potentiometric titration. The experiments were carried out by placing 0.2 g of ST or CE sludges in 50 cm^3 of deionised water [51]. The mixtures were stirred with magnetic stirrers and left to equilibrate overnight. The equilibrated suspensions were titrated downwards (0.5 mol dm^{-3} HNO_3) and upwards (0.5 mol dm^{-3} NaOH) from their natural pH in order to obtain a pH range from 1 to 12. The experiments were carried out in triplicate. The titrations were repeated in the absence of the sludges to observe the changes in pH caused by acid and base addition. The pH of equilibrated solutions and their standard deviations are shown in Table 6. The original data are shown in Appendix 1.

Table 6. The pH of equilibrated ST and CE sludge solutions with deionised water

Suspension	*Equilibrated pH Acid*	*Equilibrated pH Base*
ST + DI	5.4 ± 0.2	5.2 ± 0.1
CE + DI	8.2 ± 0.1	8.0 ± 0.1
DI	5.6	6.7

The changes in the pH of the suspensions in the potentiometric titrations with acid addition are shown in Figure 17. However, the buffering capacities are visually clearer in the expanded Figure 18 which shows that the addition of HNO_3 in small amounts in DI water immediately decreased the pH value as expected. This same phenomenon is also evident when ST sludge is present; thus ST sludge does not exhibit a buffering capacity when acid is added. However, even though the pH in the CE suspension initially decreases from 8 to 7, the addition of acid does not change the pH until 0.2 cm^3 of 0.5 mol dm^{-3} HNO_3 has been added. Since humic substances are weak acids, the buffering behaviour of CE sludge is most likely dominated by formation of OH^- as calcite dissolves (equations 2.6).

$$CaCO_3 + H_2O \leftrightarrow Ca^{2+} + OH^- + HCO_3^- \qquad (2.6)$$

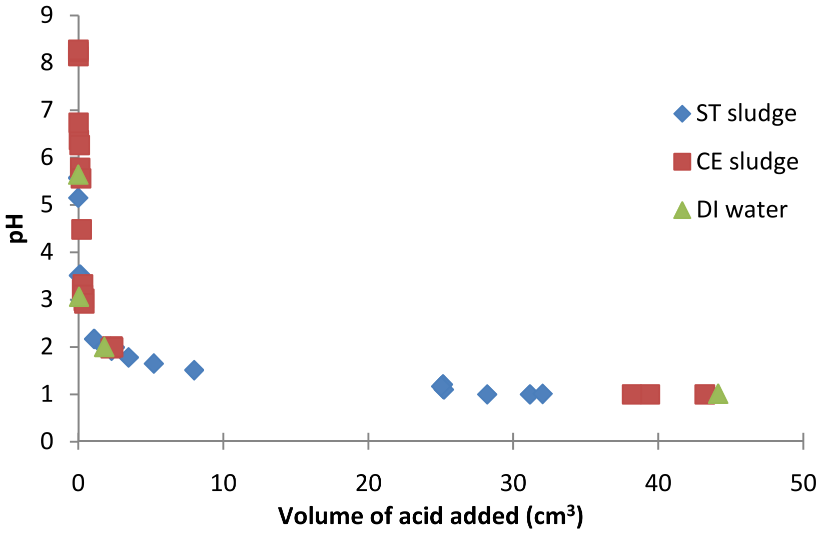


Figure 17. The evolution of pH when titrated with 0.5 mol dm^{-3} HNO_3 in three sets of samples; ST sludge in deionised water, CE sludge in deionised water and deionised water without solid matter.

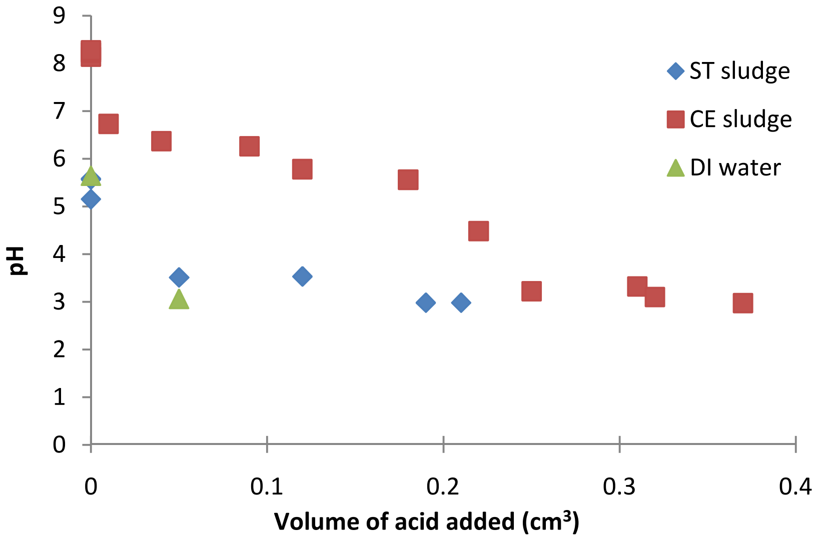


Figure 18. The evolution of pH when titrated with 0.5 mol dm^{-3} HNO$_3$ in three sets of samples; ST sludge in deionised water, CE sludge in deionised water and deionised water without solid matter. Expanded figure from Figure 17.

Figure 19 shows the changes in the pH of the ST and CE suspensions in the potentiometric titrations when base was added and Figure 20 shows in detail the pH from 0 – 0.3 cm^3 added. The evolution of pH in the ST and CE suspensions presented in Figure 20 shows that there is very little buffering capacity when sodium hydroxide is added to the CE suspension whereas ST sludge exhibits some buffering until 0.2 cm^3 of 0.5 mol dm^{-3} of NaOH solution were added. The capacity of the ST sludge to resist pH changes when base is added, is most likely caused by dissolved iron which hydrolyses water and produces H$^+$ ions according to equation 2.7. Also dissociation of COOH and OH functional groups in ST sludge may have an effect on the buffering behaviour.

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+ \qquad (2.7)$$

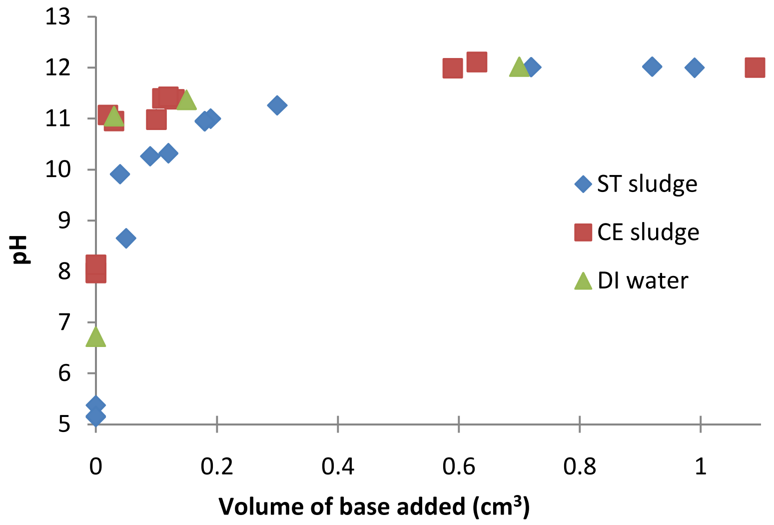


Figure 19. The evolution of pH when titrated with 0.5 mol dm^{-3} NaOH in three sets of samples; ST sludge in deionised water, CE sludge in deionised water and deionised water without solid matter.

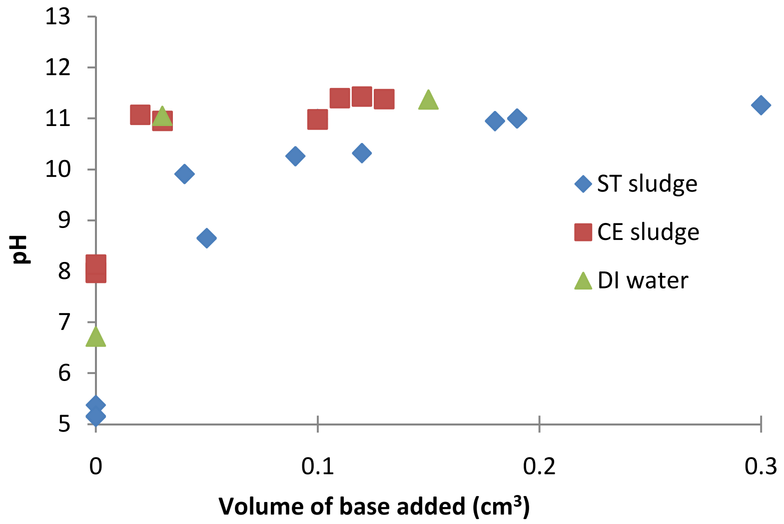


Figure 20. The evolution of pH when titrated with 0.5 mol dm^{-3} NaOH in three sets of samples; ST sludge in deionised water, CE sludge in deionised water and deionised water without solid matter. Expanded figure from Figure 19.

2.12 Solubility

One of the most important characteristics of a remediation material is its insolubility. Continuous introduction of solution through the remediation material can change the nature of the material, both chemically and physically i.e. by leaching metals, changing the pH and releasing humic substances. Therefore, performance properties of the remediation material can be significantly altered by introduction of an elution solution as a function of time.

The solubilities of ST and CE sludges were determined measuring the release of humic acid and metals (Al, Ca, K, Mg, Mn, Na and Fe) when solution was passed through columns of the materials. ST and CE sludges (100 g) were tightly packed in glass columns (Ø 2.6 cm) by mixing the sludge with DI water or 0.1 mol dm^{-3} $NaNO_3$ electrolyte to form slurries. Deionised water and 0.1 mol dm^{-3} electrolyte were used to establish a wide range of ionic strength from zero to 0.1. The slurries were poured slowly into the columns and air bubbles were removed by gentle stirring. The columns were washed with DI water or electrolyte using a flow rate of 0.2 cm^3 min^{-1}. 15 to 20 cm^3 fractions were collected by use of a fraction collector for 24 h hours (Figure 21). After this time samples were collected once a day or once every two to seven days. The experiments were carried out for 85-95 days.

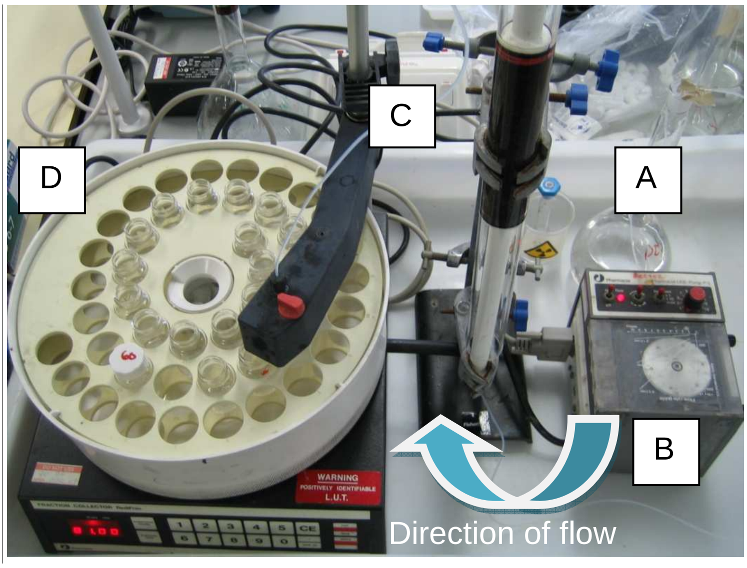


Figure 21. Experimental settings of column experiments; A) reservoir, B) peristaltic pump, C) column, and D) fraction collector.

Dissolved organic matter in the collected samples was determined as humic acid by measuring absorbance in the collected fractions at 254 nm using UV-Vis spectrophotometry. UV-Vis spectra of humic substances are broad, featureless and the absorbance decreases with increasing wavelength. A wavelength of 254 nm is commonly used since organic matter contains functional groups with structures similar to a large number of aromatic compounds (phenolic substances, anilines, benzoic acids, polyenes and polycyclic aromatic hydrocarbons with two or more rings) that absorb light around that UV region due to π- π* electronic transitions [52]. A widely used method to estimate the composition of released organic matter is to use a ratio of two absorbance measured at two wavelengths. Since the UV-Vis spectra of humic substances are broad and featureless any two wavelengths that exhibit absorbance, for example 254 nm and 354 nm, can be used. UV-Vis standard curves were prepared from twice purified humic acids (extracted from the sludges) in deionised water and electrolyte. Stocks of known amounts of twice purified HAs were dissolved in deionised water or electrolyte. A small amount of NaOH was added to encourage solubility. Standards with HA concentrations of 40, 30, 20, 10, 5, 1, 0.5 and 0.1 mg dm^{-3} were prepared from the stocks solutions and the absorbance were measured at 254 nm and 354 nm. Ratios of these were used to evaluate the composition of released organic matter. In addition, pH was monitored and the cations released (Al, Ca, K, Mg, Mn, Na and Fe) were measured using ICP-OES.

The experimental parameters of the column studies with ST and CE sludges are shown in Table 7. The dimensions of the columns were similar for all of the columns. Within the time interval of the experiments approximately 23-28 dm^3 of solution were pumped through each column which corresponds passing approximately 178 – 218 times the bed volumes of the columns through the columns.

Table 7. Detailed information on ST and CE columns

	ST + DI	***CE + DI***	***ST + electrolyte***	***CE + electrolyte***
Height (cm)	24.6	24.3	24.0	24.0
Volume of column (cm^3)	130.6	129.0	127.4	127.4
Days of experiment	93	94	85	87
Solution through (dm^3)	25.9	28.2	22.7	26.0
Washing times (day)	198	218	178	204

Table 8 shows the concentrations of aluminium, calcium, potassium, magnesium, manganese and iron impurities in the 0.1 mol dm^{-3} NaNO$_3$ electrolyte. The electrolyte contained mainly magnesium as an impurity (1.61 mg dm^{-3}) but also some calcium (0.03 mg dm^{-3}), potassium (0.27 mg dm^{-3}) and iron (0.02 mg dm^{-3}). The electrolyte did not contain significant amounts of aluminium or manganese (<0.001 mg dm^{-3}).

Table 8. Aluminium, calcium, potassium, magnesium, manganese and iron concentrations in the 0.1 mol dm^{-3} NaNO$_3$ electrolyte

Metal	***Concentration (mg dm^{-3})***
Aluminium	< 0.001
Calcium	0.033 ± 0.007
Potassium	0.272 ± 0.004
Magnesium	1.612 ± 0.225
Manganese	< 0.001
Iron	0.016 ± 0.003

The pH measurements of the collected fractions showed that the ST and CE sludges maintained their buffering capacities throughout the sampling periods (Figures 22 and 23). The original pHs of the introduced DI and electrolyte solutions were neutral, and thus ST sludge buffered the pH towards 4-5.5 and CE sludge towards pH 7-8.

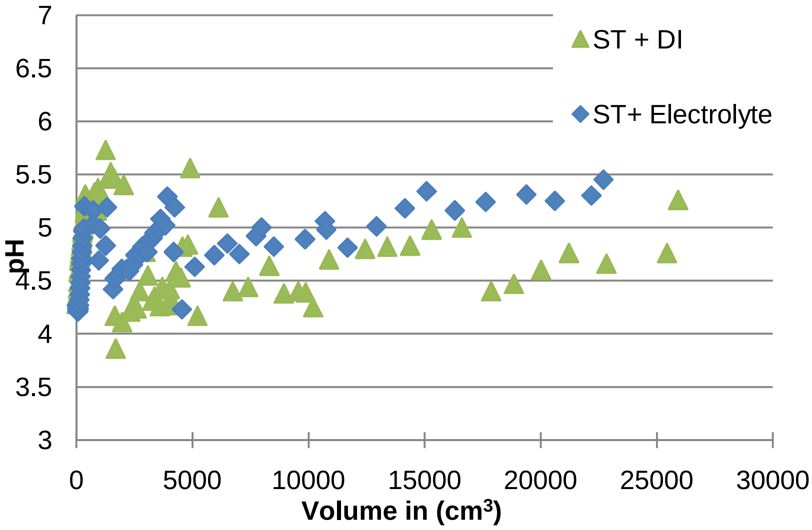


Figure 22. Evolution of pH in collected fractions from ST columns washed with deionised water (DI) and 0.1 mol dm^{-3} NaNO$_3$ electrolyte (Electrolyte).

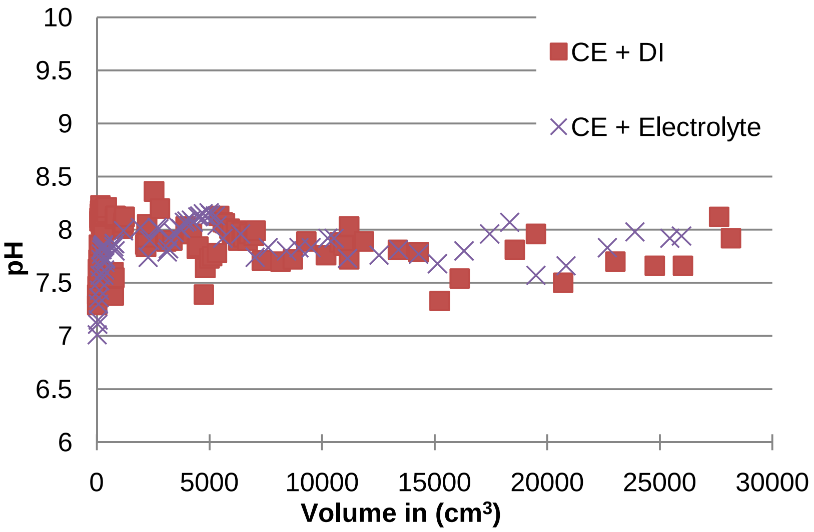


Figure 23. Evolution of pH in collected fractions from CE columns washed with deionised water (DI) and 0.1 mol dm^{-3} NaNO$_3$ electrolyte (Electrolyte).

The evolution of flow rates (Figure 24) fluctuated in the beginning of all the column experiments due to blocking or swelling of the material but then stabilised to 0.2 ± 0.05 cm^3 min^{-1} within 20 days in all columns. Clogging of the columns occurred most likely due to deposition of grains or swelling of the materials.

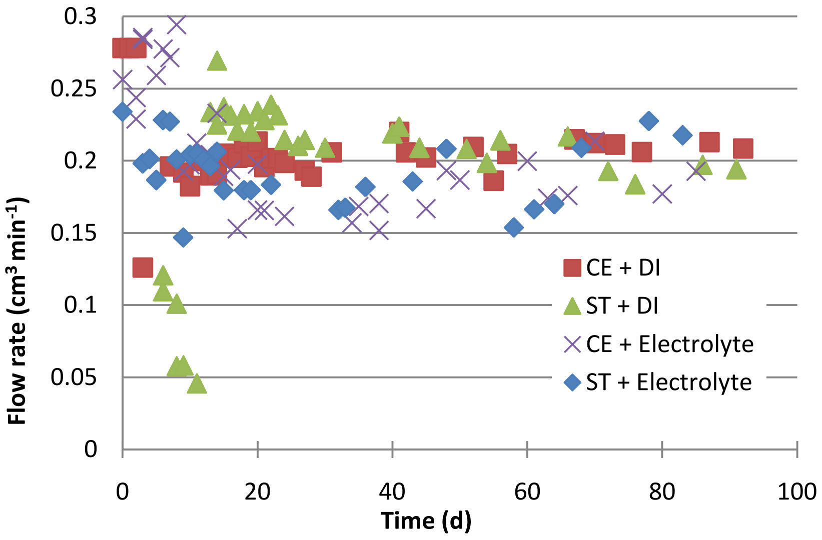


Figure 24. Evolution of flow rates in ST and CE columns.

Release of humic substances from 100 g ST packed column by deionised water detected as humic acid is shown in Figure 25. There is release of humic substances in the beginning of the experiment reaching a concentration of over 350 mg dm^{-3} after which the concentration decreases. Nevertheless, a new and higher (600 mg dm^{-3}) release occurs when 2000 cm^{3} of deionised water has passed through the column which was caused by blockage of the column when water was left stagnant inside the column for a small period of time (a few hours). Towards the end of the experiment the humic substances continue to dissolve and the HA concentration plateaus at approximately 100 mg dm^{-3}.

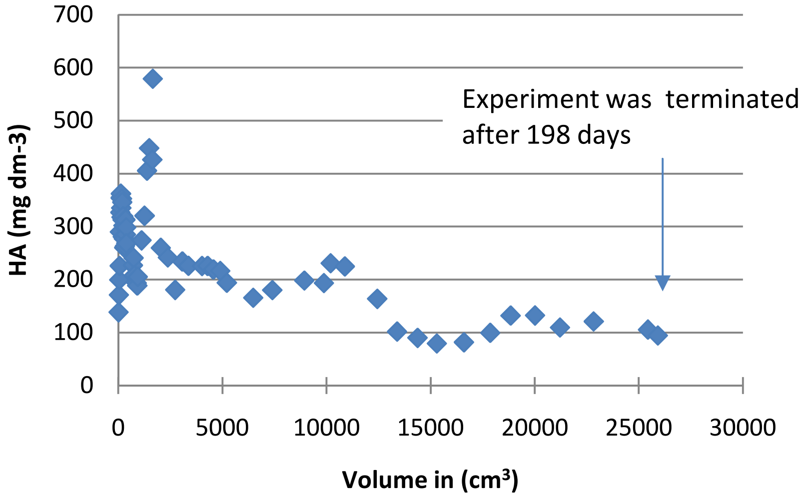


Figure 25. Humic substances released from 100 g ST column by deionised water.

The release of humic substances from 100 g ST column by 0.1 mol dm^{-3} $NaNO_3$ electrolyte exhibits (Figure 26) a similar trend. In the beginning of the experiment the release of HA reaches a maximum of 800 mg dm^{-3} but then the concentration exponentially decreases and plateaus at 100 mg dm^{-3}.

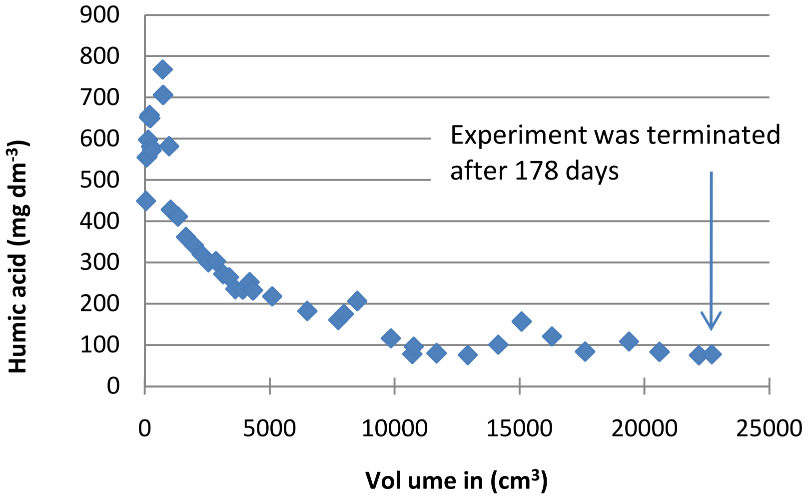


Figure 26. Humic substances released from 100 g ST column by 0.1 mol dm^{-3} $NaNO_3$ electrolyte.

The results for releases by deionised water and electrolyte from ST columns are combined in Figure 27 from which the similarity of HA release is evident. The release of humic acid is initially high after which the release plateaus to 100 mg dm^{-3}. During these 3 month experiments, approximately 4.2 % of ST sludge was dissolved by DI water and 3.8% by electrolyte. If the ST column continues to release humic acid with constant rate (100 mg dm^{-3}) when treated with deionised water or electrolyte, 846 mg of humic acid is released from the column in one month. This amount corresponds to release of 0.8% of the ST sludge in one month and 10.2% in one year.

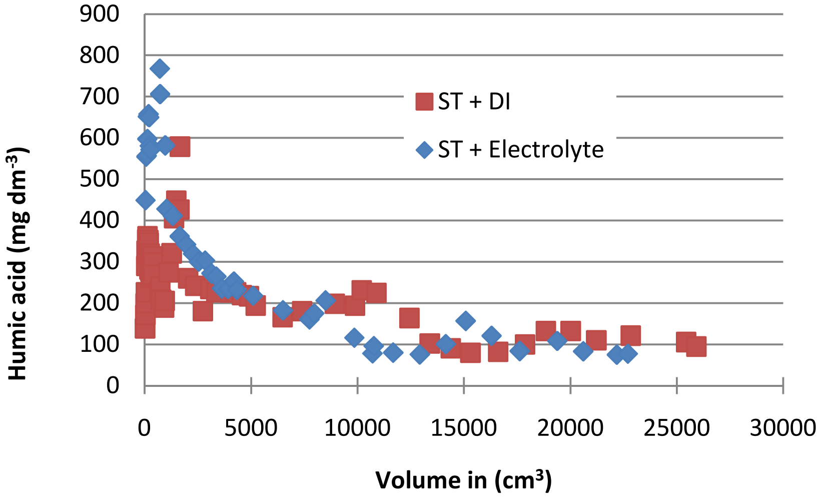


Figure 27. Humic substances released from 100 g ST columns by deionised water and 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

The 254 to 354 nm ratio of the ST sludge with DI and electrolyte (Figure 28) shows that the composition of dissolved matter in both cases is largely constant (approximately 3) after 2000 cm^{-3} of washing. It can be hypothesised that the varying 245/354 ratio in the beginning of the experiments was caused by a contribution of humic acid together with fulvic acid and other compounds containing chromophores but as the ratio changes to 3 humic acid and/or fulvic acid were released. If the observed 254/354 ratio of 3 in the plateau region is caused solely by humic acid, the purified humic acid standards should exhibit the same value. Thus, three different standards of purified humic acid from the ST sludge was prepared (1, 5, 10 mg dm^{-3}) and the ratio in the deionised water was 2.26 ± 0.04 and in electrolyte 1.9 ± 0.1. These results show that the absorbance in the collected column samples is not solely caused by humic acid but constant release of fulvic acid may also be present.

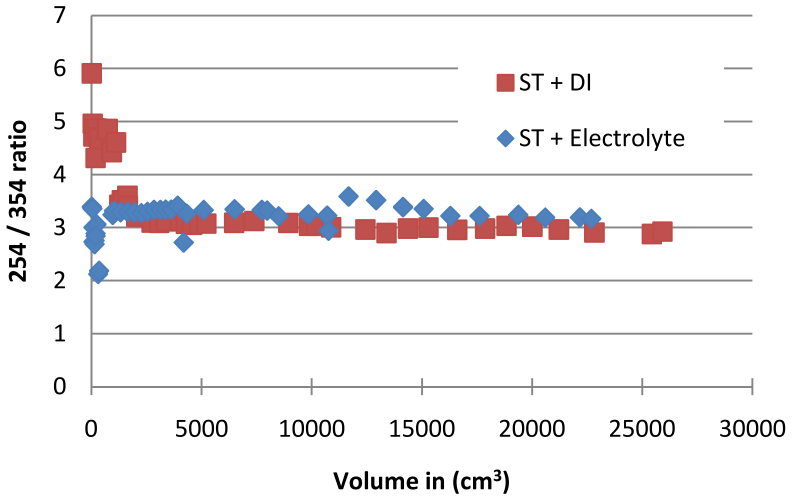


Figure 28. 254 to 354 nm ratios in the fractions collected from 100 g ST column washed by deionised water and 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

Figure 29 shows the extent of humic acid released by deionised water from 100 g CE column over time. The release was highest in the beginning of the experiment reaching 50 mg dm^{-3} release of humic acid and then exponentially decreases and plateaus at approximately 5 mg dm^{-3}.

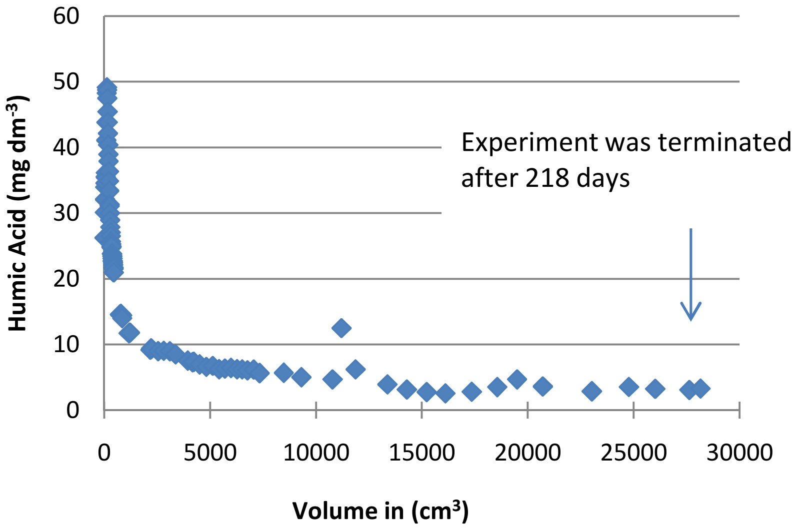


Figure 29. Humic substances released from 100 g CE column by deionised water.

The release of HA from CE sludge by electrolyte is only slightly higher (60 mg dm^{-3}) than by deionised water (50 mg dm^{-3}) in the beginning of the experiment as shown in Figure 30. However, the release does not decrease as quickly when more electrolyte is introduced to the column. Excluding peaks at 40 mg dm^{-3} and 30 mg dm^{-3} which result from blockages, humic acid at 4000 cm^3 and 18300 cm^3 respectively, the release of HA stabilises to approximately 8 mg dm^{-3}.

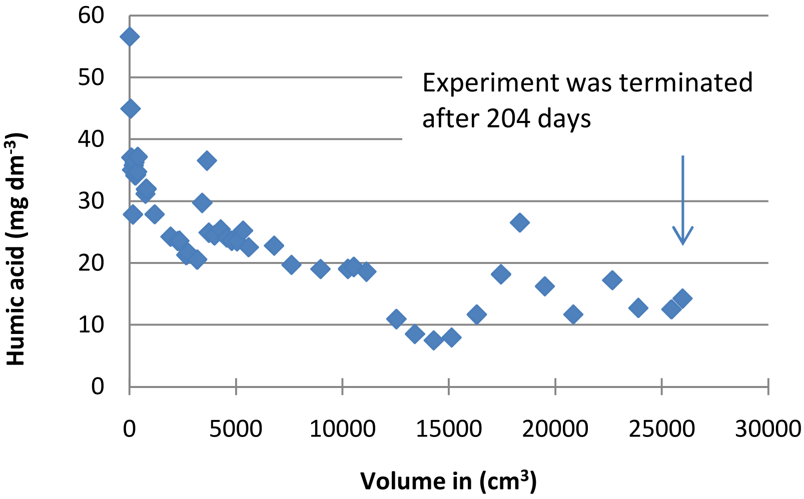


Figure 30. Humic substances released from 100 g CE column by 0.1 mol dm^{-3} $NaNO_3$ electrolyte.

When the behaviour of both the CE sludge columns are compared (Figure 31) it can be seen that the increase of ionic strength of the solution has increased the release of HA. In total, 0.1% of CE sludge was dissolved by DI water and 0.5% by electrolyte in 3 months sampling period. If DI water continues to dissolve the CE column with constant rate of 5 mg dm^{-3}, 43.2 mg of CE sludge will be released in a month and 518.4 mg in a year. These values correspond to releases of 0.04% and 0.5%, respectively. If the release rate of humic acid by electrolyte remains constant (8 mg dm^{-3}), 68.1 mg (0.07%) of CE sludge is released within a month and 829.4 mg (0.8%) within a year.

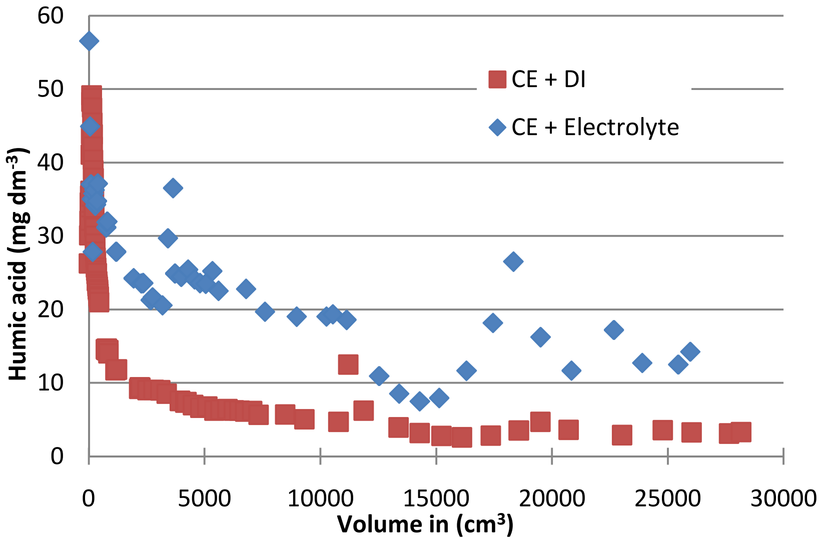


Figure 31. Humic substances released from 100 g CE column by deionised water and 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

The 254/354 ratios from the CE columns (Figure 32) show similar trends as in the ST columns; higher ratios in the beginning of the experiment and then stabilisation to 3. The ratios of the HA standards in deionised water were 2.7 ± 0.9 and in electrolyte 1.7 ± 0.3 which are different to the observed ratios of the collected CE column samples. Thus the collected samples do not only contain humic acid but may also contain fulvic acid.

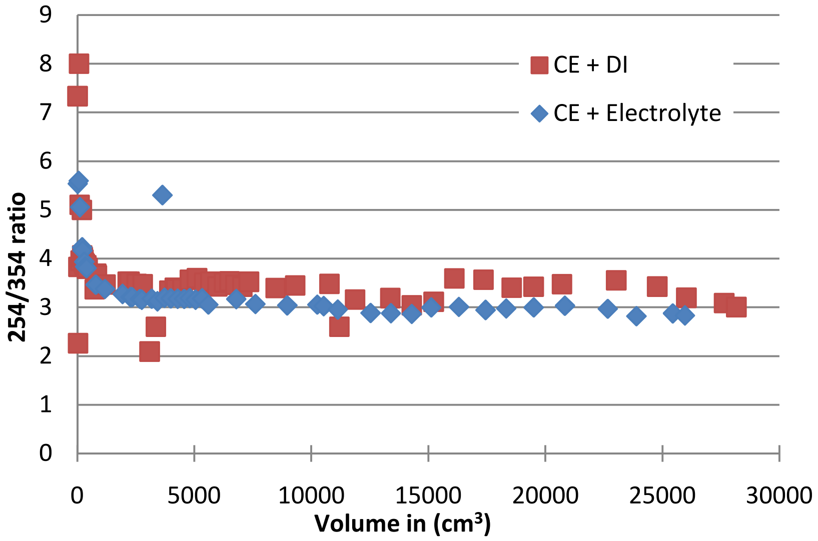


Figure 32. 254 to 354 nm ratios in the fractions collected from 100 g CE column washed by deionised water and 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

Figures 33 and 34 illustrate the colour of the fractions at the start and the end of the experiments. In the beginning of the experiments, the colours of the CE fractions are significantly lighter compared to the ST fractions. There is also a small difference in colour between CE fractions. However, the volume of deionised water pumped through the CE column at this point was almost four times higher (4.2 dm^3) compared to the other CE column (1.2 dm^3). The volumes of deionised water and electrolyte pumped through the ST columns were 1.7 dm^3 and 1.3 dm^3, respectively, and their colours are similar and strong. Even though the colours are strong in the ST sludge samples, the organic matter was not particulate. However, the organic matter starts to coagulate over period of time.

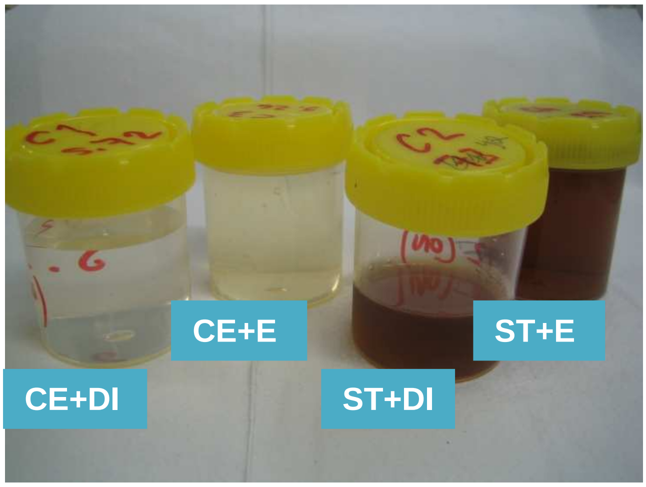


Figure 33. Picture of the collected fractions from CE and ST columns (deionised water (DI) and electrolyte (E)) in the beginning of the experiments.

The CE fractions at the end of the experiments are visually clear whereas colour remains in the ST fractions (Figure 34). However, the colours of all the samples in Figure 2.33 are significantly lighter compared to the colour of the samples collected in the beginning of the experiments (Figure 33). The final volumes passed through the CE columns were 28.2 dm^3 (DI) and 26.0 dm^3 (E) and through the ST columns 25.9 dm^3 (DI) and 22.7 dm^3 (E).

Figure 34. Picture of the collected fractions from CE and ST columns (deionised (DI) and electrolyte (E)) in the end of the experiments.

The concentrations of calcium, potassium, magnesium, manganese, sodium and iron released from the ST column washed with deionised water are shown in Figures 35 to 41 and summarised in Figures 42 and 43. All the metals except iron are initially released within the first elution volume of 2000 cm^3 (corresponding to 15.3 bed volumes) after which the concentrations in the collected fractions plateau at under 10 mg dm^{-3}. The iron concentration released is almost constant (35 mg dm^{-3}) until 10 000 cm^3 has passed through the column after which the iron concentrations decrease to 10-20 mg dm^{-3} but the release of iron does not plateau before the end of the experiment (Figure 2.41).

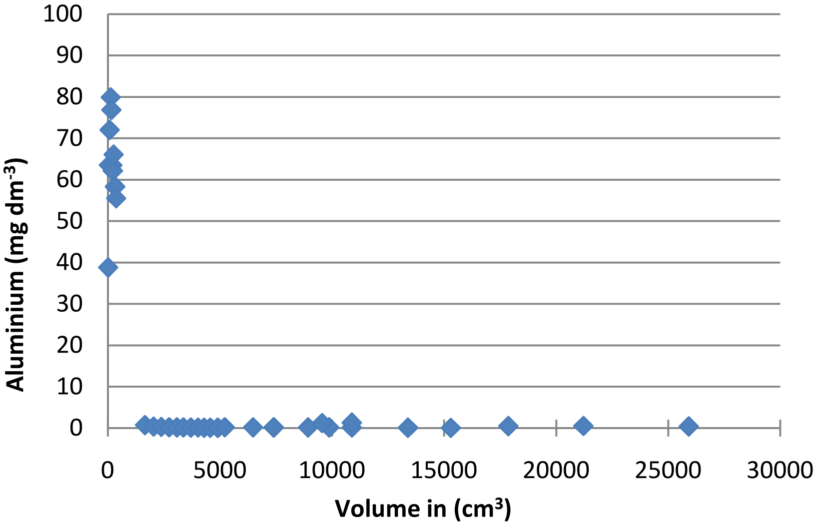


Figure 35. Release of aluminium from 100 g ST sludge column by deionised water.

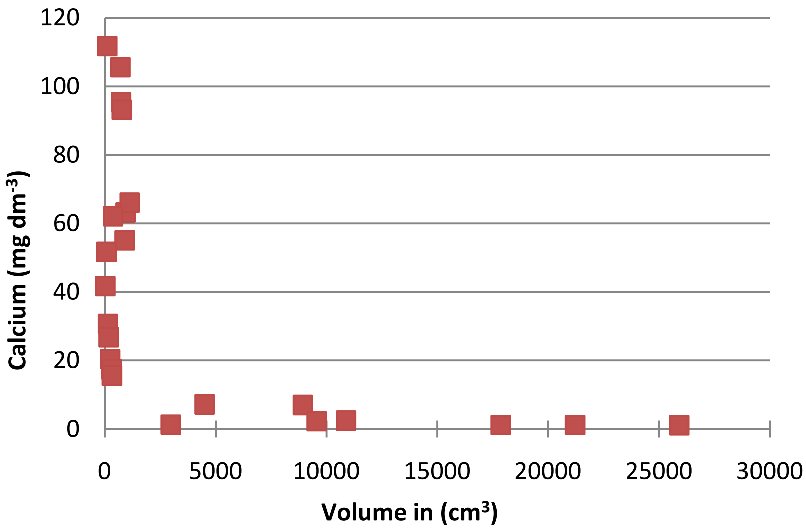


Figure 36. Release of calcium from 100 g ST sludge column by deionised water.

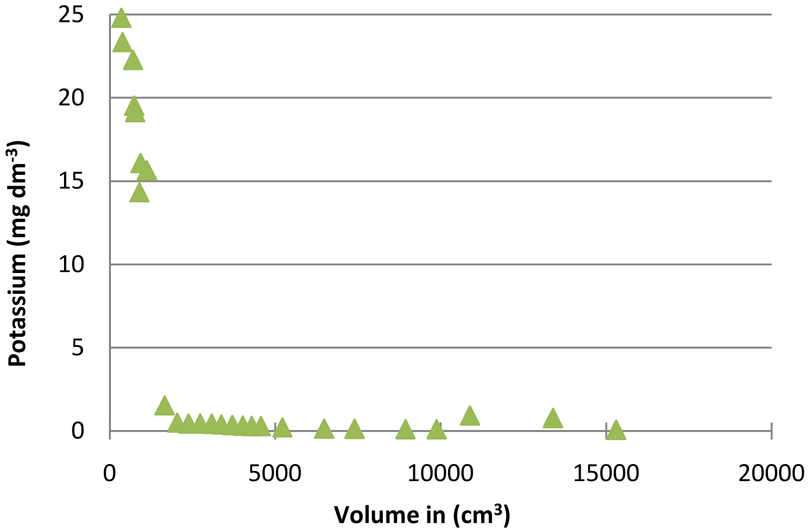


Figure 37. Release of potassium from 100 g ST sludge column by deionised water.

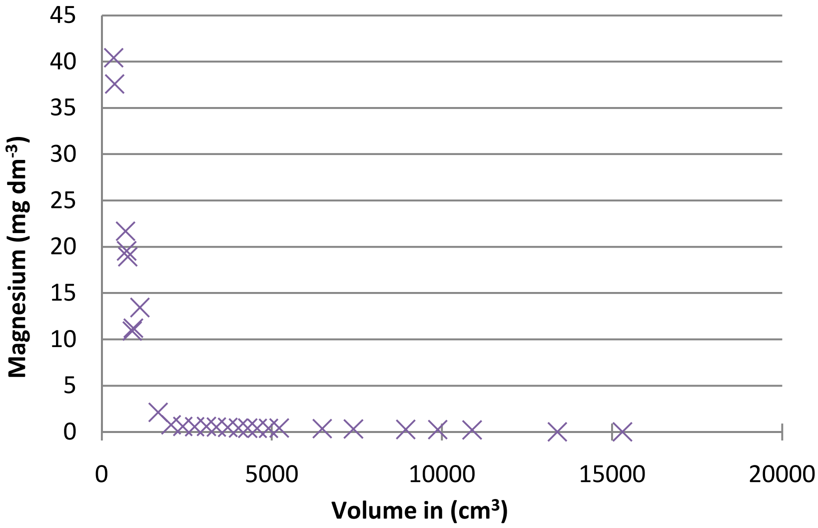


Figure 38. Release of magnesium from 100 g ST sludge column by deionised water.

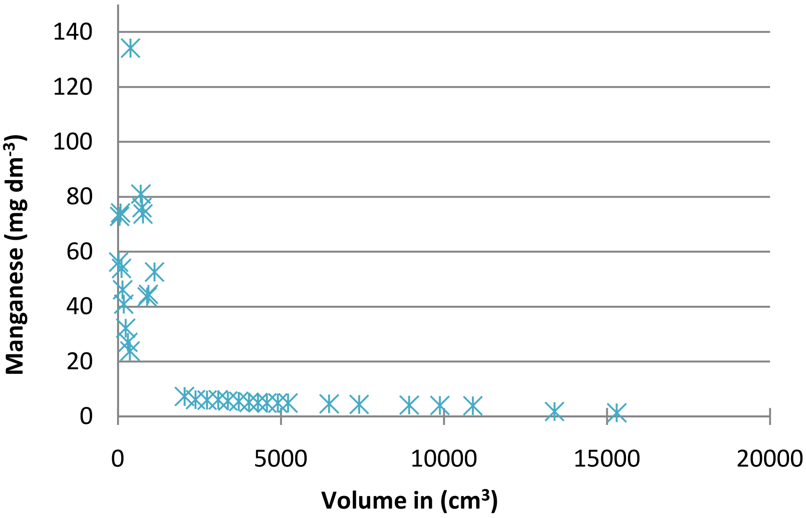


Figure 39. Release of manganese from 100 g ST sludge column by deionised water.

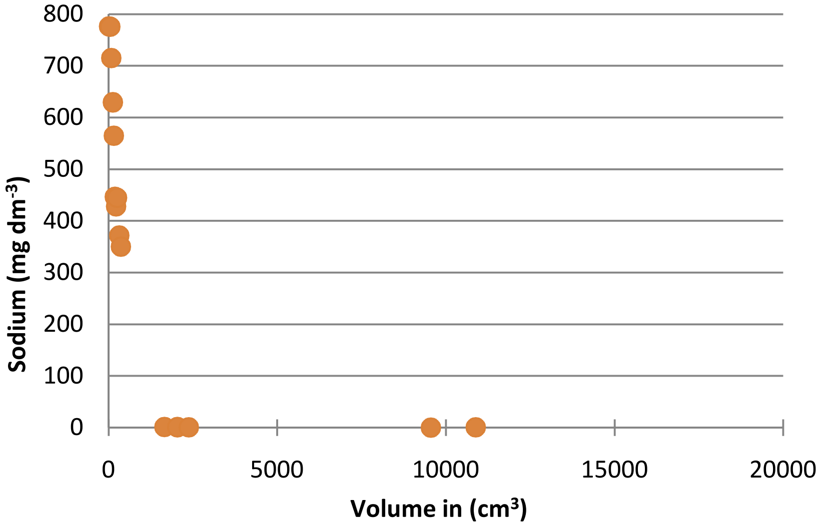


Figure 40. Release of sodium from 100 g ST sludge column by deionised water.

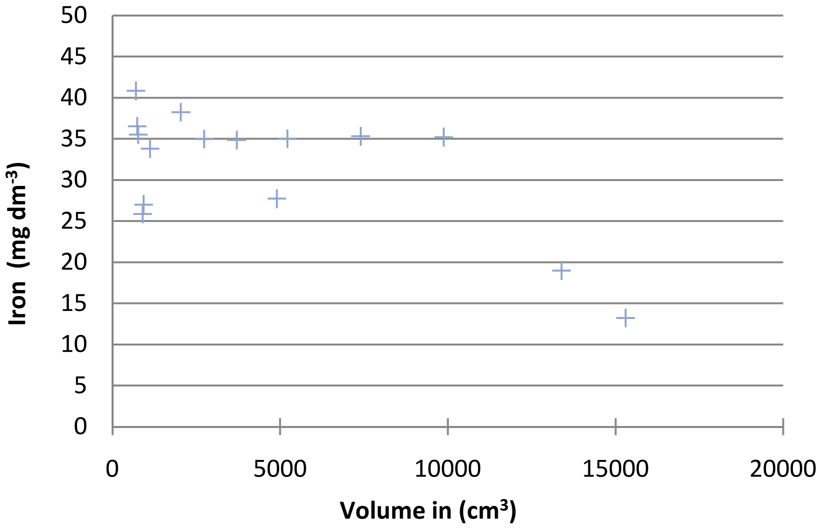


Figure 41. Release of iron from 100 g ST sludge column by deionised water.

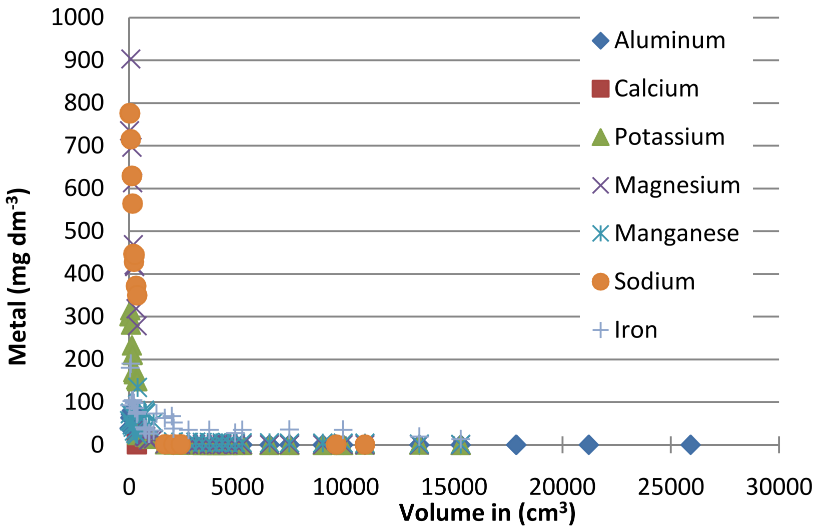


Figure 42. Release of metals from 100 g ST column by deionised water.

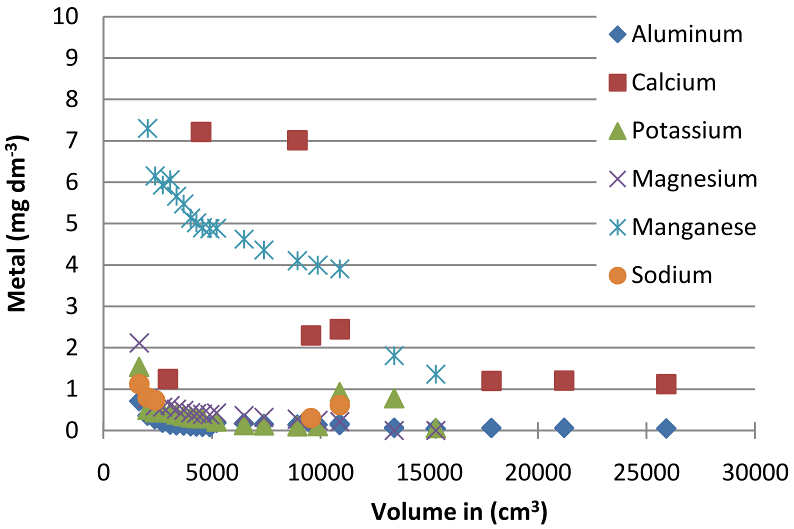


Figure 43. Release of metals from 100 g ST column by deionised water (expanded from Figure 42).

Released metal concentrations in the collected fractions of the ST column washed with 0.1 mol dm^{-3} $NaNO_3$ electrolyte are shown in Figures 44 to 49 and summarised in Figures 50 and 51. The electrolyte contained sodium, thus it was not analysed in the collected samples. All the metals, including iron, are initially released within the first elution volume of 5000 cm^3 (correspond to 39.2 bed volumes) after which the concentrations in the collected fractions plateau to different levels; Ca < 5 mg dm^{-3}, K and Mg < 1 mg dm^{-3}, Mn < 10 mg dm^{-3} and Fe (< 60 mg dm^{-3}).

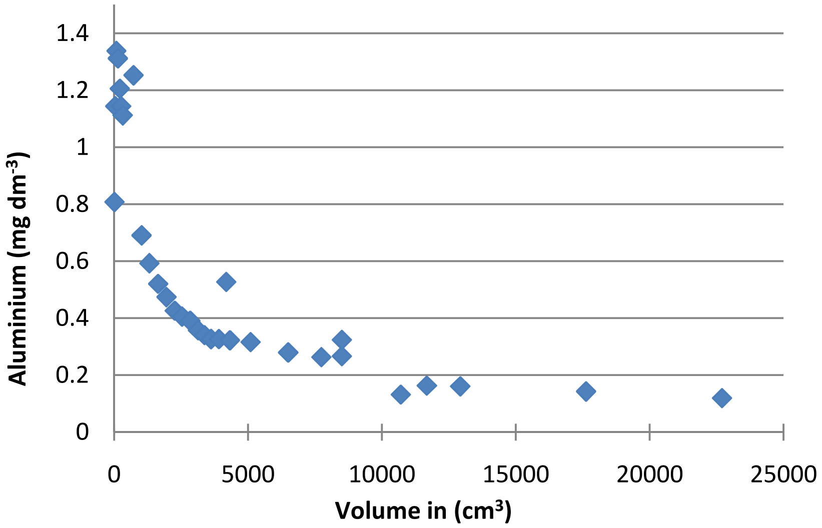


Figure 44. Release of aluminium from 100 g ST sludge column by 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

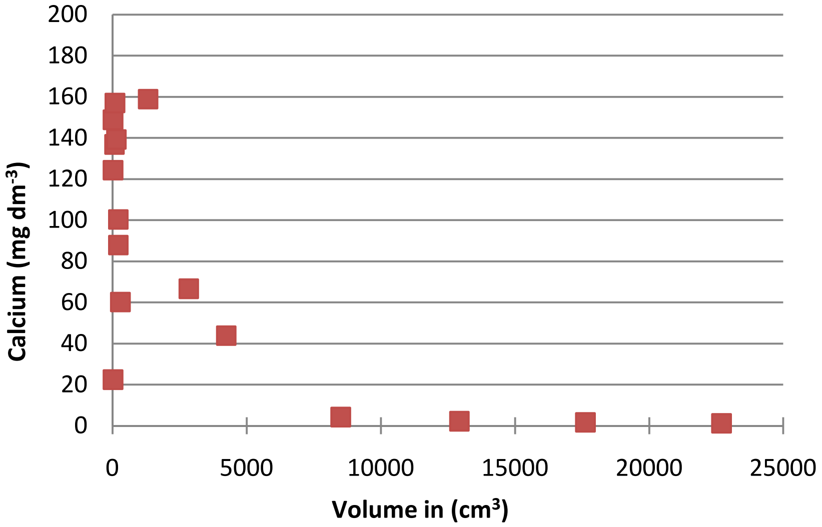


Figure 45. Release of calcium from 100 g ST sludge column by 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

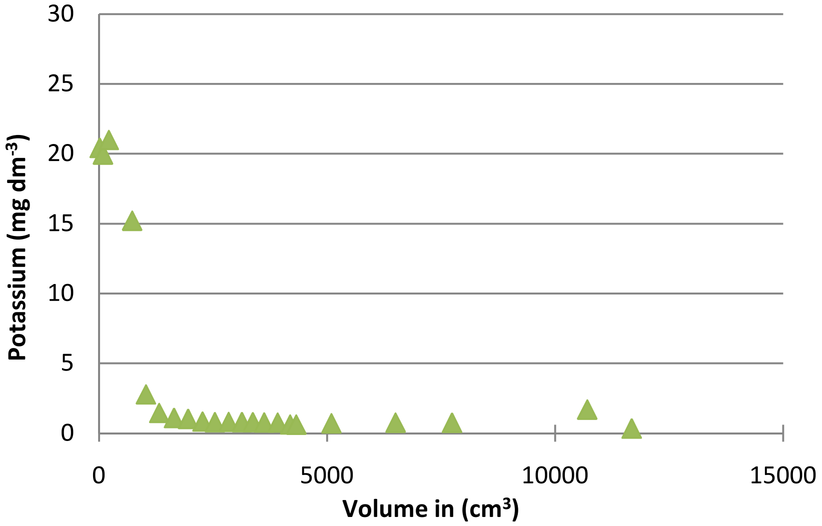


Figure 46. Release of potassium from 100 g ST sludge column by 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

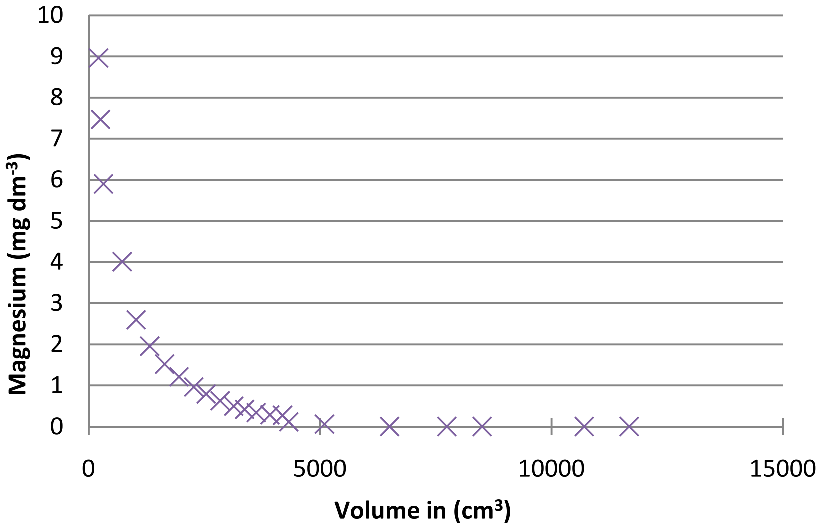


Figure 47. Release of magnesium from 100 g ST sludge column by 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

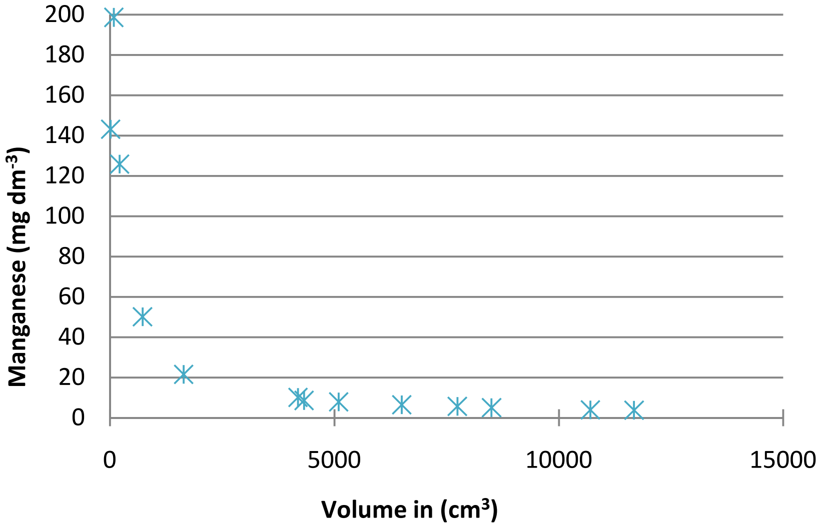


Figure 48. Release of manganese from 100 g ST sludge column by 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

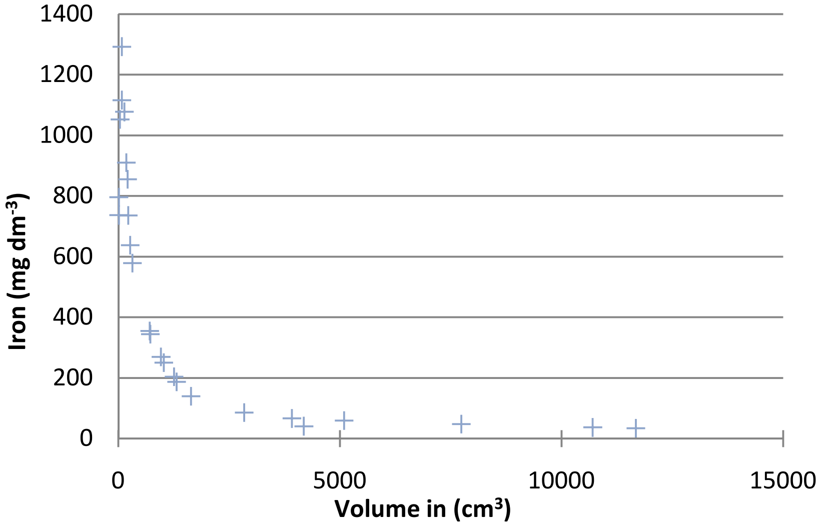


Figure 49. Release of iron from 100 g ST sludge column by 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

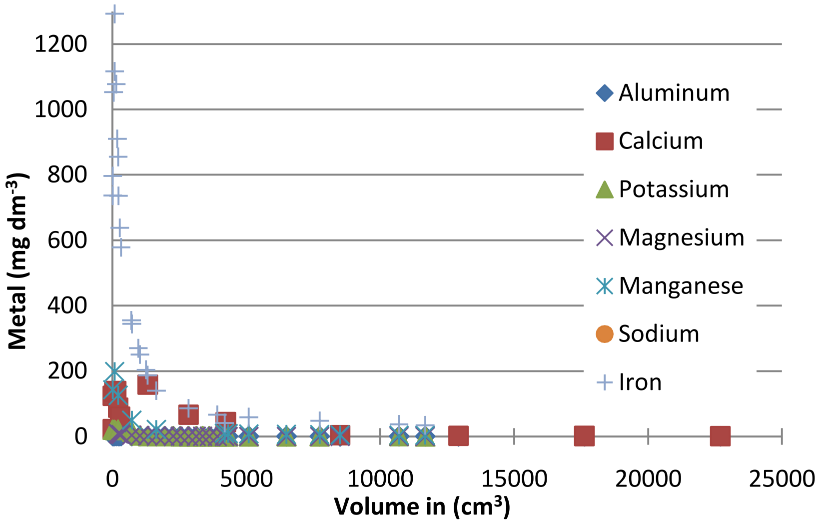


Figure 50. Release of metals from 100 g ST column by 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

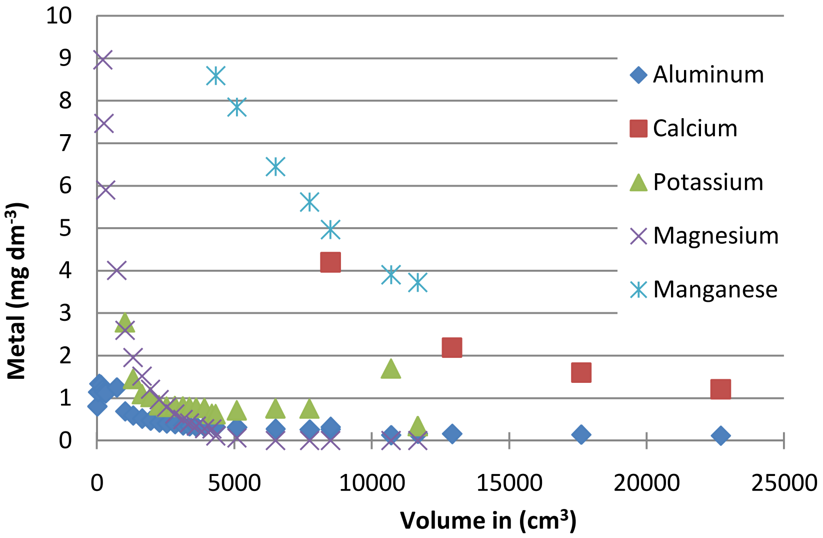


Figure 51. Release of metals from 100 g ST column by 0.1 mol dm^{-3} NaNO$_3$ electrolyte (expanded from Figure 50).

The results of metal release from the CE column by deionised water are shown in Figures 52 to 58 and summarised in Figures 59 and 60. The major metals released are calcium and magnesium with initial release concentrations of 130 mg dm^{-3} and 250 mg dm^{-3}, respectively. The release of calcium from calcite decreases until 2000 cm^3 (corresponding to 15.5 bed volumes) of DI water had been pumped through the column after which the release concentrations plateau to approximately 10 mg dm^{-3}. Magnesium is released rapidly within 200 cm^3 (correspond to 1.6 bed volumes) after which the release is insignificant. The released concentrations of aluminium (< 0.12 mg dm^{-3}), potassium (< 7 mg dm^{-3}), manganese (< 0.035 mg dm^{-3}), sodium (<5 mg dm^{-3}) and iron (< 0.3 mg dm^{-3}) are much lower than those of calcium and magnesium.

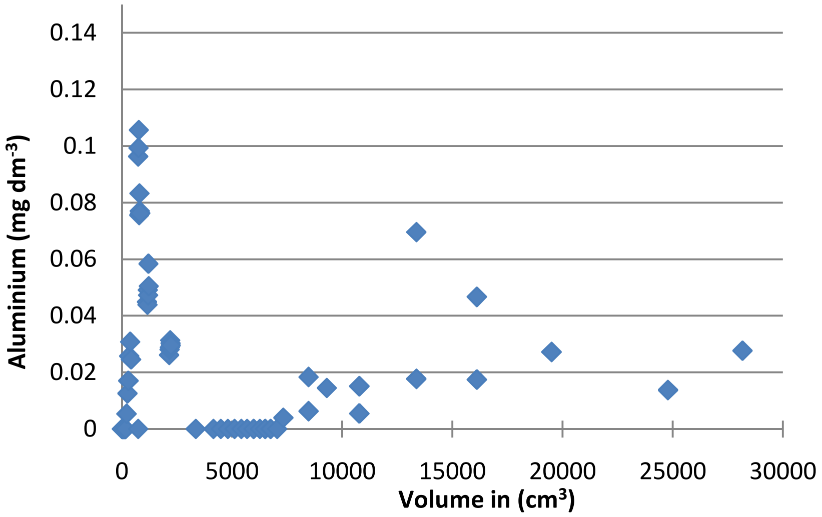


Figure 52. Release of aluminium from 100 g CE sludge column by deionised water.

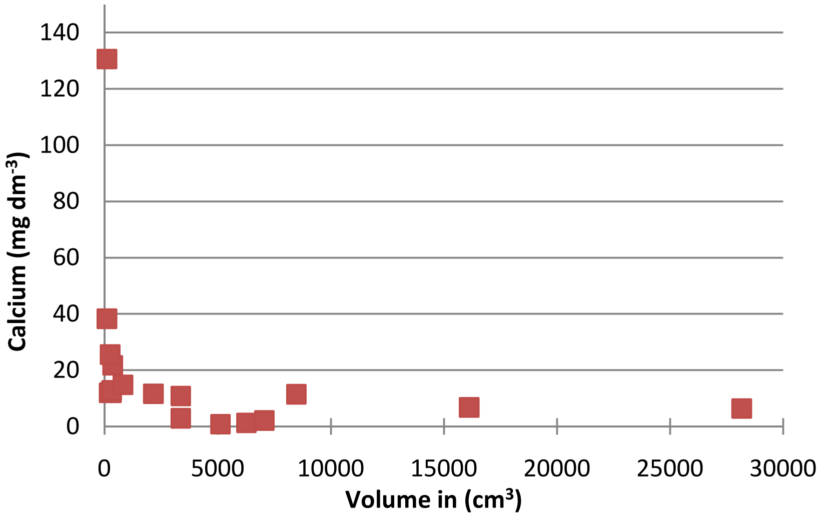


Figure 53. Release of calcium from 100 g CE sludge column by deionised water.

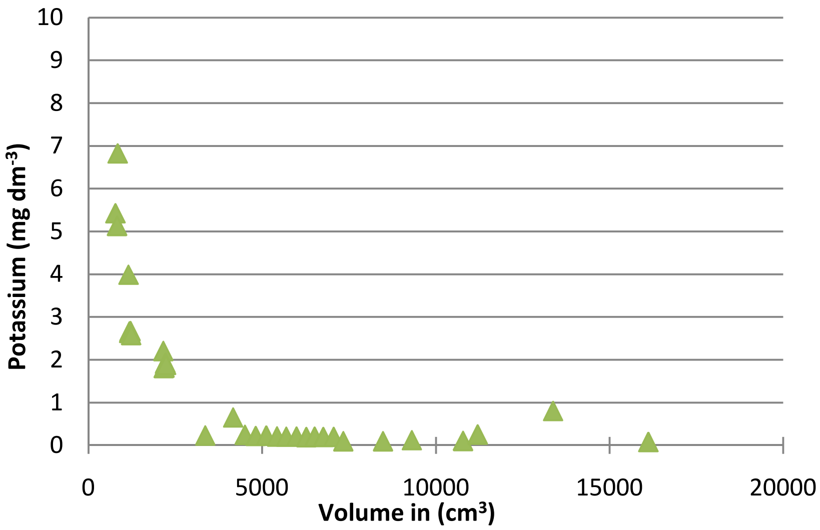


Figure 54. Release of potassium from 100 g CE sludge column by deionised water.

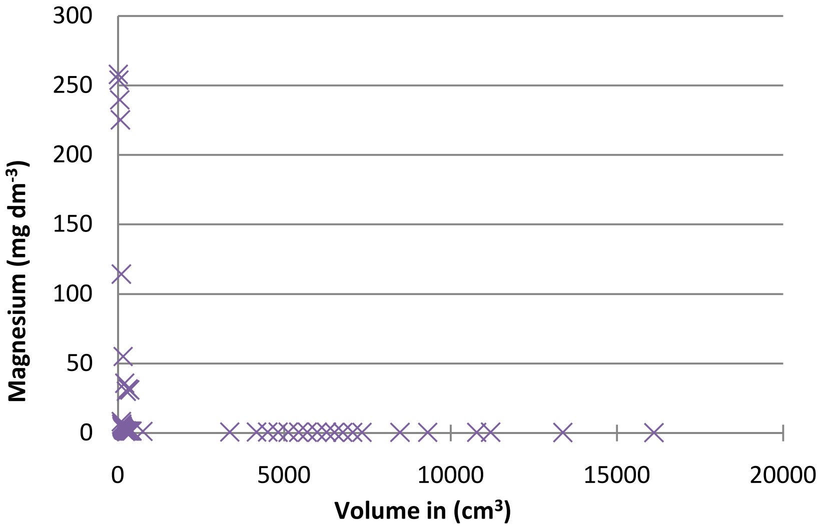


Figure 55. Release of magnesium from 100 g CE sludge column by deionised water.

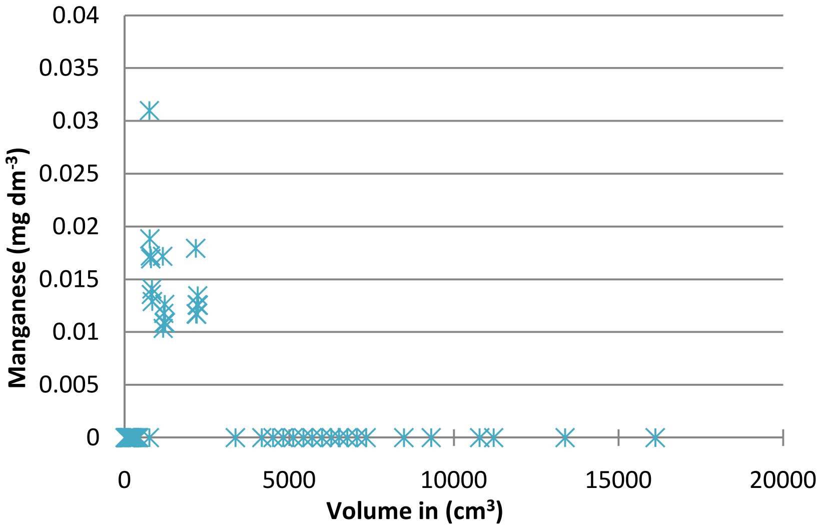


Figure 56. Release of manganese from 100 g CE sludge column by deionised water.

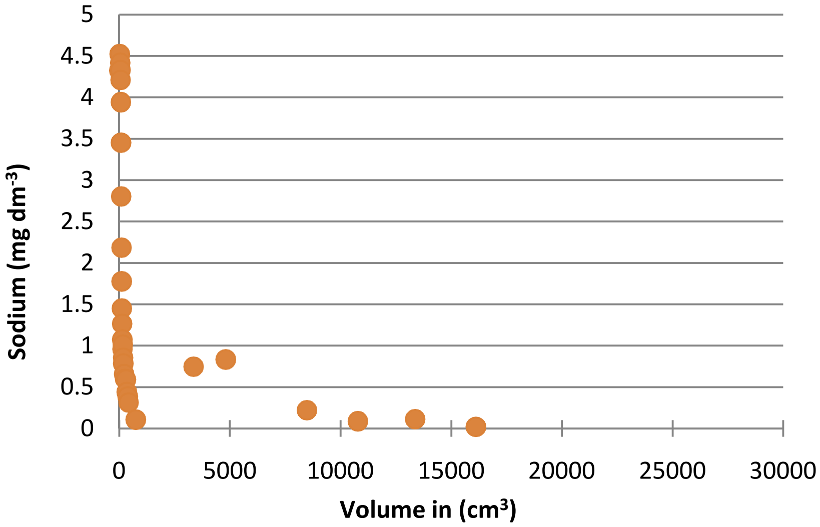


Figure 57. Release of sodium from 100 g CE sludge column by deionised water.

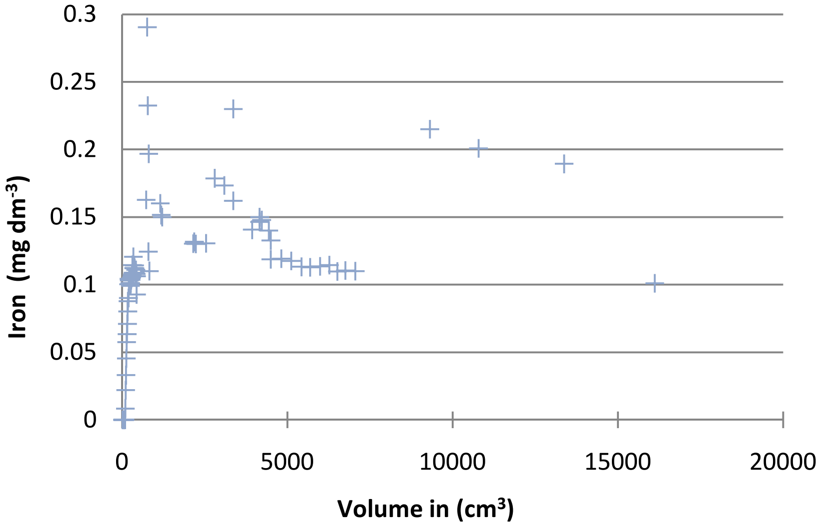


Figure 58. Release of iron from 100 g CE sludge column by deionised water.

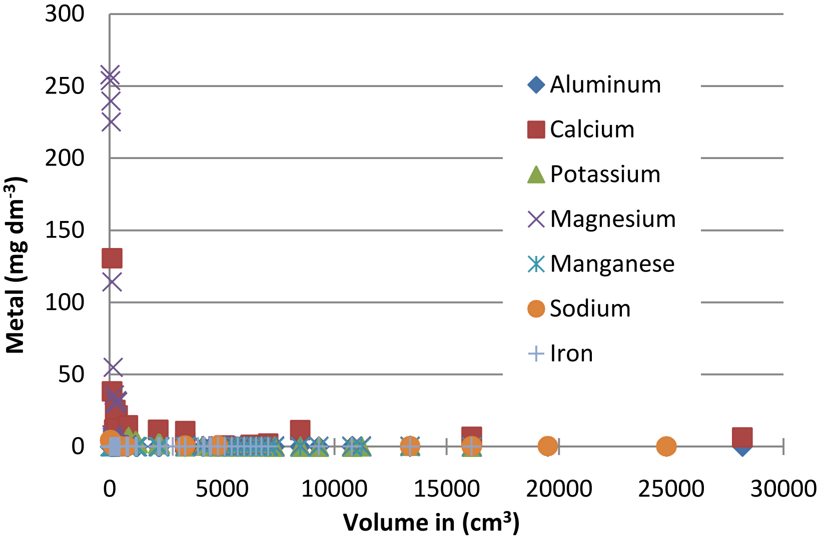


Figure 59. Release of metals from 100 g CE column by deionised water.

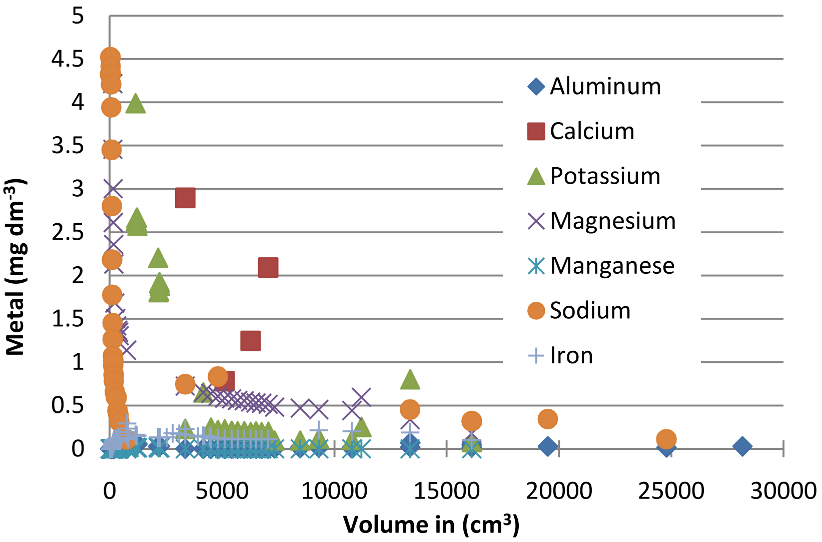


Figure 60. Release of metals from 100 g CE column by deionised water (expanded from Figure 59).

The trend of metal release from the CE column by 0.1 mol dm^{-3} $NaNO_3$ electrolyte (Figures 61 – 68) are similar to the previous CE results with the exception of magnesium release. These results show that calcium is the only major metal released (initially 140 mg dm^{-3}) whereas the releases of aluminium (< 0.1 mg dm^{-3}), potassium (< 6 mg dm^{-3}), magnesium (< 9 mg dm^{-3}), manganese (< 0.002 mg dm^{-3}), and iron (< 0.3 mg dm^{-3}) are significantly lower. The release of calcium plateaus (10 mg dm^{-3}) after 15 000 cm^3 of electrolyte had passed through the column

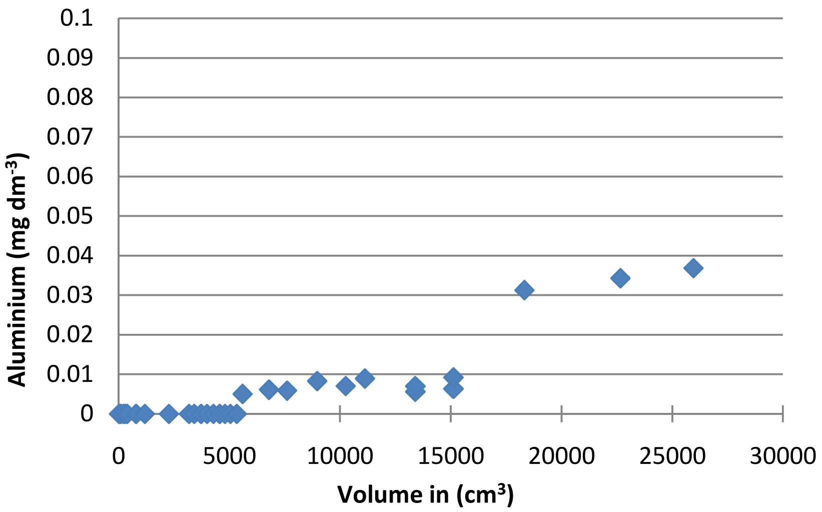


Figure 61. Release of aluminium from 100 g CE sludge column by 0.1 mol dm^{-3} $NaNO_3$ electrolyte.

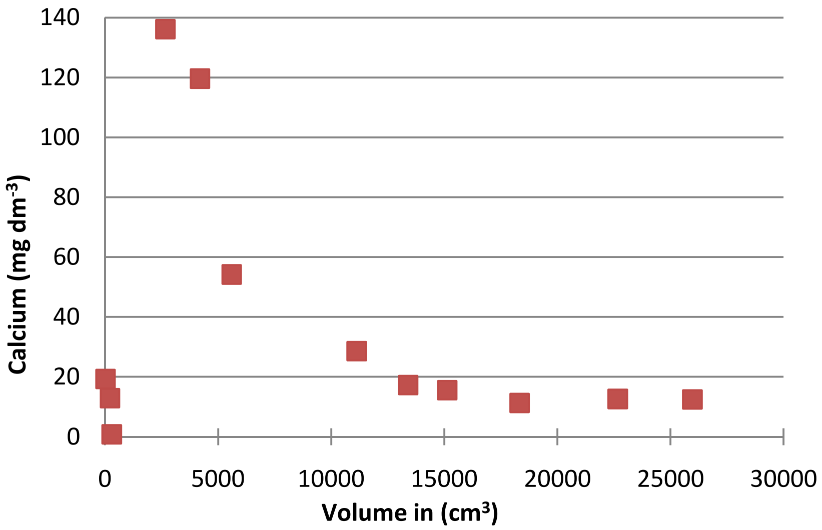


Figure 62. Release of calcium from 100 g CE sludge column by 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

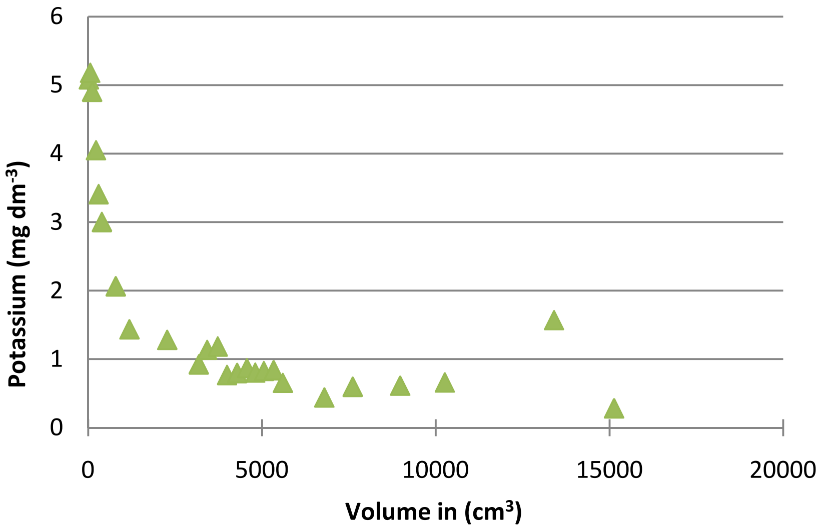


Figure 63. Release of potassium from 100 g CE sludge column by 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

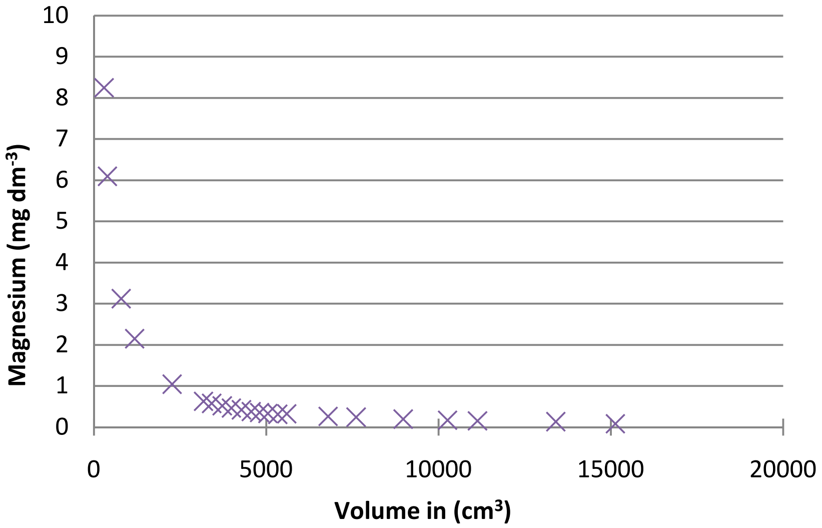


Figure 64. Release of magnesium from 100 g CE sludge column by 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

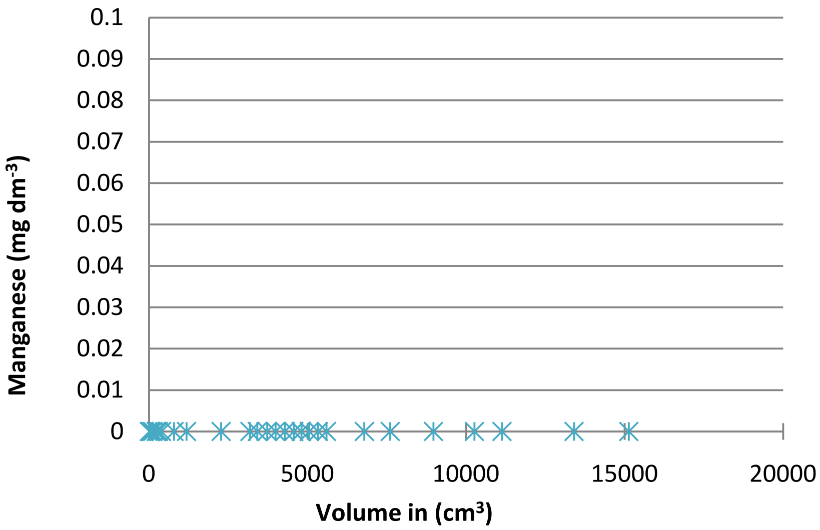


Figure 65. Release of manganese from 100 g CE sludge column by 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

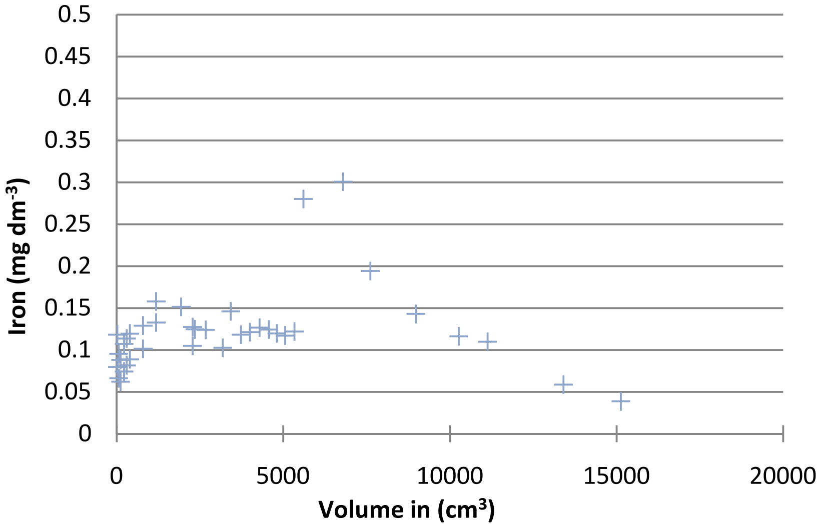


Figure 66. Release of iron from 100 g CE sludge column by 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

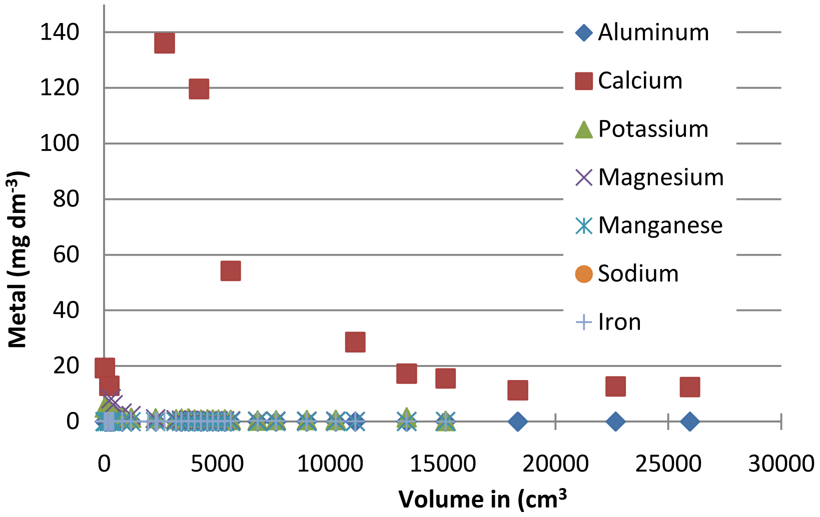


Figure 67. Release of metals from 100 g CE column by 0.1 mol dm^{-3} NaNO$_3$ electrolyte.

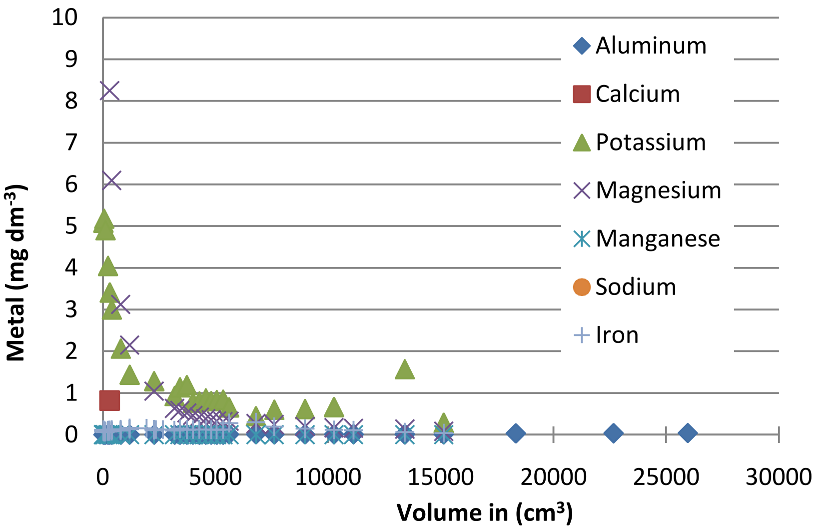


Figure 68. Release of metals from 100 g CE column by 0.1 mol dm^{-3} NaNO$_3$ electrolyte (expanded from Figure 67).

The releases of aluminium from ST and CE columns when passing deionised water and 0.1 mol dm^{-3} NaNO$_3$ electrolyte through the columns are shown in Figure 69. Initially, DI water releases significantly higher amount of aluminium (maximum of 80 mg dm^{-3}) compared to aluminium releases from CE columns (<0.2 mg dm^{-3}) or ST column by electrolyte (<0.2 mg dm^{-3}). Additionally, the releases of aluminium are higher from the ST columns compared to CE columns throughout the whole experiment (Figure 70).

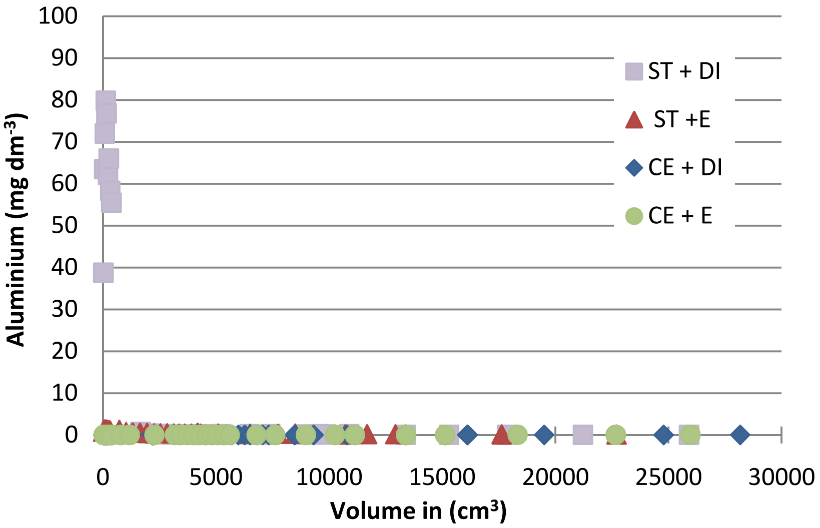


Figure 69. Aluminium releases from ST and CE columns by deionised water (DI) and 0.1 mol dm^{-3} NaNO$_3$ electrolyte (E).

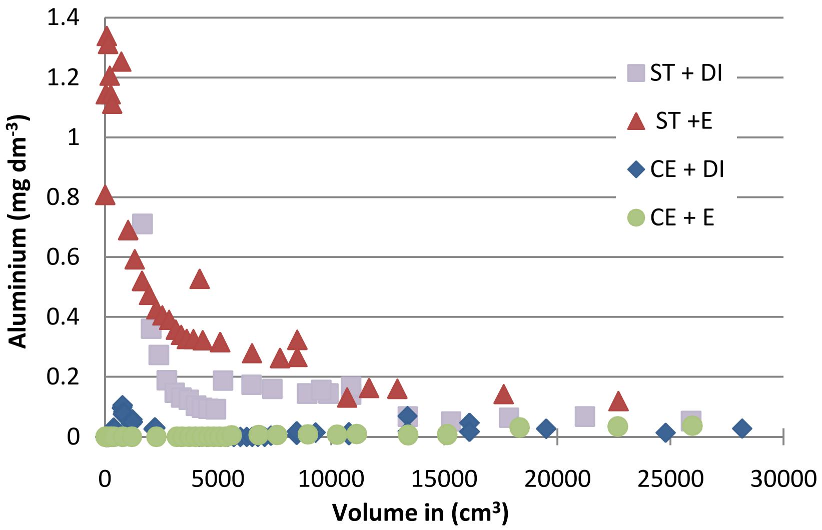


Figure 70. Aluminium releases from ST and CE columns by deionised water (DI) and 0.1 mol dm^{-3} NaNO$_3$ electrolyte (E) (expanded from Figure 69).

Figure 71 shows higher release of calcium by 0.1 mol dm^{-3} NaNO$_2$ electrolyte than by deionised water from both ST and CE columns. However, towards the end of the experiment (Figure 72) the release is highest from CE column by deionised water and electrolyte. This is most likely due to leaching of calcium from calcite present in the CE column.

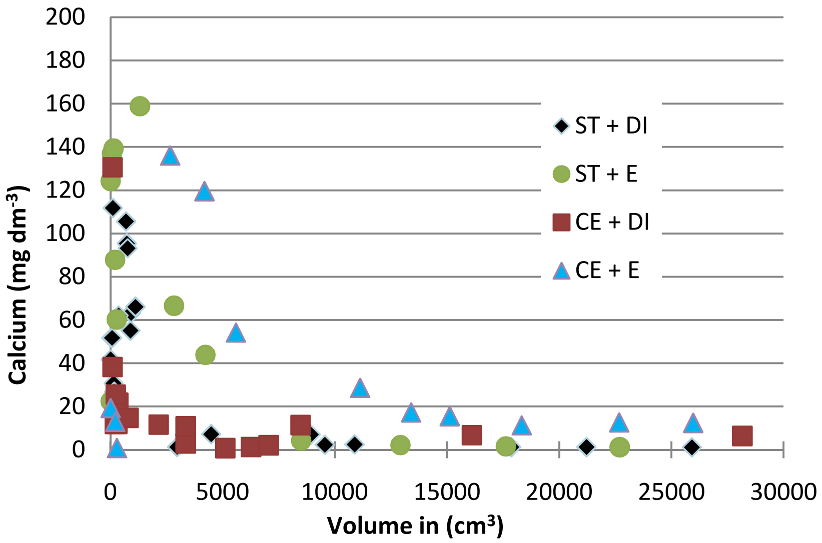


Figure 71. Calcium releases from ST and CE columns by deionised water (DI) and 0.1 mol dm^{-3} NaNO$_3$ electrolyte (E).

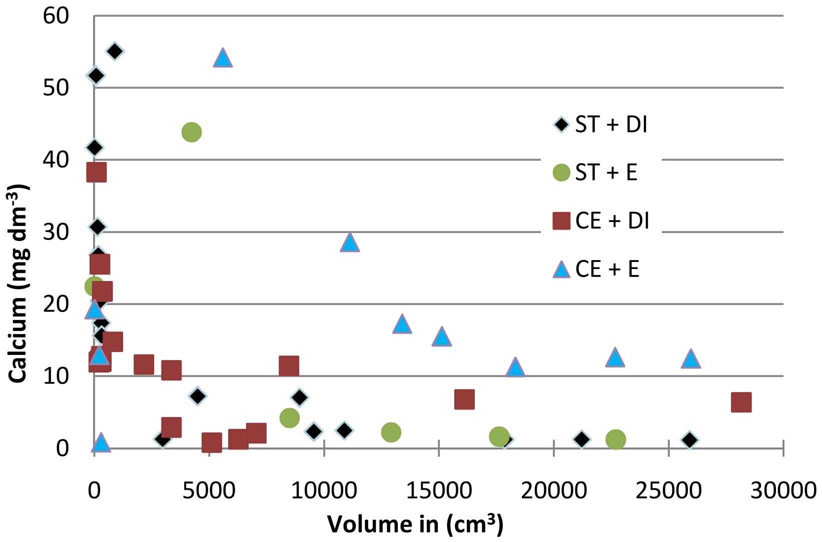


Figure 72. Calcium releases from ST and CE columns by deionised water (DI) and 0.1 mol dm^{-3} NaNO$_3$ electrolyte (E) (expanded from Figure 71).

Initial release of potassium (Figure 73) is highest from the ST column when eluting with deionised water but all releases are similarly low after passing 800 cm^3 of solutions through the columns (Figure 74).

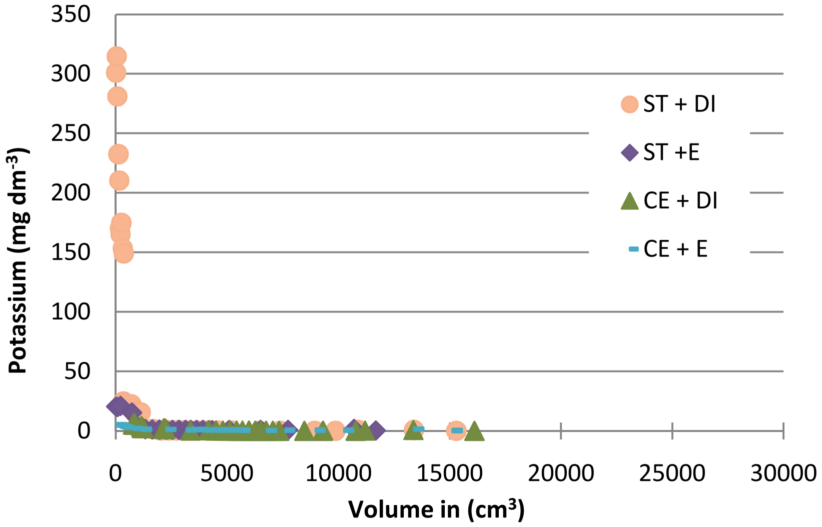


Figure 73. Potassium releases from ST and CE columns by deionised water (DI) and 0.1 mol dm^{-3} NaNO$_3$ electrolyte (E).

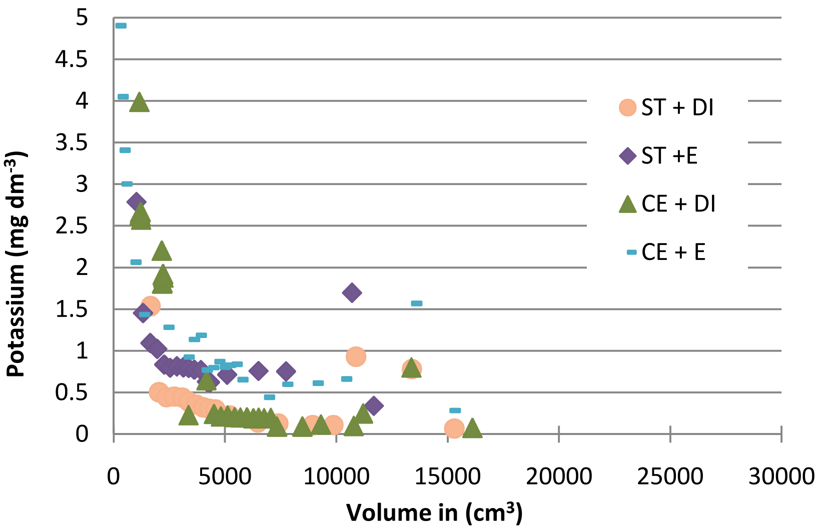


Figure 74. Potassium releases from ST and CE columns by deionised water (DI) and 0.1 mol dm^{-3} NaNO$_3$ electrolyte (E) (expanded from Figure 73).

The releases of magnesium from ST and CE columns are highest when eluted with deionised water (Figure 75) but the levels of release decrease quickly to low levels which are similar to those measured from elution with electrolyte (Figure 76).

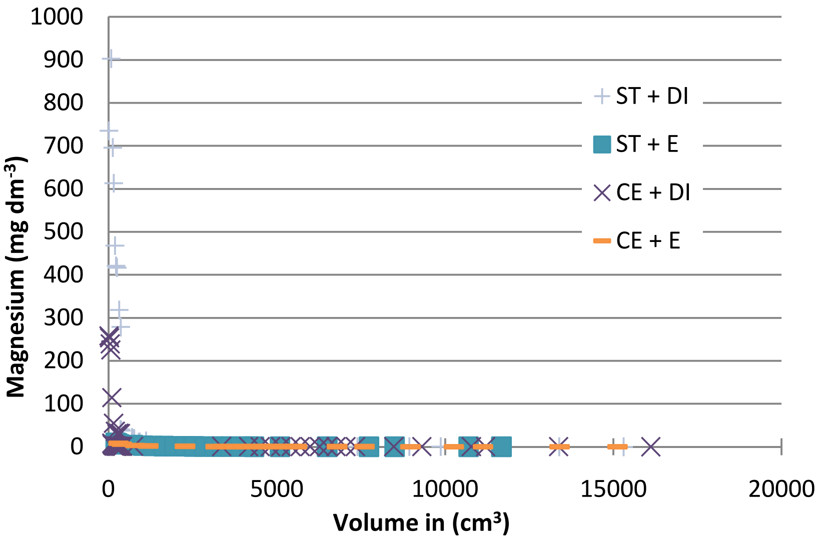


Figure 75. Magnesium releases from ST and CE columns by deionised water (DI) and 0.1 mol dm^{-3} NaNO$_3$ electrolyte (E).

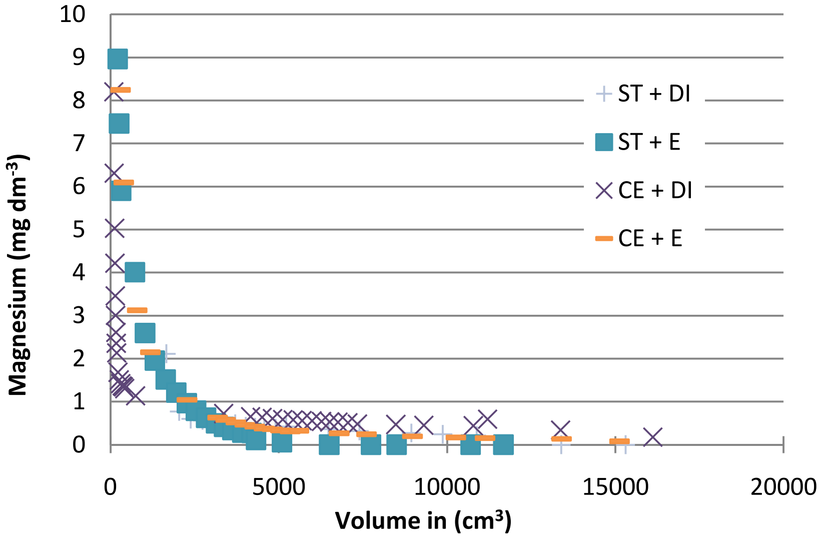


Figure 76. Magnesium releases from ST and CE columns by deionised water (DI) and 0.1 mol dm^{-3} NaNO$_3$ electrolyte (E) (expanded from Figure 75).

Figures 77 and 78 show that the CE sludge releases only minor amounts of magnesium whereas the quantities released are similar for both deionised and electrolyte elution from the ST column.

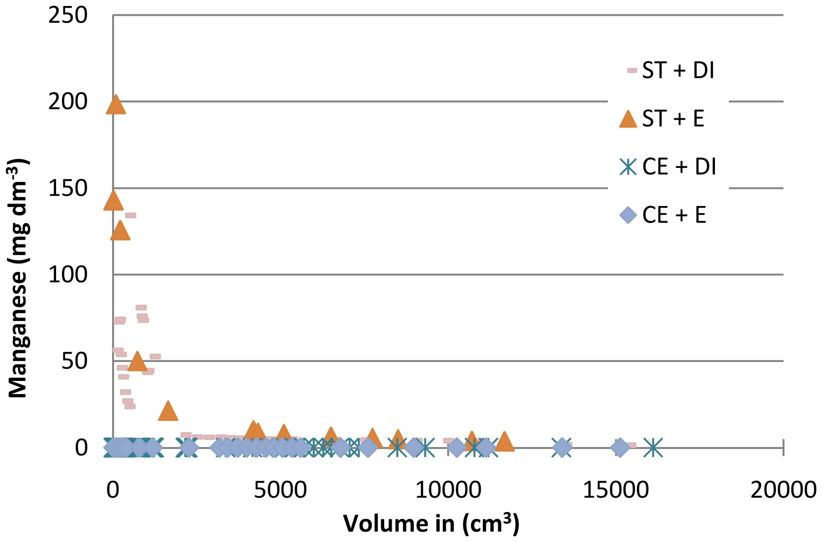


Figure 77. Manganese releases from ST and CE columns by deionised water (DI) and 0.1 mol dm^{-3} NaNO$_3$ electrolyte (E).

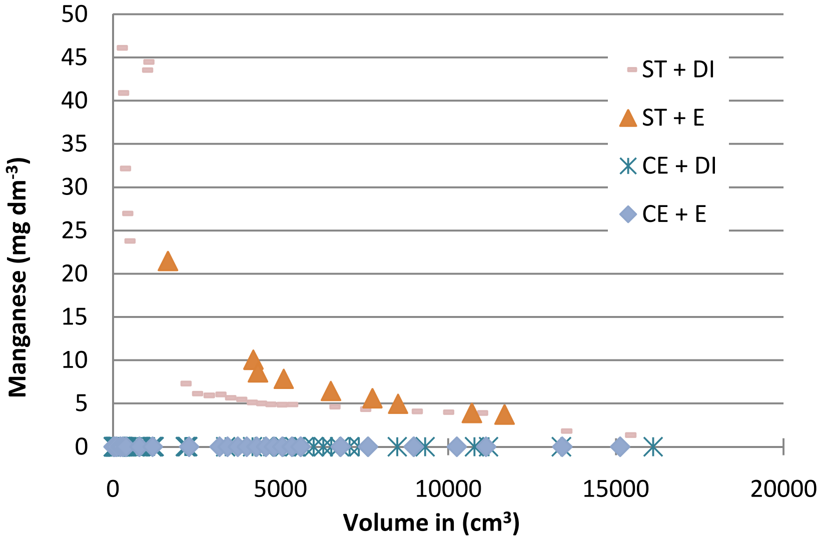


Figure 78. Manganese releases from ST and CE columns by deionised water (DI) and 0.1 mol dm^{-3} NaNO$_3$ electrolyte (E) (expanded from Figure 77).

Figure 79 shows that the initial release of sodium from ST column when eluting with deionised water is over 170 times higher than that compared to the CE column.

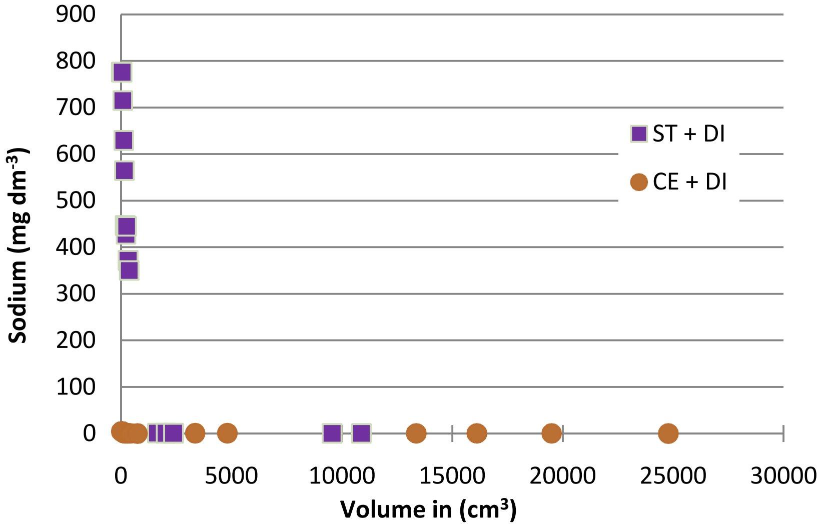


Figure 79. Sodium releases from ST and CE columns by deionised water (DI).

The major metal released from the ST sludge was unsurprisingly iron (Figure 80). In addition, the initial release was over 6 times (1300 mg dm^{-3}) higher when eluting with electrolyte compared to deionised water (200 mg dm^{-3}). Evidently, the sodium ions in the electrolyte have encouraged desorption of iron. Release of iron decreases exponentially but continues throughout the whole experiment. The releases of iron from the CE columns are insignificant compared to the releases by ST columns (Figure 81).

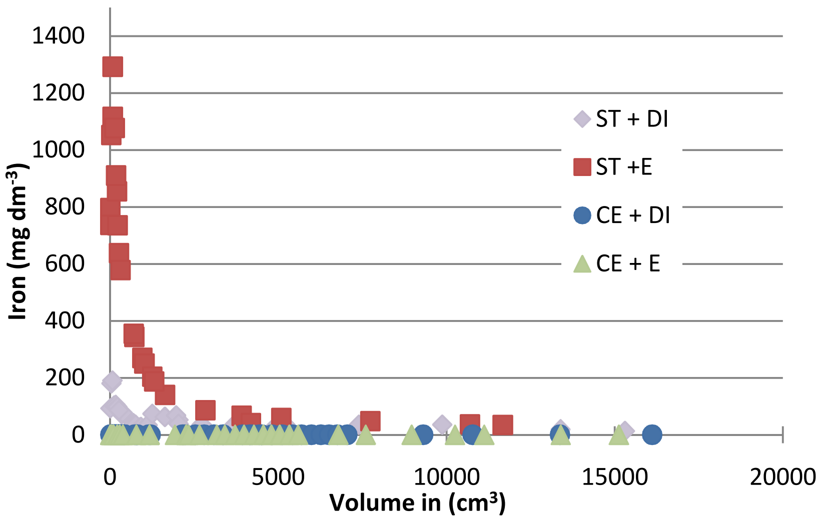


Figure 80. Iron releases from ST and CE columns by deionised water (DI) and by 0.1 mol dm^{-3} $NaNO_3$ electrolyte (E).

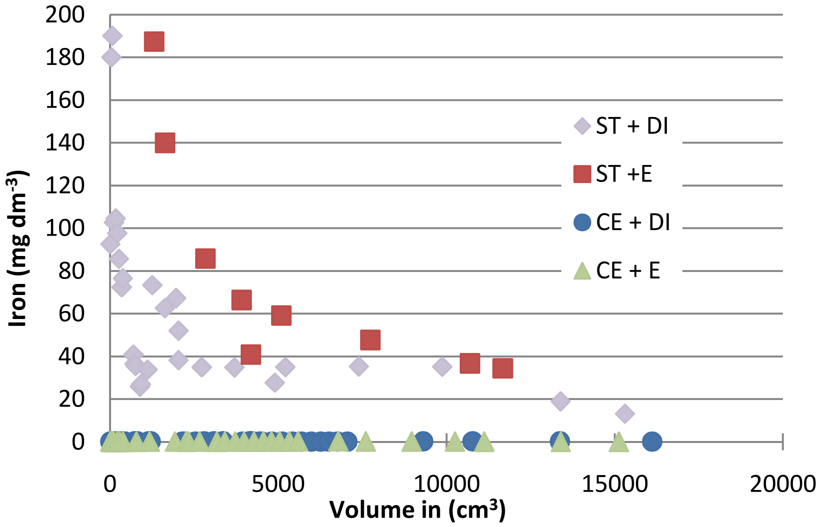


Figure 81. Iron releases from ST and CE columns by deionised water (DI) and 0.1 mol dm^{-3} $NaNO_3$ electrolyte (E) (expanded from Figure 80).

The overall results show that there were initial release of humic substances and metals from both ST and CE sludge columns with decreasing concentrations as more solution (DI or 0.1 mol dm^{-3} electrolyte) was introduced through the columns. However, much lower concentrations of metals were released from the CE sludge compared to ST sludge. In addition, both of the columns maintained their porosities and buffering capacities.

2.13 Summary

2.13.1 Characterisation of ST and CE sludges

Figure 82 summarises the iron, humic acid, inorganic matter, fulvic acid and insoluble organic matter contents of the ST and CE sludges. Almost half of the ST sludge was organic (49.7%) which contained 19% humic acid, 28% fulvic acid and 3% insoluble organic matter whereas the inorganic content (50.3%) mainly consisted of iron hydroxide (iron content 22.7 ± 3.3%) and other metals (e.g. Si, Ti, Al, Mn, Ca etc.) in significantly lower abundances. The organic matter of the ST sludge was aromatic, rich with carboxylic functional groups. The ST sludge exhibited resistance in pH change when base was added most likely due to release of iron which hydrolyses water and produces H^+ ions whereas no resistance was observed when acid was introduced to the mixture.

The CE sludge was mainly organic (82.7%) which contained 2% humic acid, 27% fulvic acid and 54% insoluble organic matter. The inorganic fraction (17.3%) mainly consisted of quartz (Si 87.2%), calcite (Ca 5.2%) and other metals (Ti, Al, Fe, Mn, Mg, K etc.) in lower abundances.

The organic fraction of CE sludge contained some OH and/or NH functionalities and aliphatic CH_2 and CH_3 groups but it was mainly aromatic rich with carboxylic groups. The CE sludge exhibited resistance in pH change when acid was added most likely due to release of CO_3^{2-} ions from calcite forming OH^-. However, no resistance in pH change was observed when base was introduced to the mixture.

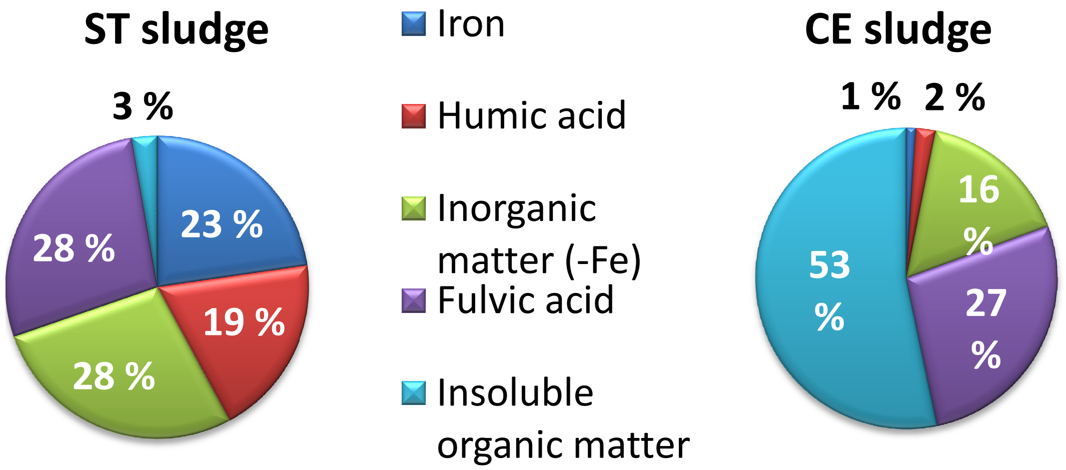


Figure 82. Iron, humic acid, inorganic matter, fulvic acid and insoluble organic matter contents of ST and CE sludge.

The values for the cation exchange capacities of ST and CE sludges were consistent when measured using UV or ICP-OES. The CEC of ST sludge was 10.1 ± 1.5 cmol$^+$ kg^{-1} when measured using UV-Vis and 8.9 ± 2.4 cmol$^+$ kg^{-1} measured using ICP-OES. The corresponding results for CE sludge were 20.6 ± 0.3 cmol$^+$ kg^{-1} and 24.2 ± 0.6 cmol$^+$ kg^{-1}.

The three major cations released from the ST sludge were potassium (13.7 ± 2.2 mg dm^{-3}), calcium (11.1 ± 1.3 mg dm^{-3}) and manganese (10.6 ± 1.4 mg dm^{-3}) whereas the three major cations released from CE sludge were magnesium (6.7 ± 0.7 mg dm^{-3}), potassium (3.5 ± 1.2 mg dm^{-3}) and calcium (1.5 ± 0.3 mg dm^{-3}).

2.13.2 Release of humic substances and metals from ST and CE columns

The release of humic substances and metals (Al, Ca, K, Mg, Mn, Na and Fe) from ST sludge in column studies was evident. Both deionised water and 0.1 mol dm^{-3} $NaNO_3$ electrolyte released significant amounts of organic matter and metals, especially iron. The releases of humic substances from ST columns by DI water and 0.1 mol dm^{-3} $NaNO_3$ electrolyte were estimated to be 0.8% of the column mass per month corresponding to 10.2% per year. In the case of CE sludge, releases of humic substances were significantly lower compared to the ST columns and the major elements released by deionised water were calcium and magnesium whereas there was only significant release of calcium by electrolyte. The releases of humic substances from CE columns were estimated to be 0.04% of the column mass per month and 0.5% per year by DI water and 0.07% per month and 0.8% per year by 0.1 mol dm^{-3} $NaNO_3$ electrolyte. The pH measurements of the collected fractions showed that the ST and CE sludges maintained their buffering capacities throughout the sampling periods ST sludge buffering the pH of the solutions towards pH 4-5 and CE sludge towards pH 7-8.

2.14 Conclusions

The ST and CE sludges under investigation were both rich in humic substances with high aromaticity. They also maintained their porosities and buffering capacities in column studies which introduce major advantages since the sludges are permeable and can buffer treated solutions. Both of the sludges exhibited release of metals and humic substances. Unfortunately, an estimated mass loss of 10% in a year may introduce a problem in long term use of ST sludge. However, the mass loss of CE sludge was insignificant (<1% in a year).
The difference in the release of humic substances from the ST and CE sludges may be explained by the significantly different volatilisation temperatures (450 ℃ for ST and 1050 ℃ for CE sludge) suggesting com pletely different characteristics of the organic matter in the sludges. As a conclusion it can be said that both of the sludges have potential to be commercialised remediation materials because of their organic content (suggesting efficient extraction of both metals and organic compounds), porosity, and buffering behaviour, if the solubility of the ST sludge can be overcome or if it is not of major concern.

CHAPTER 3

APPLICATION 1 - EXTRACTION OF ARSENIC, IRON AND URANIUM FROM INDUSTRIAL EFFLUENTS

CHAPTER 3 – APPLICATION 1 - EXTRACTION OF ARSENIC, IRON AND URANIUM FROM INDUSTRIAL EFFLUENTS

3.1 Introduction

White coloured kaolin (China Clay) is used in the paper, ceramics, paint, and rubber industries [53]. The clay often has a light brown colour due to impurities, mainly iron oxides, which affect its commercial value if present in excess [3,4]. The desired level of iron in the China Clay is less than 0.8% (w/w) [3]. Physical and chemical processes such as flotation, magnetic separation, and leaching carried out with Na_2SO_3, Cl_2, HCl, and dithionite have been used to remove the impurities [4]. In addition, in recent decades there has been an interest in finding alternative chemical processes which would be more efficient with respect to iron removal and more environmentally friendly [4]. Studies on the removal of iron by complexation or reduction using organic acids, such as oxalic, citric and ascorbic acids have been conducted [4]. The removal of colour (Fe^{3+} reduced to soluble Fe^{2+}) also releases other metals from the clay, such as arsenic and uranium. In some China Clay plants, the effluent produced after the colour removal is treated with iron precipitation to reduce metal concentrations in the discharged effluent.

3.1.1 Kaolin production

The name kaolin comes from a Chinese word “kauling” meaning “high ridge”, the name of a hill near Jauchau Fu, China, where kaolin was obtained centuries ago [54]. The most abundant mineral in China Clay is kaolinite whose structural formula is $Al_4(OH)_8[Si_4O_{10}]$ [54]. The structure of kaolinite consists of a single silica tetrahedral sheet and a single alumina octahedral sheet combined in a unit in which the tips of the silica tetrahedrons and one of the layers of the octahedral sheet form a layered structure (Figure 83) [54]. Kaolinite is a result of kaolinisation of granite [53], and it is one of the main weathering processes affecting granitic rocks in which Na-, Ca-, and K-feldspar minerals are attacked by water and carbon dioxide [55]. The idealised stoichiometry of the kaolinisation reaction for orthoclase ($KAlSi_3O_8$) and albite ($NaAlSi_3O_8$) may be written as follows [55].

$4MeAlSi_3O_8 + 4H_2O + 2\ CO_2 \rightarrow Al_4(OH)_8[Si_4O_{10}] + 2\ Me_2CO_3 + 8SiO$ (3.1)
Where Me = K, Na

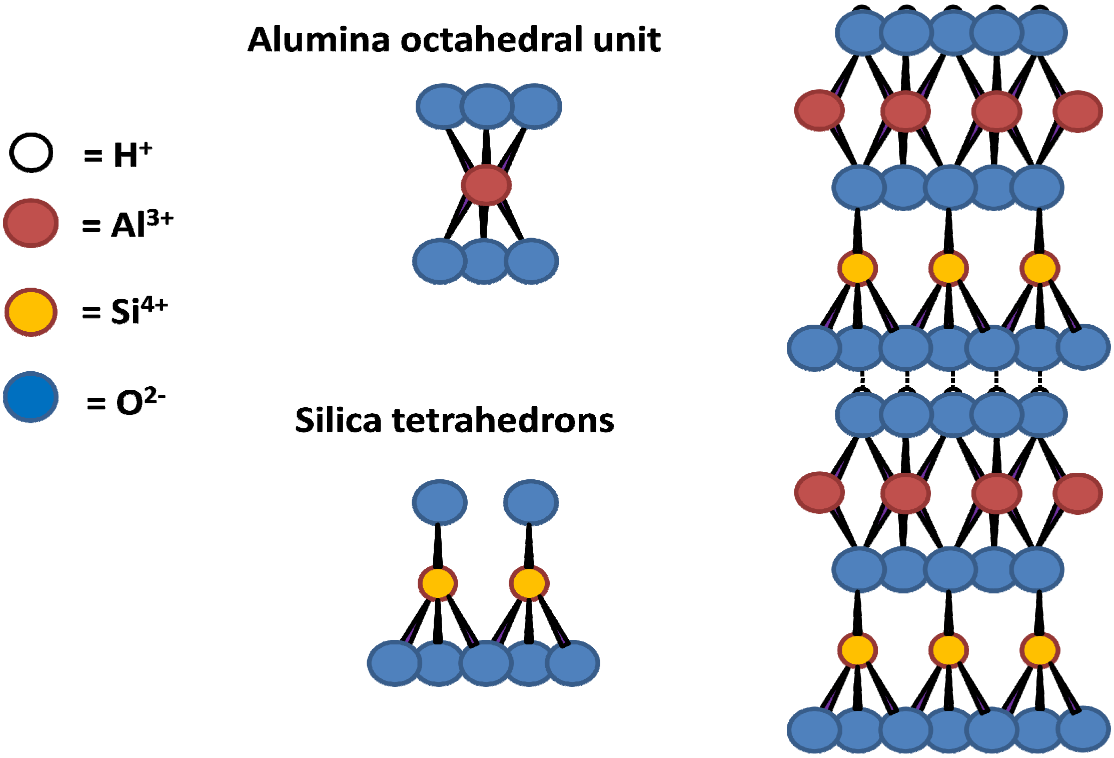


Figure 83. Schematic pictures of alumina octahedral unit and silica tetrahedrons as building blocks of kaolinite.

Mining of China Clay is often carried out by hydraulic washing of the kaolinised granite [53]. The first stage of the processing of the mined material is to remove coarse minerals that are also liberated with the clay [53]. The coarsest fraction (> 250 µm) consists mainly of quartz, mica, and un-kaolinised feldspar, and also other minerals, commonly tourmaline, topaz, and fluorite [53]. The coarse fraction is conveyed to waste tips and the finer fraction (< 250 µm) containing kaolin is pumped to a processing plant [53]. The fine-grained quartz, micas, and accessory minerals are separated from the kaolin by hydrocyclones [53].

The separated, light brown coloured kaolin is pumped to a China Clay processing plant for colour removal. An example treatment scheme is presented in Figure 84. First, the raw kaolin slurry is pumped into a Stage I reactor in which the pH is raised by addition of re-circulated slurry from the base of the clarifier chamber [56]. The suspension is mixed and the neutralised mixture gravitates into the Stage II reactor where air is introduced to ensure that the iron present is fully oxidised. The pH is raised again to a set-point of 8.0 by addition of sodium hydroxide [56]. The mixture flows into an in-line mixer where a flocculant (for example cationic polyelectrolyte) is added [56]. The mixture is fully mixed and then it flows into the clarifier chamber in which a rake directs settled solids to the clarifier hopper. The thickened solids from the clarifier are either re-circulated to the Stage I reactor or removed from the system (white coloured China Clay) [56]. The suspended solids content and pH of the effluent are monitored before transportation to an effluent treatment plant for metal removal or discharge [56].

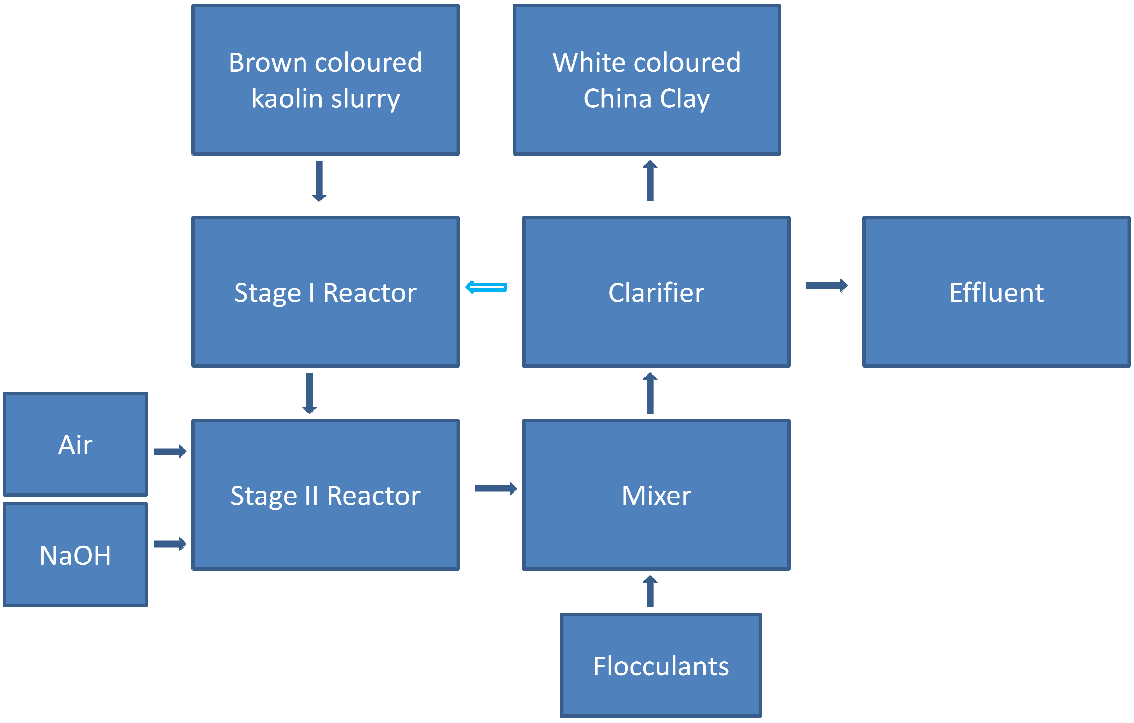


Figure 84. Example of a kaolin purification scheme in a China Clay plant.

The most common approach in chemical treatment of industrial waste waters is to produce an insoluble metal precipitate [57]. Since the salts of many heavy metals (such as hydroxides and sulphides) have very low solubilities in water, the contaminants are removed by adjusting the pH and adding the relevant anion, thus the metal precipitates out of solution [57]. Nevertheless, metal hydroxides have different solubility curves and some metals exhibit a tendency to re-dissolve at elevated pH [57]. The presence of complexing agents, such as cyanide, phosphates and ammonia, and the difference in the solubilities of the different metal hydroxides or sulphides with pH, often causes the final selection of pH to be a compromise [57]. The removal of the precipitate can be accomplished, for example, by settlement or by sand filtration [57]. There are several treatment processes that can be applied to the effluent produced in a China Clay plant such as iron precipitation or pH adjustment by liming.

The China Clay deposits in Cornwall and Devon have been mined for almost 250 years [58]. In the early 1960's, the output of China Clay in the UK was around 1.5 million tonnes and 1990 doubled to 3 million tonnes [59]. Mining produces approximately 9 tonnes of waste for one tonne of clay [59].

3.1.2 Aim and outline of this chapter

This study concentrates on removal of arsenic, iron and uranium from effluents originating from two China Clay plants in south-west England, designated here as Plant P and Plant R. Figure 85 shows the flow chart of the treatment processes in those plants. In Plant P, the effluent is treated by adding sodium carbonate and calcium hydroxide to the raw effluent (A). The addition of sodium carbonate increases the pH to 4-5 and thus some metals (e.g. iron) are precipitated. The resultant solution is designated as effluent B. In plant R, the effluent (C) is treated by iron precipitation and the majority of metals are co-precipitated resulting in cleared effluent D.

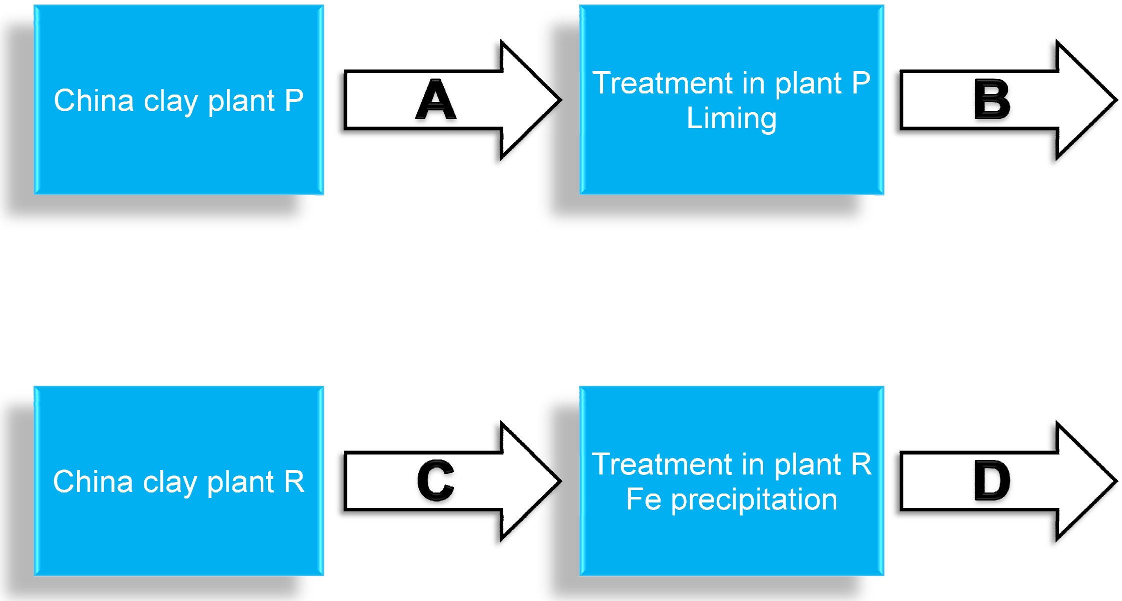


Figure 85. China clay Plants in P and R and their effluent treatment in the treatment plant. A represents the un-treated P effluent, B treated P effluent, C un-treated R effluent and D treated R effluent.

The objective of this work is to investigate the use of ST and CE sludges to remove arsenic, iron, and uranium from the Plant P and R effluents A, B and C. Thus, treatment with a sludge could replace the currently existing cleaning processes for effluent A and C, or further purify effluent B. In this chapter, the effluents A-C received from Plants P and R are named;

- A → un-treated Plant P effluent
- B → treated Plant P effluent
- C → un-treated Plant R effluent

Treated Plant R effluent (D) was not included in this study because iron precipitation is a very efficient method in removing metals. Nevertheless, the pH of the treated effluent is low and requires addition of alkali before it can be discharged.

Arsenic, iron and uranium are of interest because arsenic is a toxic element, iron is a major element in the effluent as well as a toxic metal where present in excess, and uranium is both toxic and radioactive. The current effluent treatments can cause the precipitates to clog pipelines and thus a process in which the effluent flows through the treatment zone, of CE or ST sludge, would be advantageous. In addition, both sludges exhibit buffering properties thus treated effluent could be discharged without further treatment.

The experimental work was started by determining the release of iron from both ST and CE sludges into deionised water because ST sludge contains a significant amount of iron (23%) which might be released from the material. In addition, the release of arsenic, iron and uranium into electrolyte was also measured. The elemental compositions of the effluents were determined using ICP-OES, ICP-MS and IC and their ionic strengths modelled using the JCHESS programme [7]. The molarity of background electrolyte was chosen according to the modelling results, and later the extraction capacities for arsenic, iron and uranium from electrolyte were compared to the experiments carried out in effluents. The reversibility of extraction i.e. the release from sludge is an important factor and thus studies on reversibility of the extraction for arsenic, iron and uranium in electrolyte were carried out. The JCHESS programme [7] was also used to determine the speciation of arsenic, iron and uranium in electrolyte and effluents in atmospheric conditions (0.4 V Eh and presence of $CO_{2(q)}$). The kinetics of the extraction process in electrolyte and effluents were determined on time intervals from 1 minute to 60 minutes with increasing amounts of solid matter. Column experiments were carried out to simulate extraction in a dynamic flow-through system. A schematic representation of experimental work for effluents and electrolyte is shown in Figure 86.

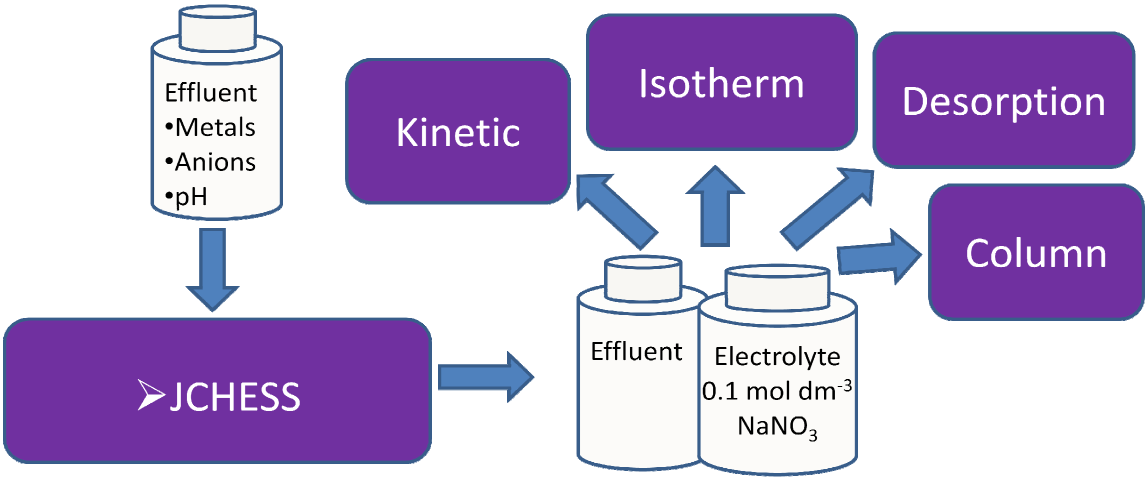


Figure 86. Schematic representation of experimental work for effluents and electrolyte in Chapter 3.

3.2 Reagents and instrumentation

3.2.1 Reagents

All reagents which have been used in this chapter are listed along with their purities and suppliers in Table 9. A Millipore Corporation™ cartridge purification system was used to produce deionised water (18 MΩ) for the preparation of solutions. All reagents were readily water soluble except arsenic trioxide which was first dissolved into concentrated sodium hydroxide and then the pH was adjusted to 3 using 1 mol dm^{-3} H_2SO_4. Arsenic trioxide was used in all experiments except for the isotherm experiments in electrolyte in which arsenic trichloride in acid was used. The samples were acidified (0.5% nitric acid) prior to ICP-OES and ICP-MS measurements unless measured immediately after they were prepared.

Table 9. Reagents, their purities and suppliers used in Chapter 3

Reagent	***Purity***	***Supplier***
$AsCl_3$	Standard in acid	BDH Chemicals
As_2O_3	99.999%	Acros
$Fe(NO_3)_3 \bullet 9H_2O$	Reagent grade	Fisher
Na_2CO_3	Standard 99.95-100.05%	Aldrich
$NaNO_3$	99+%	Acros
$UO_2(NO_3)_2 \bullet 6H_2O$	98%	BDH Chemicals
28 element standard	Multielement standard	Fisher
TraceCert standard	Multielement standard	Fluka
HNO_3 for acidification	Trace element grade	Fisher

3.2.2 Instrumentation

Elemental analyses were carried out using a Thermo Fisher's iCAP 6000 Series ICP-OES with ASX-520 autosampler or an Agilent Technologies' 7700 Series ICP-MS with ASX-520 autosampler unless samples were sent to the National Laboratory Service where anion concentrations were also measured using ion chromatography. Argon was used as a carrier gas in ICP-OES and ICP-MS measurements. The mineral compositions were determined using D8 Advice powder X-ray diffraction (XRD) manufactured by Bruker. The UV-readings were carried out using a Varian 50 Bio UV-visible spectrophotometer at room temperature in 1 cm quartz cells. pH was measured at room temperature using Jenway or Orion pH meters.

3.3 Characterisation of the un-treated and treated P and un-treated R effluents

The industrial effluents received from Plant P (15) and Plant R (2) China Clay plants were numbered as follows according to their order of arrival:

- Treated Plant P 1-14
- Un-treated Plant P 15
- Un-treated Plant R 1-2

The effluents were characterised prior to the experiments. The samples were visually observed (colour, transparency) and their pH was measured three times at room temperature using a pH meter. All the effluents contained solids which were separated by filtration (treated P, 30 kD Millipore cellulose membrane) and the mineral compositions of the solids were determined using XRD. The elemental compositions of un-treated Plant P effluent (15), treated Plant P effluents (13-14) and un-treated Plant R effluents (1-2) were measured using ICP-MS and ICP-OES. The anions were determined using ion chromatography (IC). The liming process in the Plant P effluent processing plant was mimicked by adjusting the pH of the un-treated Plant P effluent (15) to 5 using sodium carbonate. The elemental composition of treated Plant P effluent (15b) was determined immediately after the treatment.

The pH of the un-treated Plant P effluent (15) was 3.0 and the average pH of the treated Plant P effluents (1-14) was 5.3 ± 0.5 thus the “liming” had increased the pH from 3 to 5. The average pH of the Plant R effluents (1-2) was 2.7 ±0.2. The results show that the effluents transported from the China Clay plant are strongly acidic (pH 3).

All three effluents contained white solids (Figure 87). The brownish colour of the solid in the treated Plant P effluent (B) is due to precipitated iron. The XRD results showed that the solids were mainly kaolinite, quartz, and possibly feldspar. The results are in good agreement with the production of China Clay in which kaolin is separated from kaolinised granite thus fine grained kaolinite and quartz has been carried through the production process.

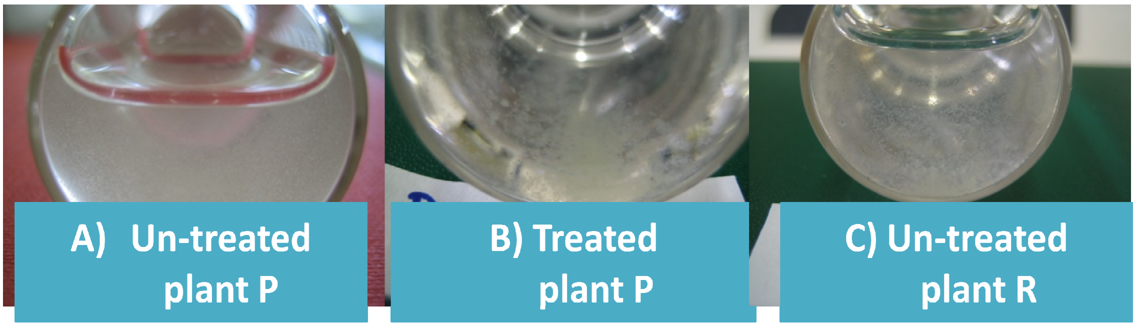


Figure 87. Examples of un-treated (A) and treated (B) P effluents and un-treated (C) R effluent.

The elemental compositions of the effluents are presented in Table 10. The elements under investigation (As, Fe and U) are underlined. The arsenic concentrations of un-treated and treated Plant P effluents were under the quantification limits of the analytical methods used at the time of measurement (1, 5 and 6 µg dm^{-3}). The arsenic concentration in Plant R effluents 1 and 2 were 132 and 24 µg dm^{-3}, respectively. The iron concentrations in the Plant R effluents (65.4 and 74.8 mg dm^{-3}) were significantly higher than in the un-treated Plant P effluent (5.7 mg dm^{-3}). The iron concentrations in the treated Plant P effluents 13-14 were lower than in un-treated Plant P effluent 15 due to iron precipitation as iron hydroxide with increasing pH from 3 to 5. The uranium concentrations in all of the effluents were at a level of 20 to 80 µg dm^{-3}.

Table 10. The elemental analysis of Plant P (13-15b) and Plant R (1-2) effluents. The results are presented in mg dm^{-3}

Analyte	*P 13 Treated**	*P 14 Treated**	*P 15*	*P 15b Treated*	*R 1**	*R 2**
Al	N/A	3.740	7.582	7.328	N/A	9.950
Ca	41.4	N/A	N/A	24.7	42.4	39.3
Fe	0.123	0.383	5.7	4.6	65.4	74.8
Mg	13.6	N/A	18.4	19.6	26.9	28.6
Mn	0.453	N/A	0.702	0.693	0.849	1.056
K	18.7	N/A	21.0	22.3	59.5	46.1
Na	282.0	N/A	258.8	315.4	483.0	276.9
N	2.610	N/A	N/A	N/A	3.04	N/A
Cl	23.2	N/A	N/A	N/A	80.9	N/A
NO_2^-	0.048	N/A	N/A	N/A	< 0.004	N/A
PO_4^{3-}	< 0.020	N/A	N/A	N/A	1.13	N/A
SO_4^{2-}	732.0	N/A	N/A	N/A	1610.0	N/A
NO_3^-	2.56	N/A	N/A	N/A	< 3.04	N/A
Sb	N/A	<0.005	N/A	N/A	N/A	0.009
As	< 0.001	<0.005	<0.006	<0.006	0.132	0.024
Ba	N/A	N/A	0.035	0.035	N/A	0.028
Be	N/A	<0.005	N/A	N/A	N/A	0.006
Cd	< 0.001	<0.001	N/A	N/A	< 0.001	<0.001
Co	N/A	0.015	0.039	0.039	N/A	0.043
Cu	0.064	0.182	0.351	0.0336	0.255	0.170
Cr	< 0.001	<0.003	0.016	0.014	< 0.005	0.009
Pb	< 0.001	<0.001	0.023	0.052	<0.001	<0.001
Li	N/A	N/A	0.187	0.185	N/A	0.461
Hg	N/A	<0.020	N/A	N/A	N/A	<0.020
Mo	N/A	<0.015	N/A	N/A	N/A	<0.015
Ni	0.009	0.008	<0.012	<0.012	0.022	0.019

* analysed by National Laboratory Service, N/A: not analysed

Table 10. The elemental analysis of Plant P (13-15b) and Plant R (1-2) effluents. The results are presented in mg dm^{-3} (continued)

Analyte	*P 13 Treated**	*P 14 Treated**	*P 15*	*P 15b Treated*	*R 1**	*R 2**
Se	N/A	<0.005	N/A	N/A	N/A	<0.005
Tl	N/A	<0.005	N/A	N/A	N/A	<0.005
Sn	N/A	<0.0125	N/A	N/A	N/A	<0.0125
Ti	N/A	0.0128	N/A	N/A	N/A	0.0168
U	0.019	0.025	0.079	0.079	0.019	0.019
V	N/A	<0.010	N/A	N/A	N/A	0.0178
Zn	0.124	0.195	0.265	0.261	0.210	0.158

* analysed by National Laboratory Service, N/A: not analysed

3.4 Ionic strength in the P and R effluents

The compositions of the effluents are more diverse than that of a background electrolyte which can be used as a simplified solution. The extraction capacities for arsenic, iron and uranium were determined both in an electrolyte and in the effluents, thus the extraction capacities can be compared between a simple solution and real solutions of similar ionic strength.

The ionic strengths of the un-treated and treated Plant P and the un-treated Plant R effluents were calculated using JCHESS 2.0 programme [7]. The major aqueous species of the effluents were inserted into the programme according to the characterisation results (see Table 10). The calculated ionic strength in the un-treated Plant P effluent was 0.009, in the treated Plant P effluent 0.023, and in the un-treated Plant R effluent 0.096. The arsenic, iron and uranium extraction studies of were carried out in 0.1 mol dm^{-3} $NaNO_3$ background electrolyte which has similar ionic strength as un-treated Plant R effluent since 0.1 mol dm^{-3} $NaNO_3$ has the ionic strength of 0.1.

3.5 Speciation of arsenic, iron and uranium in 0.1 mol dm^{-3} NaNO$_3$ electrolyte, un-treated Plant P and Plant R effluents

Speciation of metals is an important factor in their behaviour because metals can be present in a solution as free ions or they can form complexes with other species. The speciation changes as a function of pH, Eh and other species present. In this study, the speciation of arsenic, iron and uranium in 0.1 mol dm^{-3} $NaNO_3$ electrolyte, un-treated Plant P, treated Plant P, and Plant R effluents were determined using the JCHESS 2.0 programme [7] between the pH range 2 to 10. The speciation modelling was started by determining the solubility of arsenic, iron and uranium as a function of pH.

3.5.1 Solubility of arsenic, iron and uranium as a function of pH

The solubilities of arsenic, iron and uranium were determined as a function of pH at atmospheric conditions (Eh 0.4 V and presence of CO_2). Data that were inserted in the JCHESS programme are shown in Table 11. The speciation studies were carried out separately for each element (As, Fe, U) at the pH, Eh and atmospheric $CO_{2(g)}$ shown. The atmospheric carbon dioxide is shown as fugacity (dimensionless).

Table 11. Original data inserted into the JCHESS programme when modelling the solubility of arsenic, iron and uranium

Variable/species	
pH	3
Eh	0.4 V
$CO_{2(g)}$	0.000316*
As	0.1 mg dm^{-3}
Fe^{3+}	0.1 mg dm^{-3}
UO_2^{2+}	0.1 mg dm^{-3}

*dimensionless

The solubility and speciation results for arsenic (Figure 88) show that the main species present are $As(OH)_{3(aq)}$ and $HAsO_{2(aq)}$ until pH 9 above which arsenic is mainly present as AsO_2^- and $H_2AsO_3^-$. Also $HAsO_4^{2-}$, $H_3AsO_{4(aq)}$ and AsO_2OH^{2-} species are present but at lower concentration. It can be concluded that arsenic is soluble at the pH 2 to 10.

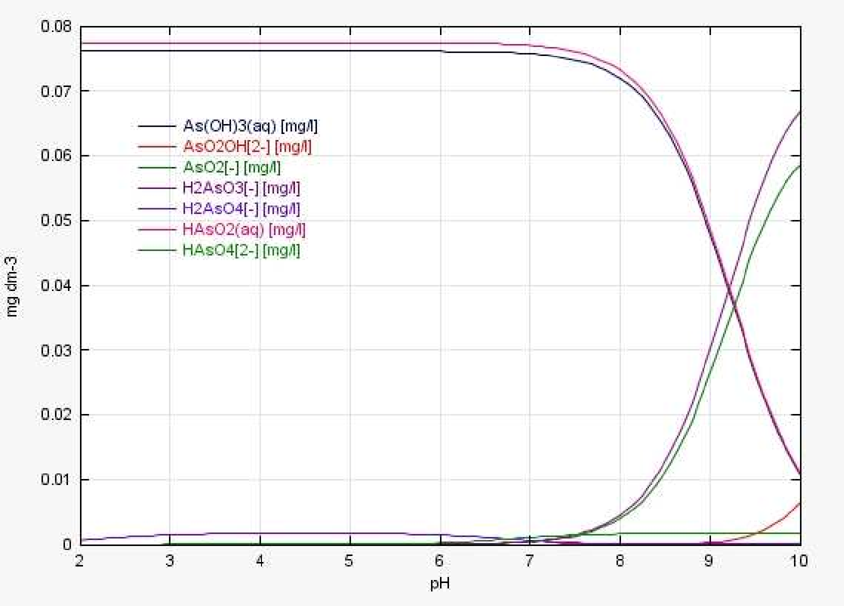


Figure 88. Speciation and solubility of arsenic as modelled by JCHESS. The original solution contained 0.1 mg dm^{-3} of arsenic.

The results in Figures 89 and 90 show that iron is mainly present as Fe^{2+} until pH 9 above which the solubility of iron rapidly decreases due to precipitation. In addition to Fe^{2+} species, also other species are present ($FeOH^+$, $FeCO_{3(aq)}$ and $FeHCO_3^+$) at much lower concentrations.

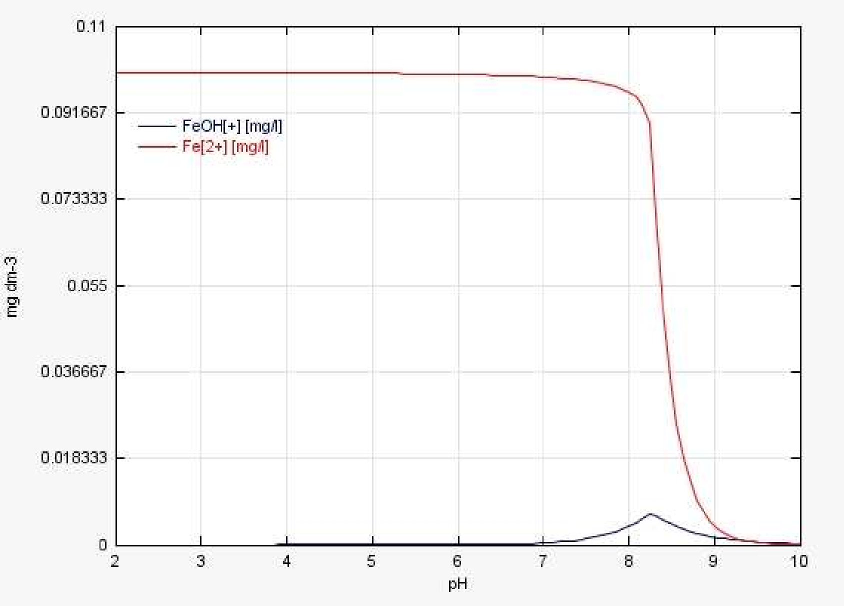


Figure 89. Speciation and solubility of iron as modelled by JCHESS. The original solution contained 0.1 mg dm^{-3} of iron.

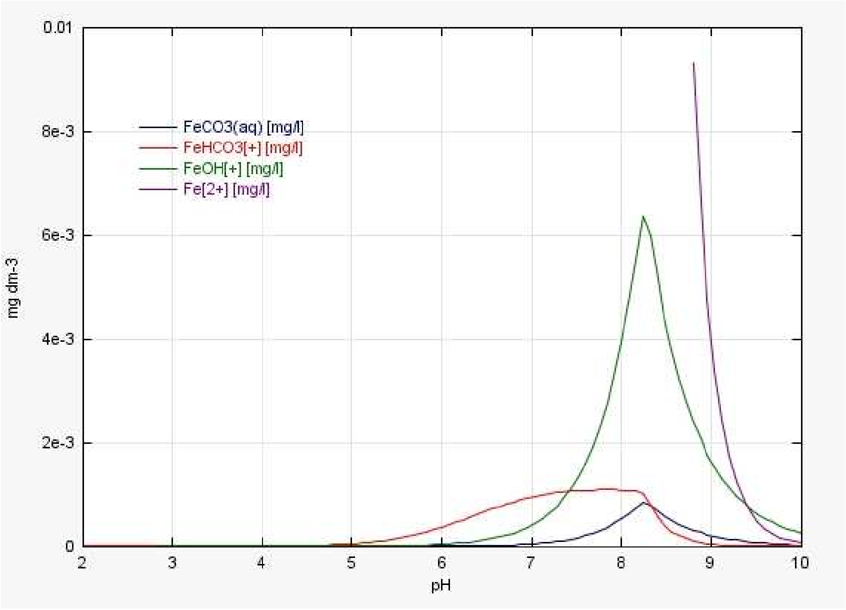


Figure 90. Speciation and solubility of iron as modelled by JCHESS. The original solution contained 0.1 mg dm^{-3} of iron.

The speciation and solubility results for uranium (Figure 91) show that the main species of uranium are UO_2^{2+} below pH 5, $UO_2(OH)_{2(aq)}$ between pH 5 and 9, and $UO_2(OH)_3^-$ above pH 9. Also significant amount of UO_2OH^+ is present around pH 5. It can be concluded that the speciation of uranium varies as a function of pH but uranium remains in the solution.

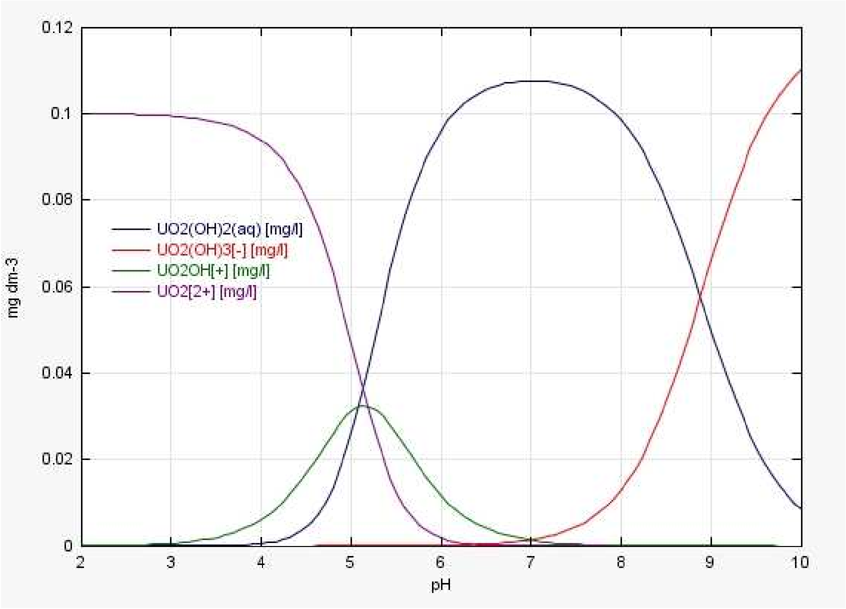


Figure 91. Speciation and solubility of uranium as modelled by JCHESS. The original solution contained 0.1 mg dm^{-3} of uranium.

3.5.2 Speciation of arsenic, iron and uranium in 0.1 mol dm^{-3} $NaNO_3$ electrolyte

The original data inserted into the JCHESS programme in modelling the speciation of arsenic, iron and uranium in 0.1 mol dm^{-3} $NaNO_3$ electrolyte are shown in Table 12. The modelling was carried out in environmental conditions (Eh 0.4 V and presence of carbon dioxide) and using the same arsenic, iron and uranium concentrations as used in following kinetic experiments in electrolyte (Table 16).

Table 12. Original data inserted into the JCHESS programme when modelling arsenic, iron and uranium speciation in 0.1 mol dm^{-3} $NaNO_3$ electrolyte

Variable/species	
pH	3
Eh	0.4 V
$CO_{2(g)}$	0.000316*
As	0.075 mg dm^{-3}
Fe^{3+}	5.585 mg dm^{-3}
UO_2^{2+}	2.38 mg dm^{-3}
Na^+	2299 mg dm^{-3}
NO_3^-	6201 mg dm^{-3}

*dimensionless

The speciation of arsenic in 0.1 mol dm^{-3} $NaNO_3$ electrolyte is shown in Figure 92. The seven arsenic species present in the solution are;

- $As(OH)_{3(aq)}$
- AsO_2^-
- AsO_2OH^{2-}
- $H_2AsO_4^-$
- $H_3AsO_{4(aq)}$
- $HAsO_{2(aq)}$
- $H_2AsO_3^-$

The predominant arsenic species below pH 4.5 is the pentavalent arsenic species $H_2AsO_4^-$. Between pH 4.5 and 9 the two main species present are the aqueous arsenious acid $As(OH)_{3(aq)}$ and $HAsO_{2(aq)}$ in which arsenic is in trivalent oxidation state. The main species above pH 9 are AsO_2^-, AsO_2OH^{2-} and $H_2AsO_3^-$.

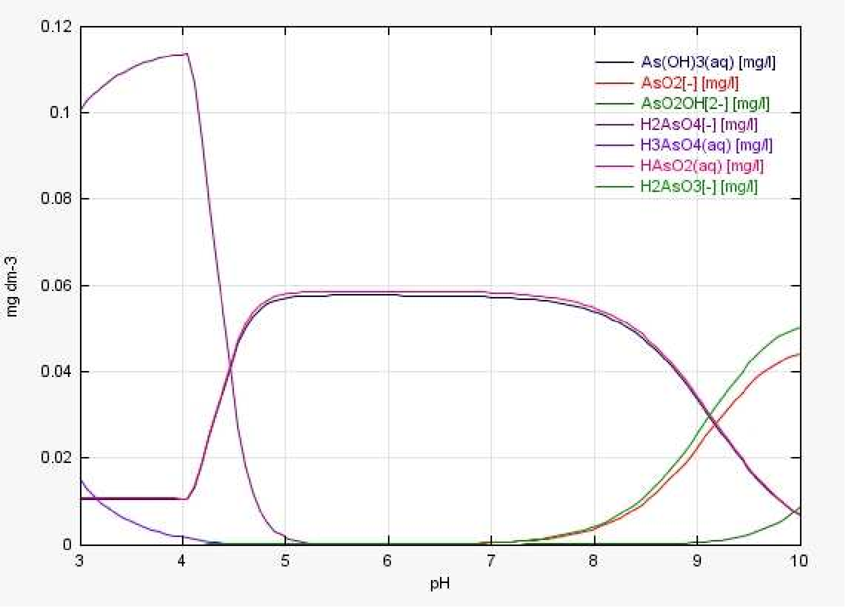


Figure 92. Speciation of arsenic in 0.1 mol dm^{-3} $NaNO_3$ modelled by JCHESS. The original solution contained 0.075 mg dm^{-3} of arsenic.

The main iron species present in the electrolyte is Fe^{2+} (Figure 93) but also iron hydroxide ($FeOH^+$) and iron bicarbonate ($FeHCO_3^+$) species are present at lower concentrations (Figure 94). However, the solubilities of iron species decrease rapidly above pH 9.

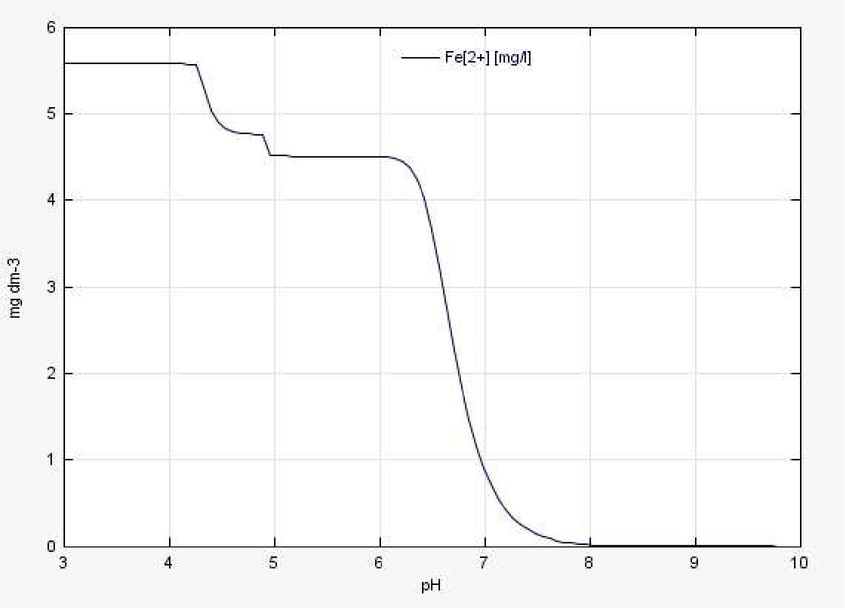


Figure 93. Speciation of iron in 0.1 mol dm^{-3} NaNO$_3$ modelled by JCHESS. The original solution contained 5.585 mg dm^{-3} of iron.

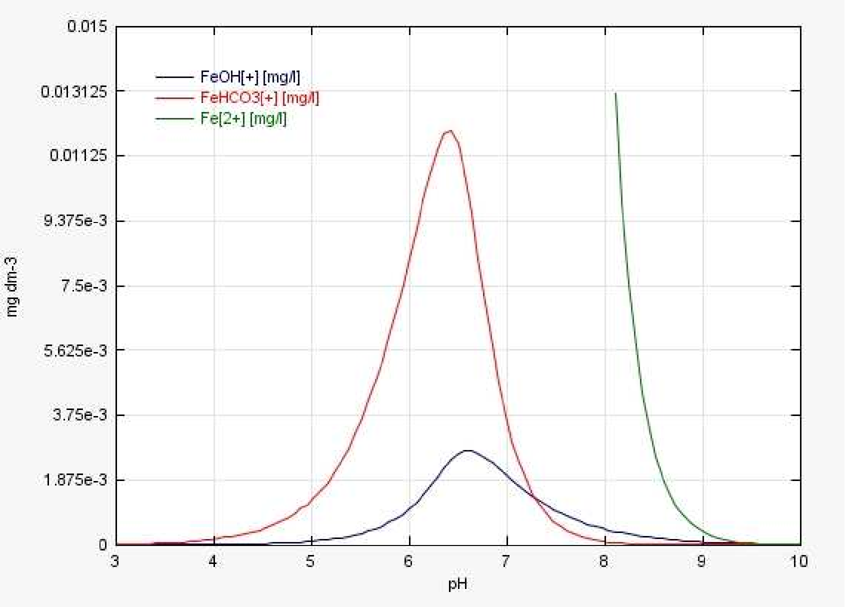


Figure 94. Speciation of iron in 0.1 mol dm^{-3} NaNO$_3$ modelled by JCHESS. The original solution contained 5.585 mg dm^{-3} of iron.

The major uranium species present in the electrolyte is the uranyl ion UO_2^{2+} below pH 5 (Figure 95) whereas uranyl hydroxides UO_2OH^+, $UO_2(OH)_{2(aq)}$ and $(UO_2)_2(OH)_2^{2+}$ are present in lower concentrations (Figure 96). The results show that uranium is less soluble in electrolyte compared to its solubility in uranium solution (Figure 91).

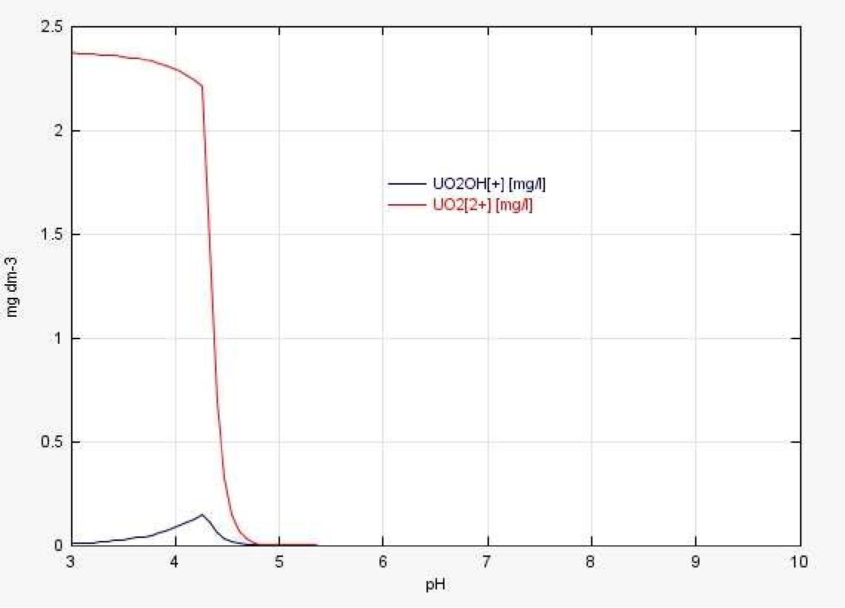


Figure 95. Speciation of uranium in 0.1 mol dm^{-3} NaNO$_3$ modelled by JCHESS. The original solution contained 2.38 mg dm^{-3} of uranyl ion.

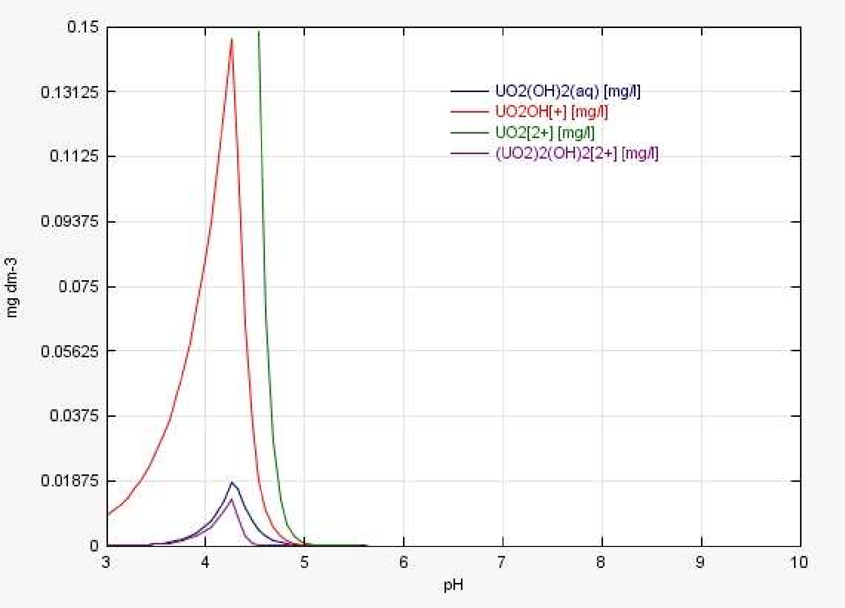


Figure 96. Speciation of uranium in 0.1 mol dm^{-3} NaNO$_3$ modelled by JCHESS. The original solution contained 2.38 mg dm^{-3} of uranyl ion.

3.5.3 Speciation of iron and uranium in un-treated Plant P effluent

Data inserted into the JCHESS programme in modelling the speciation of iron and uranium in un-treated Plant P effluent are shown in Table 13. The major cation and anion concentrations were taken from Table 10. The modelling was carried out in environmental conditions as previously in electrolyte (Eh 0.4 V and presence of carbon dioxide).

Table 13. Original data inserted into the JCHESS programme when modelling iron and uranium speciation in un-treated Plant P effluent

Variable/species	
pH	3
Eh	0.4 V
$CO_{2(g)}$	0.000316*
Fe^{3+}	0.123 mg dm^{-3}
UO_2^{2+}	0.019 mg dm^{-3}
Na^+	282 mg dm^{-3}
Ca^{2+}	41.4 mg dm^{-3}
K^+	18.7 mg dm^{-3}
Mg^{2+}	13.6 mg dm^{-3}
Mn^{3+}	0.453 mg dm^{-3}
Zn^{2+}	0.124 mg dm^{-3}
SO_4^{2-}	732 mg dm^{-3}
Cl^-	23.2 mg dm^{-3}
NO_3^-	2.56 mg dm^{-3}

*dimensionless

The results in Figure 97 show that the un-treated Plant P effluent contains Fe^{2+} and aqueous iron sulphate ($FeSO_4$) as major iron species until pH 8-9. There are also iron bicarbonate, hydroxide and carbonate ($FeHCO_3^+$, $Fe(OH)_2^+$, $FeOH^+$, and $FeCO_{3(aq)}$) species present in lower concentrations (Figure 98). Therefore, the presence of sulphate in the effluent has introduced another major species ($FeSO_{4(aq)}$) in addition to Fe^{2+} when compared to the species in 0.1 mol dm^{-3} $NaNO_3$ electrolyte (Figure 93).

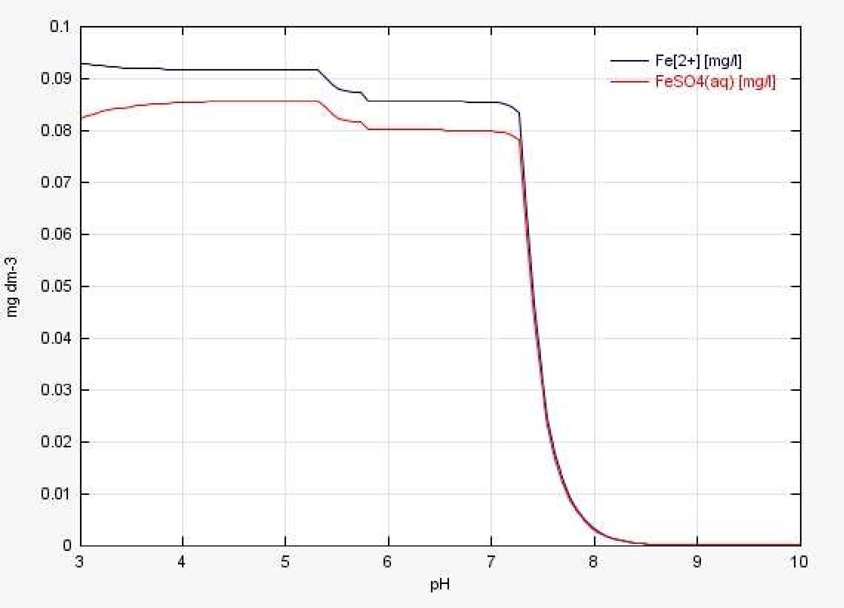


Figure 97. Speciation of iron in un-treated Plant P effluent modelled by JCHESS. The original solution contained 0.123 mg dm^{-3} of iron. Iron ions were one of the minor species in the system.

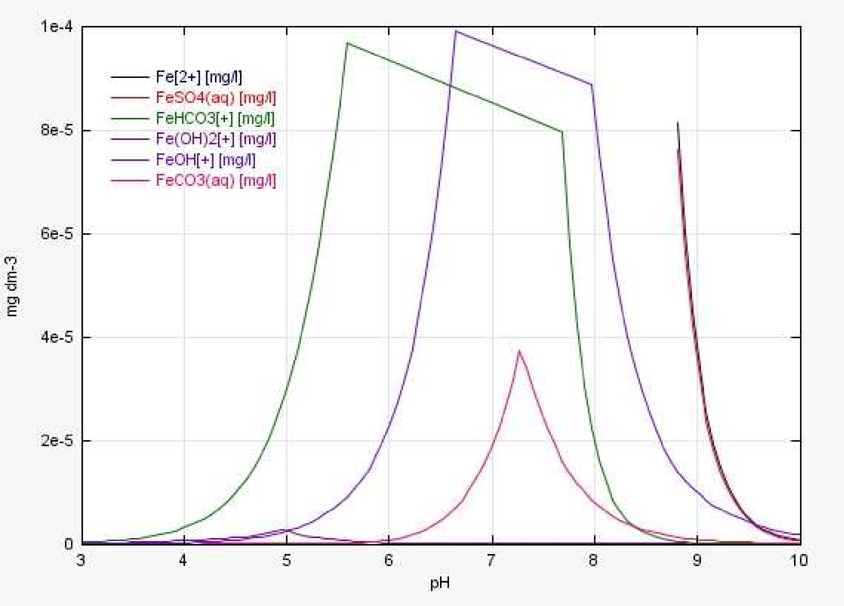


Figure 98. Speciation of iron in un-treated Plant P effluent modelled by JCHESS. The original solution contained 0.123 mg dm^{-3} of iron. Iron ions were one of the minor species in the system.

The main uranium species present until pH 6 in the un-treated Plant P effluent is aqueous uranyl sulphate (UO_2SO_4) (Figure 99). As in the case of iron speciation in the un-treated Plant P effluent, the presence of sulphate has introduced a new species of uranium (uranyl sulphate) compared to its speciation in 0.1 mol dm^{-3} $NaNO_3$ electrolyte. The effluent also contains several other uranium and uranyl species at lower concentrations (Figure 99 and 100);

- $U(OH)_{4(aq)}$
- $UO_2(OH)_{2(aq)}$
- $UO_2(SO_4)_2^{2-}$
- UO_2OH^+
- UO_2^{2+}
- $UO_2CO_{3(aq)}$
- UO_2^+
- U^{4+}

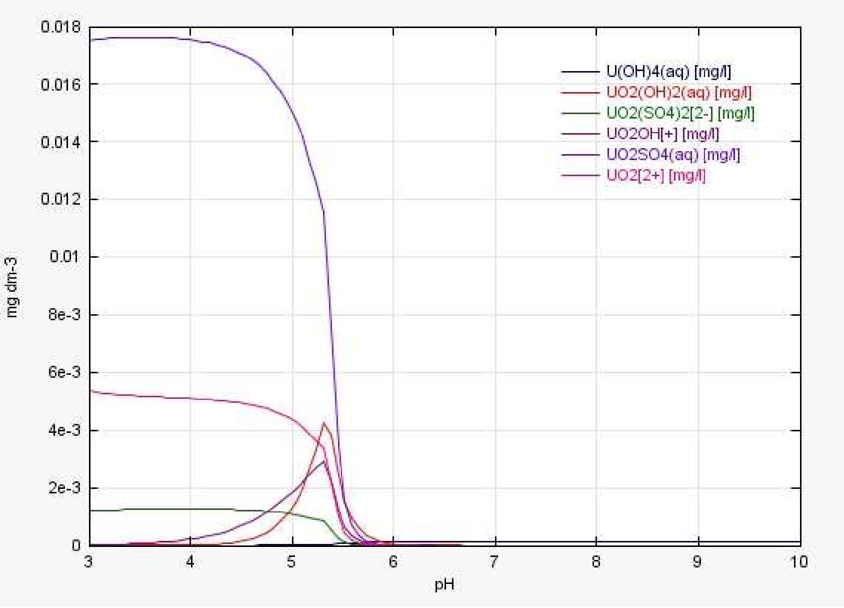


Figure 99. Speciation of uranium in un-treated Plant P effluent modelled by JCHESS. The original solution contained 0.019 mg dm^{-3} of uranyl. Uranyl ions were one of the minor species in the system.

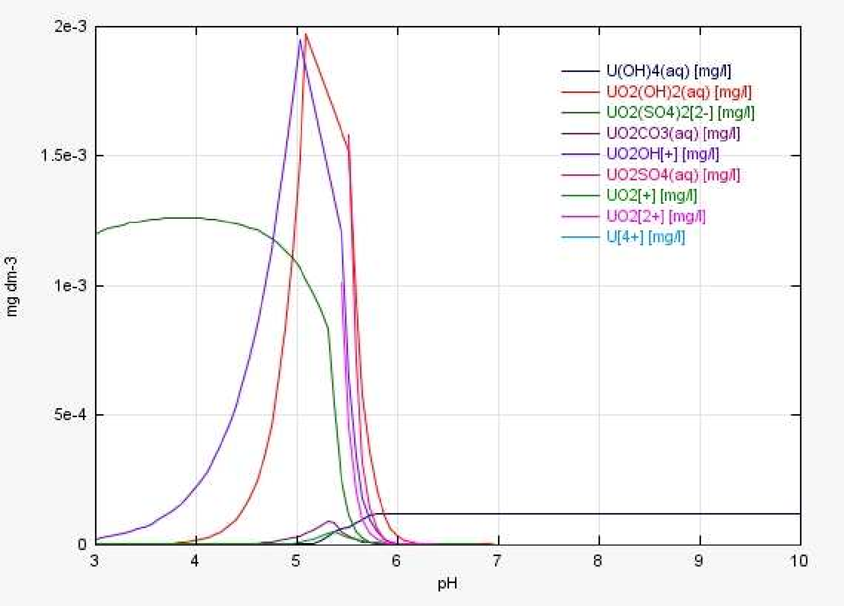


Figure 100. Speciation of uranium in un-treated Plant P effluent modelled by JCHESS. The original solution contained 0.019 mg dm^{-3} of uranyl. Uranyl ions were one of the minor species in the system.

3.5.4 Speciation of iron and uranium in treated Plant P effluent

The characterisation of treated Plant P effluent was not carried out for major anions (Table 14), therefore the speciation studies for iron and uranium were carried out by inserting the composition of un-treated Plant P effluent in the JCHESS programme and by adding carbonate in the solution (Table 10). The amount of carbonate added into the un-treated Plant P effluent (0.01 g of Na_2CO_3) was an estimation based on the experiments in which the pH of the un-treated Plant P effluent was raised from 3 to 5.

Table 14. Original data inserted into the JCHESS programme when modelling iron and uranium speciation in treated Plant P effluent

Variable/species	
pH	5
Eh	0.4 V
CO_3^{2-}	56.4 mg dm^{-3}
Fe^{3+}	0.123 mg dm^{-3}
UO_2^{2+}	0.019 mg dm^{-3}
Na^+	282 mg dm^{-3}
Ca^{2+}	41.4 mg dm^{-3}
K^+	18.7 mg dm^{-3}
Mg^{2+}	13.6 mg dm^{-3}
Mn^{3+}	0.453 mg dm^{-3}
Zn^{2+}	0.124 mg dm^{-3}
SO_4^{2-}	732 mg dm^{-3}
Cl^-	23.2 mg dm^{-3}
NO_3^-	2.56 mg dm^{-3}

The results in Figure 101 show that majority of iron has precipitated from the solution. However, there are three iron species present in the treated Plant P effluent; Fe^{2+}, $FeSO_{4(aq)}$ and $FeHCO_3^+$. The addition of carbonate has significantly decreased the iron concentration in the treated Plant P effluent but the speciation has not drastically changed when compared with the iron speciation in un-treated Plant P effluent. Nevertheless, the un-treated Plant P effluent contained some hydroxide species (Figure 98) which are not present in the treated Plant P effluent.

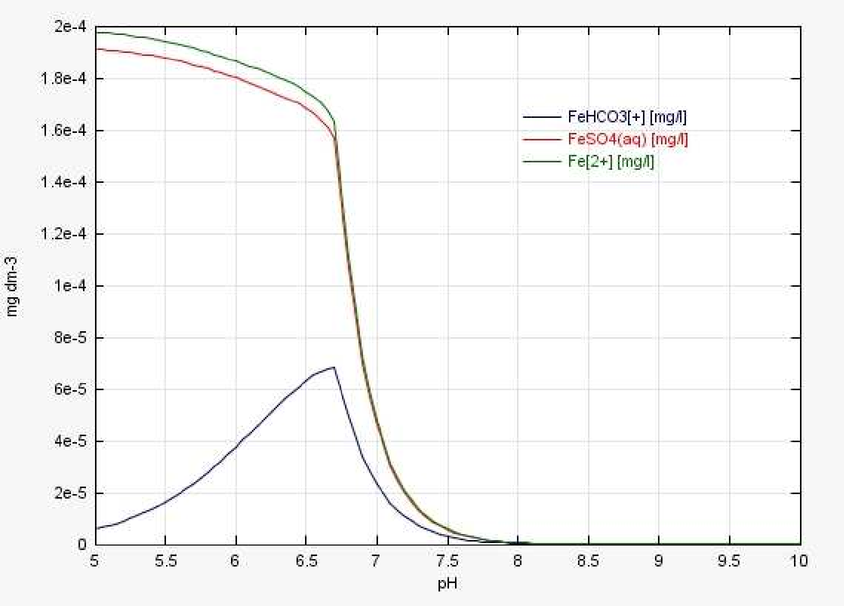


Figure 101. Speciation of iron in treated Plant P effluent modelled by JCHESS. The original un-treated Plant P effluent contained 0.123 mg dm^{-3} of iron before pH adjustment from 3 to 5. Iron ions were one of the minor species in the system.

The speciation of uranium in the treated Plant P effluent shows a large number of different type of species present in the solution between pH 5 and 10 (Figure 102). The main uranium species present between pH 5 and 6 are $UO_2SO_{4(aq)}$, $UO_2CO_{3(aq)}$ and $UO_2(OH)_{2(aq)}$. The main uranium species above pH 6 are two uranyl carbonate compounds; $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$.

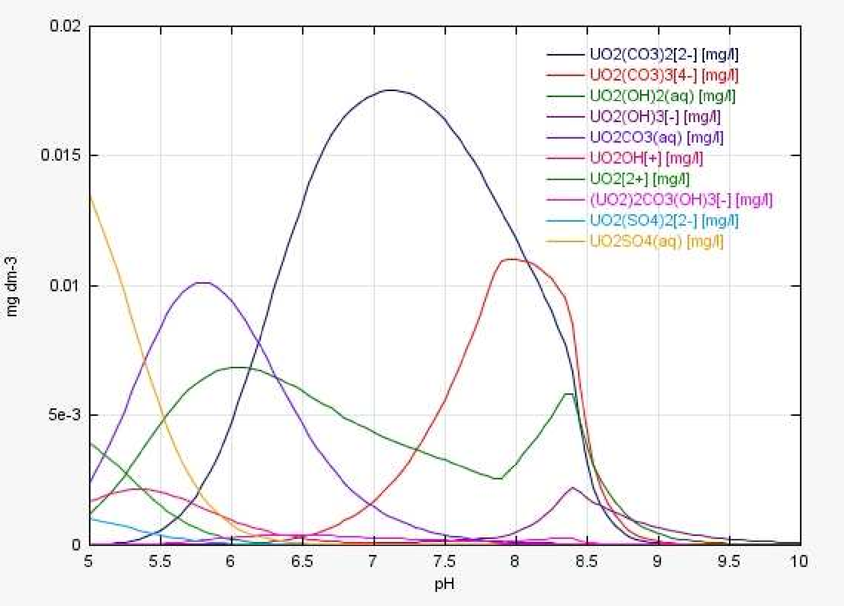


Figure 102. Speciation of uranium in treated Plant P effluent modelled by JCHESS. The original un-treated Plant P effluent contained 0.019 mg dm^{-3} of uranyl before pH adjustment from 3 to 5. Uranyl ions were one of the minor species in the system.

3.5.5 Speciation of arsenic, iron and uranium in un-treated Plant R effluent

The original data inserted into the JCHESS programme in modelling the speciation of arsenic, iron and uranium in un-treated Plant R effluent are shown in Table 15. The major cation and anion concentrations in un-treated Plant R effluent were taken from Table 10. The modelling was carried out in environmental conditions as previously in electrolyte and un-treated Plant P effluent (Eh 0.4 V and presence of carbon dioxide).

Table 15. Original data inserted into the JCHESS programme when modelling arsenic, iron and uranium speciation in un-treated Plant R effluent

Variable/species	
pH	2.7
Eh	0.4 V
$CO_{2(g)}$	0.000316*
As	0.132 mg dm^{-3}
Fe^{3+}	65.4 mg dm^{-3}
UO_2^{2+}	0.019 mg dm^{-3}
Na^+	483 mg dm^{-3}
K^+	59.5 mg dm^{-3}
Ca^{2+}	42.4 mg dm^{-3}
Mg^{2+}	26.9 mg dm^{-3}
Mn^{3+}	0.849 mg dm^{-3}
Zn^{2+}	0.210 mg dm^{-3}
Cl^-	80.9 mg dm^{-3}
SO_4^{2-}	1610 mg dm^{-3}
PO_4^{3-}	1.13 mg dm^{-3}

*dimensionless

The speciation of arsenic in un-treated Plant R effluent (Figure 103) is similar to its speciation in 0.1 mol dm^{-3} $NaNO_3$ electrolyte (Figure 92). The main arsenic species present in the un-treated Plant R effluent are similarly pentavalent arsenic as $H_2AsO_4^-$ below pH 4 and aqueous arsenious acid $As(OH)_3$ and

$HAsO_{2(aq)}$ between pH 4 and 9. However, $As(OH)_3$ and $HAsO_{2(aq)}$ are present in higher concentrations in Plant R effluent.

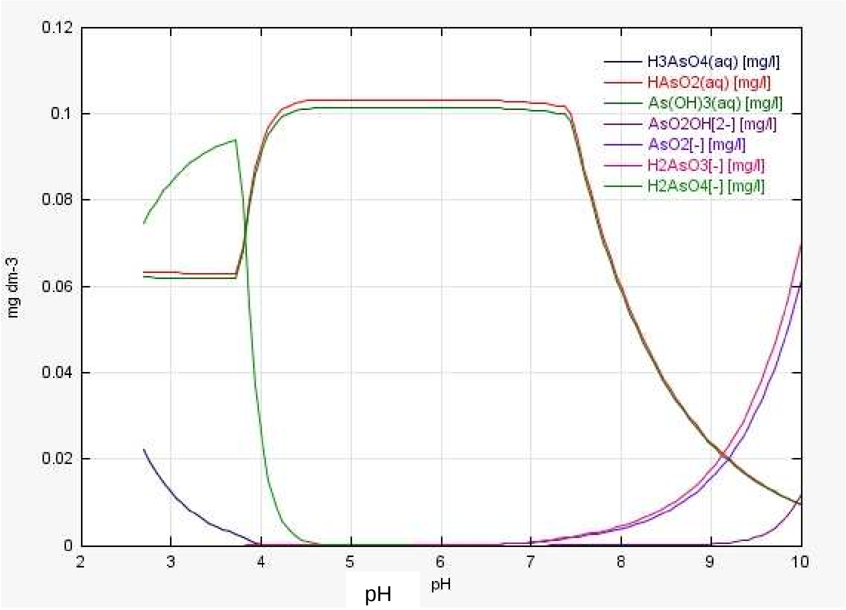


Figure 103. Speciation of arsenic in un-treated Plant R effluent modelled by JCHESS. The original solution contained 0.123 mg dm^{-3} of arsenic. Arsenic ions were one of the minor species in the system.

The main species of iron in the un-treated Plant R effluent are Fe^{2+} and aqueous $FeSO_4$ (Figure 104). The results are similar to the speciation of iron in un-treated Plant P effluent due to similarly high sulphate concentrations. However, also a new iron species, $FeCl^+$, is present along with bicarbonate, carbonate, hydroxide hydrogen phosphate and phosphate species (Figures 105-106). Iron is appreciably precipitated from the effluent above pH 7-8.

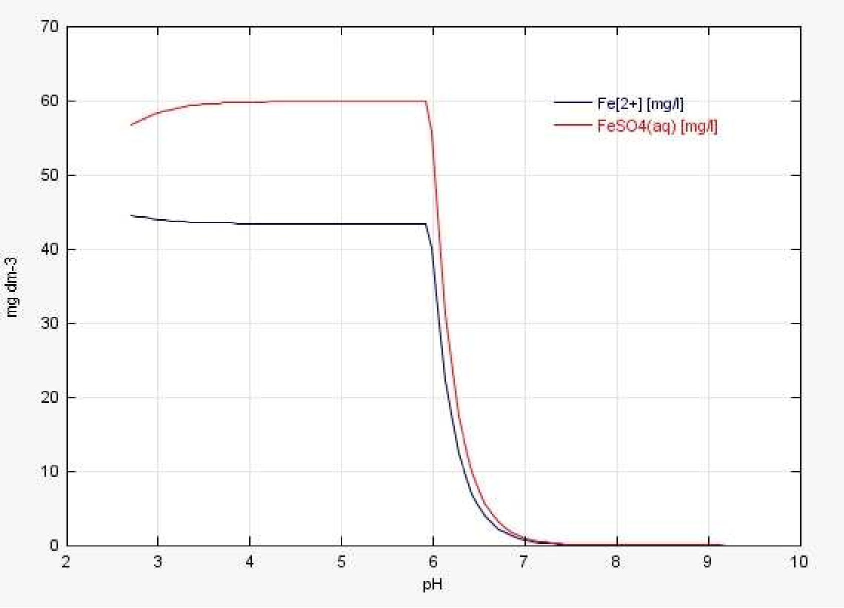


Figure 104. Speciation of iron in un-treated Plant R effluent modelled by JCHESS. The original solution contained 65.4 mg dm^{-3} of iron. Iron ions were one of the major species in the system.

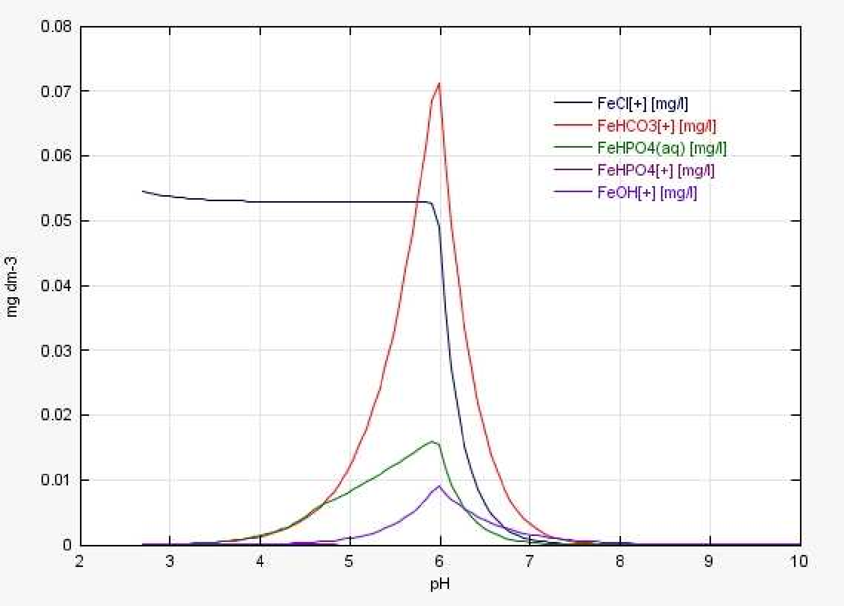


Figure 105. Speciation of iron in un-treated Plant R effluent modelled by JCHESS. The original solution contained 65.4 mg dm^{-3} of iron. Iron ions were one of the major species in the system.

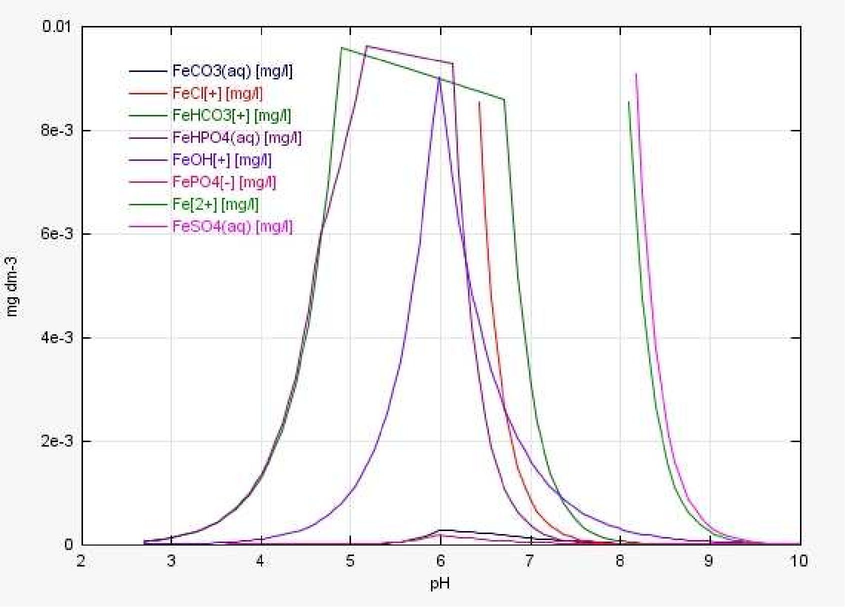


Figure 106. Speciation of iron in un-treated Plant R effluent modelled by JCHESS. The original solution contained 65.4 mg dm^{-3} of iron. Iron ions were one of the major species in the system.

The main uranium species below pH 5 in the un-treated Plant R effluent is aqueous uranyl sulphate (UO_2SO_4) (Figure 107). The results are similar to the uranium speciation results in the un-treated Plant P effluent in which aqueous uranyl sulphate was also the major uranium species. There are also many other uranyl species present such as hydroxides and hydrogen phosphates. Above pH 5 the majority of uranium is precipitated. However, a small amount of aqueous $U(OH)_4$ is present between pH 5 and 10 (Figure 108).

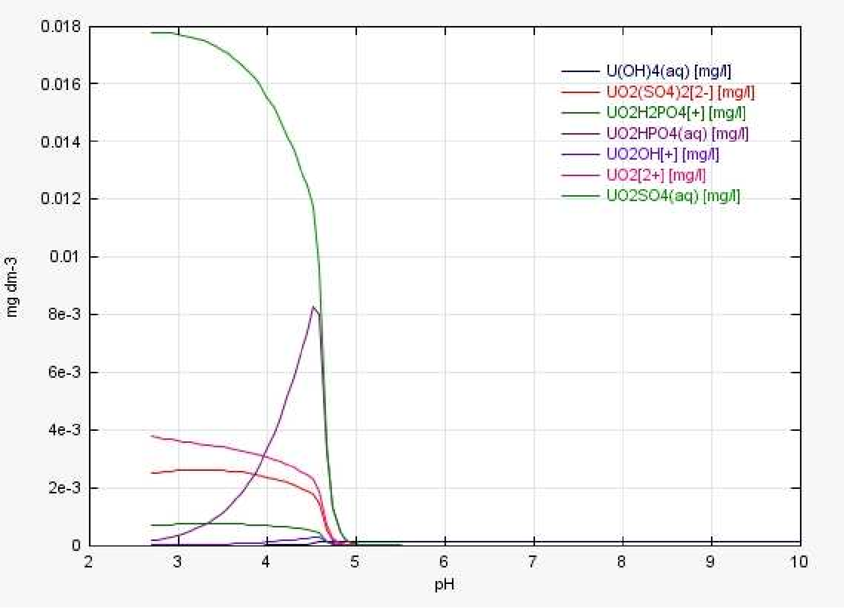


Figure 107. Speciation of uranium in un-treated Plant R effluent modelled by JCHESS. The original solution contained 0.019 mg dm^{-3} of uranyl. Uranyl ions were one of the minor species in the system.

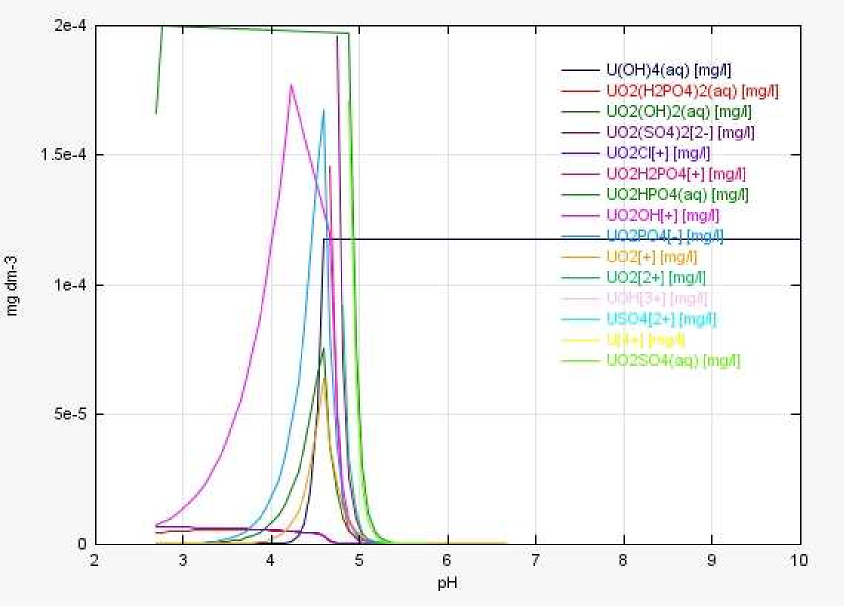


Figure 108. Speciation of uranium in un-treated Plant R effluent modelled by JCHESS. The original solution contained 0.019 mg dm^{-3} of uranyl. Uranyl ions were one of the minor species in the system.

It can be concluded that the presence of sulphate in the un-treated Plant P and R effluents has a great impact on the speciation of both iron and uranium but does not have an effect on the speciation of arsenic. The added carbonate in the treated Plant P effluent forms carbonate complexes with uranium at high pH. The uranyl carbonate complexes prevent precipitation and higher concentration of uranium remains in the treated Plant P effluent solution.

3.6 Leaching of arsenic, iron and uranium from ST and CE sludges

Leaching of iron, especially from ST sludge, is due to its high iron content (23%) which could prohibit use of the sludge in this application. The leaching experiments were firstly carried out for iron in deionised water and then in 0.1 mol dm^{-3} electrolyte for arsenic, iron and uranium.

3.6.1 Leaching of iron from ST and CE sludges into deionised water

The studies of iron leaching were carried out for both of the sludges as a function of pH. Triplicates of 2 g of sludge (ST or CE) were placed in contact with 200 cm^3 DI water and the pH was adjusted from 3 to 9 using 1 mol dm^{-3} H_2SO_4 and NaOH solutions. The samples were filtered (0.2 µm), acidified, and the iron concentrations determined using ICP-OES. Measured iron concentrations in the ST and CE leachates are shown in Figures 109 and 110. The results in Figure 109 show significant leaching of iron from the ST sludge at pH 3 (approximately 6 mg dm^{-3}) then leaching decreases rapidly with increasing pH until pH 5 after which an increasing amount of iron is released, possibly complexed with dissolved humic acid. The leaching of iron from CE sludge (Figure 110) is significantly lower than from ST sludge. The highest iron concentration released is at pH 3 (0.17 mg dm^{-3}) and it decreases constantly with increasing pH. As a reference, the behaviour of 10^{-6} mol dm^{-3} iron solution as a function of pH was investigated (Figure 111), and the results show a decrease in solubility with increasing pH until pH 5 when the solubility limit of iron hydroxide (30 µg dm^{-3}) is reached.

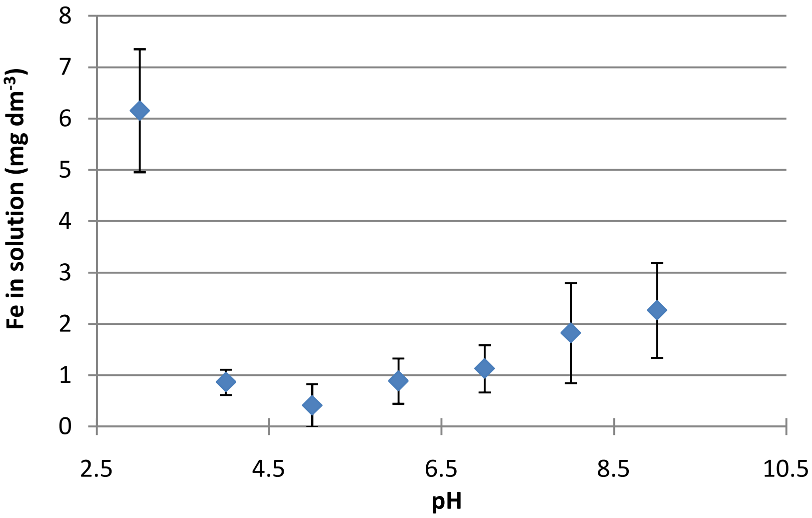


Figure 109. Leaching of iron from 2 g of ST sludge in contact with 200 cm^3 DI water as a function of pH.

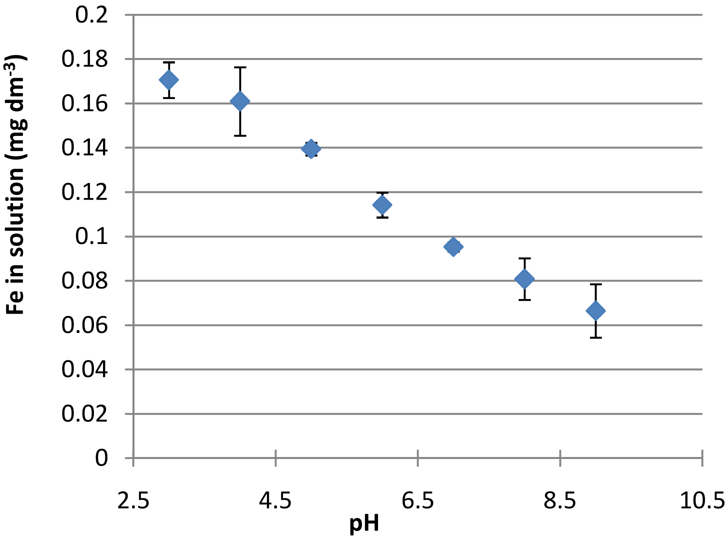


Figure 110. Leaching of iron from 2 g of CE sludge in contact with 200 cm^3 DI water as a function of pH.

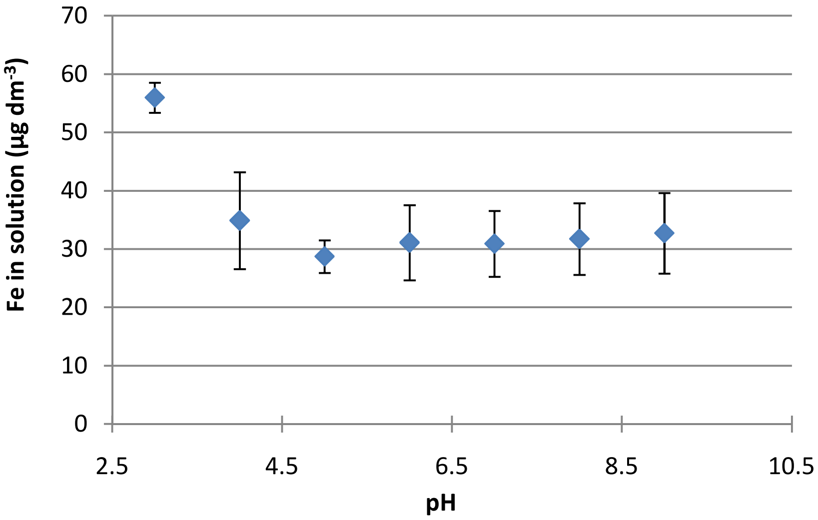


Figure 111. Iron in DI water (10^{-6} mol dm^{-3}) as a function of pH.

Since the results showed significant leaching of iron from ST sludge, an additional set of samples was prepared in which iron release at the pH of the Plant R and un-treated Plant P (~2.5) and treated Plant P (~4.5) effluents were determined. The experiments were carried out by placing 0.5 g of ST sludge into 50 cm^3 of DI water and adjusting the mixture to pH 2.7 and 4.3 using 1 mol dm^{-3} NaOH and H_2SO_4 solutions. The results showed significant release of iron to the solutions at the pH of un-treated and treated effluents; 55.5 mg dm^{-3} and 2.2 mg dm^{-3}, respectively, thus it was concluded that ST sludge releases a significant amount of iron at the pH of the effluents and therefore the following experiments were carried out using only CE sludge.

3.6.2 Leaching of arsenic, iron and uranium from CE sludge into electrolyte

Leaching tests on arsenic, iron and uranium from CE sludge were carried out in 0.1 mol dm^{-3} $NaNO_3$ electrolyte by placing 0.5 g, 1 g and 10 g of CE sludge in contact with 100 cm^3 of the electrolyte. The pH of the mixtures was measured simultaneously. Arsenic, iron and uranium concentrations in the samples collected as a function of time (1 minute to 60 minutes, 0.22 µm filter) were measured using ICP-OES (As, Fe) and ICP-MS (U).

The results of iron leaching from CE sludge in 0.1 mol dm^{-3} $NaNO_3$ electrolyte (Figure 112) show increasing iron release in the samples with increasing time. The iron concentrations in the 0.5 g and 1 g samples plateau approximately at 0.2 mg dm^{-3} and in the 10 g samples approximately to 0.3 mg dm^{-3} in 30 min. However, the levels of iron released are relatively low. The pH of the mixtures (Figure 113) increased to the natural pH of the CE sludge (pH 8) and the maximum amount of iron leached was obtained after 30 minutes. The results did not show leaching of measurable amounts of arsenic or uranium. The limit of quantification for arsenic were 6.5 µg dm^{-3} using ICP-OES and 0.4 µg dm^{-3} for uranium using ICP-MS.

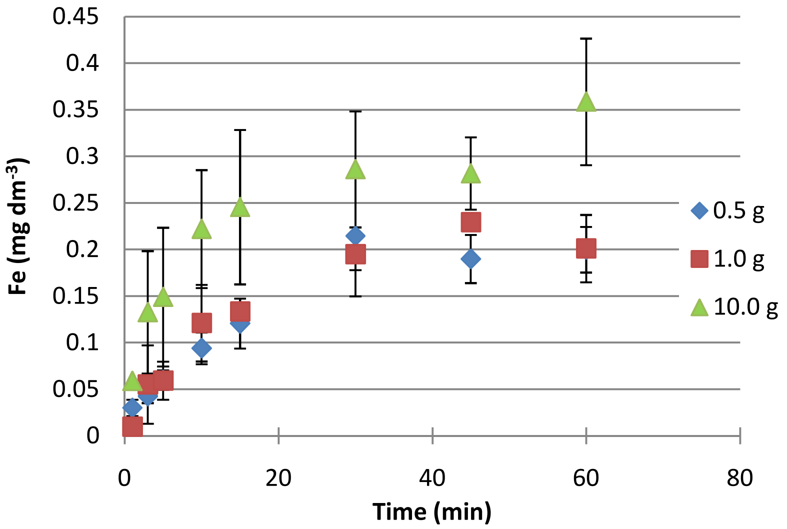


Figure 112. Leaching of iron from 0.5 g, 1 g and 10g of CE sludge in 0.1 mol dm^{-3} $NaNO_3$ electrolyte as a function of time.

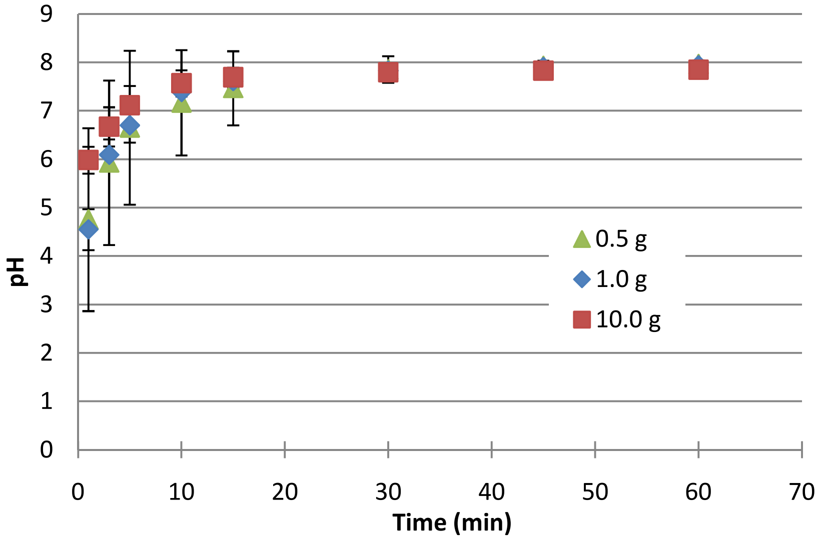


Figure 113. The pH in the samples of 0.5 g, 1 g and 10 g of CE sludge with 0.1 mol dm^{-3} $NaNO_3$ electrolyte as a function of time.

3.7 Outline of experimental studies in electrolyte, un-treated Plant P, treated Plant P and un-treated Plant R effluents

The experimental studies in electrolyte, un-treated Plant P, treated Plant P and Plant R effluents were divided into three stages (Figure 114). In the first stage, the kinetics of arsenic (when present in the original solution), iron and uranium removal from the effluents were determined by placing 0.5 g, 1 g and 10 g of CE sludge in contact with 100 cm^3 of solution giving solid:liquid ratios of 1:200, 1:100 and 1:10, respectively. The mixtures were constantly stirred using a magnetic stirrer and samples were collected as a function of time (1 minute to 60 minutes, 0.2 µm filter). The pH of the mixtures was measured simultaneously. Iron and arsenic concentrations were determined using ICP-OES and uranium concentrations using ICP-MS or ICP-OES.

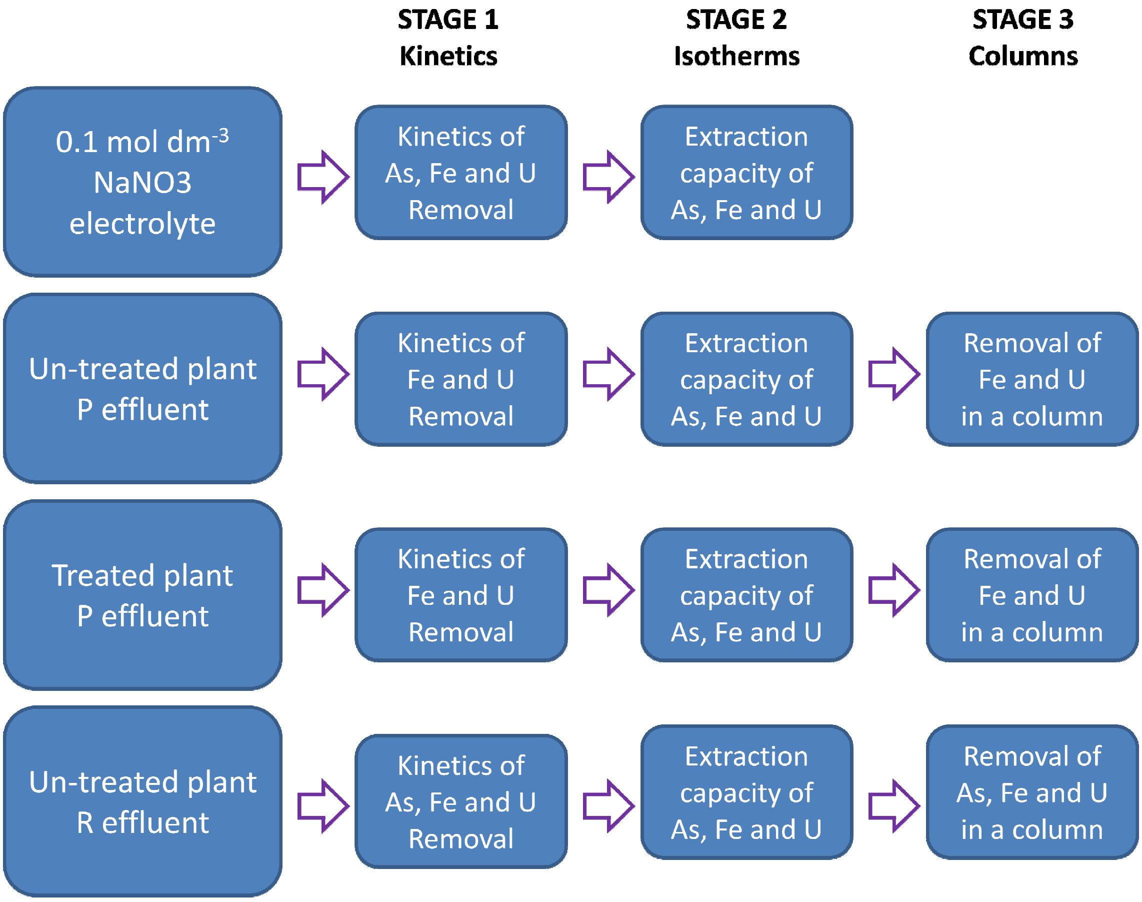


Figure 114. The experimental plan for arsenic, iron and uranium removals in electrolyte, un-treated and treated Plant P effluents and un-treated Plant R effluent.

In the second stage, the maximum capacities of arsenic, iron and uranium removal by CE sludge were determined by placing 0.2 g of CE sludge in contact with 20 cm^3 of solution with increasing concentrations of analytes (As, Fe, and U). The solid to liquid ratio of 1:100 was chosen according to the results in the first stage where the extraction was nearly as quick as in samples with 1:10 solid liquid ratios but did not require as much solid. The experiments in electrolyte were carried out using 1 hour and 24 hours contact times using constant shaking on an orbital shaker. The experiments in effluents were carried out only using 24 hours contact time due to limited amounts of effluents. The experiments were carried out without an added buffer, and the pH values of the mixtures at the end of the experiments were measured. The iron and arsenic concentrations were determined using ICP-OES and uranium concentrations using ICP-OES or ICP-MS, and results were presented as isotherm diagrams. The isotherms were plotted as analyte in the solution (mol dm^{-3}) against extracted to solid or removed from the solution (mol g^{-1}), thus in the case of arsenic for example, the x-axis is labelled as “As free mol dm^{-3}” and y-axis as “As bound mol g^{-1}”.

The third stage was carried out in columns to simulate dynamic flow through systems (Figure 115). 50 g of CE sludge were tightly packed in a glass column (Ø 2.6 cm) by mixing the sludge with DI water to form a slurry. The slurries were poured slowly into the columns and air bubbles were removed by gentle stirring. The columns were washed with DI water at least for 12 h to remove the soluble fraction (i.e. fulvic acid) with a flow rate of 0.2 cm^3 min^{-1}. The porosities of the columns were determined using tritiated water which should not interact with the column material. The porosity (ρ) can be calculated by plotting C/C_0 against volume of liquid that has passed through the column. C is the specific activity (Bq cm^{-3}) of tritium leaving the column and C_0 is the specific activity (Bq cm^{-3}) entering the column. The porosity can be calculated by using Equation 3.1 in which the break-through point of tritium is V_0 (cm^3) and volume of the column V_c (cm^3). The break-through point is shown in Figure 116 along with the dead volume of the column which refers to the volume of liquid that passes through the column before an analyte (in this case tritium) has migrated through the whole length of the column.

$$\rho\,(\%) = \frac{V_0}{V_c}\,100\% \tag{3.1}$$

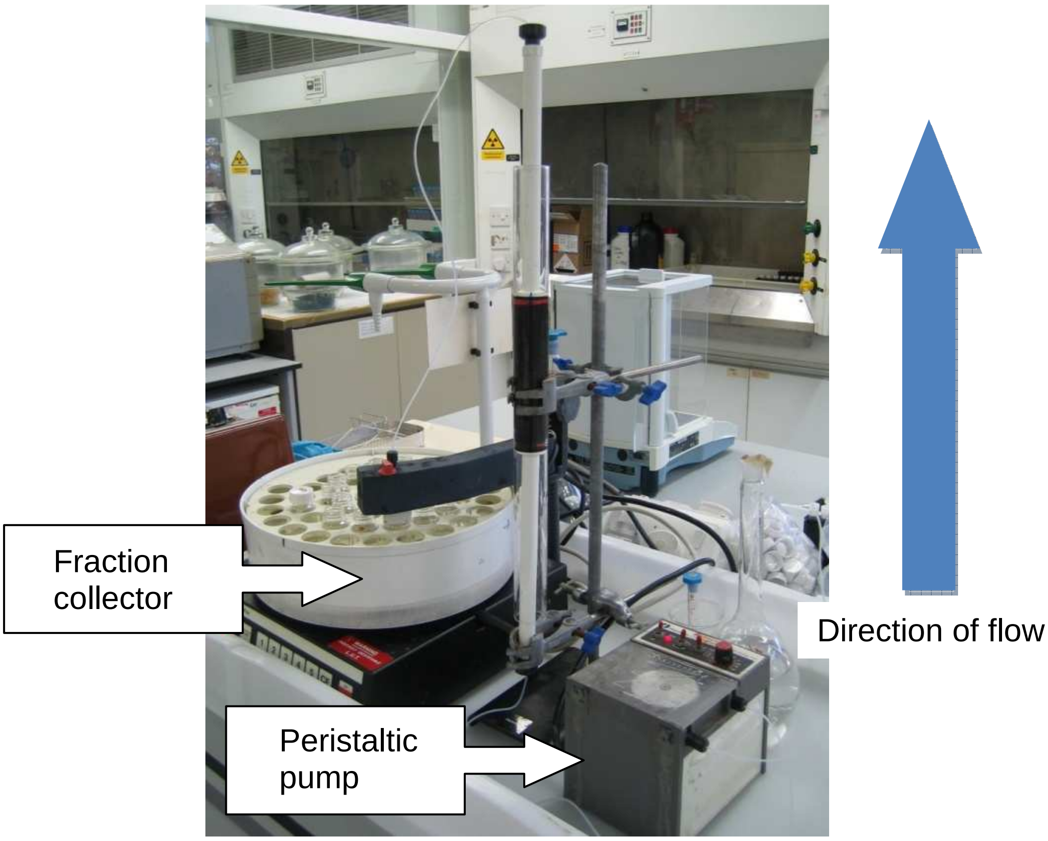


Figure 115. Experimental setup for column experiments.

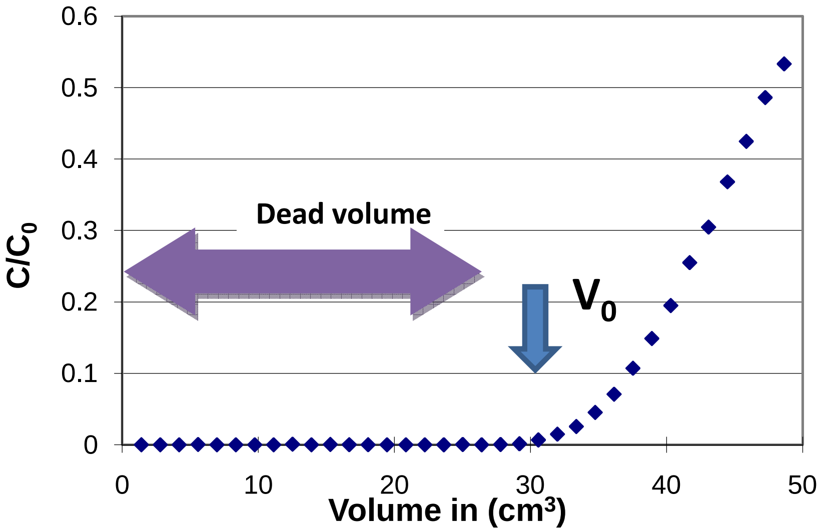


Figure 116. Example graph for determination of porosity in a column.

The porosities of the columns were determined as described above by pumping tritiated water through the columns and collecting 1 cm^3 fractions. 5 cm^3 of Multi-purpose Gold Star scintillation cocktail (manufactured by Meridian) were mixed with the fractions and tritium activity was measured using a liquid scintillation counter which had been pre-calibrated for tritium counting efficiency. The direction of flow was from bottom to top (Figure 115) to obtain constant flow rate and controlled introduction of inlet solution. The columns were further washed with DI water to remove residual amounts of tritium. Then 100 cm^3 of effluent were pumped through the column with a flow rate of 0.2 cm^3 min^{-1} and approximately 10 cm^3 fractions were collected. Fraction collection was continued when the columns were further washed with 200 cm^3 of deionised water. The pH of the collected fractions were measured prior to acidification and ICP-OES (A, Fe) or ICP-MS (U) measurements.

3.8 Extraction of arsenic, iron and uranium from electrolyte by CE sludge

The extraction experiments were firstly carried out in a simplified solution i.e. 0.1 mol dm^{-3} $NaNO_3$ electrolyte. The concentrations of the prepared arsenic, iron and uranium solutions in electrolyte are shown in Table 16. The preparations of the solutions are shown in section 3.2.1.

Table 16. Arsenic, iron and uranium concentrations in the 0.1 mol dm^{-3} $NaNO_3$ electrolyte

Solution	***pH***	***Arsenic (mol dm^{-3})***	***Iron (mol dm^{-3})***	***Uranium (mol dm^{-3})***
0.1 mol dm^{-3} $NaNO_3$	3	1E-06	1E-04	1E-05

3.8.1 Kinetics of arsenic, iron and uranium removal from 0.1 mol dm^{-3} $NaNO_3$ electrolyte

The pH of the solutions during the kinetic studies of arsenic, iron and uranium removal from 0.1 mol dm^{-3} $NaNO_3$ electrolyte by CE sludge are plotted in Figure 117. All the mixtures reach the natural pH of the CE sludge (approximately pH 8) after 30 minutes contact time.

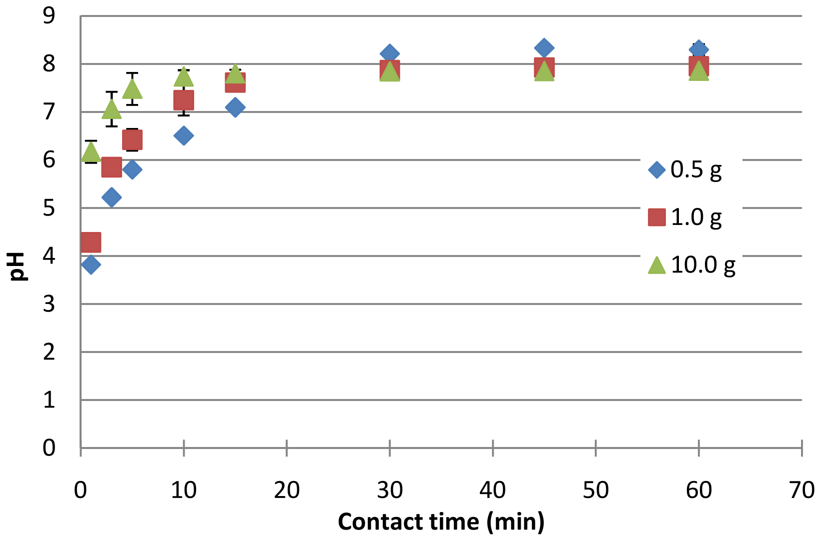


Figure 117. The pHs in the samples of 0.5 g, 1 g and 10 g of CE sludge with arsenic, iron and uranium in 0.1 mol dm^{-3} $NaNO_3$ electrolyte as a function of time.

The results of the extraction kinetics of arsenic and iron removal from the electrolyte are presented in Figures 118 and 119. The extraction of arsenic (Figure 118) reached 100% only in samples with the highest solid:liquid ratio of 1:10 (10 g to 100 cm^{-3}). The extractions with 1:200 (0.5 g to 100 cm^{-3}) and 1:100 (1 g to 100 cm^{-3}) solid:liquid ratios reached 20% and 60% extracted, respectively. The extraction of iron was efficient even in samples with lower solid liquid ratios (Figure 119). Taking experimental error into consideration, it can be seen that iron was fully removed from the electrolyte within 10 minutes in all samples with different solid to liquid ratios. Merely effect of the increasing pH causes iron to precipitate, therefore the removal of iron from the electrolyte occurred either by precipitation, by extraction by CE sludge, or both.

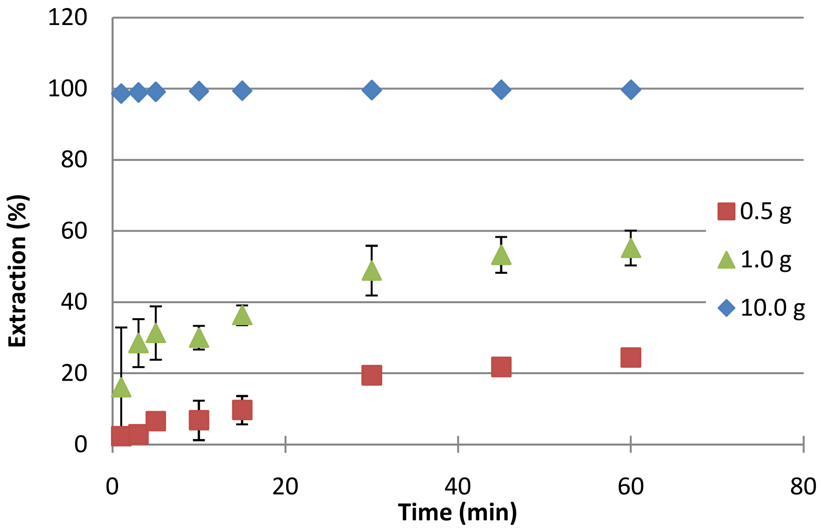


Figure 118. Extraction of arsenic by 0.5 g, 1 g and 10 g of CE sludge from 0.1 mol dm^{-3} NaNO$_3$ electrolyte. The original arsenic concentration was 10^{-6} mol dm^{-3}.

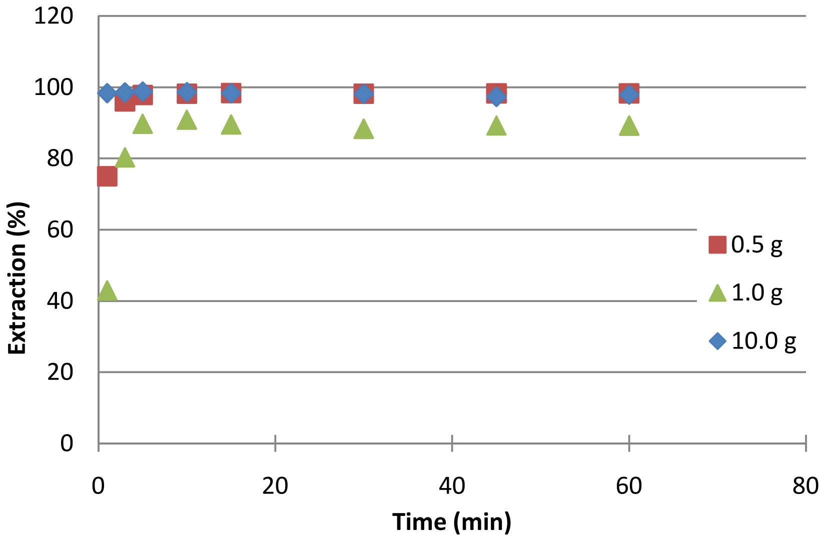


Figure 119. Extraction of iron by 0.5 g, 1 g and 10 g of CE sludge from 0.1 mol dm^{-3} NaNO$_3$ electrolyte. The original iron concentration was 10^{-4} mol dm^{-3}.

The extraction of uranium from electrolyte by CE sludge (Figure 120) reached 100% in 10 g sample sets and only 65% in the 1 g and 0.5 g sample sets. The results show that if uranium is not extracted immediately (as in 10 g sample set) uranium forms a complex with one or more species present in the solution within a couple of minutes and remains in the solution. A possible reason for the 65% extraction percentage in 0.5 g and 1 g sample sets is complexation of uranyl ion with carbonate originating from dissolved CO_2 in air. The dissolution of carbon dioxide is shown in Equations 3.2 to 3.5 and the reaction of carbonate with uranyl ions in Equations 3.6 and 3.7. However, the speciation studies carried out in section 3.5.1 do not support this theory. Another possible reason for the 65% extraction percentage is that uranium species forms a complex with dissolved organic matter and remain in the solution. However, more experiments should be carried out to confirm either hypothesis.

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \quad (3.2)$$

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \quad (3.3)$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \quad (3.4)$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \quad (3.5)$$

$$UO_2^{2+} + 2CO_3^{2-} \leftrightarrow UO_2(CO_3)_2^{2-} \quad (3.6)$$

$$UO_2^{2+} + 3CO_3^{2-} \leftrightarrow UO_2(CO_3)_3^{4-} \quad (3.7)$$

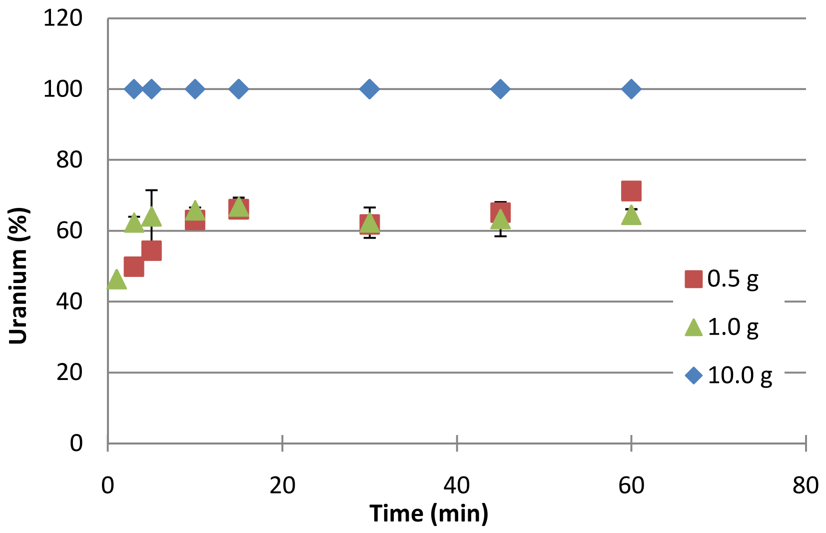


Figure 120. Extraction of uranium by 0.5 g, 1 g and 10 g of CE sludge from 0.1 mol dm^{-3} NaNO$_3$ electrolyte. The original uranium concentration was 10^{-5} mol dm^{-3}.

3.8.2 Arsenic extraction from electrolyte

The pH of the arsenic solutions in 0.1 mol dm^{-3} $NaNO_3$ electrolyte and in samples after 1 hour and 24 hours contact times are shown in Table 17. The buffering capacity of the CE sludge increases the pH of the samples but not in the 2.8E-05 to 1.35E-02 mol dm^{-3} samples in which the acid in the standard has overcome the buffering capacity of the CE sludge.

Table 17. The pH of the arsenic spiked 0.1 M $NaNO_3$ electrolyte solutions and final arsenic samples after 1 hour and 24 hours contact times with 0.2 g of CE sludge

Solution (mol dm^{-3})	***pH of original solution***	***pH in 1h samples***	***pH in 24 h sample***
Electrolyte	5.4	7.7	8.1
3.45E-07	4.7	7.7	8.2
4.03E-07	4.8	7.8	8.3
7.35E-07	4.5	7.7	8.3
1.54E-06	4.2	7.9	8.3
2.14E-06	4.1	7.8	8.3
2.8E-05	2.7	7.0	5.5
2.8E-04	1.7	2.1	2.1
8.0E-04	1.3	1.3	1.4
1.8E-03	1.0	1.0	1.1
2.4E-03	0.9	0.9	1.0
6.68E-03	0.7	0.9	0.8
1.01E-02	0.5	0.6	0.5

Figures 121 and 122 illustrate the arsenic isotherms with 1 hour and 24 hours contact times. The maximum extraction capacities were determined by calculating the average value of the samples on the plateaus in 1 hour and 24 hours samples which were 1.7E-05 ± 6.7E-06 and 1.2E-05 ± 5.2E-06 mol g^{-1}, respectively. The results show that 1 gram of CE sludge can extract 1.3 ± 0.5 mg (1 hour contact time) and 0.9 ± 0.4 mg (24 hours contact time) of arsenic from 0.1 mol dm^{-3} NaNO$_3$ electrolyte. The results are similar and therefore it can be concluded that the extraction of arsenic is fast and occurs within an hour. The original data are shown in Appendix 2.

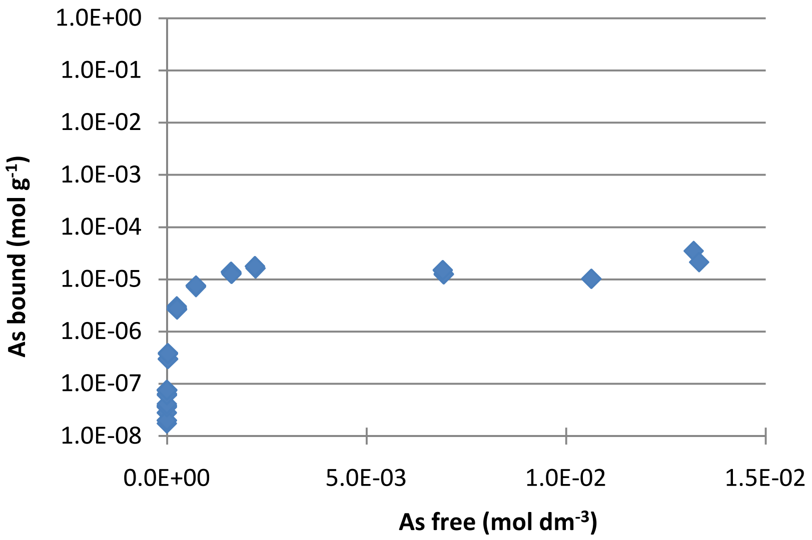


Figure 121. Extraction of arsenic by 0.2 g of CE sludge from 0.1 mol dm^{-3} NaNO$_3$ electrolyte with 1 h contact time.

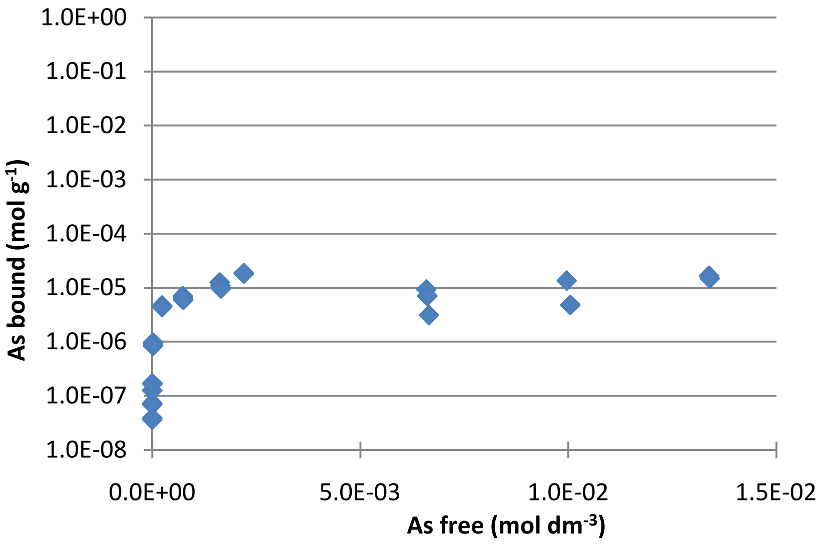


Figure 122. Extraction of arsenic by 0.2 g of CE sludge from 0.1 mol dm^{-3} NaNO$_3$ electrolyte with 24 h contact time.

3.8.3 Iron extraction from electrolyte

The pH of the iron solutions in 0.1 mol dm^{-3} $NaNO_3$ electrolyte and in the samples after 1 hour and 24 hours contact times are shown in Table 18. The pH of the original iron solutions decreased with increasing iron content from pH 4.8 to 2.2 due to iron hydrolysis in which iron(III) acts as an acid which produces protons that lower the pH. Iron(III)nitrate dissociates to iron(III) and nitrate as shown in Reaction 3.8. When iron(III) reacts with water (Reaction 3.9), iron hydroxide and protons are produced. This behaviour differs from the JCHESS modelling results since the concentrations used in the experimental solutions are much higher than in the modelling studies (Figure 89). If iron hydroxide precipitates, the equilibrium is disturbed towards the right side of the reaction thus more protons are produced.

$$Fe(NO_3)_3 \rightarrow Fe^{3+} + 3NO_3^- \qquad (3.8)$$

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+ \qquad (3.9)$$

Reaction 3.9 can also be presented as follows;

$$Fe^{3+} + nH_2O \leftrightarrow Fe(OH)_n^{3-n+} + nH^+ \qquad (3.10)$$

Where $n \leq 3$

The buffering capacity of the sludge increased the pH of the final solutions towards pH 8 in both 1 hour and 24 hours samples. Nevertheless, the final pH decreased with increasing iron concentrations and in the 1.0E-02 and 5.0E-02 mol dm^{-3} samples the pH remained almost unchanged.

Table 18. The pH of the original iron and 0.1 M $NaNO_3$ electrolyte solutions and final iron solutions after 1 h and 24 h contact times with 0.2 g of CE sludge

Solution (mol dm^{-3})	***pH of original solution***	***pH in 1h samples***	***pH in 24 h sample***
Electrolyte	5.0	7.6	7.9
1.0E-05	4.8	7.3	7.8
1.0E-04	3.7	6.5	7.6
3.0E-04	3.9	5.8	7.9
5.0E-04	3.6	5.3	7.4
7.0E-04	3.3	4.8	7.1
1.0E-03	3.0	3.7	6.3
5.0E-03	2.9	2.9	5.5
1.0E-02	2.3	2.7	2.4
3.0E-02	2.5	2.6	2.3
5.0E-02	2.2	2.3	2.6

Figures 123 and 124 show the iron isotherms in the electrolyte. The results show maximum iron extraction of 1.2E-03 ± 3.3E-04 mol g^{-1} with 1 hour contact time and 1.0E-03 ± 5.4E-04 mol g^{-1} with 24 hours contact time. The results can also be presented as grams of analyte extracted by 1 g of solid thus 66.5 mg ± 18.4 mg (1 h) and 55.6 ± 30.1 mg (24 h) of iron can be extracted by 1 g of CE sludge. The results show quick removal (< 1h) of iron from the solution. Increasing pH precipitates iron as seen in modelling studies (Figure 93). Therefore, since the CE sludge has buffering capacity towards pH 8, the iron was removed from the solution by precipitation or/and extraction by the CE sludge. The original data are shown in Appendix 2.

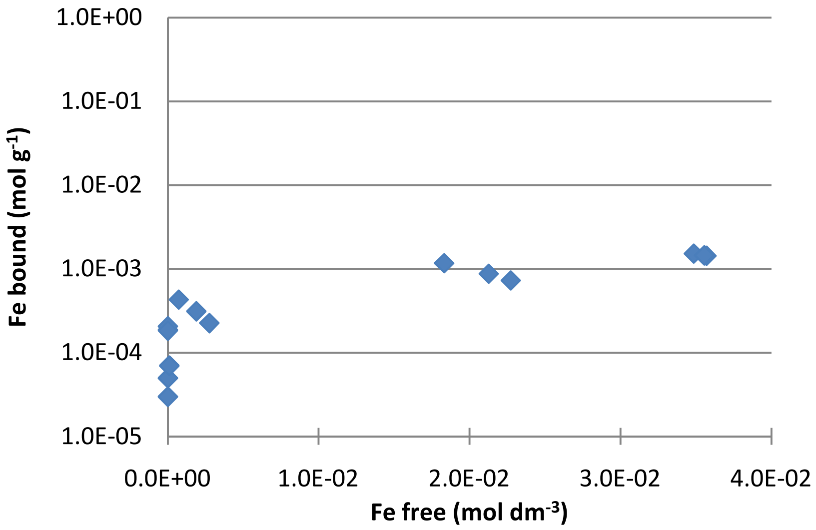


Figure 123. Extraction of iron by 0.2 g of CE sludge from 0.1 mol dm^{-3} NaNO$_3$ electrolyte with 1 h contact time.

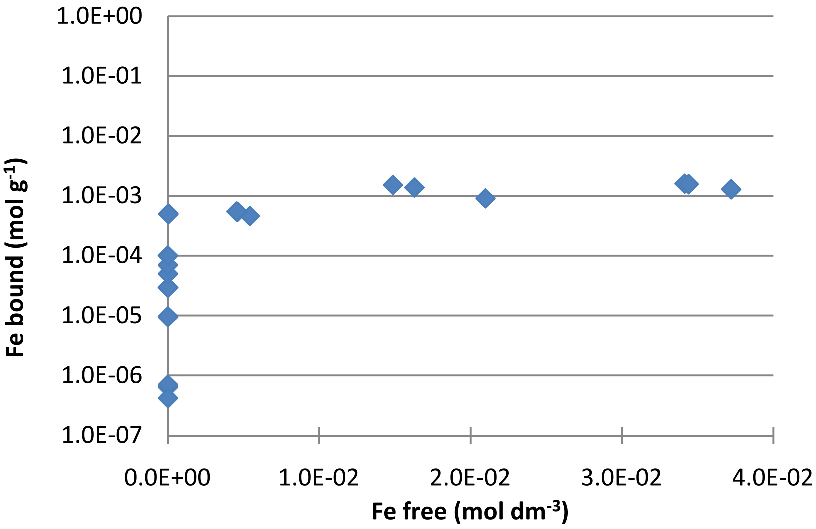


Figure 124. Extraction of iron by 0.2 g of CE sludge from 0.1 mol dm^{-3} NaNO$_3$ electrolyte with 24 h contact time.

3.8.4 Uranium extraction from electrolyte

Table 19 shows the pH of the uranium solutions in electrolyte along with the pH of the filtered 1 hour and 24 hours samples. The pH of the original solutions decreases with increasing uranium concentrations due to the acidic behaviour of uranyl ions in acidic aqueous solutions [60] when enough uranium is present (Equations 3.11-14).

$$UO_2^{2+} + H_2O \leftrightarrow UO_2OH^+ + H^+ \quad (3.11)$$

$$2UO_2^{2+} + H_2O \leftrightarrow (UO_2)_2OH^{3+} + H^+ \quad (3.12)$$

$$2UO_2^{2+} + 2H_2O \leftrightarrow (UO_2)_2(OH)_2^{2+} + 2H^+ \quad (3.13)$$

$$3UO_2^{2+} + 5H_2O \leftrightarrow (UO_2)_3(OH)_5^+ + 5H^+ \quad (3.14)$$

Mashirov *et al*. [60] postulated that above pH 3, the predominant process is spontaneous hydrolysis (Equations 3.15 and 3.16) with subsequent coagulation of neutral $(UO_2)_2(OH)_4$.

$$(UO_2)_2(OH)_2^{2+} + H_2O \leftrightarrow (UO_2)_2(OH)_3^+ + H^+ \quad (3.15)$$

$$(UO_2)_2(OH)_3^+ + H_2O \leftrightarrow (UO_2)_2(OH)_4 + H^+ \quad (3.16)$$

Table 19 also shows that the buffering capacity of the CE sludge increases the pH of the 1 hour and 24 hours uranium solutions toward pH 8. However, the increase in pH diminishes as the original uranium concentration increases.

Table 19. The pH of the original uranium and 0.1 M $NaNO_3$ electrolyte solutions and initial and final uranium solutions after 1 h and 24 h contact times with 0.2 g of CE sludge

Solution (mol dm^{-3})	***pH of original solution***	***pH in 1h samples***	***pH in 24 h sample***
Electrolyte	4.8	7.2	7.7
1.0E-05	4.6	8.2	7.5
1.0E-04	4.4	8.2	7.1
1.0E-03	3.8	7.4	5.4
3.0E-03	3.5	6.0	4.3
5.0E-03	3.3	4.8	4.0
8.0E-03	3.1	4.2	3.7

The uranium isotherms are shown in Figures 125 and 126. It can be seen that saturation of the sludge has been reached in both isotherms. The calculated averages of the maximum amount of uranium bound were 1.4E-04 ± 2.2E-05 mol g^{-1} in 1 hour samples and 3.3E-04 ± 3.1E-05 mol g^{-1} in 24 hours samples. The maximum amounts of uranium that 1 g of CE sludge can extract are 33.1 ± 5.3 mg (1 h) and 78.3 ± 7.4 mg (24 h), thus the extraction capacity is twice as high when using the longer contact time. Therefore, it can be concluded that the extraction of uranium is not as fast as the extraction of arsenic or iron (< 1 h). Uranium species are bigger molecules than arsenic or iron species and therefore extraction kinetics are slower. The original data are shown in Appendix 2.

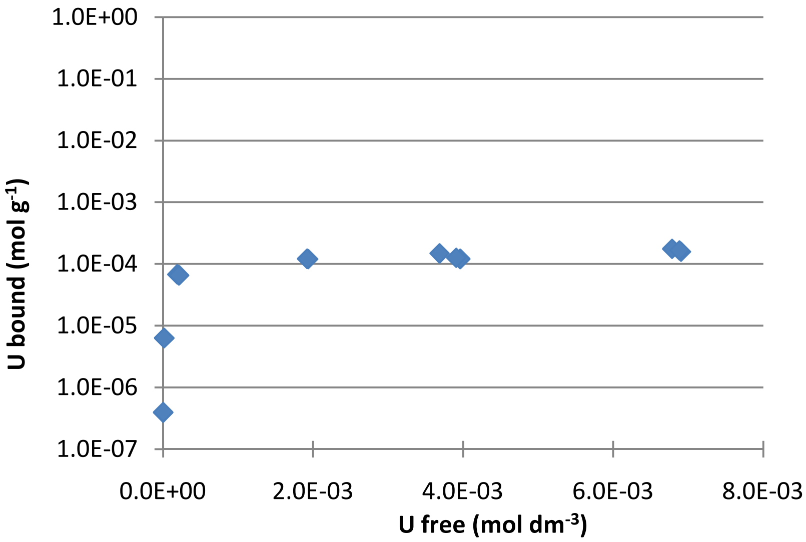


Figure 125. Extraction of uranium by 0.2 g of CE sludge from 0.1 mol dm^{-3} $NaNO_3$ electrolyte with 1 h contact time.

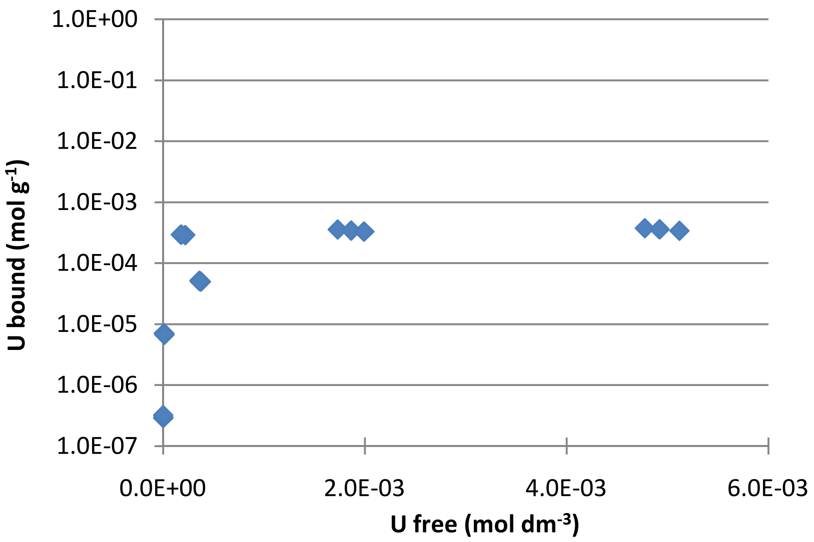


Figure 126. Extraction of uranium by 0.2 g of CE sludge from 0.1 mol dm^{-3} NaNO$_3$ electrolyte with 24 h contact time.

3.9 Extraction of arsenic, iron and uranium from un-treated Plant P effluent by CE sludge

The kinetics and extraction capacities in batches and in a column from un-treated Plant P effluent were carried out as presented in section 3.7. The original arsenic, iron and uranium concentrations in the effluent are shown in Table 20. Even though the un-treated Plant P 15 effluent did not contain a measurable amount of arsenic, the extraction capacity for arsenic was determined by adding increasing amounts of arsenic into the effluent.

Table 20. The original iron and uranium concentrations in the un-treated P 15 effluent

Effluent	*pH*	*Arsenic (mg dm^{-3})*	*Iron (mg dm^{-3})*	*Uranium (mg dm^{-3})*
Un-treated Plant P 15	3.0	< 0.006	5.7	0.079

3.9.1 Kinetics of arsenic, iron and uranium removal from un-treated Plant P effluent

Figure 127 displays the pH in the mixtures of 0.5 g, 1 g and 10 g of CE sludge and 100 cm^3 of un-treated Plant P effluent. The original pH of the un-treated Plant P effluent was 3.0 and the pH in the samples with three different solid:liquid ratios increased as a function of time until they reached pH 8 in 60 minutes. Thus the buffering capacity of the CE sludge overcame the acidity of the effluent.

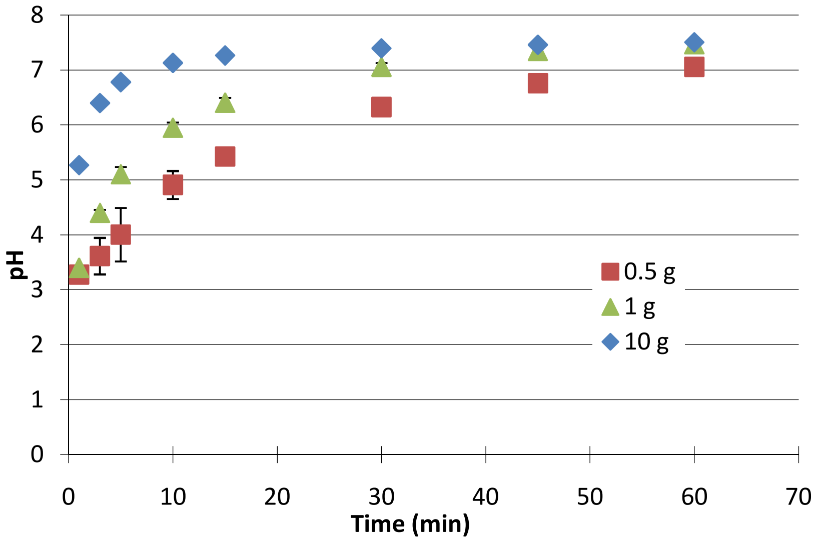


Figure 127. The pH in the samples of 0.5 g, 1 g and 10 g of CE sludge with arsenic, iron and uranium in un-treated Plant P effluent as a function of time.

The kinetics of iron and uranium removal from the un-treated effluent are presented in Figures 128 and 129. The extraction results show fast extraction of iron (100% in 10 min) and uranium (100% in 30 min) in all three sample sets.

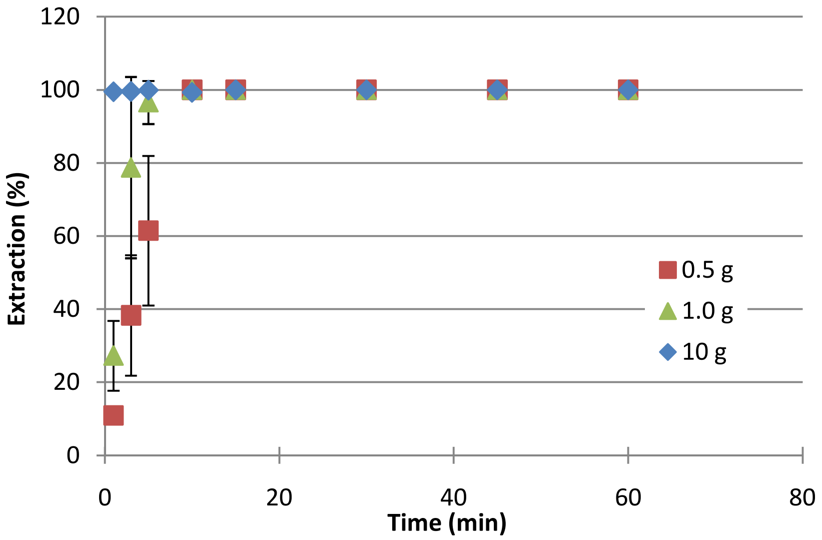


Figure 128. Extraction of iron by 0.5 g, 1 g and 10 g of CE sludge from un-treated P effluent. The original iron concentration in the un-treated Plant P effluent was 5.7 mg dm^{-3}.

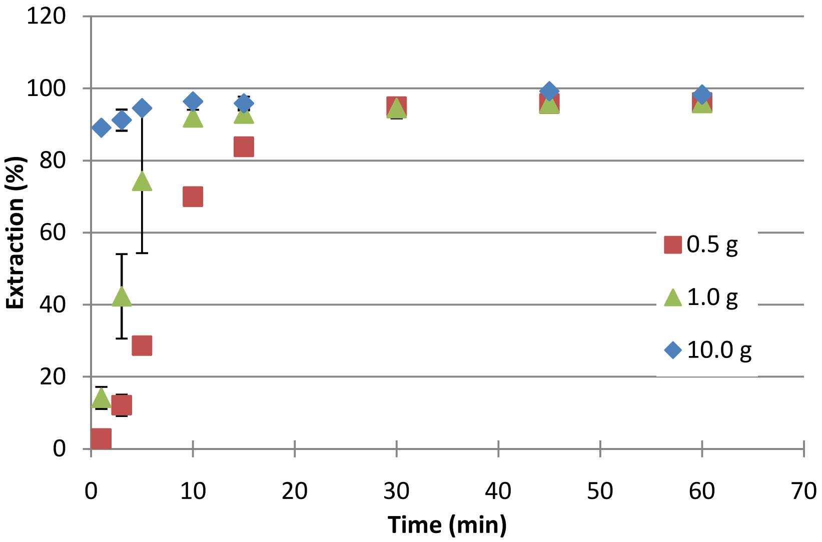


Figure 129. Extraction of uranium by 0.5 g, 1 g and 10 g of CE sludge from un-treated Plant P effluent. The original uranium concentration in the un-treated Plant P effluent was 0.079 mg dm^{-3}.

3.9.2 Arsenic extraction from un-treated Plant P effluent

Table 21 shows the added arsenic concentrations in the un-treated Plant P effluent and the final pH of the samples after 24 hours contact time. All the pHs increased from the original pH of the effluent (3.0) to between pH 6 and 7. Thus the natural pH of the CE sludge was almost reached.

Table 21. The concentrations of the arsenic spiked un-treated Plant P solutions and final pH of the solutions after 24 h contact time with 0.2 g of CE sludge

Solution (mol dm^{-3})	***pH in 24 h sample***
1.34E-03	7.0
2.64E-03	6.4
6.64E-03	6.1
1.31E-02	6.4
4.12E-02	-
7.54E-02	6.3

The maximum capacity of the CE sludge to extract arsenic from the un-treated Plant P effluent (Figure 130) could not been determined since the CE sludge was not saturated with arsenic. Nevertheless, it can be said that the extraction capacity for arsenic in un-treated P effluent is higher than 5.4E-04 ± 1.3E-05 mol g^{-1} which corresponds to 40.7 ± 1.0 mg per 1 g of CE sludge. The original data are shown in Appendix 2.

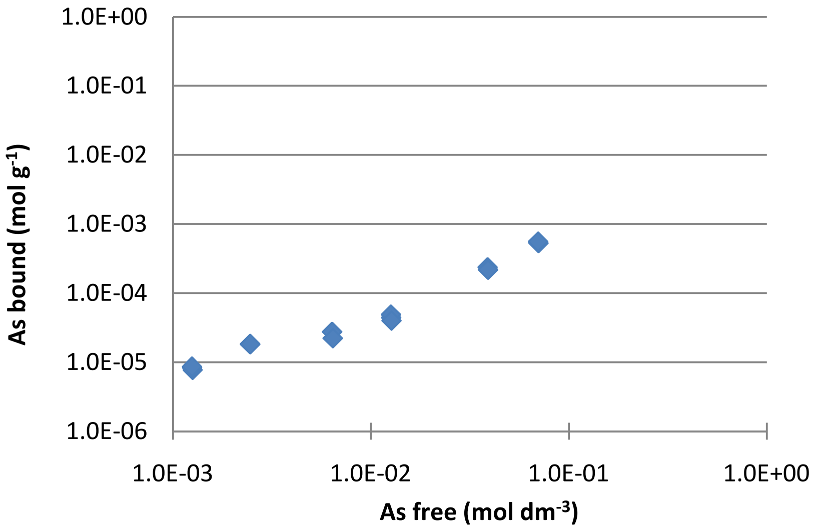


Figure 130. Extraction of arsenic by 0.2 g of CE sludge from un-treated Plant P effluent with 24 h contact time.

3.9.3 Iron extraction from un-treated Plant P effluent

The iron concentrations in the un-treated Plant P effluents after addition of iron and the pH of the mixtures after 24 hours contact times are shown in Table 22.

The results show a decrease of pH with increasing iron concentration due to hydrolysis of iron.

Table 22. The concentrations of the iron spiked un-treated Plant P solutions and final pH of the solutions after 24 h contact time with 0.2 g of CE sludge

Solution (mol dm^{-3})	***pH in 24 h sample***
2.07E-05	7.2
1.32E-03	6.4
2.70E-03	5.0
4.31E-03	3.3
6.70E-03	2.6
3.76E-02	1.8

The maximum capacity of iron removal by CE sludge from un-treated Plant P effluent is 3.0E-04 ± 1.2E-04 mol g^{-1} (Figure 131) which corresponds to an extraction of 16.7 ± 6.8 mg of iron by 1 g of CE sludge. The original data are shown in Appendix 2.

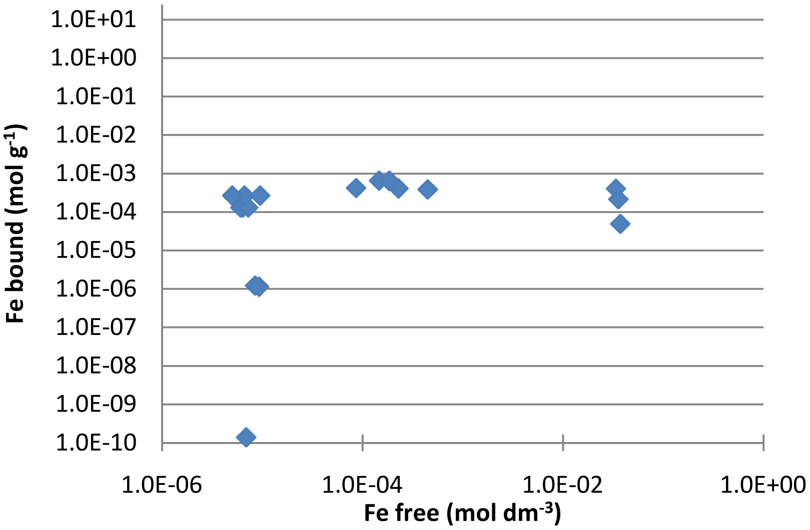


Figure 131. Extraction of iron by 0.2 g of CE sludge from un-treated Plant P effluent with 24 h contact time.

3.9.4 Uranium extraction from un-treated Plant P effluent

The uranium concentrations in the un-treated Plant P effluents after uranium addition and the pH of the 24 hours samples are shown in Table 23. The pH of the uranium samples decrease with increasing uranium concentrations.

Table 23. The concentrations of the uranium spiked un-treated Plant P solutions and final pH of the solutions after 24 h contact time with 0.2 g of CE sludge

Solution ***(mol dm^{-3})***	***pH in 24 h sample***
3.92E-04	6.9
8.26E-04	6.7
2.06E-03	5.9
4.23E-03	4.9
8.55E-03	4.3
1.17E-02	4.0

The maximum amount of uranium that can be extracted by CE sludge from un-treated Plant P effluent is 2.2E-04 ± 5.0E-05 mol g^{-1} (Figure 132), thus the maximum amount of uranium that 1 g of CE sludge can extract is 51.5 ± 11.9 mg. The original data are shown in Appendix 2.

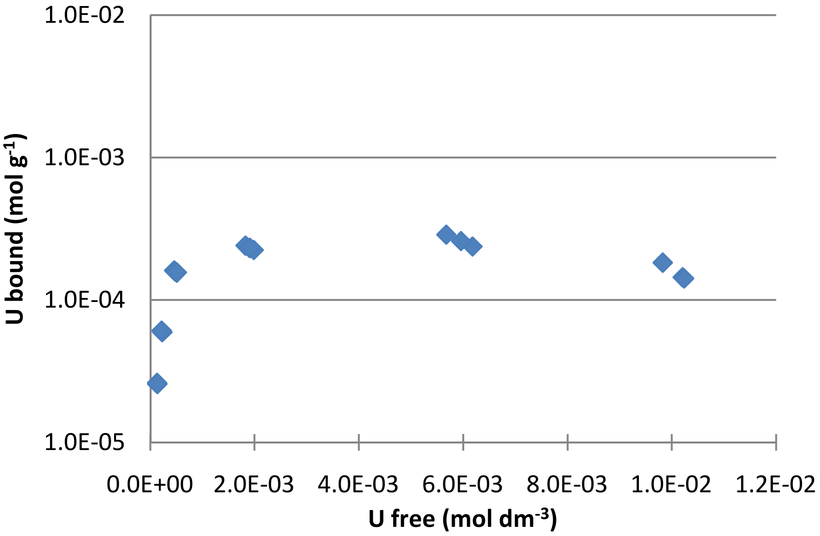


Figure 132. Extraction of uranium by 0.2 g of CE sludge from un-treated P effluent with 24 h contact time.

3.9.5 Extraction of iron and uranium from un-treated Plant P effluent by a column

The iron and uranium extraction results using the 50 g CE column (length 11.9 cm, porosity 59%) treated with un-treated Plant P effluent, and the pH, are shown in Figures 133-135. The iron concentrations in the dead volume region exhibit leaching of iron from the original column material ranging from 0.7 to 0.1 mg dm^{-3} (Figure 133). After that the extraction percentage of iron increases rapidly. When the column is washed with DI water, some loosely bound iron is released (max 0.6 mg dm^{-3}) but the extraction percentage is always above 90% (Figure 134). The total amount of iron in the collected samples was 0.1013 mg and in the 100 cm^3 effluent 0.565 mg, thus overall 82% of iron was retained in the column and 18% migrated through the column.

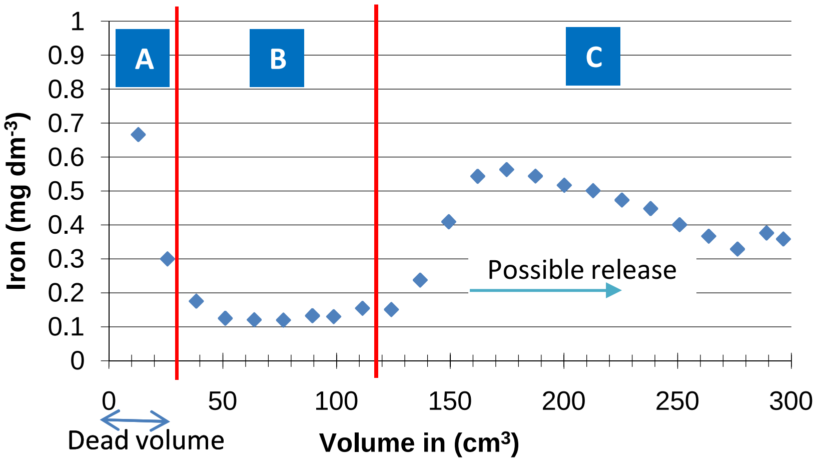


Figure 133. Iron concentrations in the fractions collected from 50 g CE column treated with 100 cm^3 un-treated Plant P effluent. The original iron concentration in the un-treated Plant P effluent was 5.7 mg dm^{-3}. Region A is the dead volume of the column, B is the region of elution with effluent and C is the region of elution with deionised water.

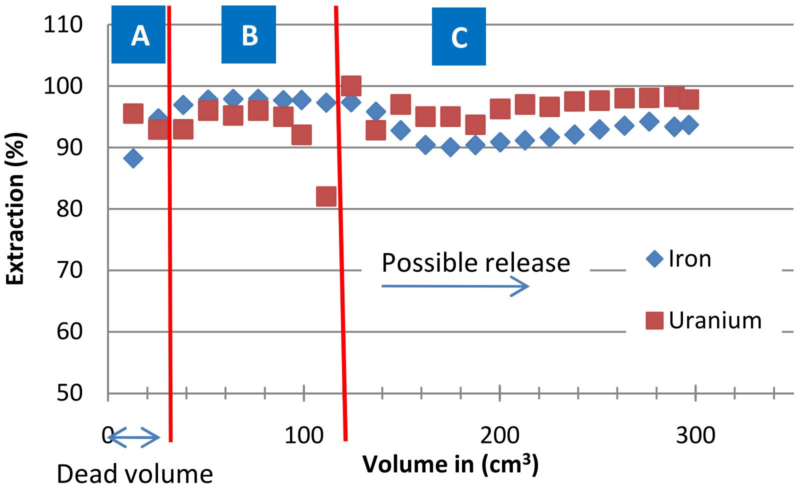


Figure 134. The extraction percentages of iron and uranium removals in the fractions collected from 50 g CE column treated with 100 cm^3 un-treated Plant P effluent. The original iron and uranium concentrations in the un-treated Plant P effluent were 5.7 mg dm^{-3} and 0.079 mg dm^{-3}, respectively. Region A is the dead volume of the column, B is the region of elution with effluent and C is the region of elution with deionised water.

The extraction of uranium was also efficient with over 80% extraction (Figure 134). Nevertheless, since the CE sludge does not release measurable uranium and some uranium was detected at low concentrations throughout the experiment it can be concluded that the uranium detected in the samples is due to experimental error (Figure 135).

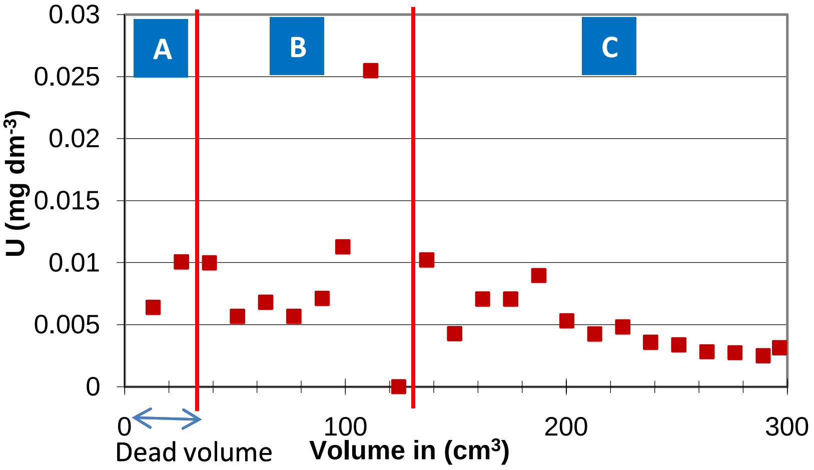


Figure 135. Uranium concentrations in the fractions collected from 50 g CE column treated with 100 cm^3 un-treated Plant P effluent. The original concentration in the un-treated Plant P effluent was 0.079 mg dm^{-3}. Region A is the dead volume of the column, B is the region of elution with effluent and C is the region of elution with deionised water.

The pH in the collected samples (Figure 136) increases from pH 7.2 to 8 as the effluent was passed through the column after which the pH remained at the buffering pH of the CE sludge (~8). Since increasing pH precipitates iron and uranium, these results suggest that their removal may have occurred by precipitation or extraction or both.

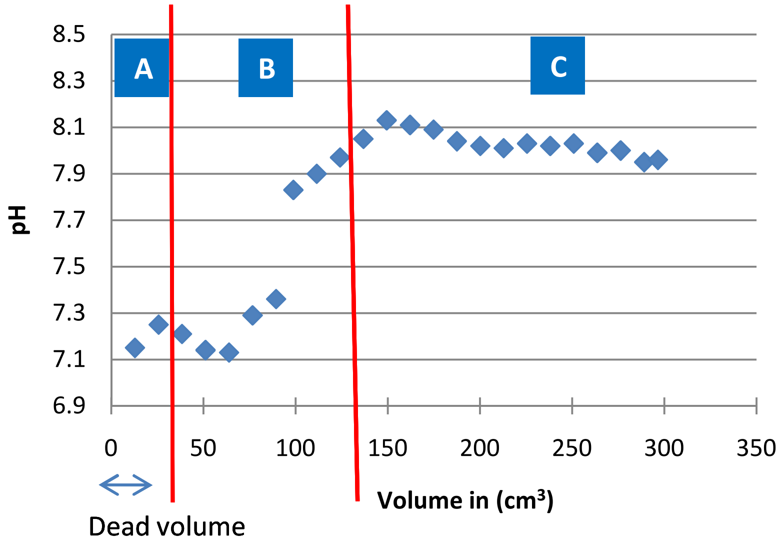


Figure 136. The pHs of fractions collected from 50 g CE column treated with 100 cm^3 untreated Plant P effluent. Region A is the dead volume of the column, B is the region of elution with effluent and C is the region of elution with deionised water.

3.10 Extraction of arsenic, iron and uranium from treated Plant P effluent by CE sludge

The kinetics and extraction capacities in batches and in a column from treated Plant P effluent were carried out as presented in section 3.7. The treatment of Plant P effluent was mimicked by adding sodium carbonate to the effluent (P 15) until the pH increased to 5. The treated Plant P effluent was named as Plant P 15b effluent. The arsenic, iron and uranium concentrations in the treated Plant P 15b effluent are shown in Table 24. Even though the treated Plant P effluent did not contain a measurable amount of arsenic, the extraction capacity for arsenic was determined.

Table 24. Original arsenic, iron and uranium concentrations in treated Plant P

Effluent	***pH***	***Arsenic (mg dm^{-3})***	***Iron (mg dm^{-3})***	***Uranium (mg dm^{-3})***
Treated P	5.3	< 0.006	4.6	0.079

3.10.1 Kinetics of arsenic, iron and uranium removal from treated Plant P effluent

The pH in all the mixtures of 0.5 g, 1 g and 10 g of CE sludge with 100 cm^3 of treated Plant P effluent (Figure 137) equilibrate to pH 7.5 within 30 minutes due to the buffering capacity of CE sludge.

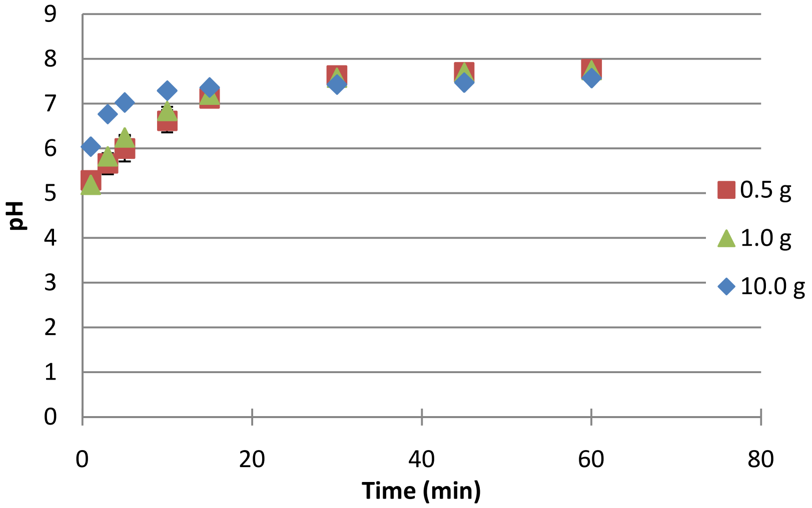


Figure 137. The pH in the samples of 0.5 g, 1 g and 10 g of CE sludge with treated Plant P effluent as a function of time.

The results of iron extraction from treated Plant P effluent are shown in Figure 138 as percentages and in Figure 139 as concentrations. The results show initially 100% extraction in all three sample sets but then increasing leaching of iron as a function of time. Sodium carbonate was added into the treated Plant P effluent and therefore carbonate may have an effect on leaching of iron from the CE sludge or it may enhance dissolution of humic acid complexed with iron. To investigate further, an additional set of experiments was undertaken to determine the effect of carbonate on the leaching of iron from the sludge as free iron or as a complex with dissolved humic acid. Triplicates of 0.2 g of CE sludge were placed in contact with 20 cm^3 0.1 mol dm^{-3} $NaNO_3$ in the presence and absence of sodium carbonate. The pH of the electrolytes were set to 3 (absence of carbonate) using 1 mol dm^{-3} H_2SO_4 and in the presence of carbonate using a sufficient amount of solid sodium carbonate to increase the pH to 5. The samples were agitated on an orbital shaker for 1 hour, the pH was measured and then samples were filtered (0.2 µm). The UV-readings were measured at 254 nm and the iron concentrations were determined using ICP-OES. After 1 hour contact time, the pH was 5.9 in the presence and 7.0 in the absence of carbonate. The UV readings at 254 nm did not exhibit a significant difference in absorbance between the samples sets (0.4476 ± 0.0059 in the absence and 0.3668 ± 0.0105 in the presence), thus carbonate has not increased the solubility of humic acid rather decreased it slightly. The samples in the presence of carbonate also showed lower iron concentrations released; 0.017 ± 0.002 mg dm^{-3} compared to 0.123 ± 0.017 mg dm^{-3} in the absence of added carbonate.

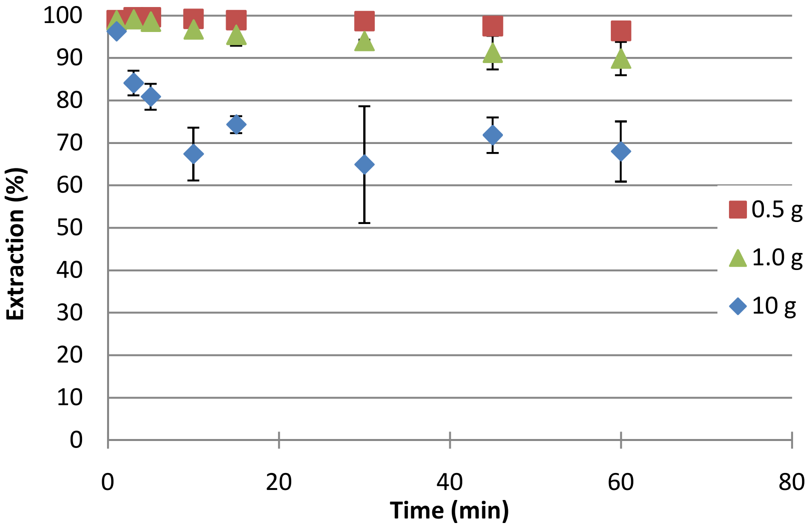


Figure 138. Extraction (%) of iron by 0.5 g, 1 g and 10 g of CE sludge from treated Plant P effluent as a function of time. Original iron concentration was 4.6 mg dm^{-3}.

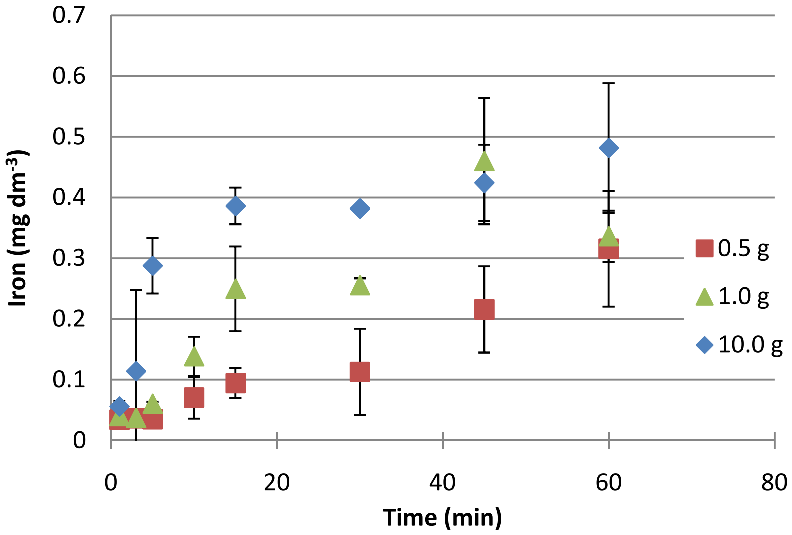


Figure 139. Extraction (mg dm^{-3}) of iron by 0.5 g, 1 g and 10 g of CE sludge from treated Plant P effluent as a function of time. Original iron concentration was 4.6 mg dm^{-3}.

Figure 140 shows the results of uranium extraction from treated Plant P effluent. The initial extraction of uranium is over 50% and then plateaus to 85% in 45 minutes. In light of the JCHESS modelling results (Figure 102), carbonate has an effect on uranium behaviour, and thus some uranium has formed a complex with carbonate and remained in the solution. The presence of carbonate and increasing pH initiate competing reactions; carbonate increases uranium solubility through complex formation and increasing pH tends to initiate precipitation.

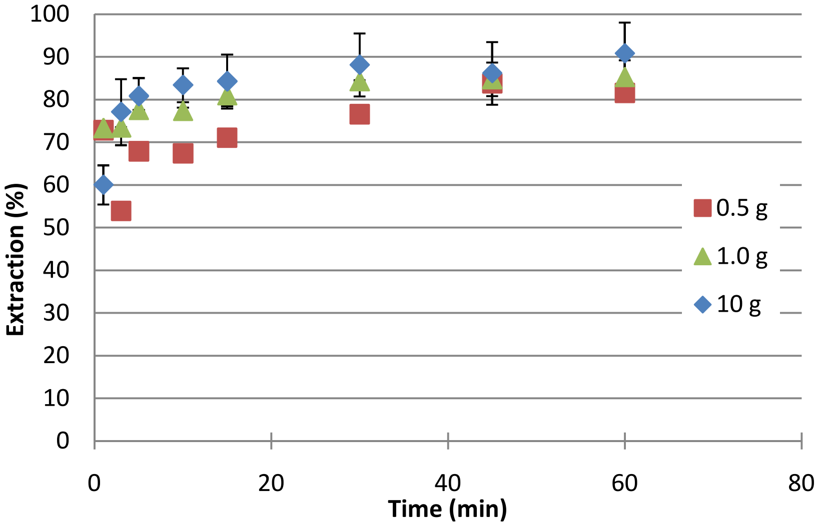


Figure 140. Extraction of uranium by 0.5 g, 1 g and 10 g of CE sludge from treated Plant P effluent as a function of time. Original uranium concentration was 0.079 mg dm^{-3}.

3.10.2 Arsenic extraction from treated Plant P effluent

The arsenic concentrations in the treated Plant P effluent after the arsenic addition and the pH of the 24 hours samples are shown in Table 25. The pH of the original treated Plant P effluent was 5, thus the buffering capacity of CE sludge has increased the pH toward 7.

Table 25. The concentrations of the arsenic spiked treated Plant P solutions and final pH of the solutions after 24 h contact time with 0.2 g of CE sludge

Solution (mol dm^{-3})	*pH in 24 h sample*
3.00E-03	6.98
6.28E-03	7.08
8.46E-03	6.65
2.91E-02	6.41
8.12E-02	6.71

The results presented in Figure 141 show that the maximum capacity of arsenic removal from treated Plant P effluent is 9.9E-05 ± 1.4E-05 mol g^{-1}. Thus, 1 g of CE sludge can extract 7.4 ± 1.1 mg of arsenic from treated Plant P effluent. The original data are shown in Appendix 2.

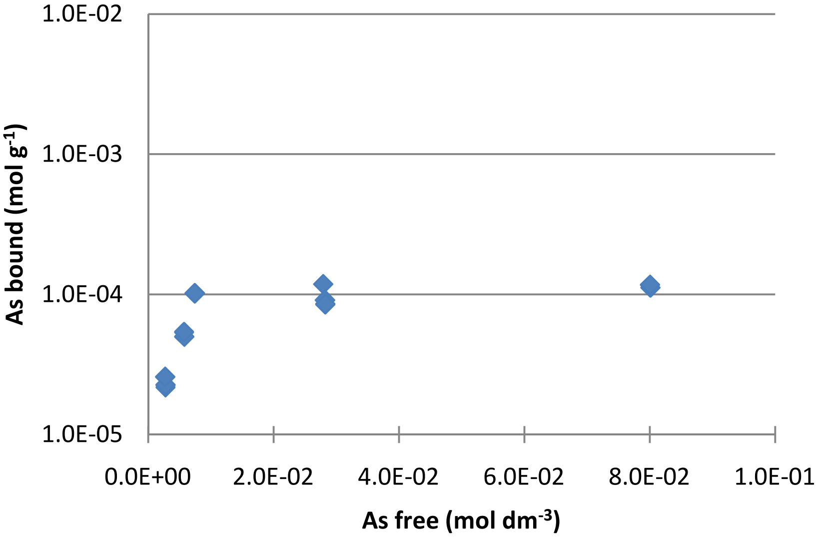


Figure 141. Extraction of arsenic by 0.2 g of CE sludge from treated Plant P effluent with 24 h contact time.

3.10.3 Iron extraction from treated Plant P effluent

Table 26 shows the concentrations of added iron in the treated Plant P solutions and the pH of the 20 cm^3 solutions after 24 hours contact times with 0.2 g of CE sludge. The final pH decrease slightly with increasing iron concentrations but the variance is only from pH 5.7 to 7.2.

Table 26. The concentrations of the iron spiked treated Plant P solutions and final pH of the solutions after 24 h contact time with 0.2 g of CE sludge

Solution ***(mol dm^{-3})***	***pH in 24 h sample***
4.98E-04	7.2
1.04E-03	6.9
3.27E-03	6.3
1.01E-02	6.6
3.30E-02	5.7

Iron precipitation is clearly observed in Figure 142. The samples were prepared by adding the iron to treated Plant P effluent (addition of iron lowered the pH) after which the pH was adjusted back to 5 ± 0.2 by the addition of Na_2CO_3. The pH adjustment precipitated most of the added iron (red precipitate). Therefore, the removal of iron from the treated Plant P effluent occurred by precipitation (Fe “bound” in Figure 142) rather than extraction. The iron concentrations in the samples are approximately the same (1.8E-05 ± 1.1E-05 mol dm^{-3}) which correspond to 1.0 ± 0.6 mg dm^{-3}. The original data are shown in Appendix 2.

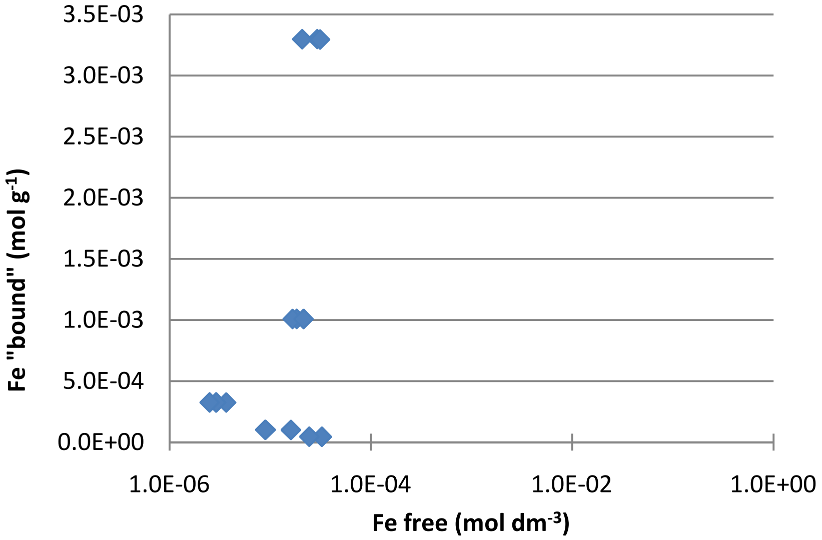


Figure 142. Extraction/precipitation of iron by 0.2 g of CE sludge from treated Plant P effluent with 24 h contact time.

3.10.4 Uranium extraction from treated Plant P effluent

Table 27 shows the concentrations of the treated Plant P solutions with added uranium and the pH of the samples after 24 hours contact time with CE sludge. The final pH of the samples rose from the original pH of 5 to 6-7.

Table 27. The concentrations of the uranium spiked treated Plant P solutions and final pHs of the solutions after 24 h contact time with 0.2 g of CE sludge

Solution ***(mol dm^{-3})***	***pH in 24 h sample***
5.89E-04	7.1
2.31E-03	6.6
5.62E-03	6.1
9.83E-03	6.0
2.38E-02	6.0

Figure 143 show the uranium isotherm for treated Plant P effluent. Since the results show that the CE sludge is not saturated with uranium the extraction capacity for uranium cannot be determined. Nevertheless, the capacity is higher than 2.1E-03 ± 1.1E-04 mol g^{-1} which corresponds to 488.8 ± 25.5 mg of uranium extracted by 1 g of CE sludge. The original data are shown in Appendix 2.

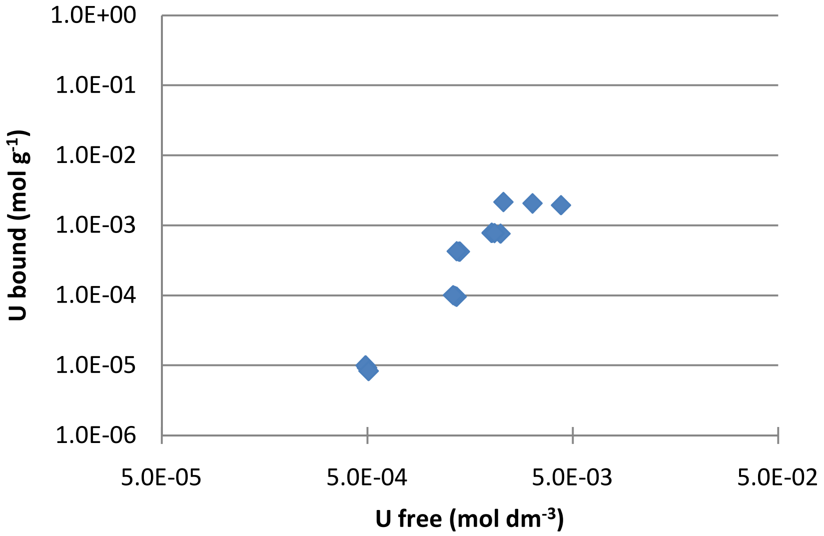


Figure 143. Extraction of uranium by 0.2 g of CE sludge from treated Plant P effluent with 24 h contact time.

3.10.5 Extraction of iron and uranium from treated Plant P effluent by a column of CE sludge

The porosity of the 50 g CE column was 52%, as measured by using tritiated water, and the length 12.5 cm. The extraction results of iron and uranium plotted in the Figures 144-146 show efficient removal of both analytes. The iron present in the samples in the dead volume region suggests leaching of iron from the column (0.3 mg dm^{-3}) but the concentration rapidly decreases to 0.2 mg dm^{-3} as the effluent begins to elute from the column (Figure 144). When the column is washed with DI water, some loosely bound iron is released but the concentration does not increase above 0.7 mg dm^{-3}. Nevertheless, the extraction percentage is above 85% throughout the whole experiment (Figure 146). The total amount of iron in the collected samples was 0.1063 mg and in the 100 cm^3 effluent 0.4630 mg thus 77% of iron was retained in the column and 23% was recovered. The uranium removal from the effluent was also significant (Figure 145 and 146). When the experimental error is taken into consideration, it can be said that the extraction of uranium was complete.

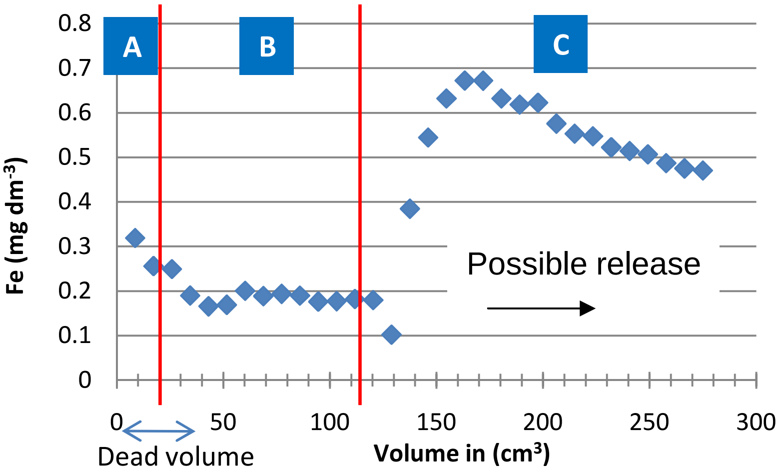


Figure 144. Iron concentrations in the fractions collected from 50 g CE column treated with 100 cm^3 treated Plant P effluent. The original iron concentration in the treated Plant P effluent was 4.6 mg dm^{-3}. Region A is the dead volume of the column, B is the region of elution with effluent and C is the region of elution with deionised water.

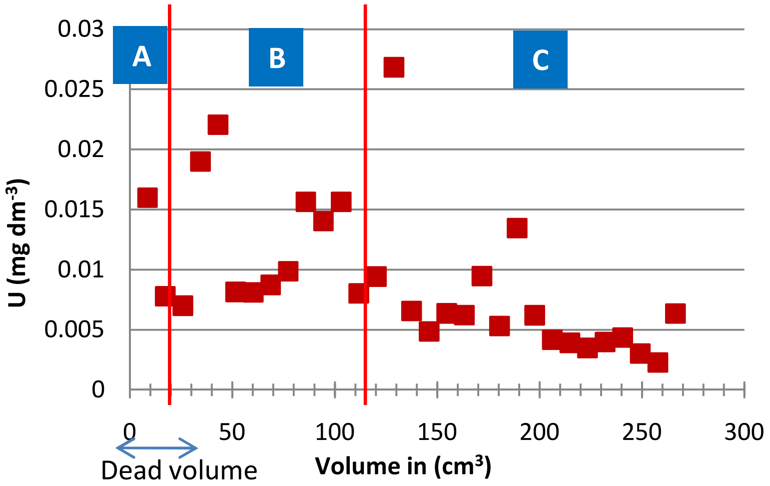


Figure 145. Uranium concentrations in the fractions collected from 50 g CE column treated with 100 cm^3 treated Plant P effluent. The original uranium concentration in the treated Plant P effluent was 0.079 mg dm^{-3}. Region A is the dead volume of the column, B is the region of elution with effluent and C is the region of elution with deionised water.

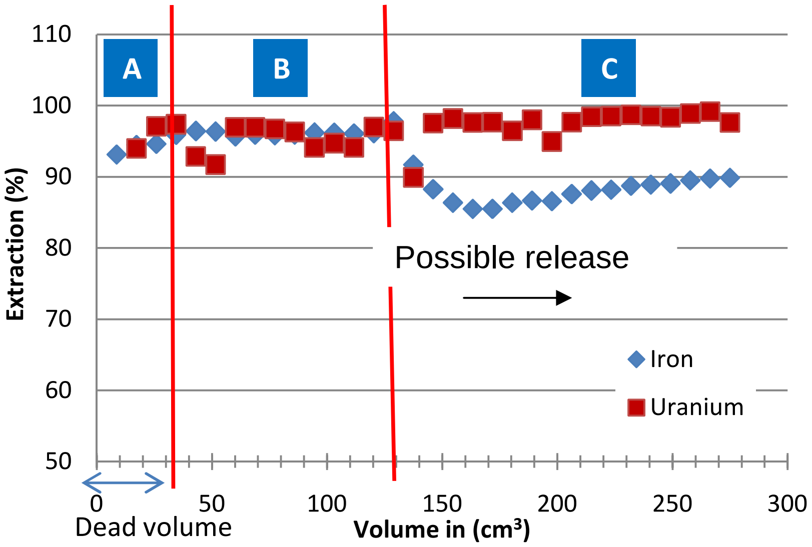


Figure 146. Iron (A) and uranium (B) concentrations in the fractions collected from 50 g CE column treated with 100 cm^3 treated Plant P effluent and their extraction percentages (C). The original iron and uranium concentrations in the treated Plant P effluent were 4.6 mg dm^{-3} and 0.079 mg dm^{-3}, respectively. Region A is the dead volume of the column, B is the region of elution with effluent and C is the region of elution with deionised water.

The pH of the collected samples (Figure 147) show an increase from 7.2 to 7.4 in the dead volume region after which it increases step-wise first to 7.9 and then to 8.0. As the washing solution comes through the column the pH begins to decrease reaching 7.8 at the end of the experiment. Increasing pH precipitates iron and uranium, therefore these results suggest that the removal of iron and uranium may have occurred by precipitation or extraction or both.

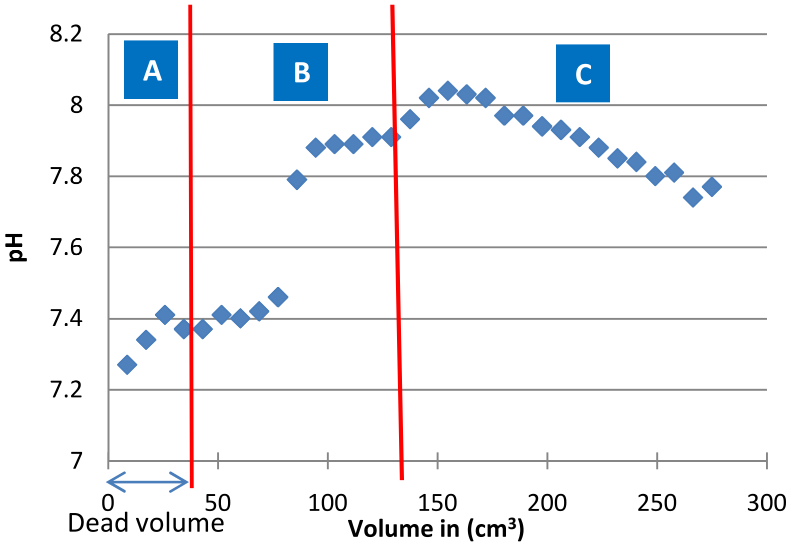


Figure 147. The pH of fractions collected from 50 g CE column treated with 100 cm^3 treated Plant P effluent. Region A is the dead volume of the column, B is the region of elution with effluent and C is the region of elution with deionised water.

3.11 Extraction of arsenic, iron and uranium from un-treated Plant R effluent by CE sludge

The kinetics and extraction capacities in batches and in a column from un-treated Plant R effluent were carried out as presented in section 3.7. The original arsenic, iron and uranium concentrations in the Plant R 1 effluent are shown in Table 28.

Table 28. The original arsenic, iron and uranium concentrations in un-treated Plant R 1 effluent

Effluent	***pH***	***Arsenic (mol dm^{-3})***	***Iron (mol dm^{-3})***	***Uranium (mol dm^{-3})***
Plant R	2.7	0.132	65.4	0.019

3.11.1 Kinetics of arsenic, iron and uranium removal from un-treated Plant R effluent

The pH of arsenic, iron and uranium kinetic samples are shown in Figure 148. In the 1 g and 10 g samples, the pH increases towards the natural pH of the sludge as a function of time and reaches pH 7 in 60 minutes. The pH in the 0.5

g sample set continues to increase during the sampling time and reaches pH 5 by the end of the experiment.

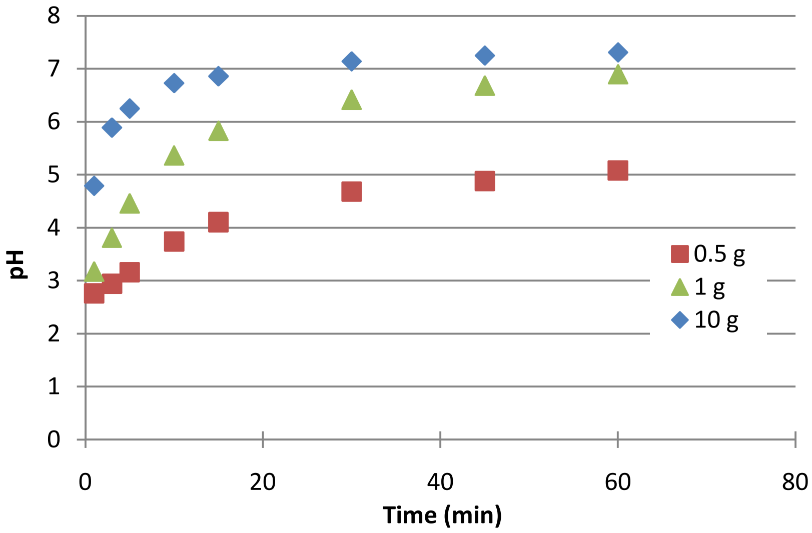


Figure 148. The pH in the samples of 0.5 g, 1 g and 10 g of CE sludge with 100 cm^3 un-treated Plant R effluent as a function of time.

Arsenic is efficiently extracted from the effluent in all the samples, even though they have different solid:liquid ratios (Figure 149). The 0.5 g samples extract arsenic within 30 minutes, 1 g samples within 15 minutes, and 10 g samples within 2 minutes. The iron in the samples with the lowest solid:liquid ratio (0.5 g to 100 cm^3) is not extracted from the effluent even after 60 minutes, while the samples with the solid:liquid ratio of 1:100 (1 g to 100 cm^3) extracts almost all of the iron in 60 minutes (Figure 150). The iron in the effluent is most efficiently removed within 15 minutes by samples with 1:10 solid:liquid ratio (10 g to 100 cm^3). The uranium in the un-treated Plant R effluent is fully extracted in 60 minutes in all three sample sets (Figure 151).

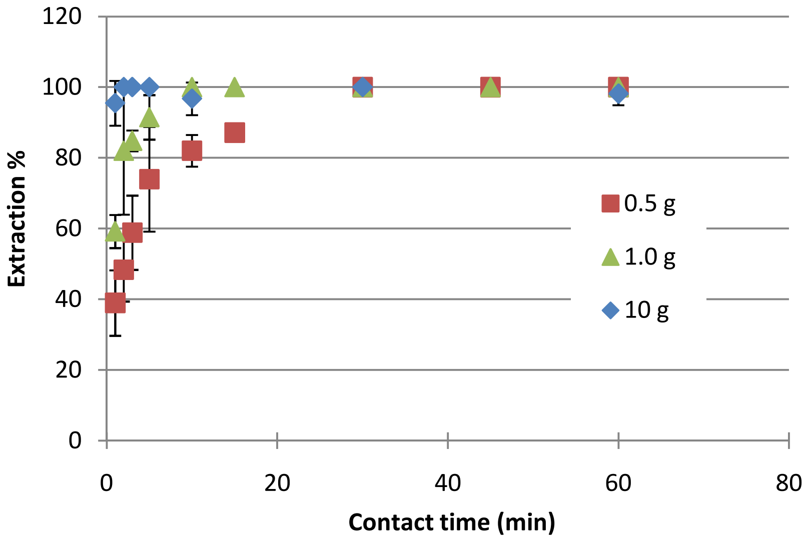


Figure 149. Extraction of arsenic by 0.5 g, 1 g and 10 g of CE sludge from 100 cm^3 un-treated Plant R effluent. The original arsenic concentration in the un-treated Plant R effluent was 0.132 mg dm^{-3}.

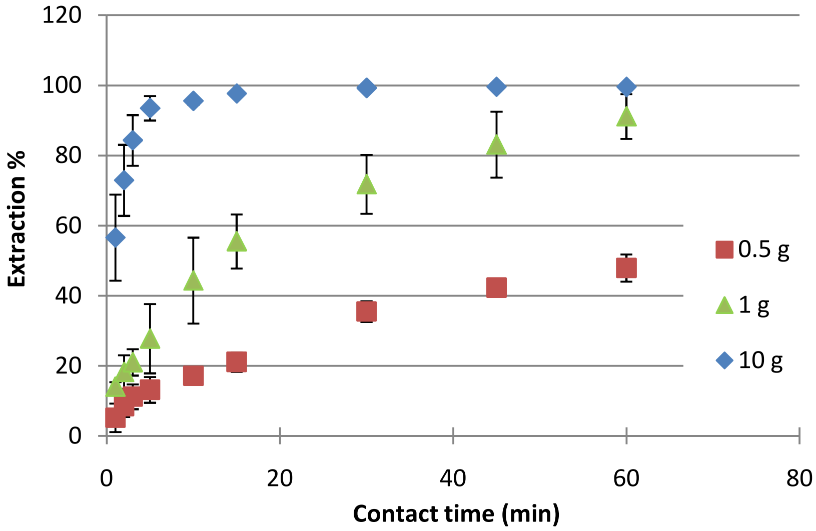


Figure 150. Extraction of iron by 0.5 g, 1 g and 10 g of CE sludge from 100 cm^3 un-treated Plant R effluent. The original iron concentration in the un-treated Plant R effluent was 65.4 mg dm^{-3}.

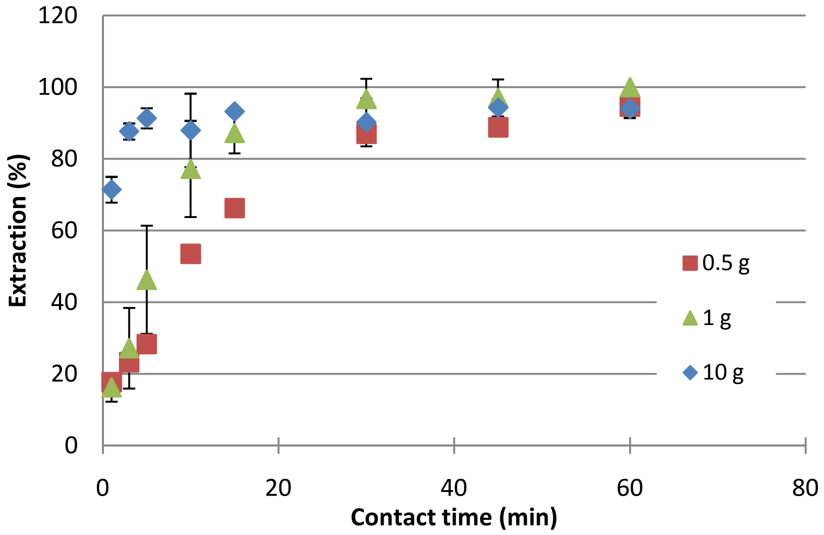


Figure 151. Extraction of uranium by 0.5 g, 1 g and 10 g of CE sludge from 100 cm^3 un-treated Plant R effluent. The original uranium concentration in the un-treated Plant R effluent was 0.019 mg dm^{-3}.

3.11.2 Arsenic extraction from un-treated Plant R effluent

The concentrations of added arsenic in un-treated Plant R solutions and the pH of the samples after 24 hours contact times (Table 29) reveal that the pH of the samples are between 1.7 – 2.6 thus the buffering capacity of CE sludge has not overcome the acidity of the un-treated Plant R effluent. Nevertheless, the added arsenic was first dissolved in strong NaOH and then the pH of the solution adjusted below 3 before being added to the un-treated Plant R effluent, thus the acidification might have enhanced the acidity of the effluent enough to overcome the buffering capacity of the sludge.

Table 29. The concentrations of the arsenic spiked un-treated Plant R solutions and final pH of the solutions after 24 h contact time with 0.2 g of CE sludge

Solution (mol dm^{-3})	***pH in 24 h sample***
1.70E-03	1.65
7.65E-03	1.58
1.44E-02	1.62
4.59E-02	1.84
7.22E-02	2.56

The arsenic isotherm in un-treated Plant R effluent (Figure 152) shows that the CE sludge has not been saturated with arsenic thus the extraction capacity for arsenic is higher than 3.4E-04 ± 3.1E-05 mol g^{-1} which corresponds to 25.5 ± 2.3 mg per 1 g of CE sludge. The original data are shown in Appendix 2.

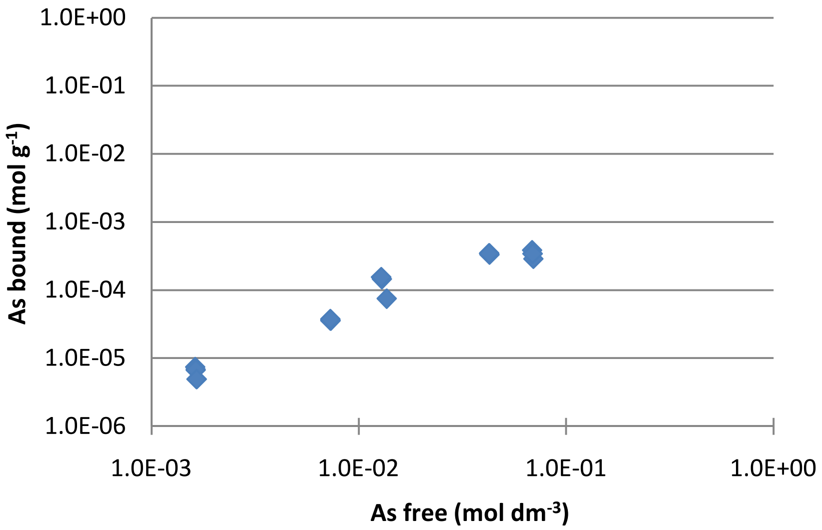


Figure 152. Extraction of arsenic by 0.2 g of CE sludge from un-treated Plant R effluent with 24 h contact time.

3.11.3 Iron extraction from un-treated Plant R effluent

Table 30 shows the concentrations of un-treated Plant R solutions with added iron and the pH of the samples after 24 hours contact times. The pH decreases with increasing iron concentrations due to hydrolysis of iron.

Table 30. The concentrations of the iron spiked un-treated Plant R solutions and final pH of the solutions after 24 h contact time with 0.2 g of CE sludge

Solution (mol dm^{-3})	***pH in 24 h sample***
1.23E-03	6.02
1.34E-03	6.14
5.16E-03	3.02
8.62E-03	2.60
9.74E-03	2.61
1.52E-02	2.22

The extraction capacity for iron from un-treated Plant R effluent is 5.1E-04 ± 5.3E-05 mol g^{-1} (Figure 153) which corresponds to an extraction of 28.3 ± 3.0 mg of iron by 1 g of CE sludge. The original data are shown in Appendix 2.

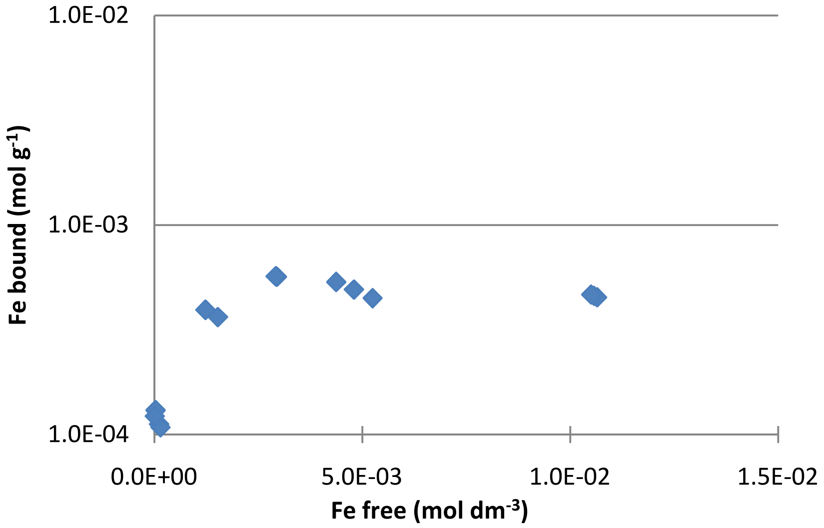


Figure 153. Extraction of iron by 0.2 g of CE sludge from un-treated Plant R effluent with 24 h contact time.

3.11.4 Uranium extraction from un-treated Plant R effluent

Table 31 shows the concentrations of uranium added to un-treated Plant R solutions and the pH of the samples after 24 hours contact times. The results show decreasing pH with increasing uranium concentrations.

Table 31. The concentrations of the uranium spiked un-treated Plant R solutions and final pH of the solutions after 24 h contact time with 0.2 g of CE sludge

Solution (mol dm^{-3})	***pH in 24 h sample***
5.80E-07	6.16
2.10E-06	5.34
4.23E-06	4.68
3.37E-04	5.94
6.42E-03	4.2
8.12E-03	4.07
1.23E-02	3.89

Figure 154 shows the uranium isotherm in un-treated Plant R effluent. The maximum capacity of uranium removal from un-treated Plant R effluent is 1.7E-04 ± 5.2E-05 mol g^{-1}. Thus, 1 g of CE sludge can extract 39.8 ± 12.4 mg of uranium from un-treated Plant R effluent. The original data are shown in Appendix 2.

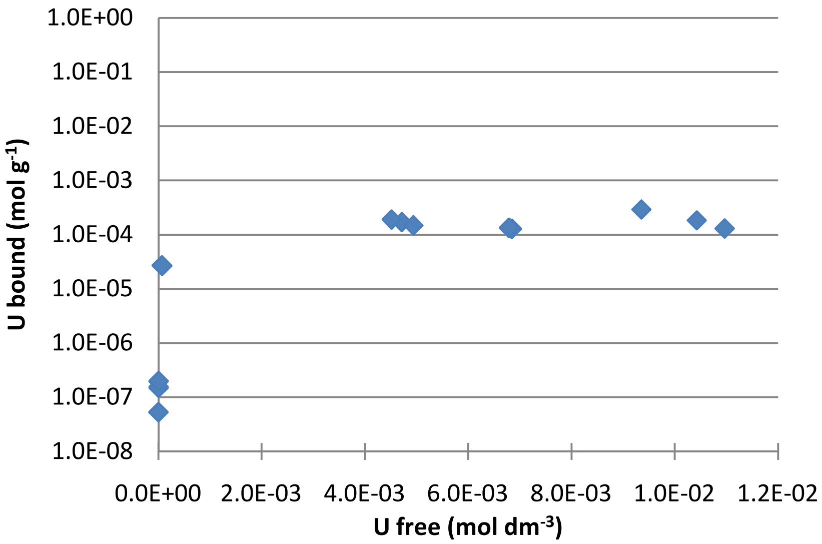


Figure 154. Extraction of uranium by 0.2 g of CE sludge from un-treated Plant R effluent with 24 h contact time.

3.11.5 Extraction of arsenic, iron and uranium from un-treated Plant R effluent by a column of CE sludge

The extraction results of arsenic, iron and uranium by a 50 g CE column with a porosity of 48% and length of 12.0 cm are shown in Figures 155 to 157. The arsenic concentrations in the collected samples were under the limit of quantification (<6 µg dm^{-3}), thus arsenic has been extracted efficiently. The iron and uranium results are presented in detail. As the un-treated Plant R effluent begins to elute from the column, the iron concentrations in the collected fraction samples decreases rapidly from 0.3 mg dm^{-3} to 0.05 mg dm^{-3} (Figure 155). Washing the column with DI water releases some loosely bound iron with a maximum of 0.3 mg dm^{-3}. Nevertheless, the extraction percentage is above 99.9% throughout the whole experiment (Figure 157). There were 7.2741 mg of iron in the original 100 cm^3 effluent and 0.0614 mg in the collected samples. Thus 99.2% of iron was retained in the column and only 0.8% migrated through the column. The extraction of uranium was very efficient with over 90%

extraction percentage (Figure 157). The measured uranium concentrations in the samples were low (Figure 156). Therefore when the experimental error is taken into consideration, it can be said that the extraction of uranium was efficient.

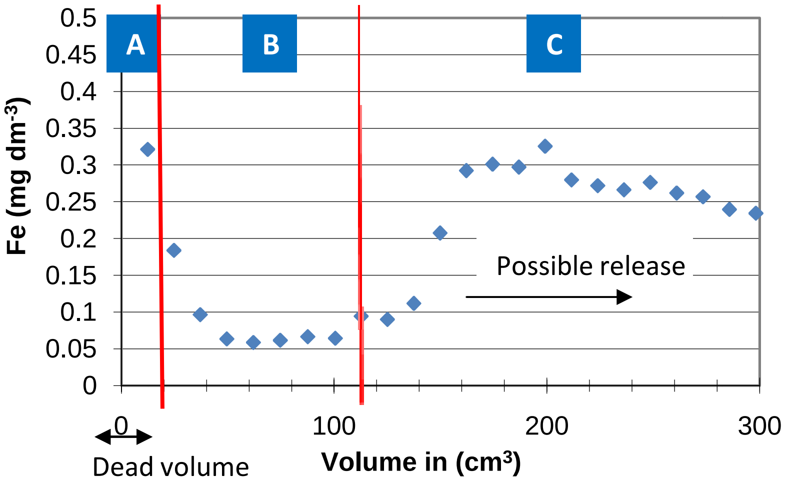


Figure 155. Iron concentrations in the fractions collected from 50 g CE column treated with 100 cm^3 un-treated Plant R effluent. The original iron concentration in the un-treated Plant R effluent was 74.8 mg dm^{-3}. Region A is the dead volume of the column, B is the region of elution with effluent and C is the region of elution with deionised water.

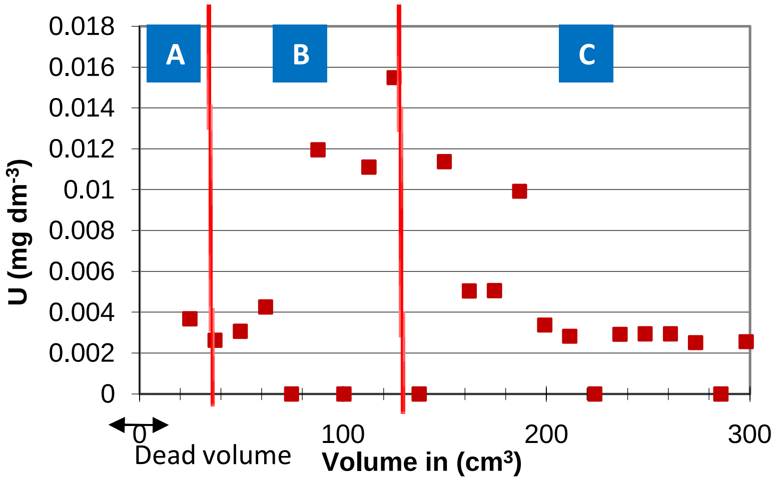


Figure 156. Uranium concentrations in the fractions collected from 50 g CE column treated with 100 cm^3 un-treated Plant R effluent. The original uranium concentration in the un-treated Plant R effluent was 0.019 mg dm^{-3}. Region A is the dead volume of the column, B is the region of elution with effluent and C is the region of elution with deionised water.

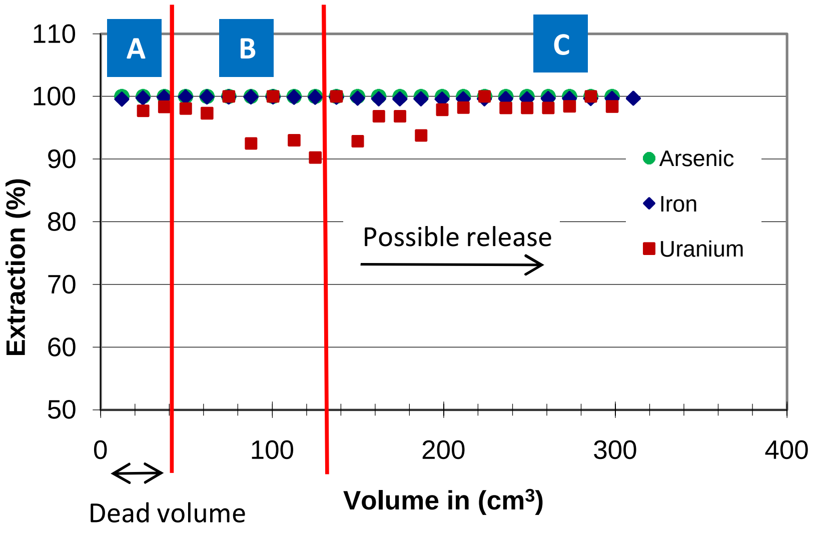


Figure 157. Arsenic, iron (A) and uranium (B) extraction percentages in the fractions collected from 50 g CE column treated with 100 cm^3 un-treated Plant R effluent. The original arsenic, iron and uranium concentrations in the un-treated Plant R effluent were 0.024 mg dm^{-3}, 74.8 mg dm^{-3} and 0.019 mg dm^{-3}, respectively. Region A is the dead volume of the column, B is the region of elution with effluent and C is the region of elution with deionised water.

The pH of the collected samples (Figure 158) show a small decrease and then an increase from 7 to 8.2 as the effluent is eluted from the column. The pH decreases again slowly during elution with DI. These results suggest that removal of iron and uranium may have occurred by precipitation or extraction or both.

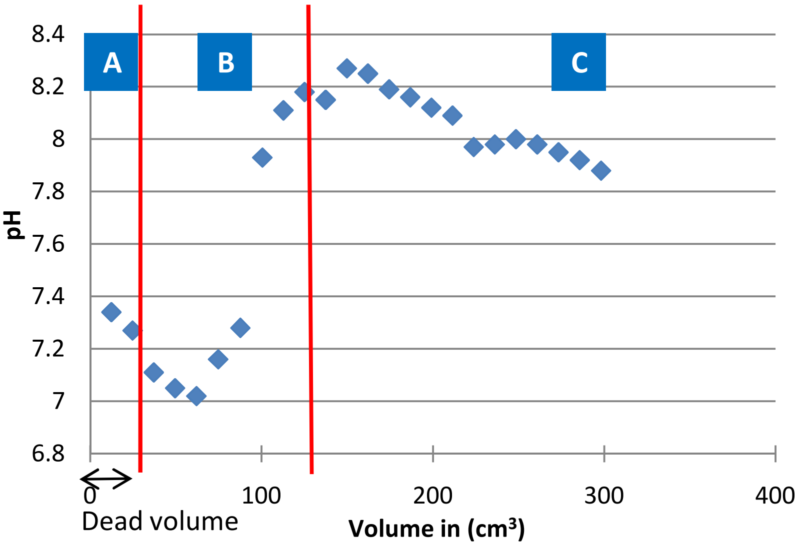


Figure 158. The pH of fractions collected from 50 g CE column treated with 100 cm^3 un-treated Plant R effluent. Region A is the dead volume of the column, B is the region of elution with effluent and C is the region of elution with deionised water.

3.12 Reversibility of arsenic, iron and uranium removal

The reversibility of extraction is an important factor when considering the stability of analyte removal. If the analyte is irreversibly bound another cation cannot replace it at the extraction site. If the analyte is reversibly bound it can be released back into solution after extraction and therefore the material can be reused.

Reversibility studies into arsenic, iron and uranium removal were investigated by placing 0.2 g of CE sludge (triplicates) in contact with arsenic (1E-02 mol dm^{-3}), iron (5E-02 mol dm^{-3}) and uranium (5E-03 mol dm^{-3}) separately in 20 cm^{3} of 0.1 mol dm^{-3} $NaNO_3$ electrolyte. The concentrations of the analytes were high enough to saturate the solid. After 24 hours of agitation on an orbital shaker, the samples were centrifuged (20 min, 6000 rpm), the solutions and solids separated and solutions filtered (0.22 µm). The solutions removed were replaced by 20 cm^{3} of electrolyte without arsenic, iron or uranium. All the solutions were adjusted to pH 3 prior to the experiments. This procedure was repeated until no significant amount of analyte was released from the sludge. Arsenic and iron concentrations were determined using ICP-MS and uranium concentrations using ICP-OES and ICP-MS.

The results of the investigation on reversibility of arsenic, iron and uranium removal (Table 32) reveal that arsenic is largely reversibly bound whereas iron and uranium are irreversibly bound by the CE sludge. The first wash with electrolyte released 76.1% of the arsenic originally extracted and the second wash released an additional 9.2%. Only 4.4% of iron is released in the first wash and 1.4% in the second wash whereas 5.3% and 2.6% of uranium are released, respectively. The pH in the arsenic samples show that buffering capacity of CE sludge has increased the pH from 3 to 7.4 in extraction samples and to 7.3 - 7.6 in desorption samples. Hydrolysis of iron has overcome the buffering capacity of the CE sludge and kept the pH in the acidic region in all samples. The pH in the uranium samples varies from pH 6.4 to 6.9, thus they have been buffered by CE sludge.

Table 32. Reversibility of arsenic, iron and uranium removal from CE sludge in 0.1 mol dm^{-3} NaNO$_3$ electrolyte

	Arsenic	***Iron***	***Uranium***
pH in extraction	7.4	1.8	6.4
1st release (%)	76.1 ± 3.6	4.4 ± 0.2	5.3 ± 1.0
pH in 1st wash	7.3	2.6	6.8
2nd release (%)	9.2 ± 1.3	1.4 ± 0.1	2.6 ± 0.2
pH in 2nd wash	7.6	3.1	6.9

As a conclusion, it can be said that arsenic was removed from the solution via ion exchange most likely by carboxylic functional groups present in the organic matter of the CE sludge because the carboxylic functional groups are considered to dominate the metal ion complexation behaviour of humic substances [43]. Even though within the pH range 2 to 5 the ion exchange processes are the major mechanism for removal of metals from solutions by formation of metal carboxylates [46], iron has been irreversibly removed from the solution (pH 1.8 to 3.1). This is most likely due to precipitation because iron precipitates to iron hydroxide at increasing pH. Above pH 5, both ion exchange and metal hydroxide precipitation become significant in the metal removal processes [46], therefore uranium was removed from the solution by precipitation as hydroxide or/and extraction by CE sludge. Extraction of uranyl ion occurs most likely by complexation with carboxylate groups acting as bidentate ligands [61].

3.13 Summary

3.13.1 The composition of un-treated and treated Plant P and R effluents

The pHs of the un-treated Plant P and R effluents were 3.0 and 2.7±0.2. Thus the effluents transported from the China Clay plant to the effluent reprocessing plant are strongly acidic. Since the average pH of the treated Plant P effluents was 5.3 ± 0.5, the "liming" has increased the pH from 3 to 5. All the effluents contained small amounts of solids, mainly kaolinite, quartz, and possibly feldspar thus they have been carried through the process possibly due to their small grain size.

The arsenic, iron and uranium concentrations in the effluents used in the kinetic, isotherm and columns experiments are presented in Table 33. The Plant P effluents did not contain measurable amounts of arsenic whereas the arsenic concentration in the un-treated Plant R effluent was 0.132 mg dm^{-3}. The iron concentrations were much lower in the Plant P effluents (5.7 and 4.6 mg dm^{-3}) compared to the Plant R effluent which contained 74.8 mg dm^{-3} of iron. The uranium concentrations in the Plant P effluents were four times higher (0.079 mg dm^{-3}) than Plant R (0.019 mg dm^{-3}) effluent.

Table 33. Arsenic, iron and uranium concentrations in the un-treated Plant P, treated Plant P and un-treated Plant R effluents. Concentrations are presented in mg dm^{-3}

Analyte	*Un-treated P*	*Treated P*	*Un-treated R*
As	<0.006	<0.006	0.132
Fe	5.7	4.6	65.4
U	0.079	0.079	0.019

3.12.2 Speciation of arsenic, iron and uranium in 0.1 mol dm^{-3} NaNO$_3$ electrolyte, un-treated Plant P and R effluents

The speciation of arsenic, iron and uranium was modelled using the JCHESS programme as a function of pH (from 2 to 10). The results showed similar speciation of arsenic in both the electrolyte and un-treated Plant R effluent. Un-treated Plant P effluent did not contain arsenic. The results showed that the high sulphate concentration in the un-treated Plant P and R effluents had an effect on the speciation of iron and uranium. The main species present in the electrolyte was Fe^{2+} whereas in the effluents the main species were Fe^{2+} and $FeSO_{4(aq)}$. The main uranium specie present in the electrolyte was UO_2^{2+} whereas in the effluents (un-treated Plant P and Plant R) the uranium was mainly present as $UO_2SO_{4(aq)}$. In the treated Plant P effluent uranyl ions formed carbonate species and remained in the solution even in increasing pH. Therefore, it was concluded that the speciation of arsenic was not affected by other species, such as sulphates, present in the solutions whereas sulphate formed species with iron and uranium in the un-treated Plant P and Plant R effluents and carbonate formed species with uranium in the treated Plant P effluent.

3.12.3 Leaching of arsenic, iron and uranium from ST and CE sludges

The leaching results of iron to deionised water from ST sludge exhibited significant release of iron (6 mg dm^{-3}) at pH 3 and above pH 6 possibly due to dissolution of humic acid complexed with iron. It was concluded that the release of iron from the ST sludge hinders the use of the sludge for extracting iron from Plant R and P effluents and therefore further experiments were only carried out using CE sludge which exhibited only a very small release of iron as a function of pH.

CE sludge released iron as a function of time at its natural pH 8 reaching a maximum of 0.35 mg dm^{-3} when 10 g of CE sludge were in contact with 100 cm^3 electrolyte for 60 minutes. No measurable amounts of arsenic or uranium were leached from the CE sludge.

3.12.4 Kinetics of arsenic, iron and uranium removal from electrolyte and effluents

The buffering capacity of CE sludge had a significant effect on the pH of the solutions. Even though the pH of the un-treated effluents were 3, the pH of the solid and solution mixture increased to above pH 7 in all cases except Plant R effluent in contact with 0.5 g of solid. The increase of pH was fastest in the electrolyte and treated Plant P effluents whose original pH was 3 and 5, respectively. The un-treated Plant P and Plant R effluents contained high amounts of sulphates, thus slower evolution of pH. For example the un-treated Plant P 13 effluent contained 732 mg dm^{-3} of sulphate and un-treated Plant R 1 effluent 1610 mg dm^{-3}.

The kinetic results in electrolyte showed almost immediate 100% extraction of arsenic and iron from sample sets which contained 10 g of solid and 100 cm^3 solution. The iron removal was also efficient at lower solid:liquid ratios (1:200 and 1:100) with 100% extraction within 5 minutes. The maximum uranium removals in 1 g and 0.5 g sample sets were 65% possibly due to complexation with carbonate or dissolved humic substances.

The removal of iron and uranium from un-treated Plant P effluent was fast; both analytes were efficiently removed from the solutions within 10 minutes and 30 minutes, respectively. Kinetic results in the treated Plant P effluent exhibited significantly different results. Initially, iron was removed from the solution but then release of some iron from the CE sludge occurred. The effect of carbonate on the release of iron from the sludge or on the complexation with dissolved humic acid was studied and concluded not to be evident. The maximum removal of uranium from treated Plant P showed a maximum of between 80-90%. In the light of the JCHESS modelling, some uranium has complexed with carbonate and remained in the solution.

Arsenic and uranium were fully removed from the un-treated Plant R effluent within 30 minutes and 60 minutes, respectively, in all sample sets. The high iron content in the 100 cm^3 effluent (74.8 mg dm^{-3}) was removed from the solution in 60 minutes by 1 g of solid and in 15 minutes by 10 g of solid whereas 0.5 g of solid removed almost 50% of iron in 60 minutes.

3.12.5 Extraction capacities for arsenic, iron and uranium in electrolyte and effluents

The extraction capacities (mol g^{-1}) for arsenic, iron and uranium from electrolyte and effluents are shown in Table 34. The extraction capacities for arsenic and iron from electrolyte in 1 hour and 24 hours contact times exhibit similar values. Therefore, it can be concluded that the extractions of arsenic and iron occur quickly (< 1h). The extraction of uranium did not occur as quickly as arsenic and iron extractions since extraction of uranium was over twice as high when using 24 hours contact time.

The arsenic isotherms in un-treated Plant P and un-treated Plant R effluents did not reach saturation thus the maximum exchange capacities are higher than 5.4E-04 ± 1.3E-05 mol g^{-1} and 3.4E-04 ± 3.1E-05 mol g^{-1}, respectively. The exchange capacity for arsenic in electrolyte was 1.2E-05 ± 5.2E-06 mol g^{-1} whereas it was 9.9E-05 ± 1.4E-05 mol g^{-1} in the treated Plant P effluent.

The maximum capacity of iron removal was highest in the electrolyte (1.0E-03 ± 5.4E-04 mol g^{-1}), second highest in the un-treated Plant R effluent (5.1E-04 ± 5.3E-05 mol g^{-1}) and then in un-treated Plant P effluent (3.0E-04 ± 1.2E-04 mol g^{-1}). Precipitation of iron occurred in the treated Plant P samples due to addition of sodium carbonate which increased the pH.

The CE sludge did not reach saturation when increasing amount of uranium was added into the treated Plant P effluent since the sodium carbonate treatment (increase of pH to 5) caused uranium precipitation. The maximum capacity of uranium removal increased in order of un-treated R (1.7E-04 ± 5.2E-05 mol g^{-1}), un-treated P (2.2E-04 ± 5.0E-05 mol g^{-1}) and electrolyte (3.3E-04 ± 3.1E-05 mol g^{-1}).

Table 34. Extraction capacities for arsenic, iron and uranium in 0.1 mol dm^{-3} NaNO$_3$ electrolyte (E), un-treated (UT) Plant P, treated (T) Plant P and un-treated (UT) Plant R effluents. Results presented as mol g^{-1}. The contact times in electrolyte are 1 h and 24 h and in effluents 24h

Solution	*Arsenic 1h*	*Arsenic 24h*	*Iron 1 h*	*Iron 24 h*	*Uranium 1 h*	*Uranium 24h*
E	1.7E-05	1.2E-05	1.2E-03	1.0E-03	1.4E-04	3.3E-04
	±6.7E-06	±5.2E-06	±3.3E-04	±5.4E-04	±2.2E-05	±3.1E-05
UT P	N/A	>5.4E-04	N/A	3.0E-04	N/A	2.2E-04
		±1.3E-05		±1.2E-04		±5.0E-05
T P	N/A	9.9E-05	N/A	*	N/A	>2.1E-03
		±1.4E-05				±1.1E-04
UT R	N/A	>3.4E-04	N/A	5.1E-04	N/A	1.7E-04
		±3.1E-05		±5.3E-05		±5.2E-05

*precipitation, > saturation of the CE sludge was not reached, N/A not analysed

3.12.6 Arsenic, iron and uranium removal in CE sludge columns

The CE sludge columns efficiently extracted arsenic (if present) and uranium from all the effluents. Nevertheless, some iron was measured in the collected samples eluting from the columns. The measured iron might have migrated through the column but also leached from the CE sludge. Table 35 shows the lengths and porosities of the columns along with the percentages of iron extraction and recovery. The columns were packed in a similar way and their porosities range from 48% to 59%. The extraction percentages for iron are high from all of the effluents. Even though un-treated Plant R contained the highest amount of iron, it exhibited the lowest amount of iron in the collected samples and highest extraction percentage (99%). Nevertheless, even in the un-treated and treated Plant P effluents the extraction percentages are 82% and 77%, respectively.

Table 35. Lengths and porosities of the 50 g CE columns treated with un-treated (UT) Plant P, treated (T) Plant P and un-treated (UT) Plant R effluents along with the masses of iron pumped through the column and in the collected samples and calculated extraction and recovery percentages

Column	*Length (cm)*	*Porosity (%)*	*Fe in (mg)*	*Fe out (mg)*	*Extraction (%)*	*Recovery (%)*
UT P	11.9	59	0.565	0.101	82.1	17.9
T P	12.5	52	0.463	0.106	77.0	23.0
UT R	12.0	48	7.274	0.061	99.2	0.8

3.12.7 Reversibility of arsenic, iron and uranium removal

Iron and uranium were irreversibly removed from the solution. In total, only 5.8% of iron and 7.9% of uranium was released in two washings of the CE sludge samples. Arsenic was reversibly bound. The first wash released 76.1% of the arsenic and the second wash released an additional 9.2%. Thus the removal of arsenic has occurred by exchange in carboxylic sites, the removal of iron by precipitation as hydroxides and uranium by complexation with carboxylate groups acting as bidentate ligands. The pH of the arsenic and uranium solutions was controlled by the CE sludge which buffers the pH towards 8. Nevertheless, the buffering capacity was overcome by iron hydrolysis in the iron samples and the pH remained in the acidic region with a maximum of 3.1.

3.14 Conclusions

The ST sludge exhibited significant release of iron from its matrix, thus it was not considered to be a good candidate as a remediation material for arsenic, iron and uranium from industrial effluents. Characterisation of the CE sludge, as described in Chapter 2, showed that the sludge contained 82.7% (w/w) organic material which contained 20% humic acid and 27% fulvic acid. Therefore, as expected, the CE sludge showed excellent extraction capacities for all three elements under investigation from 0.1 mol dm^{-3} $NaNO_3$ electrolyte and industrial effluent. The reversibility of arsenic removal enables re-use of the CE sludge. The precipitation of iron and uranium initiated by increase of pH suggests that those elements can be efficiently removed from the effluents as long as the CE sludge maintains its buffering capacity. The natural buffering capacity of the CE sludge increased the pH towards 8 even in the strongly acidic effluents with pH 3. Therefore in addition to the efficient contaminant removal, the treated effluent could be discharged without further treatment or pH adjustment.

CHAPTER 4

APPLICATION 2 - EXTRACTION OF ORGANIC COMPOUNDS INTO A PERMEABLE REACTIVE BARRIER

CHAPTER 4 – APPLICATION 2 - EXTRACTION OF ORGANIC CONTAMINANTS

4.1 Introduction

Nitrates, pesticides, hydrocarbons, chlorinated hydrocarbons, sulphate, phosphate and bacteria are the main contaminants in groundwater in Europe [62]. A permeable reactive barrier (PRB) is considered to be an innovative and green approach to remediate contaminated groundwater [8]. The concept of PRB was developed by the University of Waterloo in the early 1990s [8]. The basic aim of a PRB is to either destroy or immobilise the target contaminants that are contained in groundwater [63]. Environmental Protection Agency defines a PRB as “an emplacement of reactive media in the subsurface designed to intercept a contaminant plume, provide a flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals down-gradient of the barrier” [8]. In other words, as the groundwater flows through the PRB, the reactive material traps or degrades the compounds of concern. Once the PRB has been installed, it remains in the ground until it no longer functions as intended or until the contaminants have been degraded into less harmful components [8]. This chapter focuses on remediation of some chlorinated anilines, phenols and benzenes which are mainly pesticides.

4.1.1 Pesticides in the environment

Pesticides are substances designed to control or destroy agricultural pests [64] and they can be classified as insecticides, herbicides and fungicides [9]. However, they cause water pollution, soil degradation, and the destruction of native flora and fauna [65]. The over-use of pesticides also produces insect resistance, destruction of natural enemies and an increasing number of pest species leading to increased spraying [65]. Over 10 000 commercial formulations of around 450 pesticide compounds are used in agriculture and for other purposes all over the world [9].

With a few exceptions, herbicides are organic molecules [64]. Some herbicides disappear from the soil in a relatively short period of time, if they are suitable as a nutrient for micro-organisms [64]. However, there are a few conditions that must be met before a herbicide molecule can be microbiologically degraded [66]. First of all, the soil must contain an organism that is effective in metabolising the herbicide molecule [66]. Secondly, the compound must be in a suitable form and available to the organism [66]. Thirdly, the compound must usually be capable of inducing formation of the enzyme or enzymes appropriate for detoxification, because most of enzymes require induction [66]. Fourthly, the environmental conditions such as soil pH, temperature, and organic matter must be suitable for the micro-organism [66].

Increasing awareness of the toxic effects of chlorinated agrochemicals has limited their use [9]. In some cases, the use of the chemical has been banned completely [9]. For example, the use of dichlorodiphenyl trichloroethane (DDT) was banned in the USA in 1973 and in the UK in 1984 [9]. Even though the use of these chemicals has been banned, they will persist in the environment for a period of time depending on temperature, rainfall and soil type [9]. DDT (Figure 159), polychlorinated biphenyls (PCB) and polychlorinated dibenzodioxins have very slow decomposition rates because the carbon-chlorine bond is not found in nature and most micro-organism species do not possess the enzymes to break it [9]. Nevertheless, some species of bacteria and fungi have evolved the ability to decompose chlorinated organic compounds [9].

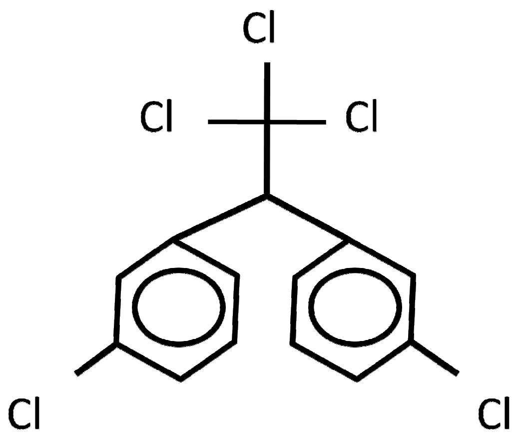


Figure 159. Structure of DDT.

4.1.2 Permeable reactive barrier

Several methods have been developed for installation of permeable treatment walls [67], but the two traditional and most commonly used PRB configurations are the continuous wall and the funnel and gate (Figure 160) [8,62]. The continuous wall PRB is a wall of reactive material that has been placed in a trench [8]. The height, depth and length of the continuous wall are designed to prevent over- and underflows [8]. The width of the wall is determined according to the required residence time of the contaminants and groundwater velocity [8].

The funnel and gate PRB consists of an impermeable side walls that direct the contaminated plume into a reactive gate [8]. The permeability of the gate must be equal or greater than the aquifer permeability to prevent overflows [8]. As with the continuous wall PRBs, the width of the reactive gate is determined according to the required residence time of the contaminants and groundwater velocity [8]. Since the groundwater is directed to a gate, the amount of reactive material is smaller than with the continuous wall PRB [8]. However, construction cost of the continuous wall type barrier is much cheaper than the funnel and gate system [62].

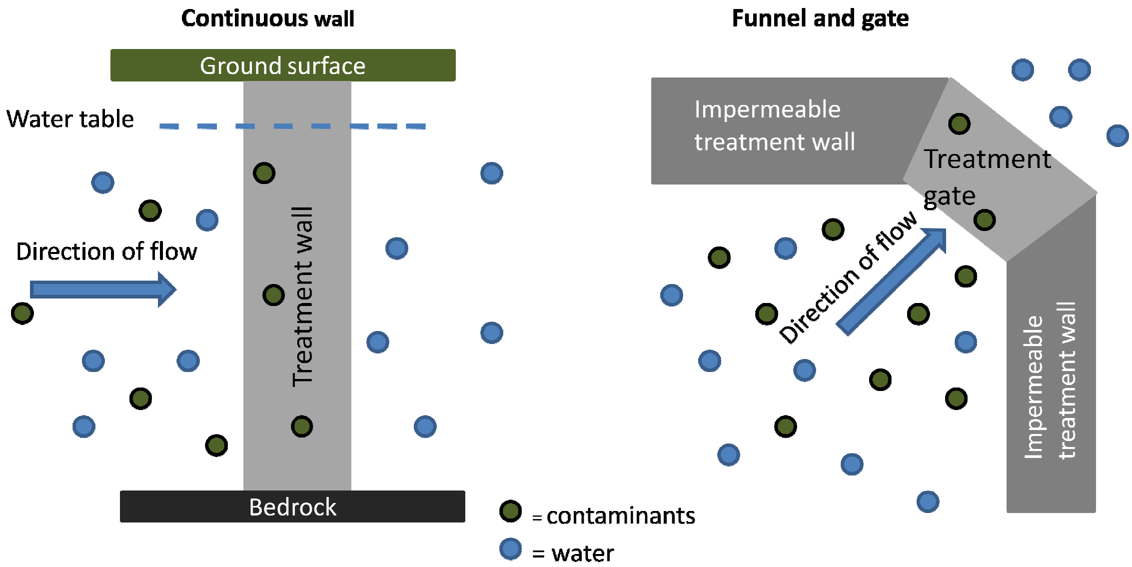


Figure 160. Illustration of continuous wall and funnel and gate PRBs.

There are also some more recent and advanced configurations of a PRB [62]:

1. Injection system which involves creating a treatment zone within the contaminant boundary by drilling series of bore holes or injection wells and injecting the reactive material (chemical/particulate mixture) into the treatment zone.
2. Hydraulic/pneumatic fracturing which involves intentional fracturing of the barrier using pumped water and/or air under high pressure after which the evolved fractures are filled with reactive medium.
3. Passive groundwater capture and treatment by reactor cells involves emplacement of reactor cell(s) in the subsurface consisting of reactive medium and capturing the contaminated plume into the reactor for treatment.

Sometimes the contaminant source area is isolated with a low permeability barriers or covers to prevent contaminant migration [68]. However, the pollution remains on site [68].

PRBs are potentially cost-effective, because they are operated *in situ* and the water is allowed to run through the zone [8] [69]. However, due to the lack of long-term data the cost-effectiveness has not been proven [8]. Nevertheless, in several sites the cost of the clean-up was up to 50% less when a PRB was used than it would have been with a “pump-and-treat” method [8].

In addition to the potential cost effectiveness, the advantages of a PRB are that it is a passive treatment system, able to treat a wide range of contaminants (inorganics, organics and radionuclides), they reduce exposure to contaminants, they clean the groundwater on site, they have relatively low maintenance and operational costs, and they enable the site to be in use at the same time [8]. However, the disadvantages are that for example large rocks can present problems when installing the PRB, the permeability might change over time, the clean-up is a long process and changes in water levels can introduce alternative pathways for the water to flow outside the barrier [8].

The first pilot-scale PRB was installed in 1991 in Ontario, US and the first full-scale commercial PRB in 1994 in California, US [8]. Since then PRBs have been installed throughout the world. In 2005, there were as many as 200 PRB applications with different reactive materials worldwide [63]. Nearly 120 of these had zero-valent iron as the reactive material [63].

4.1.3 Reactive materials and reaction processes in PRBs

Several issues need to be taken into consideration when choosing the type of reactive material in a PRB [8]:

1. It needs to bind the contaminants of concern at an effective rate
2. It needs to be stable over the amount of time needed
3. It needs to be readily available at reasonable cost
4. Its permeability needs to be the same or greater than the aquifer permeability to minimize flow restrictions
5. It cannot produce unwanted by-products

Zero-valent iron (ZVI) is the most common reactive material but other types of materials, such as organic based (activated carbon, leaf, peat, sewage sludge, and sawdust), alkaline- complexing agents (hydrated lime, ferrous sulphate), phosphate minerals (fish bone), zeolites, clay, metal oxides, microorganisms, polymers, innovative polymer membrane containing iron, are also being investigated [62],[63] [70]. In recent years, the search for low-cost adsorbents with metal-binding capacities has intensified [71]. For example, some natural materials, agricultural wastes and industrial by-products have been under investigation [71].

The prevalent use of zero-valent iron (ZVI) is due to its documented suitability for remediation of a variety of types of contaminants [63]. As ZVI oxidises it passes its electrons to contaminants which undergo reductive processes resulting in precipitation or degradation [62]. Activated carbon is also widely considered as a suitable adsorbent for polluted groundwater [62]. Activated carbon presents a high extraction capacity for many organic and inorganic contaminants largely due to its high surface area (~1000 m^2 g^{-1}) [62]. There is a vast amount of data on *ex situ* water and wastewater treatment by activated carbon but very limited data on *in situ* treatment under field conditions [62]. There is also a growing interest in bio-barriers in which compounds are removed by biodegradation [69,72].

The treatment zone of the PRB can function directly as in the iron zone or indirectly by using materials designed to stimulate secondary processes such as by adding carbon substrate and nutrients to enhance microbial activity [63]. The reactive material of a PRB can also be sequenced to treat different types of contaminants [63].

The reaction processes of contaminant removal can be classified broadly into three categories [62];

1. Degradation through chemical or biological reactions leading to decomposition or degradation of contaminants into harmless compounds.
2. Precipitation as immobilisation of contaminants within the reaction zone by formation of insoluble compounds.
3. Sorption as immobilisation of contaminants within the reaction zone by adsorption or complex formation.

In general, the reactive materials used for the construction of PRB are the ones that change pH or redox potential, cause precipitation, possesses materials with high sorption capacity and materials which release nutrients/oxygen to enhance biological degradation [62]. These processes can be presented more specifically;

1. Reductive degradation of organic contaminants [62]. Abiotic reduction consists of chemical reactions in which contaminants are converted to harmless compounds which are either immobilised in the barrier or permeate through it in a reduced form [8].
2. Oxidative degradation of organic contaminants [62].
3. Retardation and biodegradation of organic contaminants [62]. Biotic reduction is initiated by supplying electron donors and nutrient materials that are used by micro-organisms to break down contaminants [8,73]. The electron donors can be leaf mulch, saw dust, wheat straw, or alfalfa hay and the nutrient materials municipal waste and compost [8]. However, microbial decomposition has an initial time lag, while the micro-organisms become adapted to the substrate [9].
4. Sorption of organic and inorganic contaminants [62]. Sorption may occur when the contaminant interacts with the surface of the solid material such as amorphous ferric oxyhydroxide, zeolites and ZVI fillings [8]. Most of the reactions are reversible and rapid [8].
5. Reduction and/or precipitation of heavy metal compounds [62]. Chemical precipitation of some species is a process initiated by an increase in pH [8]. The contaminants can also be reduced to less-soluble species and retained in the barrier as minerals [8].
6. Ion exchange processes are reversible reactions in which similar ions are exchanged between the solid and solution [8]. Naturally occurring inorganic zeolites are commonly used as ion exchangers, but new synthetic ion exchangers which can be adapted to specific contaminants are available [8].

4.1.4 Aim and outline of this chapter

The aim of this chapter is to investigate whether ST and CE sludges could be used as remediation materials in permeable reactive barriers designed to treat metals and/or organic compounds. Both of the sludges can efficiently extract metals [1,2], therefore the investigations reported in this chapter are widened to organic compounds, concentrating on chlorinated aromatic hydrocarbons. The organic compounds under investigation were chosen from Groundwater Regulations 1998 List 1 [5] (Appendix 3). These regulations were established to prevent direct and indirect discharges of harmful substances to groundwater and it reflects the Groundwater Directive 80/68/EEC.

The experimental work was carried out in batches to determine the extraction capacities for organic compounds by the ST and CE sludges. The organic compounds were dissolved in deionised water, placed in contact with increasing amounts of ST and CE sludges and stirred for 1 day and 1 week to obtain information on extraction kinetics. The remaining amounts of organic compounds in the solutions were measured using GC-MS. The experiments were not carried out in electrolyte due to the scoping nature of the studies and because addition of salt into GC-MS may block the thin GC capillary column. The results were interpreted according to their octanol-water partition coefficient, K_{ow}, which can be used to predict the fate of a chemical in the environment. Decreasing K_{ow} value presents increasing water solubility. Also column experiments were carried out to simulate extraction in a dynamic flow through system.

4.2 Reagents and instrumentation

4.2.1 Reagents

The organic compounds investigated in this chapter are shown in Table 36 along with their purities and suppliers. A Millipore Corporation^{TM} cartridge purification system was used to produce deionised water (18 MΩ) for the preparation of solutions containing organics.

Table 36. Reagents, their purities and suppliers used in Chapter 4

Reagent	*Purity*	*Supplier*
4-chloro-3-methyl phenol	≥99%	Fisher Scientific
2,4,6-trichlorophenol	98%	Fisher Scientific
trichlorfon		Fisher Scientific
dichlorprop	97%	Sigma Aldrich
2,4-dichlorophenol	99%	Sigma Aldrich
1,3-dichloropropene	97%	Sigma Aldrich
DDT	98%	Sigma Aldrich
hexachloroethane	98%	Sigma Aldrich
lindane	≥99%	Sigma Aldrich
pentachlorophenol	98%	Sigma Aldrich
trichloroethylene		Sigma Aldrich
2,4-dichloro-1-nitrobenzene	97%	Sigma Aldrich
1,2,4,5-tetrachlorobenzene	98%	Sigma Aldrich
2,3,5-trichlorophenol		Sigma Aldrich
3,4,5-trichlorophenol		Sigma Aldrich
2,3,4-trichlorophenol		Sigma Aldrich
chloro-2-nitrobenzene	≥98%	BDH laboratory chemicals
2-chloroaniline	A.S.	Fluka
chlorathalonil	A.S.	Fluka
1-chloro-2,4-dinitrobenzene	≥98%	Fluka
chloro-4-nitrobenzene	≥98%	Fluka

*A.S. analytical standard

Table 36. Reagents, their purities and suppliers used in Chapter 4 (continued)

Reagent	***Purity***	***Supplier***
2-chlorophenol	≥99%	Fluka
2-chlorotoluene	A.S.	Fluka
2,3-dichloroaniline	A.S.	Fluka
1,2-dichlorobenzene	A.S.	Fluka
hexachlorobenzene	97%	Fluka
tetrachloroethylene	≥99.5%	Fluka
1,2,4-trichlorobenzene	A.S.	Fluka
$MgCl_2 \times 6H_2O$	99.0-102.0%	BDH laboratory chemicals
$KHCO_3$	99.9%	Fisher Scientific
$CaSO_4 \times 2H_2O$	99.92%	Fisher Scientific
$NaHCO_3$	99.7%	Aldrich
$CaCl_2 \times 2H_2O$	99.5%	BDH laboratory chemicals
$NaNO_3$	99%	Sigma Aldrich

*A.S. analytical standard

4.2.2 Instrumentation

Gas chromatographic analyses coupled with a mass spectrometer were performed on a Fisons Instruments' GC 8000 Series 8060 gas chromatograph equipped with a silica capillary column (Rtx®-5MS, 30 m x 0.32 mm, purchased from Restek) and a Fisons Instruments' MD 800 mass spectrometer. The temperature programme for organic compounds was increased stepwise from 50 to 250 ℃ and the temperature was lowered to 50 ℃ for 10 minutes between samples. The injected sample size was 1 μ dm^3, the ionisation mode was EI^+, detector voltage 350 V, emission current 150 μA, and helium was used as a carrier gas. The pH of the solutions were measured at room temperature using a Jenway or Orion pH meter.

4.3 Selection of organic compounds

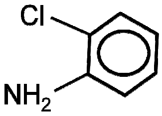
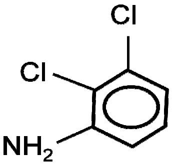
In total 28 key contaminants (Table 37) were chosen from the Groundwater Regulations 1998 List 1 [5] according to their water solubilities and accessibilities. The compounds were dissolved into deionised water to produce saturated solutions. The concentrations of saturated water solutions were determined by preparing standards in dichloromethane. The samples and standards were measured using GC/MS.

Table 37. Organic compounds chosen from Groundwater Regulation List 1 for solubility experiments

Anilines	***Phenols***	***Benzenes***	***Others***
2-chloroaniline	2-chlorophenol	hexachlorobenzene	chlorathalonil
2,3-dichloroaniline	4-chloro-3-methylphenol	1-chloro-2-nitrobenzene	2-chlorotoluene
	2,4-dichlorophenol	1-chloro-4-nitrobenzene	DDT
	pentachlorophenol	2,4-dichlorobenzene	1,3-dichloropropene
	2,3,5-trichlorophenol	2,4-dichloro-1-nitrobenzene	dichlorprop
	2,4,6-trichlorophenol	chloro-2,4-dinitrobenzene	hexachloroethane
	3,4,5-trichlorophenol	1,2,4,5-tetrachlorobenzene	lindane
	2,3,4-trichlorophenol	1,2,4-trichlorobenzene	tetrachloroethylene
		1,2-dichlorobenzene	trichloroethylene

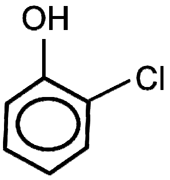
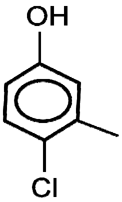
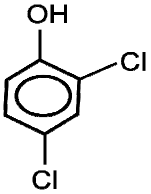
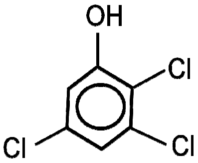
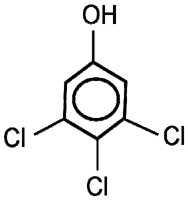
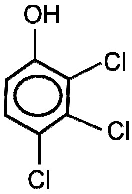
The low water solubility of some organic compounds prohibited their detection by GC-MS, thus the organic compounds investigated were narrowed to contain chlorinated anilines, chlorinated phenols, and chlorinated benzenes. In total, extraction investigations were carried out for 14 organic compounds. The structures and the octanol-water partition coefficients (log K_{ow}) of the organic compounds are shown in Tables 38-40.

Table 38. Structures and octanol-water partition coefficients of chlorinated anilines under investigation

Compound	***Structure***	***Log K_{ow}***
2-chloroaniline		1.92*
2,3-dichloroaniline		2.78*

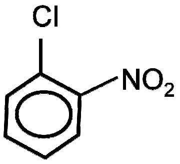
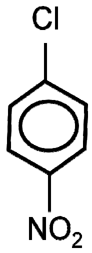
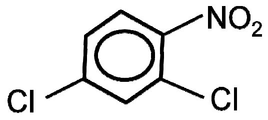
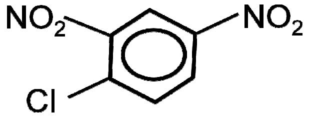
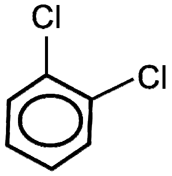
*Value provided by [74]

Table 39. Structures and octanol-water partition coefficients of chlorinated phenols under investigation

Compound	Structure	Log K_{ow}
2-chlorophenol		2.15*
4-chloro-3-methylphenol		3.1*
2,4-dichlorophenol		3.06*
2,3,5-trichlorophenol		4.56*
3,4,5-trichlorophenol		4.41**
2,3,4-trichlorophenol		3.61***

*Value provided by [74], ** [75], *** [76]

Table 40. Structures and octanol-water partition coefficients of chlorinated nitrobenzenes under investigation

Compound	***Structure***	***Log K_{ow}***
1-chloro-2-nitrobenzene		2.24*
1-chloro-4-nitrobenzene		2.39*
2,4-dichloro-1-nitrobenzene		3.1*
1-chloro-2,4-dinitrobenzene		2.17**
1,2-dichlorobenzene		3.38*

*Value provided by [74], ** [77]

4.4 Outline of extraction studies for chlorinated anilines, phenols and benzenes by ST and CE sludges

The extractions of the chlorinated aromatic hydrocarbons from deionised water by ST and CE sludges were determined at their natural pH. Increasing amounts of the sludges were placed in contact with 20 cm^3 of aqueous solution containing a constant amount of organic compound. The mixtures were shaken for 1 day and 1 week to obtain information on the kinetics, after which the samples were filtered through 0.45 µm filters and pH was measured. The remaining amounts of organic compounds in the solutions were measured using GC/MS. Extraction capacities for different organic compounds calculated from the results were interpreted according to their octanol-water partition coefficients (Figure 161).

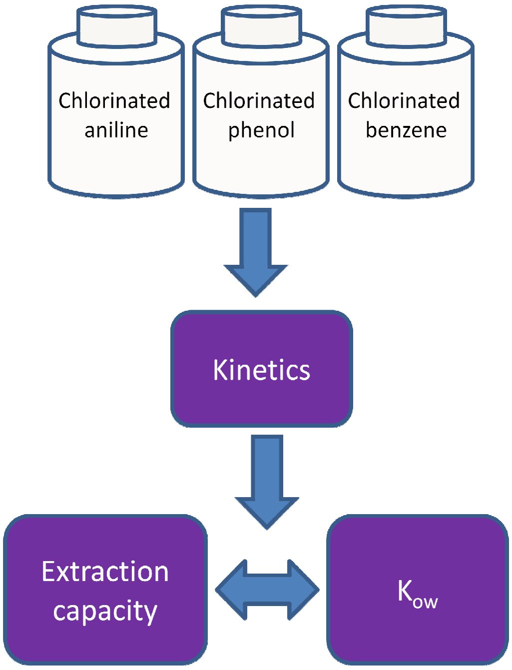


Figure 161. Schematic picture of batch experiments and interpretation of results.

The column experiments were carried out by mixing 50 g of ST and CE sludges with deionised water to form slurries and then packing them in glass columns (Ø 2.6 cm) and then washing them with DI water with a constant flow rate of 0.2 cm^3 min^{-1} for at least 12 h to remove the soluble fraction (i.e. fulvic acid). The porosities of the columns were determined as described in Chapter 3. Known amounts of organic compounds (representatives from the groups of chlorinated anilines, phenols and benzenes) were dissolved in 500 cm^3 synthetic groundwater. The synthetic groundwater chosen for these studies has previously been used in studies carried out in the same research group [78]. The synthetic groundwater was introduced into the column (flow rate of 0.2 cm^3 min^{-1}) and 20 cm^3 fractions eluting were collected by a fraction collector (Figure 162). The amount of chlorinated contaminants in the fractions were measured using GC-MS. pH in the collected fractions was also measured.

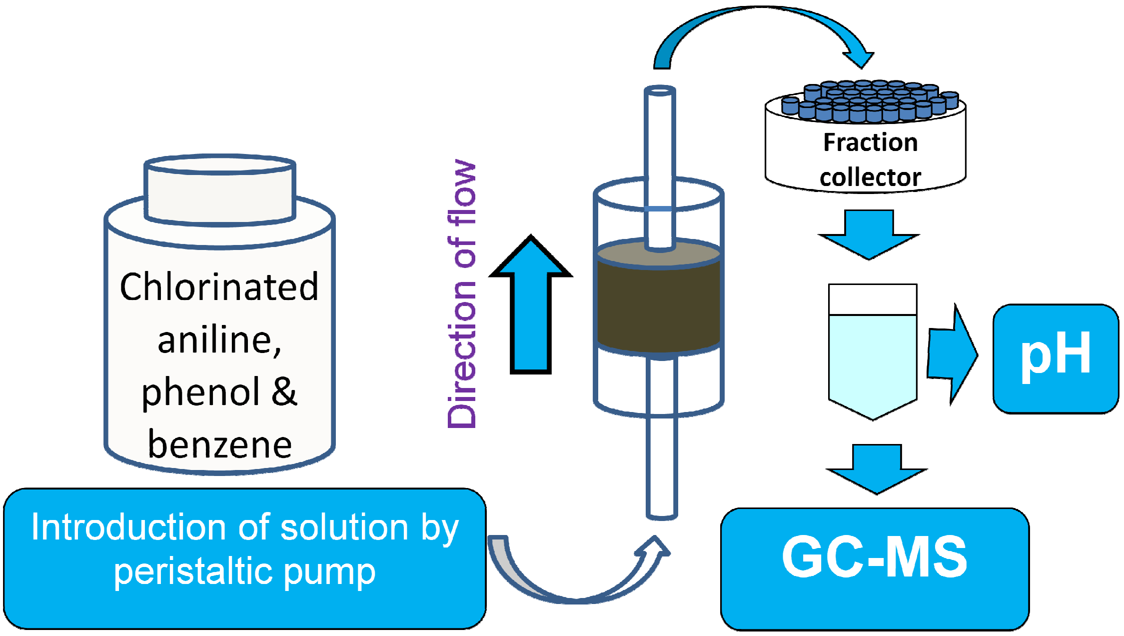


Figure 162. Schematic picture of column experiments.

4.5 Calculation of results and errors

The extraction percentages were calculated by comparing the GC-MS peak areas of the organic compound in samples to the original solutions. The results were plotted as mass of sludge against extraction percentage. The minimum amounts of solid needed to extract 100% of the organic compound from the 20 cm^3 solutions were calculated using linear fit. For example, studies by Karickhoff *et al*. showed linear extraction for chlorinated hydrocarbons [79]. The extraction capacities were calculated by multiplying the concentration of the original solution with volume and dividing it by the minimum amount of solid needed to extract 100% of the organic compound from the 20 cm^3 solution.

The errors for the masses (s_x) were calculated using the following equations 4.1-3. The errors in the extraction capacities were calculated by determining the percentage of error in masses and applying the same percentage of error to the extraction capacities.

$$s_x = \frac{s_y}{|m|}\sqrt{\frac{1}{k} + \frac{x^2 n}{D} + \frac{\Sigma(x_i^2)}{D} - \frac{2\, x\, \Sigma x_i}{D}} \qquad (4.1)$$

Where s_y and D are determined as

$$s_y = \sqrt{\frac{\Sigma(d_i^2)}{n - 2}} \qquad (4.2)$$

$$D = [\Sigma\,(x_i^2)]\,n - \Sigma\,(x_i)\,\Sigma\,(x_i) \qquad (4.3)$$

In which

m = slope of linear fit (% g^{-1})

k = instrumental replicates (3)

x = calculated x-value (g)

n = number of points on the graph (3-4)

x_i = values on x-axis (g)

$d_i = y_i - y$ = difference between determined and calculated y-values (%)

4.6 Extraction of chlorinated anilines by ST sludge using 1 day and 1 week contact times

The extractions of the two chlorinated anilines (2-chloroaniline and 2,3-dichloroaniline) from deionised water by ST sludge were determined as described in section 4.4. The extraction results are shown in Figures 163-164 for 1 day and 1 week contact times. The results show linear relationships between extraction percentages and increasing amounts of ST sludge exhibiting R^2 values from 0.8517 to 0.9834. The original data are shown in Appendix 4.

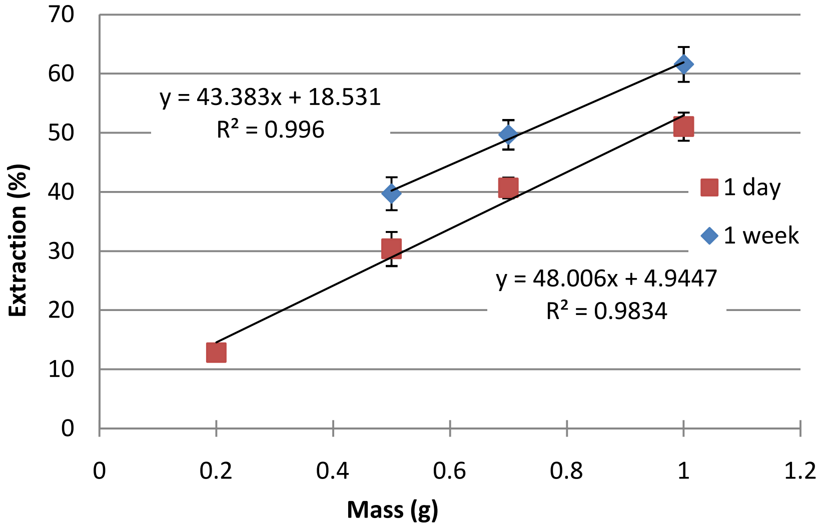


Figure 163. Extraction of 2-chloroaniline from 20cm^3 of deionised water by increasing amount of ST sludge using 1 day and 1 week contact times.

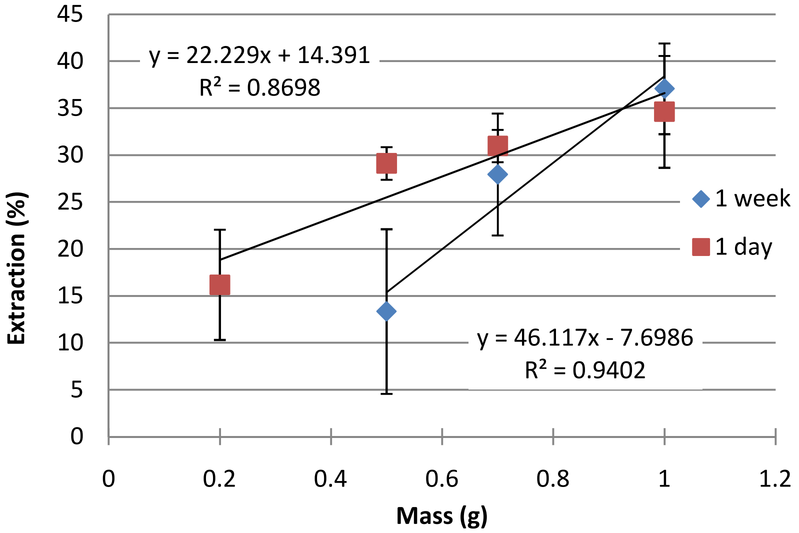


Figure 164. Extraction of 2,3-dichloroaniline from 20cm^3 of deionised water by increasing amount of ST sludge using 1 day and 1 week contact times.

The calculated masses of ST sludge needed to extract 100% of the chlorinated aniline from 20 cm^3 aqueous solution are shown in Table 41 along with the solution concentrations, contact times, extraction capacities and errors. The errors were calculated as explained in section 4.5. The extraction capacities are also shown in Figure 165 which clearly exhibit rapid removal of 2-chloroaniline (maximum reached within 1 day contact time) whereas removal of 2,3-dichloroaniline increases with increasing contact time.

Table 41. The concentrations of original chlorinated aniline solutions, contact times, masses of ST sludge needed to extract 100% of organic compound from the 20 cm^3 solution, extraction capacities and errors

Chlorinated anilines	*Solution ($mg\ dm^{-3}$)*	*Contact time (d)*	*Mass (g)*	*Capacity ($mg\ g^{-1}$)*	*Error (%)*
2-chloroaniline	331.8	1	1.98 ± 0.09	3.4 ± 0.2	4.6
2-chloroaniline	318.4	7	1.9 ± 0.1	3.4 ± 0.2	5.9
2,3-dichloroaniline	200	1	3.85 ± 0.09	1.04 ± 0.02	2.3
2,3-dichloroaniline	211.2	7	2.3 ± 0.3	1.8 ± 0.3	13.7

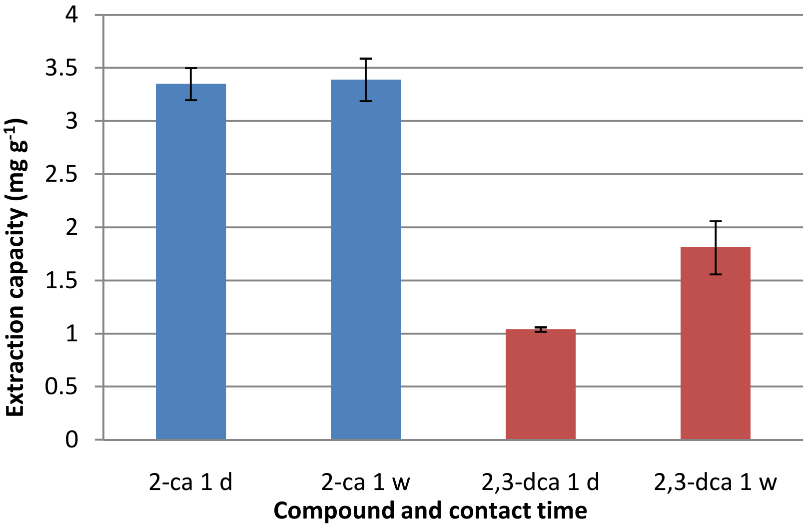


Figure 165. Extraction capacity of chlorinated anilines by ST sludge and contact time (1 day and 1 week). Abbreviations: 2-chloroaniline (2-ca) and 2,3-dichloroaniline (2,3-dca).

The correlation between the water solubility of the chlorinated anilines (K_{ow}) and the extraction capacities by ST sludge (Figure 166) show an increasing trend in the extraction capacity with increasing water solubility. However, more experiments using other chlorinated anilines should be carried out before firm conclusions can be drawn.

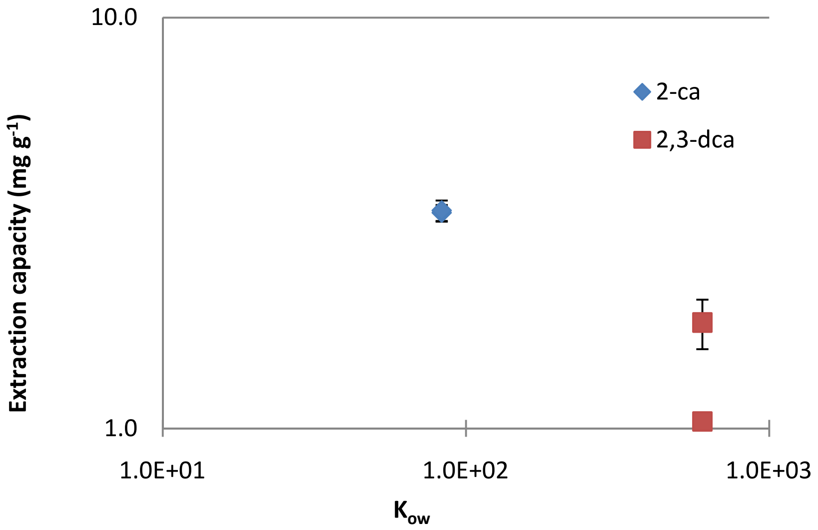


Figure 166. Extraction capacity for chlorinated anilines by ST sludge using 1 day and 1 week contact times versus octanol-water distribution coefficient K_{ow}. Abbreviations: 2-chloroaniline (2-ca) and 2,3-dichloroaniline (2,3-dca).

4.7 Extraction of chlorinated anilines by CE sludge using 1 day and 1 week contact times

The extractions of 2-chloroaniline and 2,3-dichloroaniline from deionised water by CE sludge were determined as described previously in section 4.4. The results in Figures 167-168 show good linearity in the extraction of chlorinated anilines by CE sludge R^2 values ranging from 0.8766 to 0.9932. The original data are shown in Appendix 4.

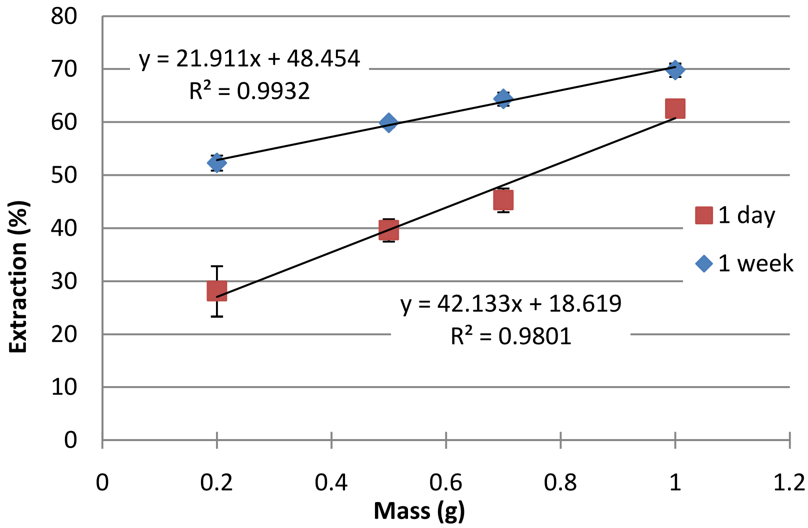


Figure 167. Extraction of 2-chloroaniline from 20cm^3 of deionised water by increasing amount of CE sludge using 1 day and 1 week contact times.

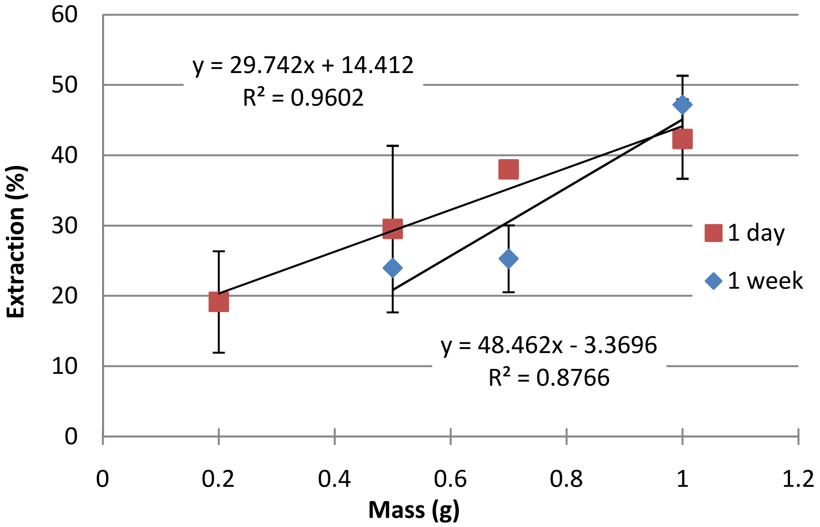


Figure 168. Extraction of 2,3-dichloroaniline from 20cm^3 of deionised water by increasing amount of CE sludge using 1 day and 1 week contact times.

The extraction results for chlorinated anilines by CE sludge are summarised in Table 42 and the extraction capacities are shown in Figure 169. The results show that 2-chloroaniline is more efficiently extracted from deionised water using 1 day contact time whereas the extraction capacity is lower in samples using 1 week contact time. However, there is over 100 mg dm^{-3} difference in the original concentrations of the 2-chloroaniline solution which may explain the decrease in the extraction capacity. Increasing contact time increased the extraction of 2,3-dichloroaniline by CE sludge.

Table 42. The concentrations of original chlorinated aniline solutions, contact times, masses of CE sludge needed to extract 100% of organic compound from the 20 cm^3 solution, extraction capacities and errors

Chlorinated anilines	***Solution (mg dm^{-3})***	***Contact time (d)***	***Mass (g)***	***Capacity (mg g^{-1})***	***Error (%)***
2-chloroaniline	331.8	1	1.9 ± 0.1	3.4 ± 0.2	6.2
2-chloroaniline	187.6	7	2.35 ± 0.09	1.60 ± 0.06	3.8
2,3-dichloroaniline	200	1	2.9 ± 0.3	1.4 ± 0.2	11.8
2,3-dichloroaniline	211.2	7	2.1 ± 0.2	2.0 ± 0.2	8.9

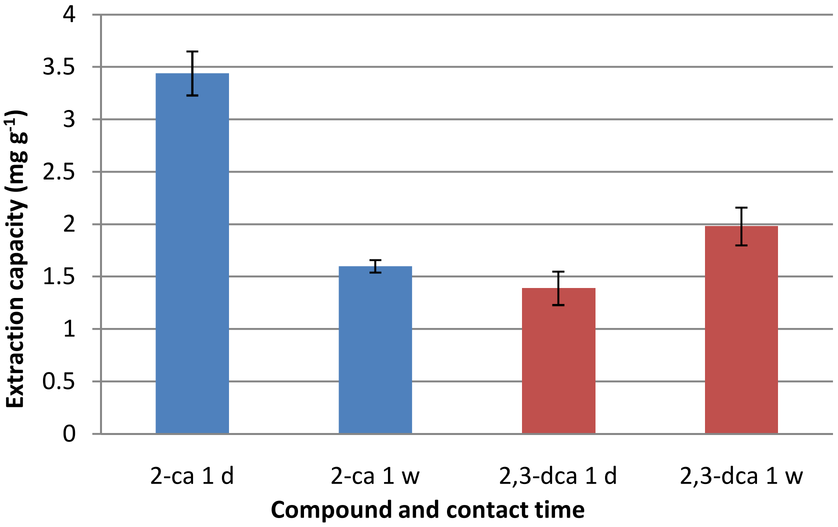


Figure 169. Extraction capacity of chlorinated anilines by CE sludge and contact time (1 day and 1 week). Abbreviations: 2-chloroaniline (2-ca) and 2,3-dichloroaniline (2,3-dca).

The K_{ow} values of the chlorinated anilines and extraction capacities by CE sludge (Figure 170) show similar trend as seen earlier with ST sludge in Figure 166. However, the trend is not as clear as in ST sludge samples and further studies in chlorinated aniline solutions should be carried out.

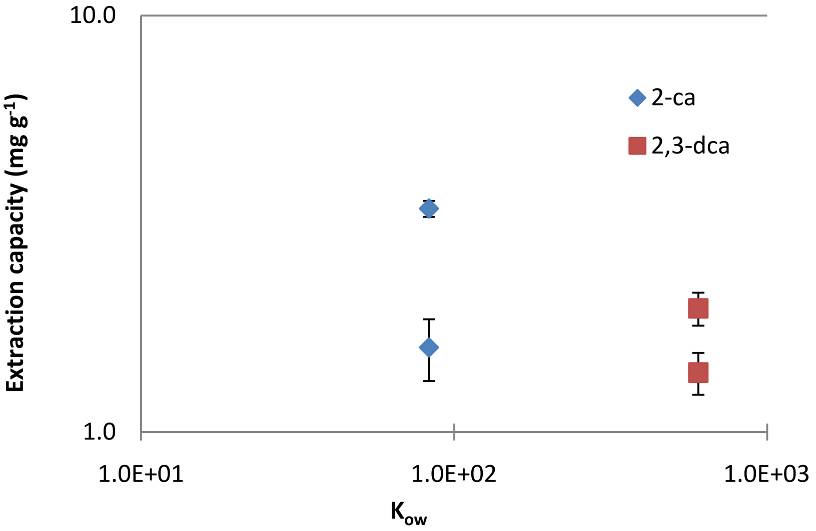


Figure 170. Extraction capacity for chlorinated anilines by CE sludge using 1 day and 1 week contact times versus octanol-water distribution coefficient K_{ow}. Abbreviations: 2-chloroaniline (2-ca) and 2,3-dichloroaniline (2,3-dca).

The octanol-water partition coefficient of chlorinated anilines and extraction capacities by ST and CE sludges are shown in Table 43. The results show similar extraction capacities for 2-chloroaniline and 2,3-dichloroaniline by both of the sludges. NH_2 groups present in the chlorinated anilines are common examples of polar groups [23] and therefore they increase the polarity of the compound and consequently their water solubility. Since polar interactions (mainly H bonding) with the O- and N- containing groups of humic acids contribute significantly to the sorption processes of highly polar solutes [80], it indicates that the extraction of chlorinated anilines by ST and CE sludges occurred via hydrogen bonding. It can also be suggested that increasing solubility (hydrophilicity) of any chlorinated aniline has a positive effect on the extraction capacity by both ST and CE sludges. However, further studies with other chlorinated anilines are required to confirm this tendency.

Table 43. Octanol-water partition coefficient and extraction capacities of chlorinated anilines by ST and CE sludges

Compound	K_{ow}	ST sludge Extraction capacity (mg g^{-1})		CE sludge Extraction capacity (mg g^{-1})	
		1 day	1 week	1 day	1 week
2-chloroaniline	1.92	3.4 ± 0.2	3.4 ± 0.2	3.4 ± 0.2	1.60 ± 0.06
2,3-dichloroaniline	2.78	1.04 ± 0.02	1.8 ± 0.3	1.4 ± 0.2	2.0 ± 0.2

4.8 Extraction of chlorinated phenols by ST sludge using 1 day and 1 week contact times

The capacities of ST sludge to extract chlorinated phenols from deionised water at its natural pH were determined as described in section 4.4 by placing increasing amounts of sludge in contact with 20 cm^3 of aqueous solution containing 2-chlorophenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, 2,3,5-trichlorophenol, 3,4,5-trichlorophenol, or 2,3,4-trichlorophenol. The mixtures were shaken for 1 day and 1 week, filtered through 0.45 µm filters and the remaining amounts of phenols in the solutions were measured using GC/MS. The results (Figures 171-176) show good linearity, R^2 value ranging from 0.8619 to 0.999. Only one graph (Figure 175) show poorer linearity with R^2 value of 0.5904. The original data are shown in Appendix 4.

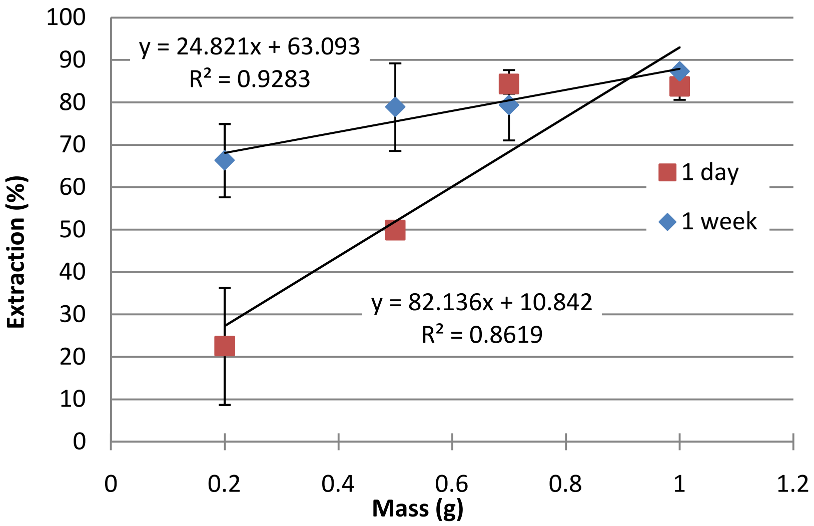


Figure 171. Extraction of 2-chlorophenol from 20cm^3 of deionised water by increasing amount of ST sludge using 1 day and 1 week contact times.

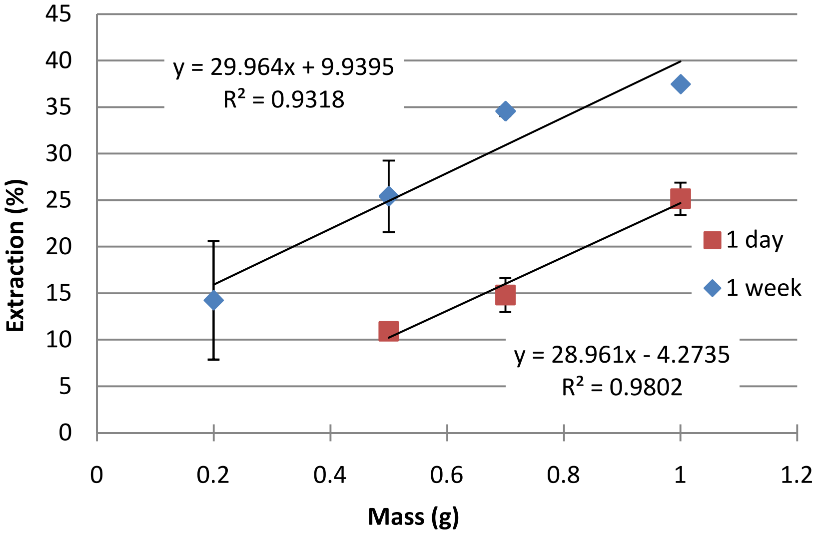


Figure 172. Extraction of 4-chloro-3-methylphenol from 20cm^3 of deionised water by increasing amount of ST sludge using 1 day and 1 week contact times.

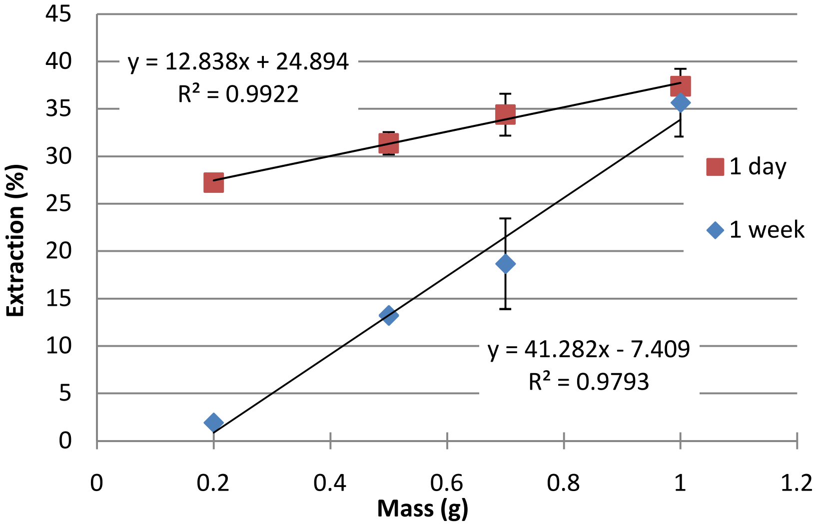


Figure 173. Extraction of 2,4-dichlorophenol from 20cm^3 of deionised water by increasing amount of ST sludge using 1 day and 1week contact times.

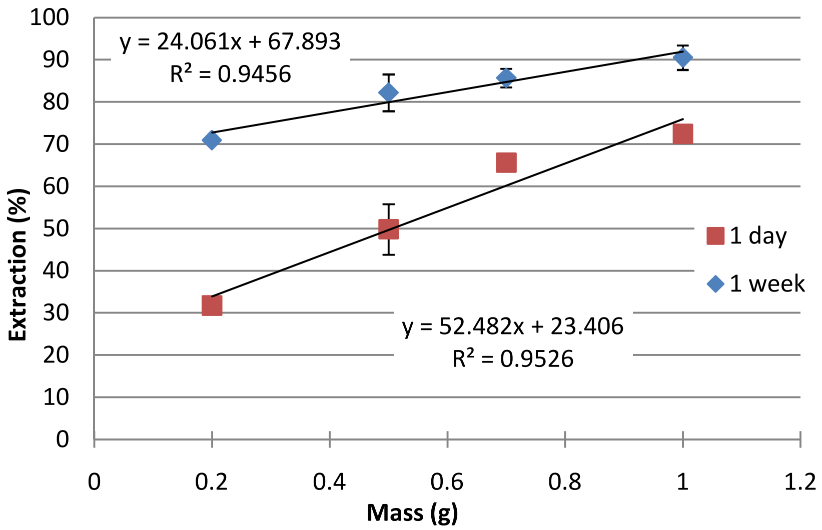


Figure 174. Extraction of 2,3,5-trichlorophenol from 20cm^3 of deionised water by increasing amount of ST sludge using 1 day and 1 week contact time.

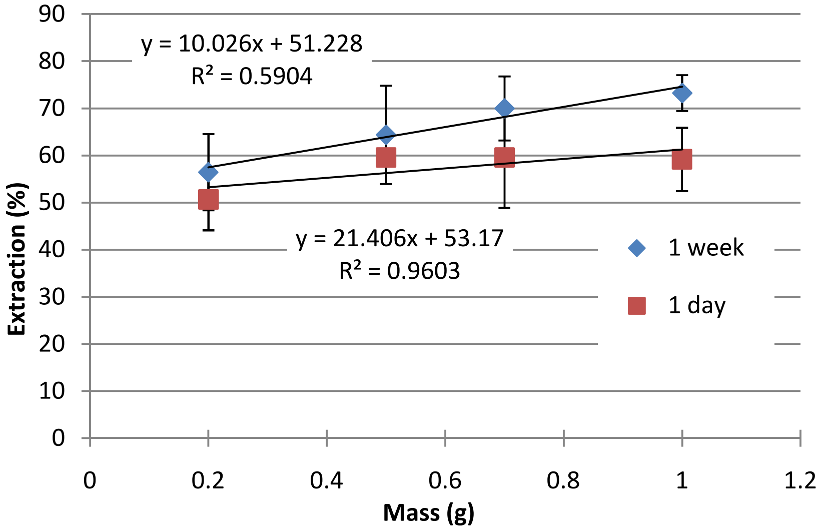


Figure 175. Extraction of 3,4,5-trichlorophenol from 20 cm^3 of deionised water by increasing amount of ST sludge using 1 day and 1 week contact time.

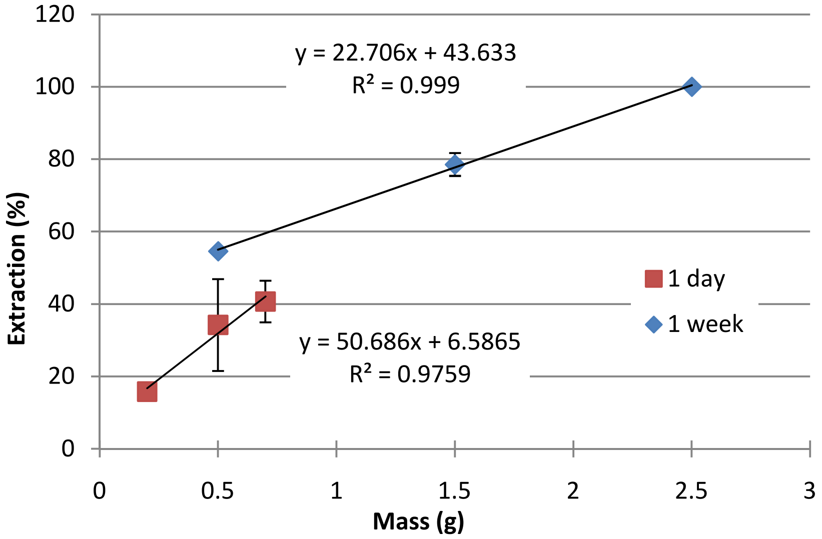


Figure 176. Extraction of 2,3,4--trichlorophenol from 20 cm^3 of deionised water by increasing amount of ST sludge using 1 day and 1 week contact times.

The calculated masses of ST sludge needed to extract 100% of the chlorinated phenols under investigation from 20 cm^3 aqueous solutions are shown in Table 44 along with the original concentrations, contact times, extraction capacities, and errors. The effect of contact time on the extraction capacities are shown in Figure 177. The results show that, within the error, increasing contact time has not significantly changed the extraction capacities for 2-chlorophenol, 2,3,5-trichlorophenol, and 3,4,5-trichlorophenol. Therefore, the results suggest fast (< 1 day) extraction for these organic compounds. The extraction capacities for 4-chloro-3-methylphenol, 2,4-dichlorophenol and 3,4,5-trichlorophenol increased with increasing contact time.

Table 44. The concentrations of original chlorinated phenol solutions, contact times, masses of ST sludge needed to extract 100% of organic compound from the 20 cm^3 solution, extraction capacities and errors

Chlorinated phenols	*Solution (mg dm^{-3})*	*Contact time (d)*	*Mass (g)*	*Capacity (mg g^{-1})*	*Error (%)*
2-chlorophenol	2994.6	1	1.1 ± 0.2	55.5 ± 12.3	22.2
2-chlorophenol	3024	7	1.5 ± 0.2	40.6 ± 6.0	14.8
4-chloro-3-methylphenol	1550	1	3.6 ± 0.2	8.6 ± 0.4	5.0
4-chloro-3-methylphenol	1485.2	7	3.01 ± 0.09	9.9 ± 0.3	3.0
2,4-dichlorophenol	1801.4	1	5.85 ± 0.05	6.16 ± 0.05	0.9
2,4-dichlorophenol	1807.6	7	2.6 ± 0.2	13.9 ± 1.2	8.5
2,3,5-trichlorophenol	467.8	1	1.5 ± 0.2	6.2 ± 0.6	10.0
2,3,5-trichlorophenol	359.8	7	1.3 ± 0.2	5.4 ± 0.9	15.8
3,4,5-trichlorophenol	372.3	1	4.9 ± 0.2	1.53 ± 0.08	4.9
3,4,5-trichlorophenol	372.4	7	2.2 ± 0.4	3.4 ± 0.5	16.0
2,3,4-trichlorophenol	477.8	1	1.8 ± 0.2	5.2 ± 0.5	9.8
2,3,4-trichlorophenol	505.5	7	2.5 ± 0.3	4.1 ± 0.5	12.5

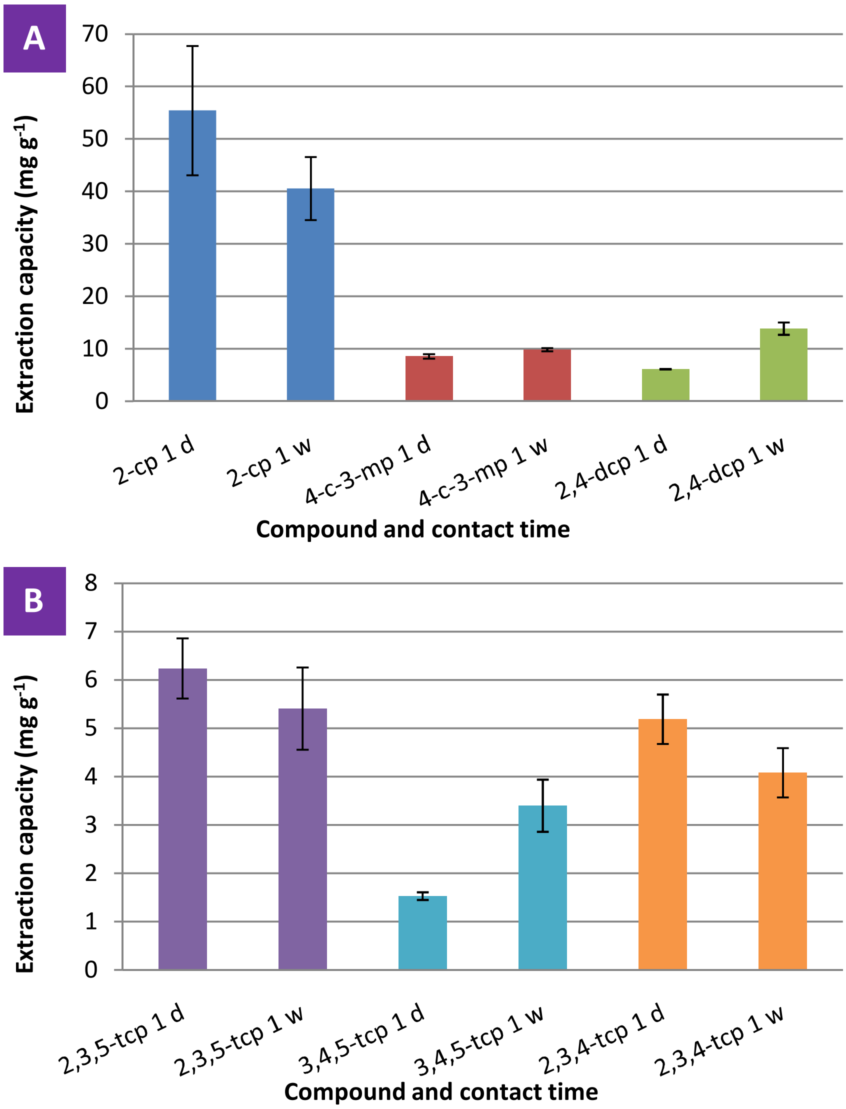


Figure 177. Extraction capacity of chlorinated phenols (A,B) by ST sludge and contact time (1 day and 1 week). Abbreviations: 2-chlorophenol (2-cp), 4-chloro-3-methylphenol (4-c-3-mp), 2,4-dichlorophenol (2,4-dcp), 2,3,5-trichlorophenol, (2,3,5-tcp), 3,4,5-trichlorophenol (3,4,5-tcp), and 2,3,4-trichlorophenol (2,3,4-tcp).

The extraction capacities for chlorinated phenols by ST sludge are shown in Figure 178 with their octanol-water partition coefficients K_{ow}. The results show a trend exhibiting a clear relationship between the water solubility and extraction capacity as shown by decreasing K_{ow}. Therefore, increasing water solubility of the chlorinated phenol corresponds to increasing extraction capacity by ST sludge.

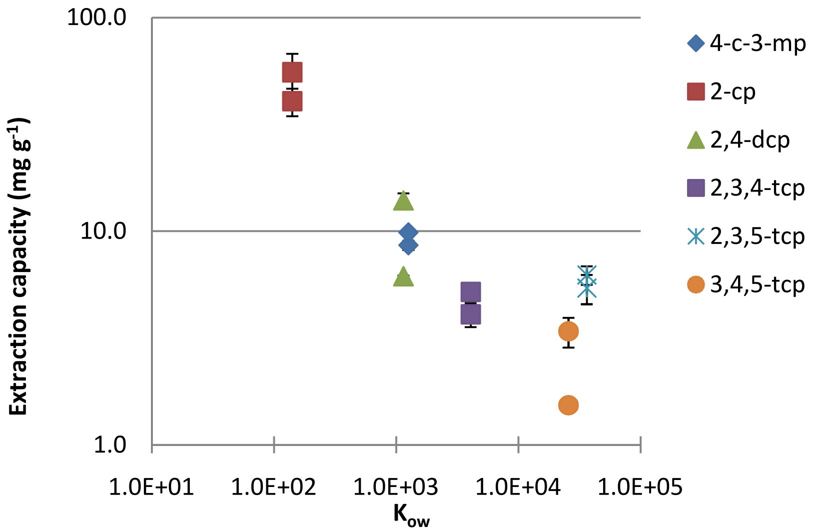


Figure 178. Extraction capacity for chlorinated phenols by ST sludge using 1 day and 1 week contact times versus octanol-water distribution coefficient K_{ow}. Abbreviations: 4-chloro-3-methylphenol (4-c-3-mp), 2-chlorophenol (2-cp), 2,4-dichlorophenol (2,4-dcp), 2,3,4-trichlorophenol (2,3,4-tcp), 2,3,5-trichlorophenol, (2,3,5-tcp), and 3,4,5-trichlorophenol (3,4,5-tcp).

4.9 Extraction of chlorinated phenols by CE sludge using 1 day and 1 week contact times

The extractions of chlorinated phenols (2-chlorophenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, 2,3,5-trichlorophenol, 3,4,5-trichlorophenol, and 2,3,4-trichlorophenol) from deionised water by CE sludge were carried out as presented in section 4.4. The extraction results by CE sludge are shown in Figures 179-184 and they show good linearity with R^2 value ranging from 0.9491 to 0.9896. Only extraction of 4-chloro-3-methylphenol results using 1 week contact time (Figure 180) show lower linearity with R^2 value 0.6499. The original data are shown in Appendix 4.

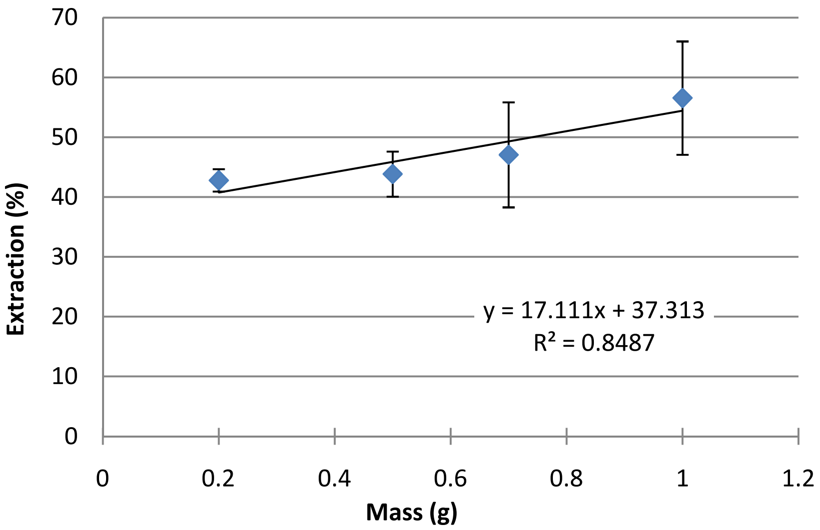


Figure 179. Extraction of 2-chlorophenol from 20 cm^3 of deionised water by increasing amount of CE sludge using 1 day contact time.

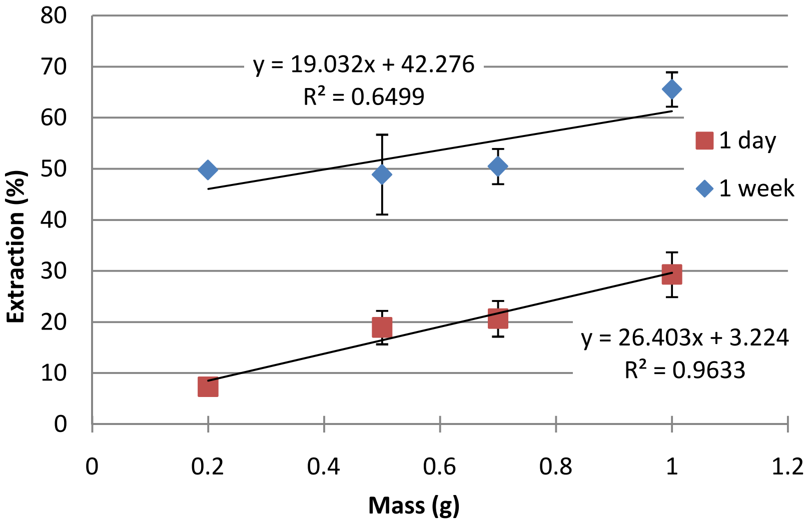


Figure 180. Extraction of 4-chloro-3-methylphenol from 20 cm^3 of deionised water by increasing amount of CE sludge using 1 day and 1 week contact times.

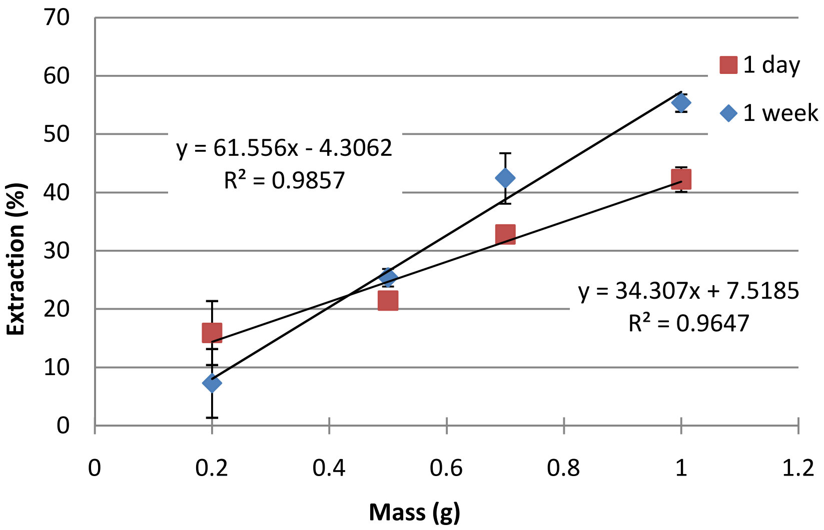


Figure 181. Extraction of 2,4-dichlorophenol from 20 cm^3 of deionised water by increasing amount of CE sludge using 1 day and 1 week contact times.

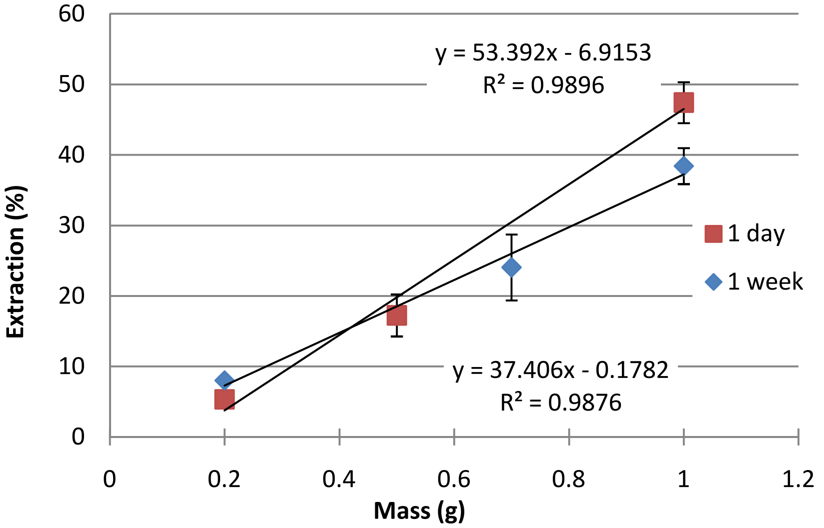


Figure 182. Extraction of 2,3,5-trichlorophenol from 20 cm^3 of deionised water by increasing amount of CE sludge using 1 day and 1 week contact times.

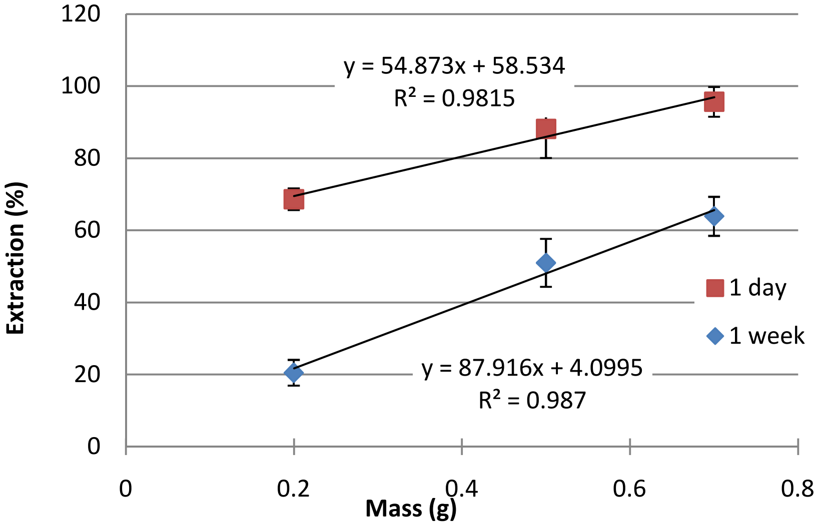


Figure 183. Extraction of 3,4,5-trichlorophenol from 20 cm^3 of deionised water by increasing amount of CE sludge using 1 day and 1 week contact times.

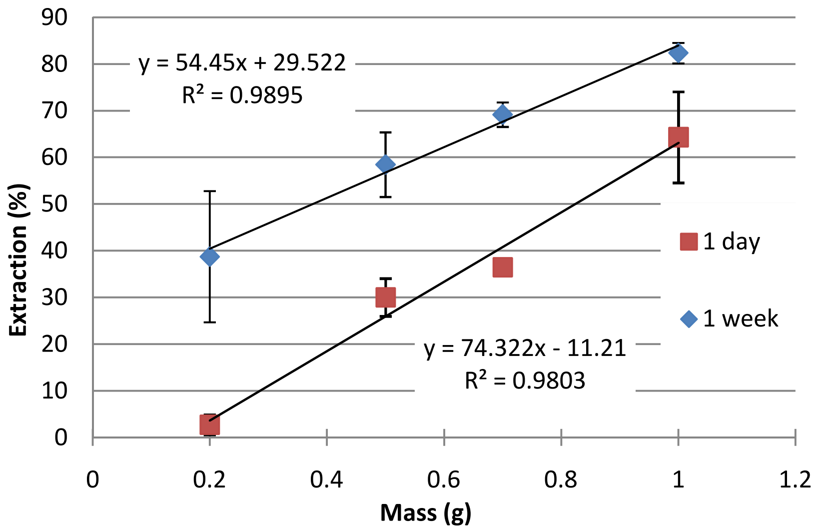


Figure 184. Extraction of 2,3,4-trichlorophenol from 20 cm^3 of deionised water by increasing amount of CE sludge using 1 day and 1 week contact times.

The amount of CE sludge needed to extract 100% of the chlorinated phenols from 20 cm^3 aqueous solutions, original concentrations, contact times, errors and extraction capacities are shown in Table 45. The extraction capacity results in Figure 185 show that increasing contact time increases the extraction capacity of 2,4-dichlorophenol whereas increasing contact time does not have a significant effect on the extraction of 4-chloro-3-methylphenol and the three trichlorophenols. Extractions of the latter compounds were rapid and occurred within 1 day.

Table 45. The concentrations of original chlorinated phenol solutions, contact times, masses of CE sludge needed to extract 100% of organic compound from the 20 cm^3 solution, extraction capacities and errors

Chlorinated phenols	*Solution (mg dm^{-3})*	*Contact time (d)*	*Mass (g)*	*Capacity (mg/g)*	*Error (%)*
2-chlorophenol	2994.6	1	3.7 ± 0.3	16.4 ± 1.4	8.5
2-chlorophenol	N/A	7	N/A	N/A	N/A
4-chloro-3-methylphenol	1550	1	3.7 ± 0.1	8.5 ± 0.2	2.7
4-chloro-3-methylphenol	1099.6	7	3.0 ± 0.4	7.3 ± 0.9	12.5
2,4-dichlorophenol	1801.4	1	2.7 ± 0.2	13.3 ± 0.7	5.6
2,4-dichlorophenol	1731.2	7	1.7 ± 0.1	20.5 ± 1.3	6.5
2,3,5-trichlorophenol	359.8	1	2.0 ± 0.1	3.6 ± 0.2	5.5
2,3,5-trichlorophenol	378	7	2.7 ± 0.2	2.8 ± 0.2	6.0
3,4,5-trichlorophenol	1273.6	1	0.8 ± 0.2	33.5 ± 8.4	25.0
3,4,5-trichlorophenol	1329.2	7	1.1 ± 0.1	24.4 ± 2.9	11.9
2,3,4-trichlorophenol	477.8	1	1.5 ± 0.1	6.4 ± 0.6	8.7
2,3,4-trichlorophenol	492.4	7	1.3 ± 0.2	7.6 ± 1.3	17.1

N/A: not analysed

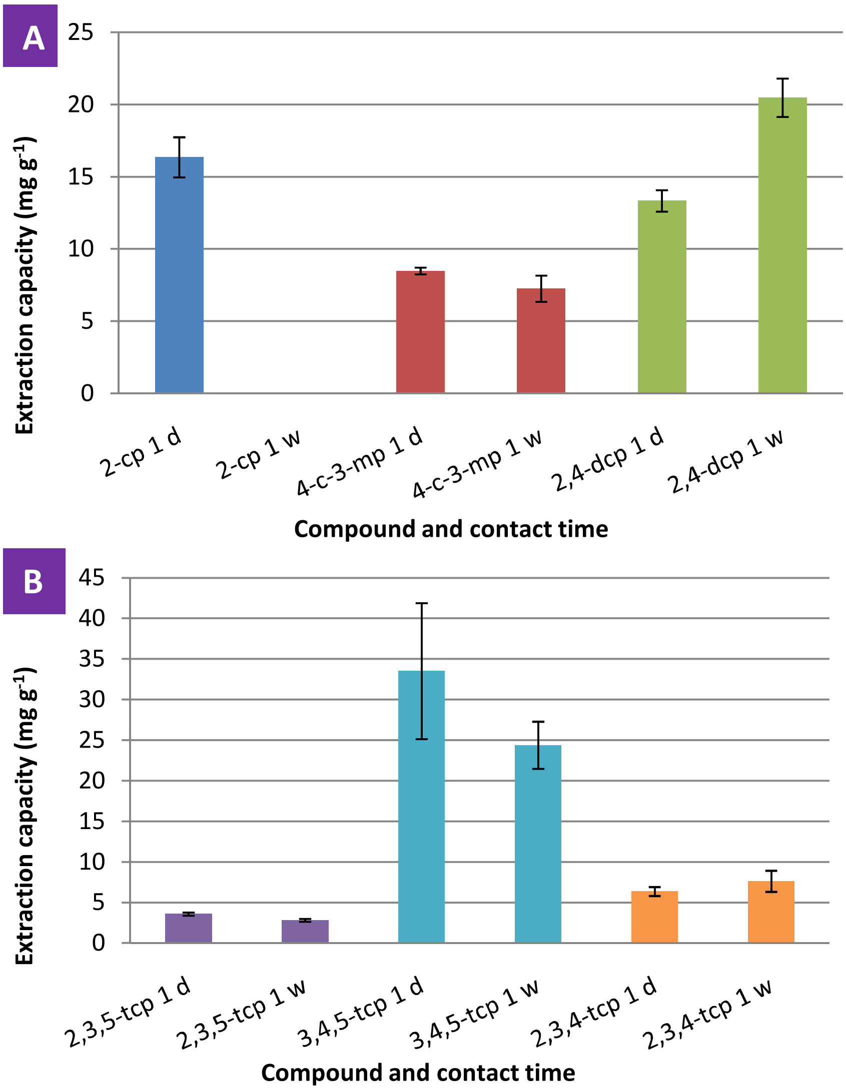


Figure 185. Extraction capacity of chlorinated phenols (A,B) by CE sludge and contact time (1 day and 1 week). Abbreviations: 2-chlorophenol (2-cp), 4-chloro-3-methylphenol (4-c-3-mp), 2,4-dichlorophenol (2,4-dcp), 2,3,5-trichlorophenol, (2,3,5-tcp), 3,4,5-trichlorophenol (3,4,5-tcp), and 2,3,4-trichlorophenol (2,3,4-tcp).

The extraction capacities shown with the octanol-water partition coefficient K_{ow} in Figure 186 exhibit a trend between the water solubilities of the chlorinated phenols and the extraction capacities by CE sludge. However, the trend is not as clear as in the corresponding results when using ST sludge (Figure 178).

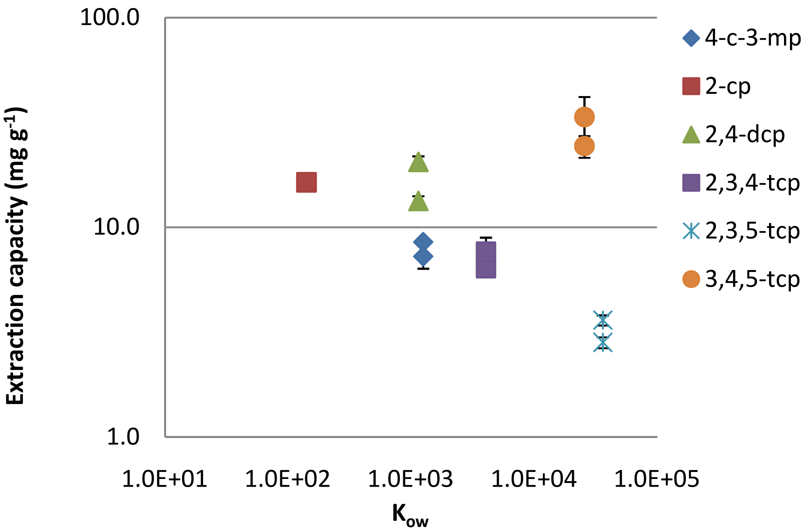


Figure 186. Extraction capacity for chlorinated phenols by CE sludge using 1 day and 1 week contact times versus octanol-water distribution coefficient K_{ow}. Abbreviations: 4-chloro-3-methylphenol (4-c-3-mp), 2-chlorophenol (2-cp), 2,4-dichlorophenol (2,4-dcp), 2,3,4-trichlorophenol (2,3,4-tcp), 2,3,5-trichlorophenol, (2,3,5-tcp), and 3,4,5-trichlorophenol (3,4,5-tcp).

The extraction results for ST and CE sludges show (Table 46) significantly higher extraction capacity for 2-chlorophenol and higher for 2,3,5-trichlorophenol by ST sludge compared to CE sludge whereas the extraction capacity is higher for 2,4-dichlorophenol and significantly higher for 3,4,5-trichlorophenol by CE sludge. The extraction capacities for 4-chloro-3-methylphenol and 2,3,4-trichlorophenol are similar for both of the sludges. Chlorinated phenols contain OH groups which are one of the common examples of polar groups (OH, NH_2, and >C=O) [23]. Hydrogen donor-acceptor interactions have been found to play an important role in the partitioning of polar compounds [80], thus, it can be assumed that the extraction of polar chlorinated phenols to ST and CE sludges occurred via hydrogen bonding. Carboxyls and alcohols are polar functional groups present in organic matter and they may invoke polar interactions with polar solutes [80].

Table 46. Octanol-water partition coefficient and extraction capacities of chlorinated phenols by ST and CE sludges

Compound	K_{ow}	ST sludge Extraction capacity (mg g^{-1})		CE sludge Extraction capacity (mg g^{-1})	
		1 day	1 week	1 day	1 week
2-chlorophenol	2.15	55.5 ± 12.3	40.6 ± 6.0	16.4 ± 1.4	N/A
4-chloro-3-methylphenol	3.1	8.6 ± 0.4	9.9 ± 0.3	8.5 ± 0.2	7.3 ± 0.9
2,4-dichlorophenol	3.06	6.16 ± 0.05	13.9 ± 1.2	13.3 ± 0.7	20.5 ± 1.3
2,3,5-trichlorophenol	4.56	6.2 ± 0.6	5.4 ± 0.9	3.6 ± 0.2	2.8 ± 0.2
3,4,5-trichlorophenol	4.41	1.53 ± 0.08	3.4 ± 0.5	33.5 ± 8.4	24.4 ± 2.9
2,3,4-trichlorophenol	3.61	5.2 ± 0.5	4.1 ± 0.5	6.4 ± 0.6	7.6 ± 1.3

4.10 Extraction of chlorinated benzenes by ST sludge using 1 day and 1 week contact times

The extraction studies of five different chlorinated benzenes (1-chloro-2-nitrobenzene, 1-chloro-4-nitrobenzene, 2,4-dichloro-1-nitrobenzene, and 1-chloro-2,4-dinitrobenzene) from deionised water by ST sludge were carried out as explained in section 4.4. The results (Figures 187-190) show good linearity, R^2 value ranging from 0.9115 to 0.9931. The original data are shown in Appendix 4.

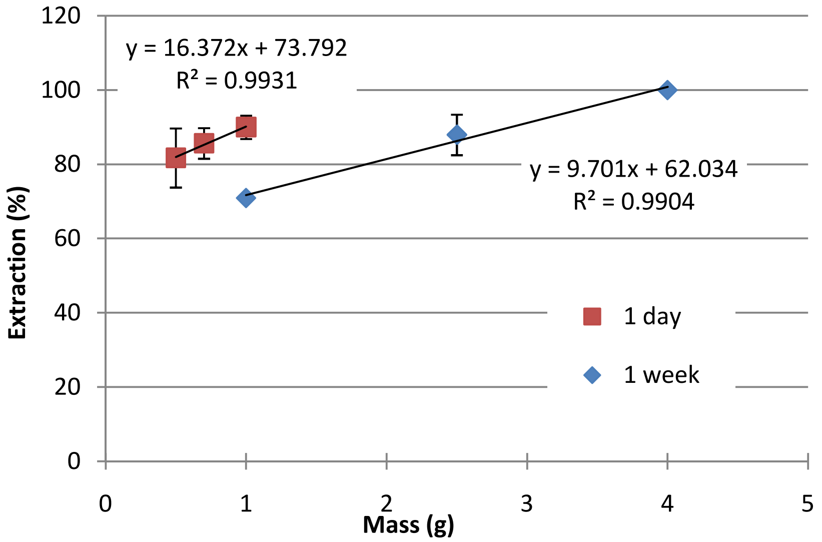


Figure 187. Extraction of 1-chloro-2-nitrobenzene from 20 cm^3 of deionised water by increasing amount of ST sludge using 1 day and 1 week contact times.

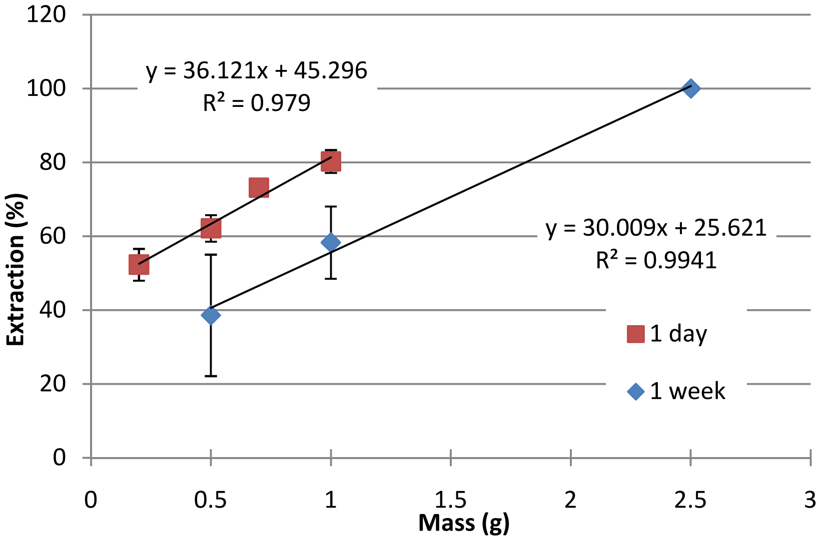


Figure 188. Extraction of 1-chloro-4-nitrobenzene from 20 cm^3 of deionised water by increasing amount of ST sludge using 1 day and 1 week contact times.

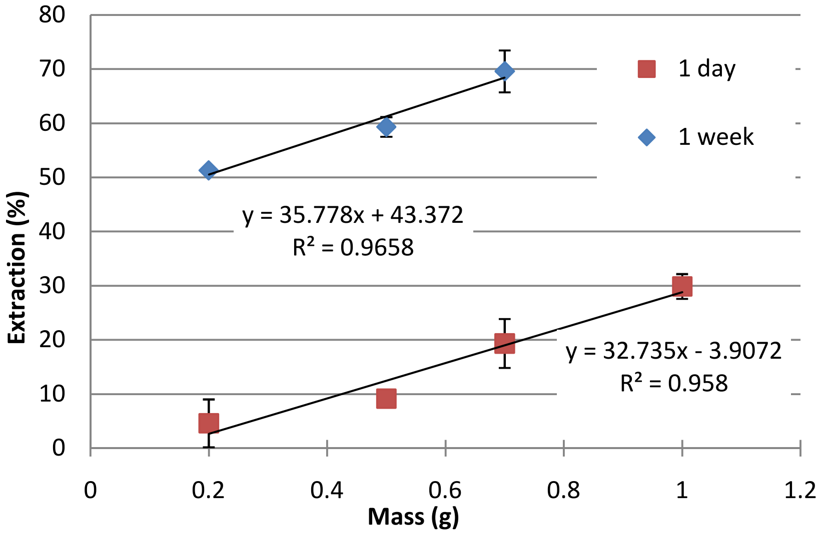


Figure 189. Extraction of 1-chloro-2,4-dinitrobenzene from 20 cm^3 of deionised water by increasing amount of ST sludge using 1 day and 1 week contact times.

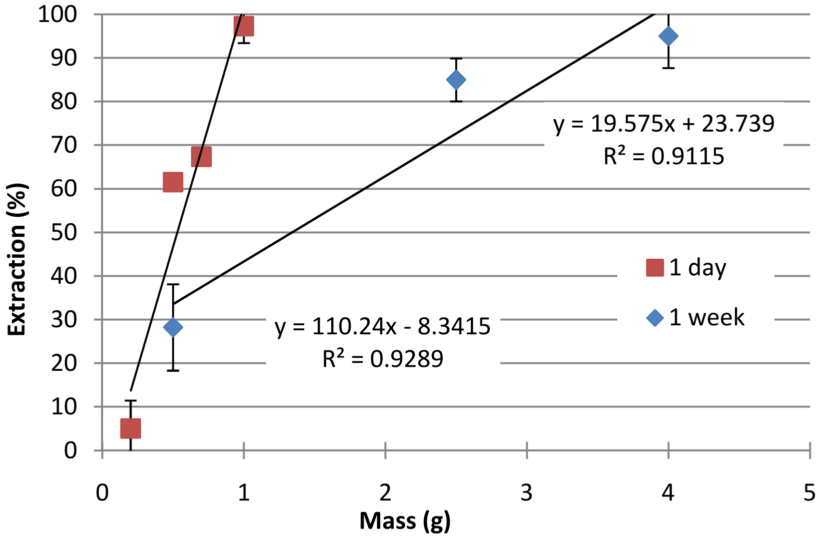


Figure 190. Extraction of 2,4-dichloro-1-nitrobenzene from 20 cm^3 of deionised water by increasing amount of ST sludge using 1 day and 1 week contact times.

The extraction results, presented as calculated masses of ST sludge needed to extract 100% of the chlorinated benzenes from 20 cm^3 aqueous solutions along with their extraction capacities, are shown in Table 47. The extraction capacity results are also plotted in Figure 191 and they show rapid extraction of 1-chloro-2-nitrobenzene and 1-chloro-4-nitrobenzene (< 1 day). The extraction of 1-chloro-2,4-dinitrobenzene was increased with increasing contact time whereas the extraction of 2,4-dichloro-1-nitrobenzene was significantly decreased.

Table 47. The concentrations of original chlorinated benzene solutions, contact times, masses of ST sludge needed to extract 100% of organic compound from the 20 cm^3 solution, extraction capacities and errors

Chlorinated benzenes	*Solution (mg dm^{-3})*	*Contact time (d)*	*Mass (g)*	*Capacity (mg g^{-1})*	*Error (%)*
1-Chloro-2-nitrobenzene	439.4	1	1.6 ± 0.4	5.5 ± 1.3	23.8
1-Chloro-2-nitrobenzene	679.7	7	3.9 ± 0.7	3.5 ± 0.7	18.7
1-Chloro-4-nitrobenzene	219.2	1	1.5 ± 0.2	2.9 ± 0.3	10.6
1-Chloro-4-nitrobenzene	235	7	2.5 ± 0.7	1.9 ± 0.5	28.2
1-Chloro-2,4-dinitrobenzene	198	1	3.2 ± 0.1	1.25 ± 0.05	4.1
1-Chloro-2,4-dinitrobenzene	206	7	1.6 ± 0.3	2.6 ± 0.5	19.6
2,4-dichloro-1-nitrobenzene	393.2	1	1.0 ± 0.2	8.0 ± 1.8	22.5
2,4-dichloro-1-nitrobenzene	396	7	2.5 ± 0.4	3.1 ± 0.5	17.1

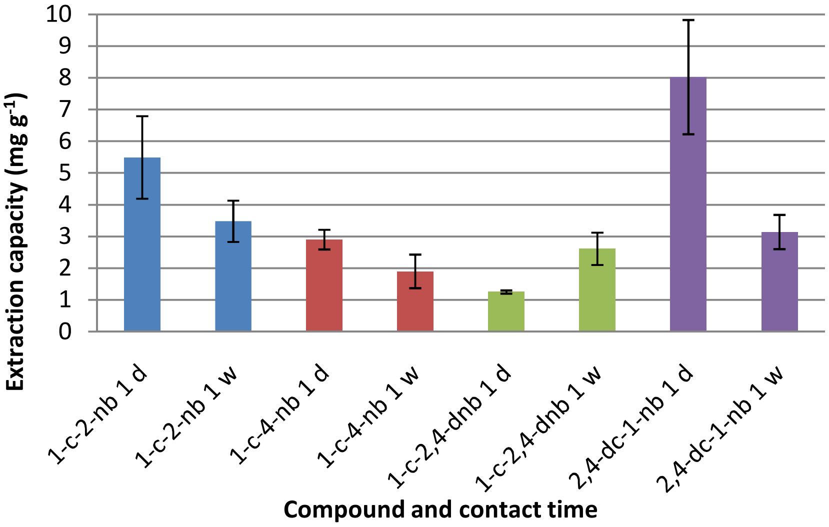


Figure 191. Extraction capacity of chlorinated benzenes (A,B) by ST sludge and contact time (1 day and 1 week). Abbreviations: 1-chloro-2-nitrobenzene (1-c-2-nb), 1-chloro-4-nitrobenzene (1-c-4-nb), 2,4-dichloro-1-nitrobenzene (2,4-dc-1-nb), and 1-chloro-2,4-dichlorobenzene (1c-2,4-dcb).

The extraction capacities plotted against the octanol-water partition coefficient K_{ow} in Figure 192 form a clear trend a suggesting relationship between the hydrophobicity of the compound and the extraction capacity i.e. increasing hydrophobicity of the chlorinated benzene enhances the extraction by ST sludge.

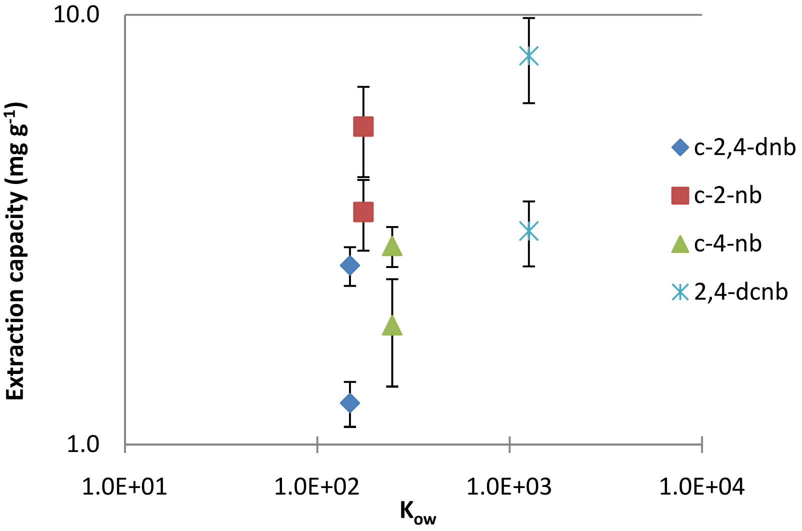


Figure 192. Extraction capacity for chlorinated benzenes by ST sludge using 1 day and 1 week contact times versus octanol-water distribution coefficient K_{ow}. Abbreviations: 1-chloro-2,4-dichlorobenzene (c-2,4-dcb), 1-chloro-2-nitrobenzene (c-2-nb), 1-chloro-4-nitrobenzene (c-4-nb), and 2,4-dichloro-1-nitrobenzene (2,4-dcnb).

4.11 Extraction of chlorinated benzenes by CE sludge using 1 day and 1 week contact times

The extraction capacities of chlorinated benzenes by CE sludge from deionised water were determined as presented in section 4.4. The organic compounds under investigation were 1-chloro-2-nitrobenzene, 1-chloro-4-nitrobenzene, 2,4-dichloro-1-nitrobenzene, 1-chloro-2,4-dichlorobenzene, and 1,2-dichlorobenzene. The results are shown in Figures 193-197 and they exhibit good linearity, R^2 values ranging from 0.9227 to 0.9995 except in 1 week 1-chloro-2-nitrobenzene sample (Figure 193) which showed poorer linearity (0.6095). The original data are shown in Appendix 4.

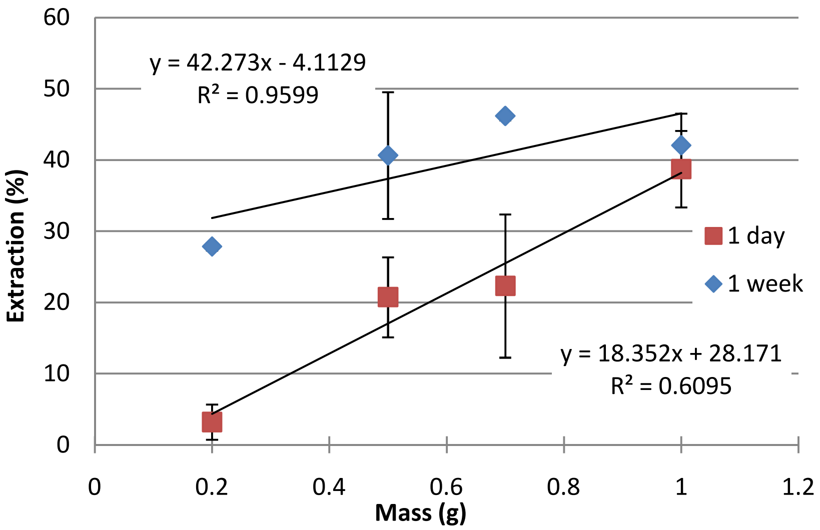


Figure 193. Extraction of 1-chloro-2-nitrobenzene from 20 cm^3 of deionised water by increasing amount of CE sludge using 1 day and 1 week contact times.

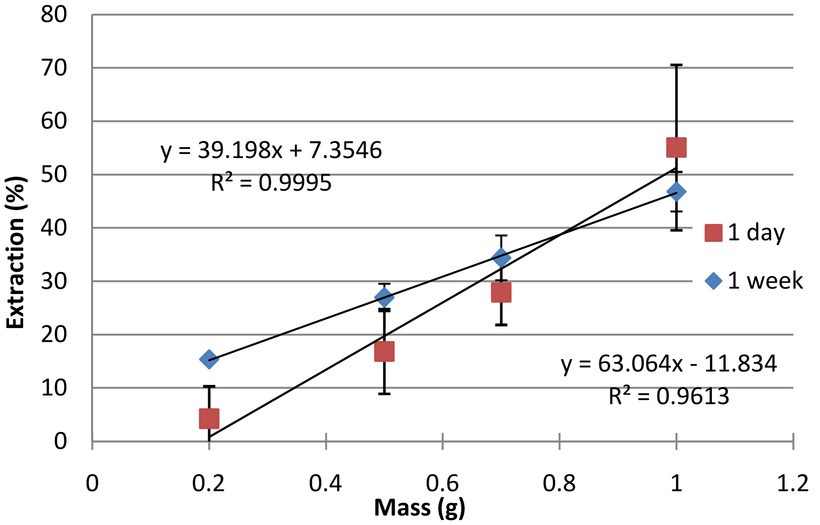


Figure 194. Extraction of 1-chloro-4-nitrobenzene from 20 cm^3 of deionised water by increasing amount of CE sludge using 1 day and 1 week contact times.

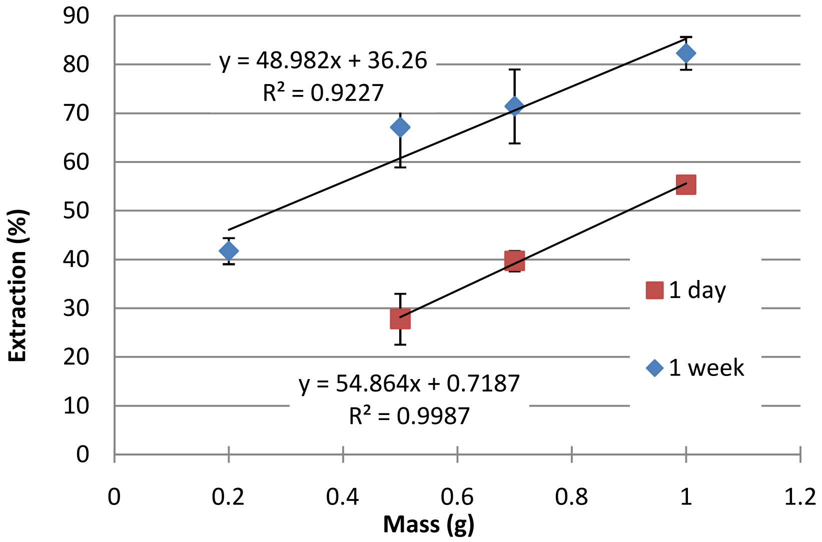


Figure 195. Extraction of 2,4-dichloro-1-nitrobenzene from 20 cm^3 of deionised water by increasing amount of CE sludge using 1 day and 1 week contact time.

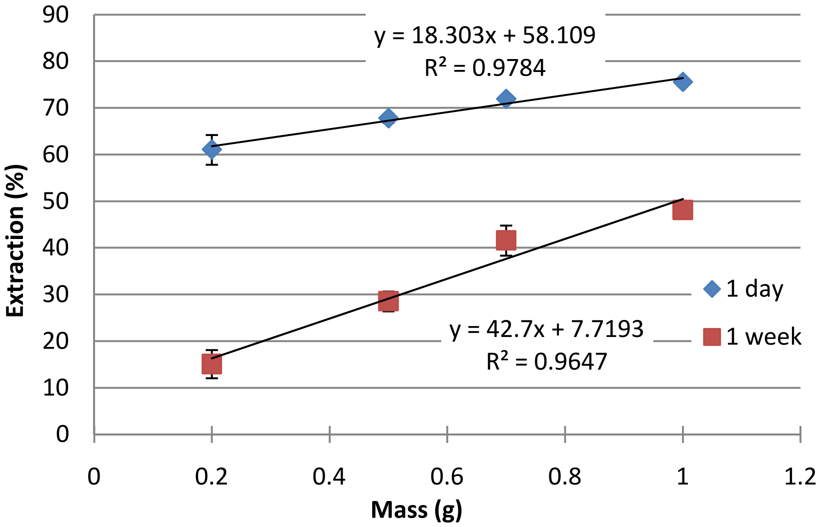


Figure 196. Extraction of 1-chloro-2,4-dinitrobenzene from 20 cm^3 of deionised water by increasing amount of CE sludge using 1 day and 1 week contact times.

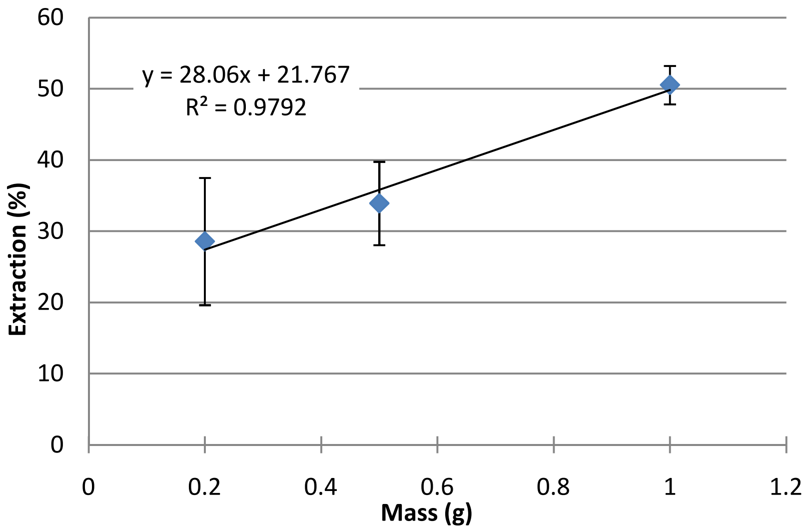


Figure 197. Extraction of 1,2-dichlorobenzene from 20 cm^3 of deionised water by increasing amount of CE sludge using 1 day contact time.

The extraction results are presented as calculated masses of CE sludge needed to extract 100% of the chlorinated benzenes from 20 cm^3 aqueous solutions along with concentrations, contact times, extraction capacities, and errors. These are shown in Table 48. The extraction results are also shown in Figure 198. There is a decrease in extraction capacity of 1-chloro-2-nitrobenzene and 1-chloro-4-nitrobenzene with increasing contact time whereas the extraction capacities are not changed for 2,4-dichloro-1-nitrobenzene and 1-chloro-2,4-dinitrobenzene.

Table 48. The concentrations of original chlorinated benzene solutions, contact times, masses of CE sludge needed to extract 100% of organic compound from the 20 cm^3 solution, extraction capacities and errors

Chlorinated benzenes	***Solution ($mg\ dm^{-3}$)***	***Contact time (d)***	***Mass (g)***	***Capacity ($mg\ g^{-1}$)***	***Error (%)***
1-Chloro-2-nitrobenzene	388	1	2.5 ± 0.2	3.2 ± 0.3	9.8
1-chloro-2-nitrobenzene	439.4	7	3.9 ± 0.4	2.3 ± 0.2	10.7
1-chloro-4-nitrobenzene	319.4	1	1.8 ± 0.3	3.6 ± 0.6	15.8
1-chloro-4-nitrobenzene	210.4	7	2.4 ± 0.1	1.78 ± 0.08	4.7
2,4-dichloronitrobenzene	251.6	1	1.81 ± 0.09	2.8 ± 0.1	5.0
2,4-dichloronitrobenzene	254.4	7	1.5 ± 0.2	3.5 ± 0.6	16.3
1-chloro-2,4-dinitrobenzene	222.8	1	2.3 ± 0.2	2.0 ± 0.1	7.0
1-chloro-2,4-dinitrobenzene	198	7	2.2 ± 0.2	1.8 ± 0.1	7.4
1,2-dichlorobenzene	562.6	1	2.5 ± 0.4	4.6 ± 0.8	17.1

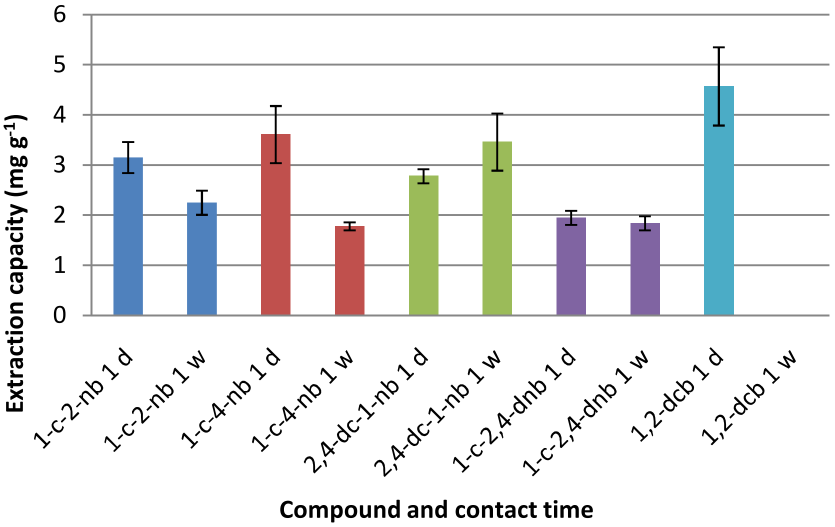


Figure 198. Extraction capacity of chlorinated benzenes (A,B) by CE sludge and contact time (1 day and 1 week). Abbreviations: 1-chloro-2-nitrobenzene (1-c-2-nb), 1-chloro-4-nitrobenzene (1-c-4-nb), 2,4-dichloro-1-nitrobenzene (2,4-dc-1-nb), 1-chloro-2,4-dichlorobenzene (1c-2,4-dcb), and 1,2-dichlorobenzene (1,2-dcb).

The extraction capacities are plotted against the octanol-water partition coefficient K_{ow} and Figure 199 shows a clear, positive trend between hydrophobicity and extraction capacity for the CE sludge. The results are in good agreement with the corresponding results using ST sludge (Figure 192).

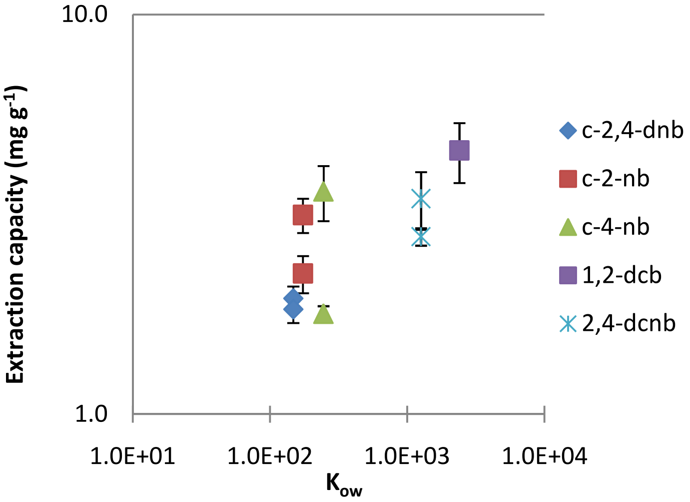


Figure 199. Extraction capacity for chlorinated benzenes by CE sludge using 1 day and 1 week contact times versus octanol-water distribution coefficient K_{ow}. Abbreviations: 1-chloro-2,4-dichlorobenzene (c-2,4-dcb), 1-chloro-2-nitrobenzene (c-2-nb), 1-chloro-4-nitrobenzene (c-4-nb), 1,2-dichlorobenzene (1,2-dcb), and 2,4-dichloro-1-nitrobenzene (2,4-dcnb).

These results (Table 49) suggest different extraction mechanisms for chlorinated benzenes compared to chlorinated anilines and phenols. The lower polarity of the NO_2 group in the nitrobenzenes compared to the NH_2 and OH groups in anilines and phenols may initiate nonpolar behaviour for chlorinated nitrobenzenes. Previous studies by Sun *et al.*, for example, have stated that sorption of nonpolar solutes are driven predominantly by hydrophobic partition [80]. Therefore, it can be concluded that the hydrophobicity of the chlorinated benzene increase their extraction from aqueous solution into ST and CE sludges. These results show opposite behaviour for chlorinated benzenes compared to chlorinated anilines and phenols which exhibited increasing extraction capacity with increasing water solubility (hydrophilicity).

Table 49. Octanol-water partition coefficient and extraction capacities of chlorinated benzenes by ST and CE sludges

Compound	K_{ow}	ST sludge Extraction capacity (mg g^{-1})		CE sludge Extraction capacity (mg g^{-1})	
		1 day	1 week	1 day	1 week
1-Chloro-2-nitrobenzene	2.24	5.5 ± 1.3	3.5 ± 0.7	3.2 ± 0.3	2.3 ± 0.2
1-Chloro-4-nitrobenzene	2.39	2.9 ± 0.3	1.9 ± 0.5	3.6 ± 0.6	1.78 ± 0.08
1-Chloro-2,4-dinitrobenzene	2.17	1.25 ± 0.05	2.6 ± 0.5	2.0 ± 0.1	1.8 ± 0.1
2,4-dichloro-1-nitrobenzene	3.1	8.0 ± 1.8	3.1 ± 0.5	2.8 ± 0.1	3.5 ± 0.6
1,2-dichlorobenzene	3.38	N/A	N/A	4.6 ± 0.8	N/A

4.12 pH buffering studies in chlorinated aniline, phenol and benzene solutions with ST sludge

The buffering behaviour of the ST sludge is evident in the extraction samples with chlorinated anilines, phenols and benzenes (Figures 200-202). The pH in the chlorinated aniline and benzene samples show a small decrease of pH as a function of increasing amount of ST sludge. The pH in the chlorinated phenol samples are more scattered. The original pHs of the solutions (Table 50) were between 8.1 - 8.8 for anilines, between 5.1 - 7.4 for phenols, and between 7.0 - 8.6 for benzenes. It can be concluded that the buffering capacity of ST sludge has efficiently lowered the pH in the chlorinated aniline, phenol and benzene sample solutions to the natural pH of the ST sludge.

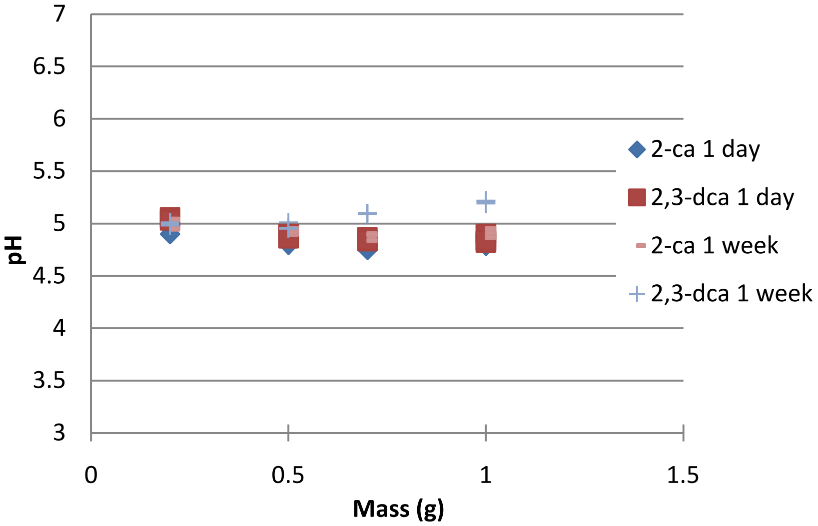


Figure 200. pH in the extraction samples of chlorinated anilines by ST sludge (1 day and 1 week contact times). Abbreviations: 2-chloroaniline (2-ca) and 2,3-dichloroaniline (2,3-dca).

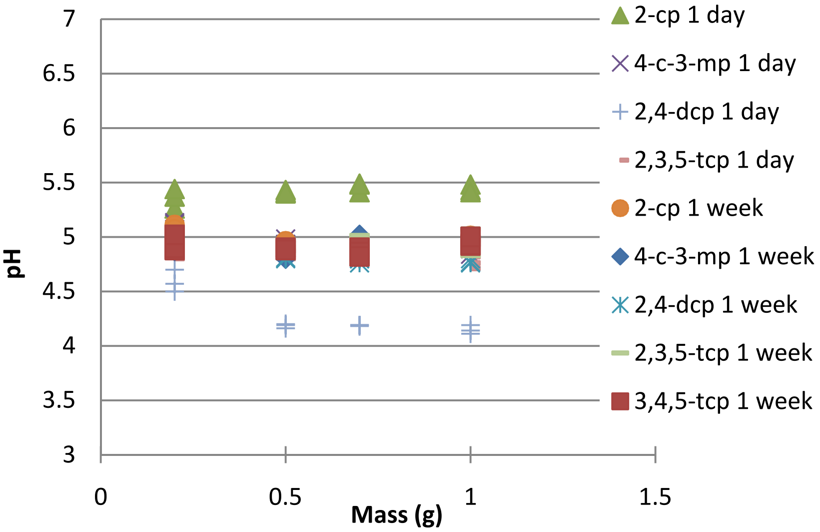


Figure 201. pH in the extraction samples of chlorinated phenols by ST sludge (1 day and 1 week contact times). Abbreviations: 2-chlorophenol (2-cp), 4-chloro-3-methylphenol (4-c-3-mp), 2,4-dichlorophenol (2,4-dcp), 2,3,5-trichlorophenol, (2,3,5-tcp), and 3,4,5-trichlorophenol (3,4,5-tcp).

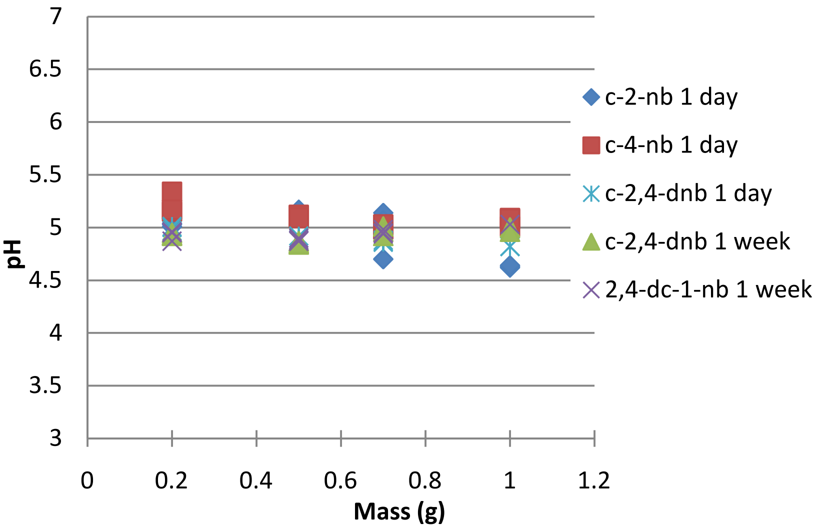


Figure 202. pH in the extraction samples of chlorinated benzenes by ST sludge (1 day and 1 week contact times). Abbreviations: 1-chloro-2-nitrobenzene (c-2-nb), 1-chloro-4-nitrobenzene (c-4-nb), 1-chloro-2,4-dichlorobenzene (c-2,4-dnb), and 2,4-dichloro-1-nitrobenzene (2,4-dc-1-nb).

Table 50. pH in the original solutions containing chlorinated anilines, phenols and benzenes used in the CE extraction studies

Compound	pH of the original solution	
	1 day	1 week
2-chloroaniline	8.2	8.1
2,3-dichloroaniline	8.8	8.2
2-chlorophenol	6.8	6.4
4-chloro-3-methylphenol	N/A	7.4
2,4-dichlorophenol	N/A	6.0
2,3,5-trichlorophenol	5.1	N/A
3,4,5-trichlorophenol	N/A	6.7
2,3,4-trichlorophenol	N/A	N/A
1-Chloro-2-nitrobenzene	7.0	N/A
1-Chloro-4-nitrobenzene	8.0	N/A
1-Chloro-2,4-dinitrobenzene	7.9	8.5
2,4-dichloro-1-nitrobenzene	N/A	8.6

The average pH in the 1 day and 1 week samples are shown in Table 51 which show buffering of pH to 5 in all sample sets. The averaged pH is 4.9 ± 0.3 in 1 day samples and 5.0 ± 0.1 in 1 week samples.

Table 51. Averaged pH in the extraction samples of chlorinated anilines, phenols and benzenes by ST sludge using 1 day and 1 week contact times

Compounds	ST sludge 1 day	ST sludge 1 week
Chlorinated anilines	4.9 ± 0.1	5.0 ± 0.1
Chlorinated phenols	4.9 ± 0.4	4.9 ± 0.1
Chlorinated benzenes	5.0 ± 0.2	4.9 ± 0.1

4.13 pH buffering studies in chlorinated aniline, phenol and benzene solutions with CE sludge

Figures 203 to 205 show the buffering behaviour of the CE sludge in extraction samples of chlorinated anilines, phenols and benzenes. The results show that the sample sets with anilines and benzenes show a clear decrease of pH with increasing amount of CE sludge whereas the pH in the samples sets with phenols are not significantly affected by the increasing amount of CE sludge. The original pH of the solutions (Table 52) were between 8.0 - 8.7 for anilines, between 5.5 - 7.5 for phenols, and between 7.9 - 8.6 for benzenes. Therefore, the increasing amount of CE sludge has buffered the pH in the chlorinated aniline and benzene sample solutions towards the natural pH of the CE sludge whereas the original pH in the phenol solutions were already at the pH region of the CE sludge.

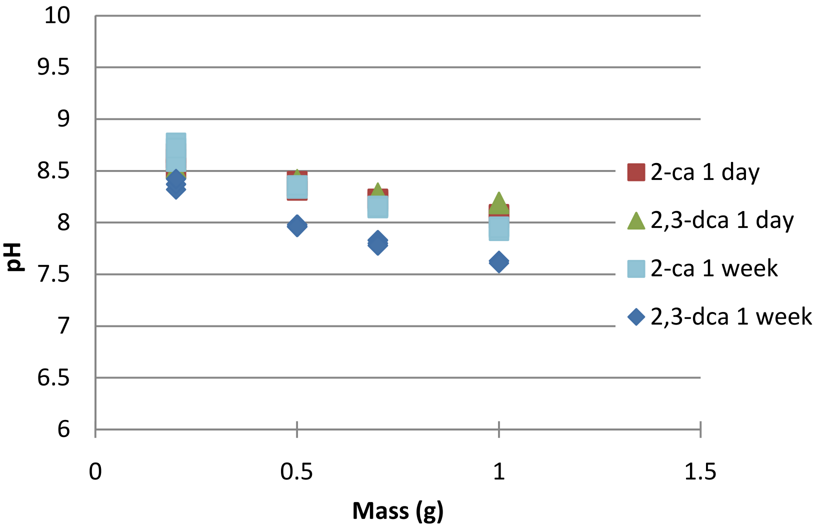


Figure 203. pH in the extraction samples of chlorinated anilines by CE sludge (1 day and 1 week contact times). Abbreviations: 2-chloroaniline (2-ca) and 2,3-dichloroaniline (2,3-dca).

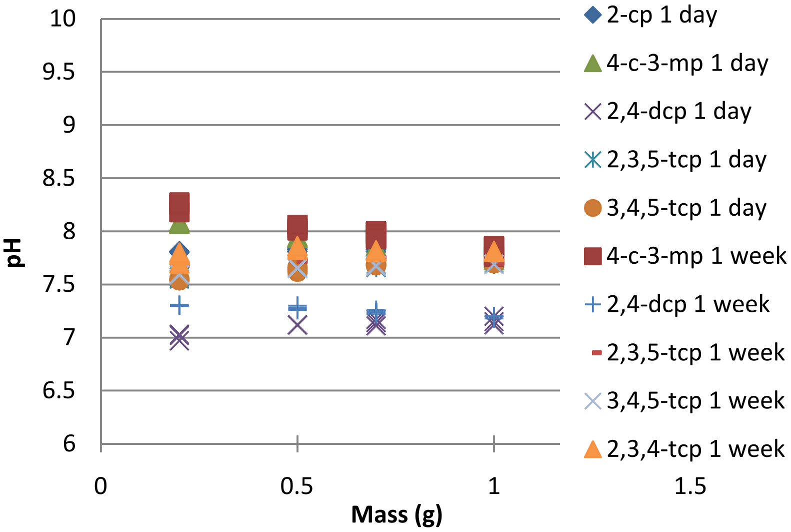


Figure 204. pH in the extraction samples of chlorinated phenols by CE sludge (1 day and 1 week contact times). Abbreviations: 2-chlorophenol (2-cp), 4-chloro-3-methylphenol (4-c-3-mp), 2,4-dichlorophenol (2,4-dcp), 2,3,5-trichlorophenol, (2,3,5-tcp), 3,4,5-trichlorophenol (3,4,5-tcp), and 2,3,4-trichlorophenol (2,3,4-tcp).

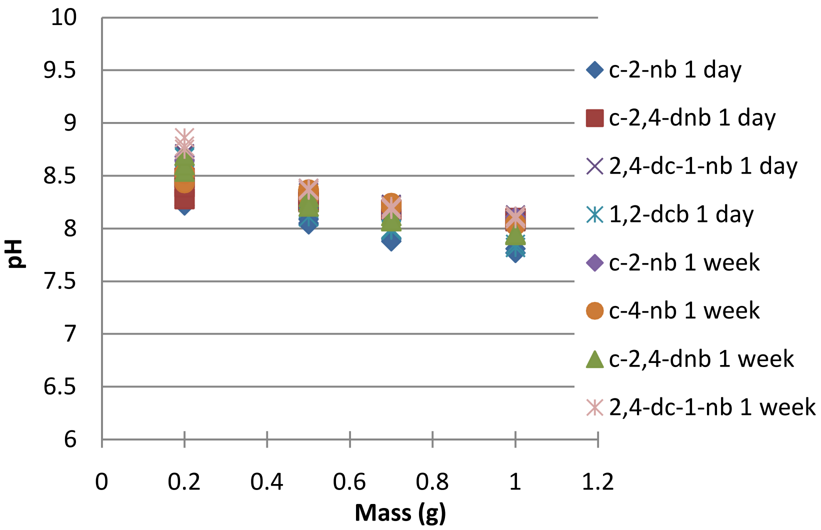


Figure 205. pH in the extraction samples of chlorinated benzenes by CE sludge (1 day and 1 week contact times). Abbreviations: 1-chloro-2-nitrobenzene (c-2-nb), 1-chloro-4-nitrobenzene (c-4-nb), 2,4-dichloro-1-nitrobenzene (2,4-dc-1-nb), 1-chloro-2,4-dichlorobenzene (c-2,4-dcb), and 1,2-dichlorobenzene (1,2-dcb).

Table 52. pH in the original solutions containing chlorinated anilines, phenols and benzenes used in the CE extraction studies

Compound	pH of the original solution	
	1 day	1 week
2-chloroaniline	8.2	8.0
2,3-dichloroaniline	8.7	8.2
2-chlorophenol	6.8	N/A
4-chloro-3-methylphenol	N/A	7.5
2,4-dichlorophenol	N/A	6.1
2,3,5-trichlorophenol	5.5	5.6
3,4,5-trichlorophenol	6.2	6.1
2,3,4-trichlorophenol	N/A	6.4
1-Chloro-2-nitrobenzene	N/A	7.9
1-Chloro-4-nitrobenzene	N/A	N/A
1-Chloro-2,4-dinitrobenzene	8.0	8.4
2,4-dichloro-1-nitrobenzene	8.2	N/A
1,2-dichlorobenzene	8.6	N/A

The averaged pH in the 1 day and 1 week sample sets show (Table 53) that the pH in the samples sets with phenols are little lower than in the sample sets with anilines and benzenes but there is no significant difference between them.

Table 53. Averaged pH in the extraction samples of chlorinated anilines, phenols and benzenes by CE sludge using 1 day and 1 week contact times

Compounds	CE sludge 1 day	CE sludge 1 week
Chlorinated anilines	8.3 ± 0.2	8.1 ± 0.3
Chlorinated phenols	7.6 ± 0.3	7.7 ± 0.3
Chlorinated benzenes	8.2 ± 0.3	8.3 ± 0.2

4.14 Extraction of 2-chloroaniline, 3,4,5-trichlorophenol and 2,4-dichloro-1-nitrobenzene by a 50 g ST column

The column study to simulate a dynamic flow through system was carried out as described in section 4.4 by packing 50 g of ST in a glass column (Ø 2.6 cm). First the sludge was mixed with DI water to form a slurry after which it was poured slowly into the column and air bubbles were removed by gentle stirring. The column was washed with DI water at least for 12 h to remove the soluble fraction (i.e. fulvic acid) with a flow rate of 0.2 cm^3 min^{-1}. The porosity of the column was measured using tritiated water as described in Chapter 3.

One representative from each group of chlorinated anilines, phenols and benzenes was chosen according to their retention times on the GC-MS chromatograms in a way that their response peaks do not overlap. Therefore known amounts of 2-chloroaniline (178.9 mg dm^{-3}), 3,4,5-trichlorophenol (101.2 mg dm^{-3}) and 2,4-dichloro-1-nitrobenzene (104.4 mg dm^{-3}) were dissolved into 500 cm^3 of synthetic groundwater [78]. The composition of the synthetic groundwater is shown in Table 54 and the pH of the solution was 7.4. The prepared synthetic ground water was introduced to the pre-treated 11 cm long 50 g ST column with a constant flow rate of 0.2 cm^3 min^{-1}. The porosity of the column was 56.3%. 20 cm^3 fractions were collected by a fraction collector and the amounts of organic compounds in the fractions were measured using GC-MS.

Table 54. The composition of 2 dm^3 of synthetic ground water

Reagent	Mass (g)
$MgCl_2$	0.1065
$KHCO_3$	0.0126
$CaSO_4$ x $2H_2O$	0.0775
$NaHCO_3$	0.1127
$CaCl_2$ x $2H_2O$	0.2248
$NaNO_3$	0.0030

The extraction results for 2-chloroaniline, 3,4,5-trichlorophenol and 2,4-dichloro-1-nitrobenzene by 50 g ST column (Figure 206) show efficient extraction of the organic compounds under investigation. The results show 100% extraction within experimental error for all the compounds. The ST sludge also buffered the solution from pH 7.4 to between pH 4.5 and 5 (Figure 207).

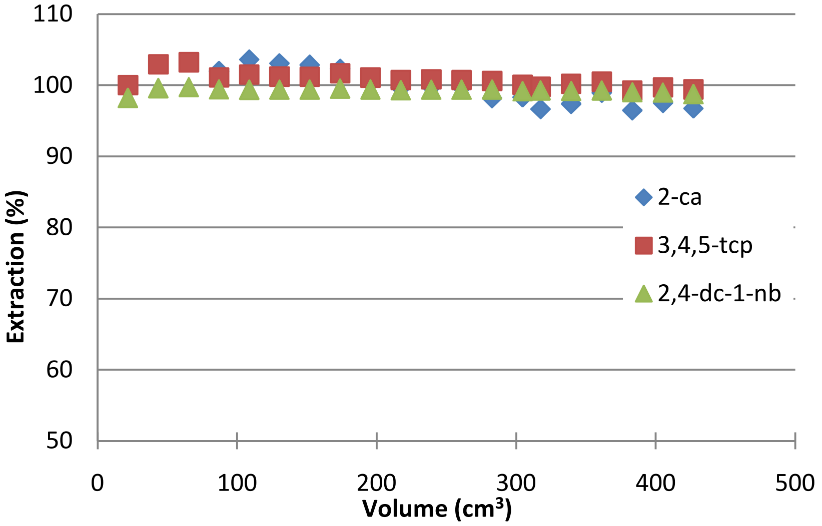


Figure 206. Extraction of 2-chloroaniline, 3,4,5-trichlorophenol and 2,4-dichloro-1-nitrobenzene by 50 g ST column. Abbreviations: 2-chloroaniline (2-ca), 3,4,5-trichlorophenol (3,4,5-tcp), and 2,4-dichloro-1-nitrobenzene (2,4-dc-1-nb).

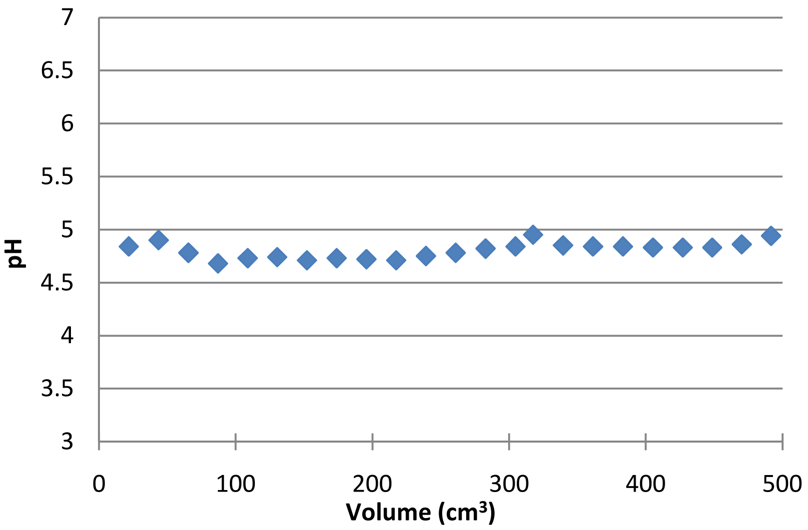


Figure 207. pHs in the fractions collected from 50 g ST column treated with deionised water containing 2-chloroaniline, 3,4,5-trichlorophenol and 2,4-dichloro-1-nitrobenzene.

4.15 Extraction of 2-chloroaniline, 3,4,5-chlorophenol and 2,4-dichloro-1-nitrobenzene by a 50 g CE column

The 50 g CE column was prepared in the same way as the 50 g ST column in the previous section by mixing the sludge with DI water to form a slurry, packing it into a glass column (Ø 2.6 cm) and then washing it with DI water at least for 12 h to remove the soluble fraction (i.e. fulvic acid) with a constant flow rate of 0.2 cm^3 min^{-1}. Known amounts of 2-chloroaniline (124.5 mg dm^{-3}) , 3,4,5-trichlorophenol (85.2 mg dm^{-3}) and 2,4-dichloro-1-nitrobenzene (90.7 mg dm^{-3}) were dissolved into 1000 cm^3 of synthetic groundwater [78]. The solution (pH 7.5) was introduced to the pre-treated 11.5 cm long 50 g CE column (flow rate of 0.2 cm^3 min^{-1}) and 20 cm^3 fractions were collected by a fraction collector. The porosity of the column was 35.3%. The amounts of chlorinated contaminants in the fractions were measured using GC-MS. However, due to samples not being measured immediately the organic compounds may have deteriorated and consequently the data has not been represented. The pH results in the collected samples show increase of pH from 7.5 to around pH 8.2 (Figure 208). Therefore, the CE sludge has efficiently buffered the pH.

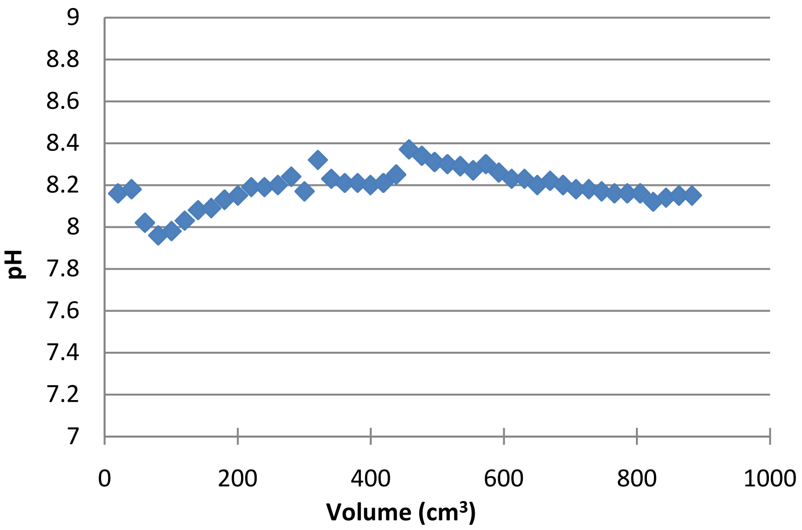


Figure 208. pHs in the fractions collected from 50 g CE column treated with deionised water containing 2-chloroaniline, 3,4,5-trichlorophenol and 2,4-dichloro-1-nitrobenzene.

4.16 Summary

4.16.1 Comparison of extraction capacities for chlorinated anilines, phenols and benzenes by ST and CE sludges

The extraction capacities of chlorinated anilines, phenols and benzenes by ST and CE sludges using 1 day and 1 week contact times are summarised in Table 55. The extractions of chlorinated anilines showed overall similar extraction capacities by both of the sludges. Only extraction of 2-chloroaniline by CE sludge using 1 week contact time differed from this statement which can be explained by lower concentration of the original solution (~330 mg dm^{-3} compared to ~1900 mg dm^{-3}). The extraction capacities of 2-chloroaniline were almost three times higher than of 2,3-dichloroaniline due to the higher polarity of the 2-chloroaniline. The extractions also occurred rapidly within 1 day contact times.

The extraction capacities for chlorinated phenols showed varying results; in some cases the extraction capacity was higher by ST sludge (2-chlorophenol and 2,3,5-trichlorophenol), in other cases by CE sludge (2,4-dichlorophenol and 3,4,5-trichlorophenol) and in some cases they were similar (4-chloro-3-methylphenol and 2,3,4-trichlorophenol). The significantly higher extraction capacity for 2-chlorophenol by ST sludge was unclear but the significantly higher extraction capacity for 3,4,5-trichlorophenol by CE sludge was due to higher original concentration of the solution (~350 mg dm^{-3} compared to ~1200 mg dm^{-3}).

The results of chlorinated benzenes showed mainly rapid extraction (< 1 day) and increasing extraction capacities when longer contact times were used. However, decrease on extraction capacity of 2,4-dichloro-1-nitrobenzene by ST sludge and of 1-chloro-2-nitrobenzene and 1-chloro-4-nitrobenzene by CE sludge were observed. The extraction capacities were higher by ST sludge for chloro-2-nitrobenzene and 2,4-dichloro-1-nitrobenzene whereas the extraction capacities were similar by both of the sludges for chloro-4-nitrobenzene and chloro-2,4-dinitrobenzene.

The pH in the extraction samples exhibited clear buffering of pH to 5 in ST samples and to pH 8 in CE samples.

Table 55. Summary of extraction capacities for chlorinated anilines, phenols and benzenes by ST and CE sludges using 1 day and 1 week contact times

Compound	ST sludge Extraction capacity (mg g^{-1})		CE sludge Extraction capacity (mg g^{-1})	
	1 day	1 week	1 day	1 week
2-chloroaniline	3.4 ± 0.2	3.4 ± 0.2	3.4 ± 0.2	1.60 ± 0.06
2,3-dichloroaniline	1.04 ± 0.02	1.8 ± 0.3	1.4 ± 0.2	2.0 ± 0.2
2-chlorophenol	55.5 ± 12.3	40.6 ± 6.0	16.4 ± 1.4	N/A
4-chloro-3-methylphenol	8.6 ± 0.4	9.9 ± 0.3	8.5 ± 0.2	7.3 ± 0.9
2,4-dichlorophenol	6.16 ± 0.05	13.9 ± 1.2	13.3 ± 0.7	20.5 ± 1.3
2,3,5-trichlorophenol	6.2 ± 0.6	5.4 ± 0.9	3.6 ± 0.2	2.8 ± 0.2
3,4,5-trichlorophenol	1.53 ± 0.08	3.4 ± 0.5	33.5 ± 8.4	24.4 ± 2.9
2,3,4-trichlorophenol	5.2 ± 0.5	4.1 ± 0.5	6.4 ± 0.6	7.6 ± 1.3
1-Chloro-2-nitrobenzene	5.5 ± 1.3	3.5 ± 0.7	3.2 ± 0.3	2.3 ± 0.2
1-Chloro-4-nitrobenzene	2.9 ± 0.3	1.9 ± 0.5	3.6 ± 0.6	1.78 ± 0.08
1-Chloro-2,4-dinitrobenzene	1.25 ± 0.05	2.6 ± 0.5	2.0 ± 0.1	1.8 ± 0.1
2,4-dichloro-1-nitrobenzene	8.0 ± 1.8	3.1 ± 0.5	2.8 ± 0.1	3.5 ± 0.6
1,2-dichlorobenzene	N/A	N/A	4.6 ± 0.8	N/A

N/A not analysed

4.16.2 The correlation of K_{ow} and extraction capacities of chlorinated anilines, phenols and benzenes by ST and CE sludges

The extraction results showed clear, positive correlation between water solubility and extraction capacity of chlorinated anilines (Figure 209) and of chlorinated phenols (Figure 210) by ST and CE sludges whereas the extraction capacities for the chlorinated benzenes (Figure 211) showed clear, negative correlation. Therefore, it was concluded that the polar groups in chlorinated anilines (NH_2) and phenols (OH) increased the polarity of the chlorinated anilines and phenols and formed strong hydrogen bonds with the polar groups (especially carboxyl and alcohol groups) in the organic fraction of the sludges. The hydrophobicity of the chlorinated benzenes initiated partition to the ST and CE sludges. These results can be used in predicting the extraction behaviour of different chlorinated hydrocarbons; increasing hydrophilicity of chlorinated anilines/phenols and increasing hydrophobicity of chlorinated benzenes enhance their extraction by ST and CE sludges.

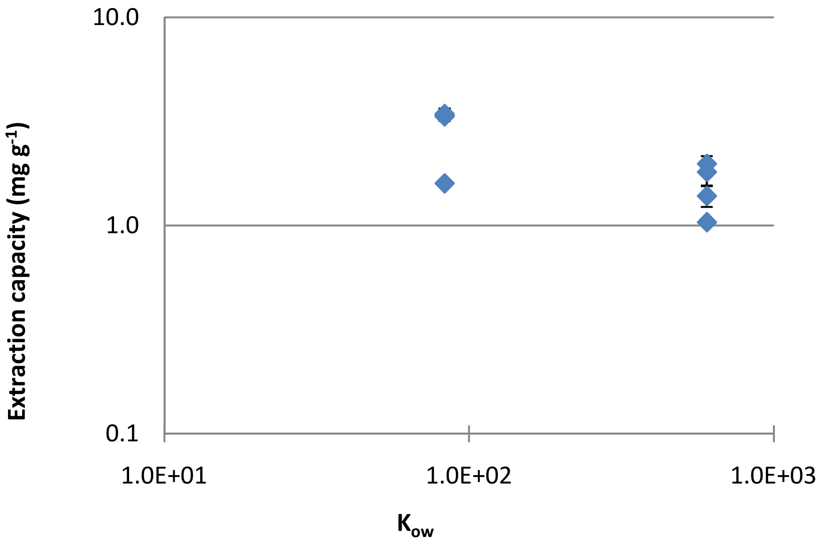


Figure 209. Extraction capacity for chlorinated anilines by ST and CE sludges using 1 day and 1 week contact times versus octanol-water distribution coefficient K_{ow}.

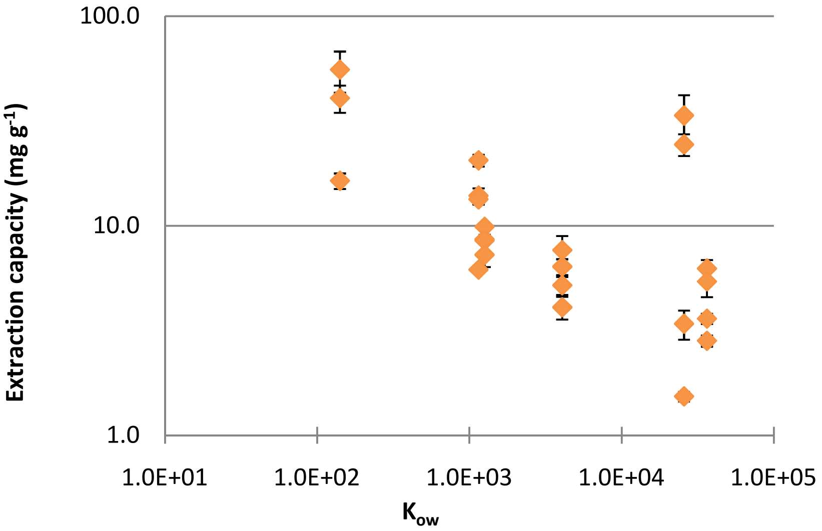


Figure 210. Extraction capacity for chlorinated phenols by ST and CE sludges using 1 day and 1 week contact times versus octanol-water distribution coefficient K_{ow}.

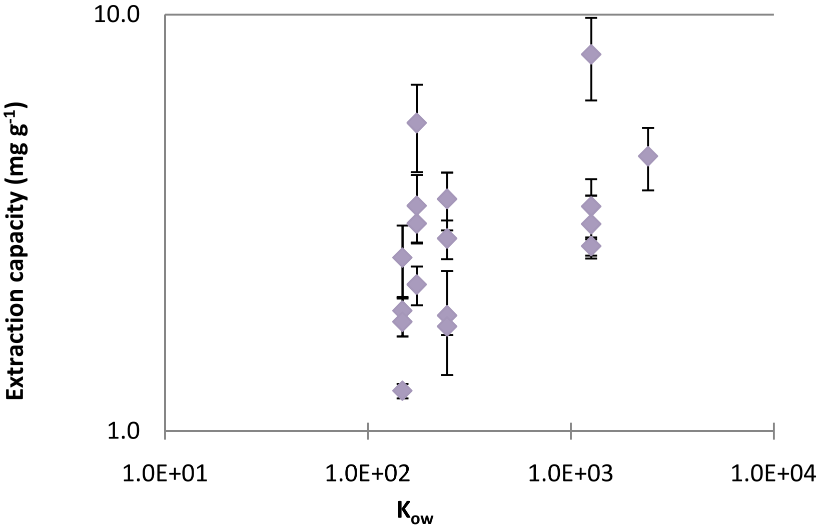


Figure 211. Extraction capacity for chlorinated benzenes by ST and CE sludges using 1 day and 1 week contact times versus octanol-water distribution coefficient K$_{ow}$.

In addition, a power equation was plotted into the extraction results (Figures 212 to 214) giving an indication on the predictive power of the data. Power equation was used since it exhibited the best fit. However, there is a considerable scatter in the data due (R^2 values ranging from 0.2744 to 0.5328), it is believed, to a combination of errors in extraction capacity determinations. The predictive equations were;

For chlorinated anilines $y = 11.28x^{-0.314}$ (4.4)

For chlorinated phenols $y = 87.2x^{-0.28}$ (4.5)

For chlorinated nitrobenzenes $y = 0.7013x^{0.2422}$ (4.6)

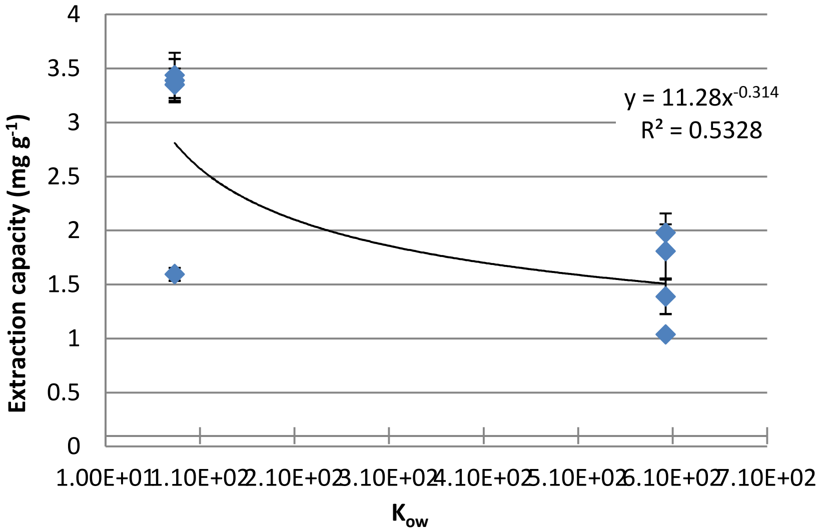


Figure 212. Power equation fitted into the extraction capacity versus octanol-water distribution coefficient Kow for chlorinated anilines by ST and CE sludges using 1 day and 1 week contact times.

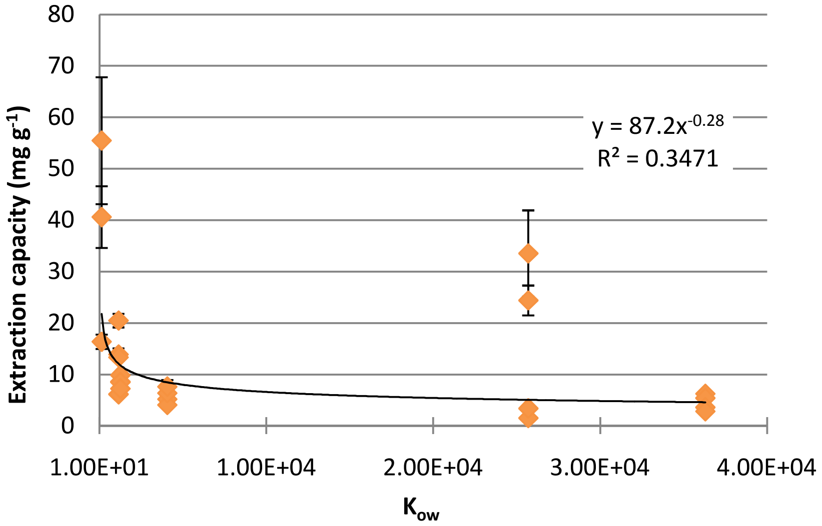


Figure 213. Power equation fitted into the extraction capacity versus octanol-water distribution coefficient K_{ow} for chlorinated phenols by ST and CE sludges using 1 day and 1 week contact times.

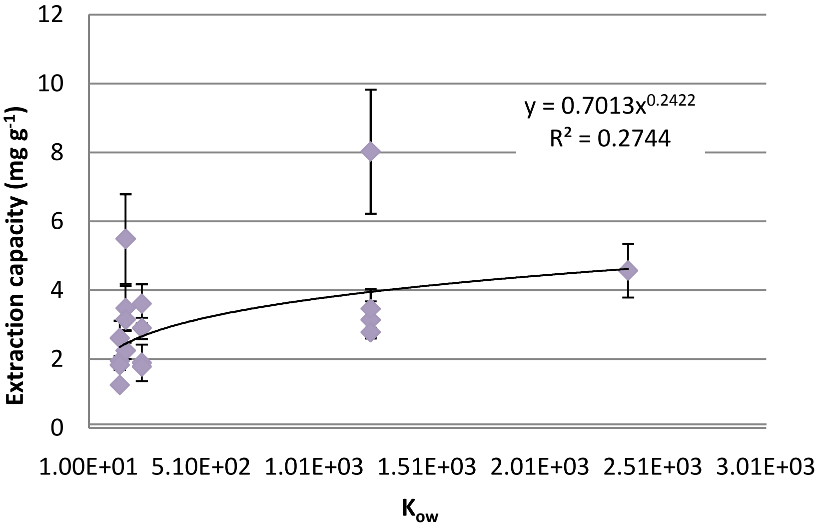


Figure 214. Power equation fitted into the extraction capacity versus octanol-water distribution coefficient K$_{ow}$ for chlorinated benzenes by ST and CE sludges using 1 day and 1 week contact times.

4.16.3 Extractions of chlorinated aniline, phenol and benzene by 50 g ST and CE columns

The extractions of 2-chloroaniline, 3,4,5-trichlorophenol and 2,4-dichloro-1-nitrobenzene by 50 g ST column showed 100% extraction for all the organic compounds under investigation. Due to technical problems, data on the corresponding extraction experiments by 50 g CE column were not available. The buffering capacities of the ST and CE sludges changed the pH of the synthetic ground water from 7.5 to between 4.5 and 5 by the ST sludge and to around pH 8.2 by the CE sludge.

4.17 Conclusions

Both ST and CE sludges showed efficient extractions of the chlorinated hydrocarbons under investigation. In some cases the extraction capacities were higher by ST sludge whereas in other cases the extraction capacities were higher by CE sludge. Therefore, it can be concluded that both of the sludges exhibit preferable extractions depending on the organic compound. A tendency of initial extraction and then release of chlorinated benzenes was observed originating from the decrease of hydrophobic extraction sites as a function of time. A clear, positive relationship between the polarity (water solubility, hydrophility) and extraction capacity was established for polar chlorinated anilines and phenols. A clear, positive correlation between the non-polarity (water insolubility, hydrophobicity) and extraction capacity was observed for the nonpolar chlorinated benzenes. These results can be used to estimate the behaviour of other chlorinated hydrocarbons.

CHAPTER 5

APPLICATION 3 - EXTRACTION OF IODINE SPECIES FROM URINE

CHAPTER 5 – APPLICATION 3 - EXTRACTION OF IODINE SPECIES FROM URINE

5.1 Introduction

Iodine is an important trace element in human nutrition because of its physiological function as a constituent of hormones excreted by the thyroid gland [81]. These hormones such as thyroxine (T_4) and tri-iodothyronine (T_3) regulate the metabolism of virtually all cells in the body [82] controlling human development and growth [83]}. Iodine enters the human body via food and inhalation of atmospheric iodine. More than 80% of it is transported to the thyroid gland [84] and the rest to muscles and various endocrine tissues [85].

When the thyroid gland is severely dysfunctional or has a tumour, radioactive iodine (^{131}I) can be given to the patient to destroy the gland tissue. The doses of radioiodine prescribed to patients in the UK vary between 200 – 800 MBq [86] and in USA between 1.85 – 7.4 GBq [87]. Nevertheless, it has been estimated that 35% to 75% of the administered dose is excreted in urine, perspiration and saliva within the first 24 h after dosing [6]. In some parts of Europe, the radioactive urine is collected in tanks in the hospital and stored until the activity of the urine has decayed to below regulation limits.

5.1.1 Radioiodine treatment

The majority of thyroid gland tumours maintain the ability to transport and concentrate iodine, a factor that allows the use of radioisotopes of iodine for both diagnosis and therapy [88]. ^{123}I and ^{131}I are the two radioactive isotopes of iodine in medical use [89]. Whereas the radiation of ^{123}I is harmless to the thyroid cells, ^{131}I radiation destroys them [89]. ^{123}I is used for thyroid imaging in which small amount of ^{123}I is given to the patient and the thyroid gland is imaged 3-6 h later [89].

Radiation therapy attempts to deliver the necessary dose of radiation to a defined tumour site while causing minimal damage to surrounding healthy tissue [90]. In the treatment of thyroid disorders, a small amount of ^{131}I (0.185 – 1.11 GBq) is given to patients with overactive thyroid glands and larger doses (1.11 – 7.4 GBq) to patients with thyroid cancer [89]. The regulations may require a short period of isolation of the patient in the medical facility, typically 2 to 3 days until radiation exposure rates decrease to acceptable levels [6]. Post-surgical ^{131}I treatments are also given to destroy the remaining thyroid tissue [88].

Radioiodine treatment has been prescribed to millions of people since it was introduced in the early 1940s [86]. The treatment is based on radiation-induced cell damage caused by the high-energy β-radiation emitted [87]. The half life of ^{131}I is 8 days and the primary emissions are the β particles (maximum energy 606 keV) and the gamma rays (364 keV) [6]. The β particles deliver the major portion of the radiation dose to the thyroid tissue of the patient while the gamma radiation can not only affect the patient but potentially also be a hazard to others nearby [6]. The β particles travel a maximum of 2 mm in tissue and have an average path length of 400 μm [91], thus virtually no beta particles escape from the thyroid tissue where it is concentrated. The biological half life of ^{131}I depends on the rates of internalisation and externalisation, and whether the isotope has been organified [92].

Therapeutic doses of ^{131}I are administered orally in liquid or capsule form [6]. The ^{131}I-labelled sodium iodide is readily absorbed from the gastrointestinal tract and distributed in the extracellular fluid of the body, concentrating in thyroid tissue, the stomach, and salivary glands, with a portion re-circulated back to these tissues [6]. For most patients, 35%-75% of the administered dose is excreted in the urine, perspiration and saliva within the first 24 h after dosing [6] but significant amounts also enter the gastrointestinal tract via salivary excretion and gastric secretion [87].

According to a European Association of Nuclear Medicine survey, approximately 6 000 doses of radioiodine were administrated in the UK in 2002 [86]. In recent years (2007), the radioiodine doses given have been even higher, with about 10 000 doses per year, since radioiodine treatment is the most cost effective and precise treatment for an overactive thyroid [82]. In most cases, the dose of radioactivity given is sufficient to destroy gradually the thyroid tissue, over 6 weeks to 6 months following a single dose [82]. The majority (80-90%) of radioiodine treated patients suffering from hyperthyroidism are cured by a single dose [86].

In the USA until a few years ago, radioiodine therapy using higher doses than 1.11 GBq of ^{131}I required hospitalisation of patients to minimise radiation exposure to others [87]. In 1997, the U.S. Nuclear Regulatory Commission (USNRC) allowed the release of patients immediately after the ^{131}I therapy if the total effective dose equivalent from the patient to an individual did not exceed 5 mSv in any 1 year [87]. USNRC Regulatory Guide 8.39 recommends that the patient can be released from the hospital when activity levels within the patient are less than 1221 MBq or a dose rate at 1 m is less than 70 μSv h^{-1} for ^{131}I [6]. The maximum activity per administration for patient released home in the UK is 800 MBq [86].

5.1.3 Iodine chemistry

Iodine is a halogen with atomic number 53. It exhibits some metal-like properties and forms compounds with many elements but it is less reactive than the lighter halogens [93]. There are 42 isotopes and isomers, but only one stable isotope, ^{127}I, is found in nature [93]. Iodine is an electronegative element with oxidation states of -1, 0, +1, +3, +5, and +7 and it can exist in various species in aqueous solutions [94]. Iodine is a biophilic element, thus it occurs in many organic compounds in nature, such as polyphenols and humic substances and can be incorporated in biomolecules, such as proteins [94].

5.1.3.1 Iodine species in environment

Since iodine is a redox sensitive element, it can form a wide variety of organic and inorganic compounds [94]. The most common inorganic forms are iodide (I^-), hypoiodous acid (HOI), elemental iodine (I_2) and iodate (IO_3^-) under natural environmental Eh-pH conditions [94]. In reducing environments, aqueous iodine usually occurs as the mobile, monovalent anion, I^-, whereas under more oxidising conditions, iodine is present as the more reactive iodate, IO_3^- [95]. The predominant states of iodine in aqueous systems are -1 (iodide, I^-), and +5 (iodate, IO_3^-) [95]. Iodate is usually the most abundant species in seawater whereas iodide is often the most abundant species in fresh water [96]. However, substantial amounts of organoiodine species can be found in fresh waters [96]. Volatile organoiodine compounds such as methyl iodide are produced in the marine environment [96].

5.1.3.2 Iodine species and humic substances

Discussion of the interaction mechanisms of iodine with humic substances (HS) can be found in the literature [97]. In some studies, it was observed that iodate (IO_3^-) was readily retained by sedimentary HS whereas little reaction was observed with iodide [97]. It was also proposed that iodate would be reduced to an electrophilic species such as $I_{2(aq)}$ or HIO that would later react with natural organic matter [97]. The cause for the higher sorption of iodate than iodide is not known but is presumably due to the “harder” base nature of iodate, which would favour “hard-hard” interactions with the “hard” acid sites on mineral surfaces [98]. Even though iodide is often employed as a non-reactive tracer, an increasing amount of evidence indicates appreciable sorption of iodide in a variety of geological media [95].

Several studies have shown that iodine species can be strongly retained in surface soils rich in organic matter [99]. Reactions of iodine with HS can follow three pathways: methylation of inorganic iodine by biomass, iodination of phenolic moieties, and iodination of amines [97]. The occurrence of alkylated volatile iodide has been investigated in water, sediment and the atmosphere, and up to eight volatile species were observed; methyl-iodide (MeI) being the major species (40%) [100]. Whitehead suggested in 1974 that sorption of I^- by organic matter probably involves the reaction of molecular iodine (resulting from the redox equilibrium $2I^- + 2e^- \rightarrow I_2$) with amino acid and phenolic components of the organic matter [99]. The retention mechanism for an anionic species such as I^- could be as simple as anionic exchange or incorporation into the organic structure by physical entrapment in the water of the organic matrix [99]. In addition, halogens can also react with phenolic moieties through an electrophilic substitution mechanism [97].

There has been discussion on the effect of pH on iodine retention. Some studies proposed that there is no significant correlation between retention and pH whereas other research have shown that I^- sorption is pH-dependent [99]. In some studies iodide was not sorbed above pH 7 possibly due to the significantly large number of hydroxyl ions present for the number of sorption sites available [99]. Sheppard *et al*. suggested that iodine retention is primarily through physical association with the surfaces and the intricate structure of the organic matter [99]. Iodide sorption to natural sediments has been correlated to organic content and Fe-oxide concentrations as well as to pH levels [98]. The sorption to organic matter and Fe-oxides, which are pH-dependent charge materials, has been attributed to interaction with their positively charged surface sites [98]. As the pH decreases, the number of positively charged surface sites increases [98].

5.1.3.3 Iodine species and minerals

Iodide sorption on many minerals has been reported to be low or insignificant by several authors. For example, Kaplan *et al.* concluded from their studies that there was little or no iodide sorption to montmorillonite, quartz, vermiculite, calcite, goethite, or chlorite whereas a significant amount of iodide was sorbed to illite [98]. It has also been postulated that iodide ($I^{-}_{(aq)}$) in soils is transformed to $I_{2(aq)}$ species through oxidation by Mn(IV) and Fe(III)-containing mineral phases [101]. In soils, iodate commonly exhibits more retention than iodide due to its stronger interactions not only with organic matter but also with clays in which positively charged adsorption sites may exist on the edges of 2:1 clays, on Al- and Fe-oxide surfaces and on 1:1 clays [95].

However, the behaviour of trace level iodine often differs from the behaviour of iodine at macro concentrations [102].

5.1.4 Iodine intake and speciation in urine

The concentration of stable iodine in a normal thyroid is approximately 1 mg per gram of wet mass [84]. WHO recommends 120-150 mg per day intake of iodine for adults and the EU 130 mg per day [84]. The corresponding urinary iodine level is 100 -200 µg dm^{-3} [84]. Intake of iodine into the human body mainly comes from food and inhalation of atmospheric iodine [84] but iodine excretion varies largely among individuals [103]. Around 90% of dietary iodine is eventually excreted in the urine, and variable urine volumes cause variable dilution of the iodine excreted in urine, and thus its concentration [103]. In urine, iodine predominantly exists as iodide [104] [94] [105] but a small amount of organic iodine is also present [94].

5.1.5 Radiolabeling using Chloramine T

Sodium N-chloro-p-toluenesulfonamide is the IUPAC name for a widely used oxidising agent known as Chloramine T, which is often abbreviated as CAT or CT. The structure of Chloramine T is shown in Figure 215 [106]. Chloramine T has an electronegative chlorine which attracts electrons, thus has high oxidising power [107]. It is also a strong oxidant in both acidic and alkaline media; E_{red} = 1.138 V at pH 0.65 and 0.5 V at pH 12 [106].

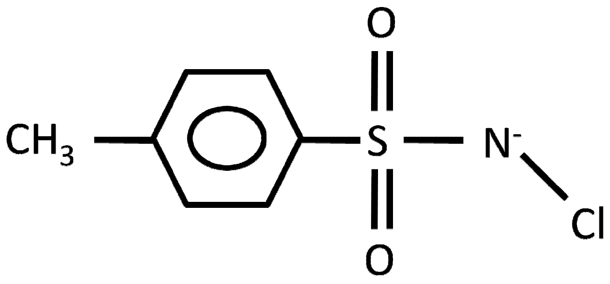
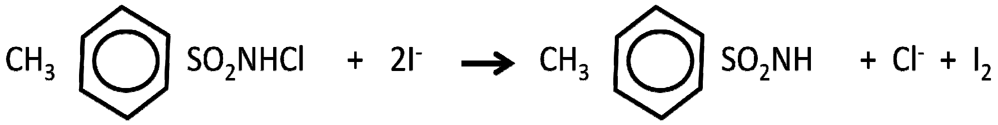


Figure 215. Structure of Chloramine T.

Radioiodination of biomolecules using Chloramine T has been carried out by several authors ([108-110]) since the method was developed by Hunter *et al.* in 1960s [111]. The mechanism for this reaction is unclear due to the lack of spectroscopic evidence. For example, Warwick *et al.* suggest formation of iodine radicals and iodinium ions [108] whereas Hallaba *et al*. , and more recently Tashtoush *et al*. , postulate oxidation to diatomic iodine (reaction 5.1) [110,109]. Therefore, there is no consensus on the speciation of the oxidised iodine species. For this work, an oxidised form of iodine by Chloramine T will be referred as the reactive iodine.



(5.1)

5.1.6 Aim and outline of this chapter

The objective of this investigation is to determine whether radioactive iodide can be extracted from urine by ST and CE sludges, and thereby concentrate the radioactivity into a smaller volume of solid. A litre of urine was estimated to contain 22.6 MBq of radioactive iodine (^{131}I), however, for safety reasons, the experiments were carried out using an equivalent amount of stable iodide spiked with ^{125}I.

The experimental work was divided into three phases (Figure 216). In Phase 1, the extraction experiments were carried out in deionised water. At this stage, extraction of iodide was expected to be low even though humic substances can extract anions due to their polyelectric nature. Efficiency of extraction was expected to increase when iodide was oxidised to reactive iodine using an oxidising agent. In the present work, Chloramine T was used as an oxidant, since it has been applied successfully in previous studies for the labelling of humic material with ^{125}I and ^{131}I [112]. The oxidation is carried out to achieve iodine incorporation via electrophilic aromatic substitution at phenolic sites on the humic molecules [112]. The experiments were carried out in batches and columns.

In Phase 2, similar experimental work was carried out using synthetic urine. This was the second step towards a more realistic medium and finally in Phase 3 the experiments were carried out in real urine. At the end of the experiments, the use of a stronger oxidising agent was also investigated and batch experiments in urine were repeated using potassium permanganate.

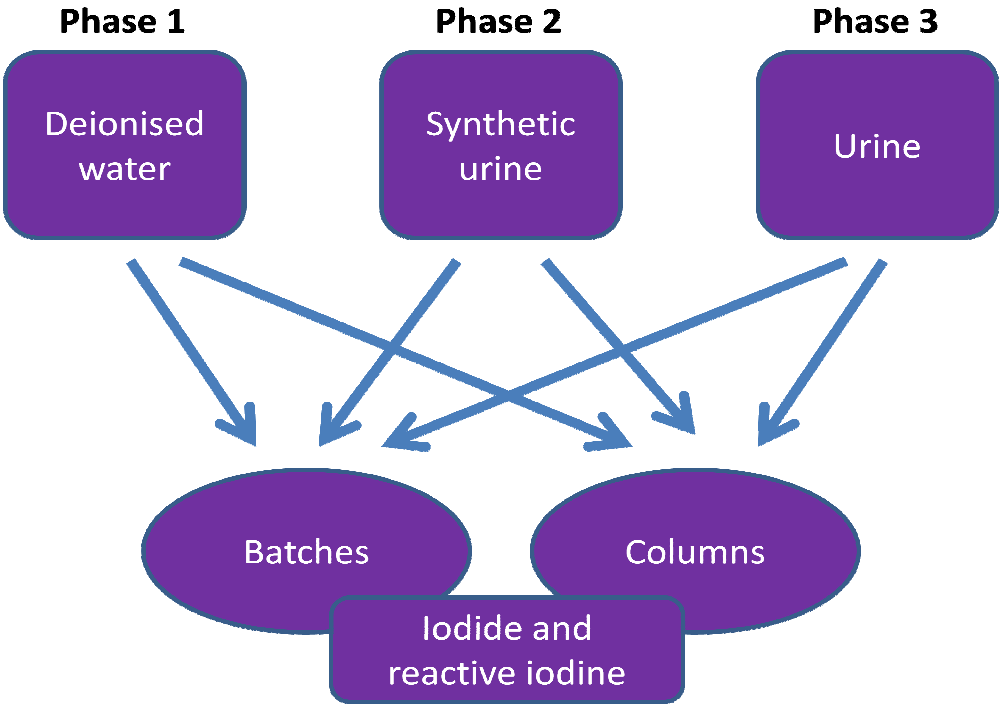


Figure 216. Three phases of experimental work in Chapter 5.

5.2 Reagents and instrumentation

5.2.1 Reagents

All reagents used in this chapter are listed along with their purities and suppliers in Table 56. A Millipore Corporation^{TM} cartridge purification system was used to produce deionised water (18 MΩ) which was used for preparation of solutions.

Table 56. Reagents, their purities and suppliers used in Chapter 5

Reagent	*Purity*	*Supplier*
Lactic acid	Technical	Lancaster Synthesis
Uric acid	Approx 99%	Sigma Aldrich
Urea	99.9%	BDH Chemicals
Glucose	General purpose	Hopkin & Williams Ltd
Chloramine T hydrate	98%	Aldrich
$KMnO_4$	Min 99%	BDH Chemicals
NaCl	Analytical reagent	Fisher
KCl	Min 99%	Fisons scientific
$CaCl_2\ 2H_2O$	98+%	Sigma Aldrich
KH_2PO_4	99%	Acros

5.2.1.1 Radioactive iodine

The half-life of ^{131}I is inconveniently short (8.0 days) for these studies. In addition, the activities needed are high (22.6 MBq of ^{131}I). Consequently, investigations were carried out with an equivalent amount of stable iodide spiked with ^{125}I (59.4 d). The mass of 22.6 MBq of ^{131}I was calculated using equation 5.2 as 4.9×10^{-9} g. Thus, during these experiments, 4.9×10^{-9} g of iodide was estimated to be excreted in 1 dm^3 of urine, and the solution was prepared by dissolving sodium iodide into deionised water. Approximately 5000 cpm cm^{-3} spikes (mass insignificant) were used.

$$m = \frac{At_{1/2}M}{\ln 2 N_A} \tag{5.2}$$

m = mass (g)
A = activity (Bq)
$t_{1/2}$ = half-life (s)
M = molecular concentration (g mol^{-1})
N_A = Avogadro's constant (6.022×10^{23} mol^{-1})

5.2.1.2 Synthetic urine

The synthetic urine [113] contained the components shown in Table 57. Due to its low solubility, hippuric acid was not added to the synthetic urine.

Table 57. Composition of synthetic urine used in Chapter 5

Compound	***Molarity (mol dm^{-3})***	***Compound***	***Concentration (mg cm^{-3})***
Lactic acid	5×10^{-4}	Cl^-	5.15
Uric acid	2×10^{-4}	PO_4^{3-}	0.5
Urea	3×10^{-4}	Na^+	4
Glucose	3×10^{-4}	K^+	0.5
		Ca^{2+}	0.5

5.2.1.3 Oxidising agents

Two oxidising agents were used; Chloramine T (CT) and potassium permanganate ($KMnO_4$). CT undergoes a two-electron change in its reactions forming a reduction product p-toluenesulfoaminide (PTS) and sodium chloride

[114]. The oxidation potential of the CT-PTS couple varies according to the pH of the medium [114]:

1.139 V at pH 0.65
0.778 V at pH 7.0
0.614 V at pH 9.7

The second oxidising agent, potassium permanganate, is a strong oxidising agent [115]. In acid solutions, the reduction can be represented by equation 5.3 [115];

$$MnO_4^- + 8H^+ + 5e \leftrightarrow Mn^{2+} + 4H_2O \qquad (5.3)$$

Nevertheless, potassium permanganate can also be used in strongly alkaline solutions in which the following reactions occur [115];

$$MnO_4^- + e \leftrightarrow MnO_4^{2-} \text{ (rapid)} \qquad (5.4)$$

$$MnO_4^{2-} + 2H_2O + 2e \leftrightarrow MnO_2 + 4OH^- \qquad (5.5)$$

In moderate alkaline solutions permanganate is reduced quantitatively to manganese dioxide [115];

$$MnO_4^- + 2H_2O + 3e \leftrightarrow MnO_2 + 4OH^- \qquad (5.6)$$

5.2.1.4 Reduction potentials for iodine reactions

The normal reduction potential of a reversible iodine system (saturated aqueous solution in the presence of solid iodine) is 0.5345 V and the reaction can be expressed as [115];

$$I_{2(solid)} + 2e^- \leftrightarrow 2I^- \quad (5.7)$$

The above reaction occurs, for example, towards the end of a titration of iodide with an oxidising agent such as potassium permanganate, when the iodide concentration becomes relatively low [115]. Near the beginning of titrations, when an excess of iodide ion is present, the tri-iodide ion is formed since iodine is readily soluble in a solution of iodide [115];

$$I_{2(aq)} + I^- \leftrightarrow I_3^- \quad (5.8)$$

The standard reduction potential is 0.5355 V and it can also be written as [115];

$$I_3^- + 2e^- \leftrightarrow 3I^- \quad (5.9)$$

Iodine and tri-iodide ion is a much weaker oxidising agent than for example potassium permanganate [115].

5.2.1.5 Urine

In an average Western diet urinary pH is between 5.6 and 6.8 [116]. The volume and content of the urine depends on what has been eaten, drunk and produced by metabolism, and hence varies enormously under different circumstances [117]. Four examples of urine composition for different diets are shown in Table 58 [118].

Table 58. Urine composition of 10 healthy male consuming a self-selected diet (SD), a western-type diet (WD), normal mixed diet (ND) and an ovo-lacto-vegetarian diet (VD) in 24 h urine [118]

	Diet SD	***Diet WD***	***Diet ND***	***Diet VD***
Urine volume (dm^3)	1.29 ± 0.15	1.48 ± 0.12	2.30 ± 0.12	2.45 ± 0.24
pH	6.01 ± 0.15	5.95 ± 0.11	6.51 ± 0.07	6.80 ± 0.07
Na (mmol)	159 ± 24	176 ± 13	146 ± 4	102 ± 15
K (mmol)	84 ± 7	60 ± 3	77 ± 5	110 ± 6
Ca (mmol)	4.68 ± 0.76	4.48 ± 0.39	3.09 ± 0.44	2.46 ± 0.42
Mg (mmol)	4.60 ± 0.44	4.63 ± 0.21	5.09 ± 0.35	5.40 ± 0.52
Ammonium (mmol)	30.8 ± 3.9	38.7 ± 1.6	25.6 ± 2.0	18.7 ± 1.9
Chloride (mmol)	164 ± 21	169 ± 12	139 ± 5	106 ± 14
Phosphate (mmol)	32.6 ± 2.6	35.4 ± 1.7	29.4 ± 1.1	25.2 ± 2.0
Sulphate (mmol)	18.5 ± 2.9	22.5 ± 1.0	18.1 ± 0.6	16.1 ± 1.2
Creatinine (mmol)	10.09 ± 1.38	16.88 ± 0.62	15.32 ± 0.41	13.78 ± 1.00
Uric acid (mmol)	3.59 ± 0.30	3.91 ± 0.21	2.93 ± 0.10	2.58 ± 0.16
Oxalic acid (mmol)	0.317 ± 0.021	0.281 ± 0.020	0.287 ± 0.018	0.376 ± 0.039
Citric acid (mmol)	2.863 ± 0.315	2.331 ± 0.189	3.226 ± 0.247	4.233 ± 0.356

The urine samples used in this chapter were collected from five 25-65 year old adults (200 cm^3 to 1000 cm^3) and refrigerated prior to the experiments.

5.2.2 Instrumentation

The pH was measured at room temperature using Jenway or Orion pH meters which were calibrated daily using a buffered pH solution (4, 7, and 10). ^{125}I activities were measured using a Packard Cobra II Auto-Gamma gamma counter and 3 min counting time. The measurement window (channels 15-75) was determined by using a ^{125}I standard.

5.3 *Extraction of iodide from deionised water by ST and CE sludges*

The experimental studies were started in simplified medium by preparing the ^{125}I spiked iodide solution (4.9 x 10^{-9} g dm^{-3}) in deionised water (DI). The experiments were carried out first in batches by placing increasing amounts of ST and CE sludge in contact with 20 cm^3 of iodide solution. All batch experiments were performed in triplicate and results are shown as averages with standard deviation. In addition, an iodide extraction isotherm was prepared using the ST sludge. The experiments were continued in column studies by passing the iodide solution once through the columns and then re-circulating the solution. Experiments on the effect of the oxidising agent Chloramine T on reactive iodine extraction using a column were investigated.

5.3.1 Extraction of iodide from deionised water by ST and CE sludge batches

Batch experiments were carried out to establish the minimum amount of ST and CE sludges needed to extract 22.6 MBq of iodide, which is the amount of iodide predicted to be in a litre of urine excreted by an iodine-treated patient on the first day after treatment. The equivalent amount of iodide was prepared as sodium iodide solution (4.9 x 10^{-9} g dm^{-3}) spiked with ^{125}I (~5000 cpm cm^{-3}). Increasing amounts of ST and CE sludges (0.2, 0.7, 1.5, and 3 g) were placed in contact with 20 cm^3 of the spiked iodine solution, stirred for 24 h, filtered through 0.45 µm filter and the remaining amount of iodide in solution was measured using a gamma spectrometer.

Figures 217 and 218 show the extraction results as percentage of iodide extracted by increasing amounts of ST and CE sludges. As the results show, the experiments using CE sludge exhibit better reproducibility. CE sludge also shows significantly higher extraction by 3 g solid (90-95%) compared to ST sludge (15-20%). The original data are shown in Appendix 5.

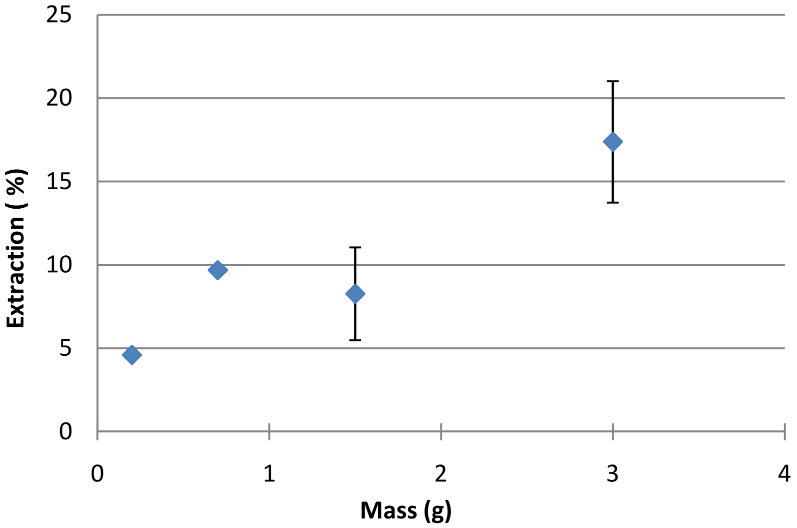


Figure 217. Extraction of iodide from deionised water by ST sludge using 24 h contact time.

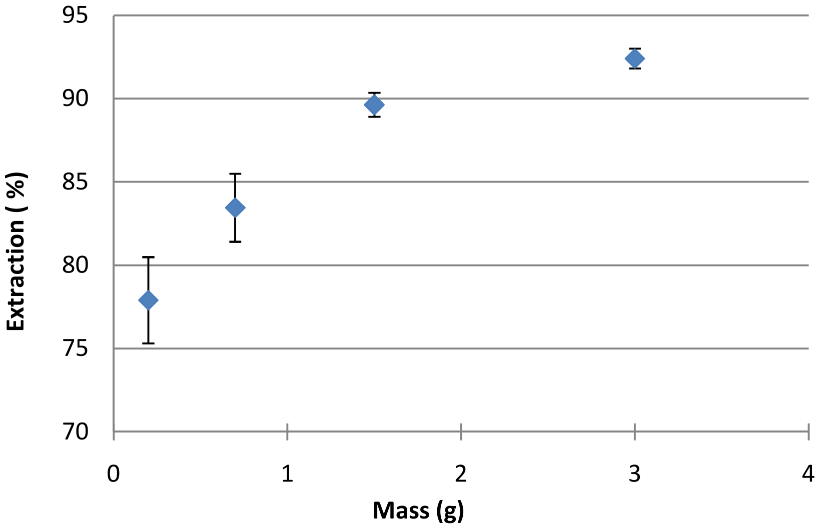


Figure 218. Extraction of iodide from deionised water by CE sludge using 24 h contact time.

The maximum capacity of the ST sludge to immobilise iodide was determined by creating an isotherm as described in Chapter 3. 31 cm^3 of ^{125}I spiked NaI solution were placed in contact with 2 grams of ST sludge and the samples were left to equilibrate for 1 week. Solutions were filtered through a 0.45 µm filter and ^{125}I activity remaining in solution was counted by gamma spectrometry. The initial iodide concentrations were increased until a saturation level for the sludge was found.

The iodide isotherm for the ST sludge is plotted in Figure 219. According to the isotherm, the maximum amount of iodide extracted is 3.86E-07 mol g^{-1} and thus 1 g of ST sludge can extract 48.2 µg of iodide, which corresponds to 222.2 GBq of ^{131}I.

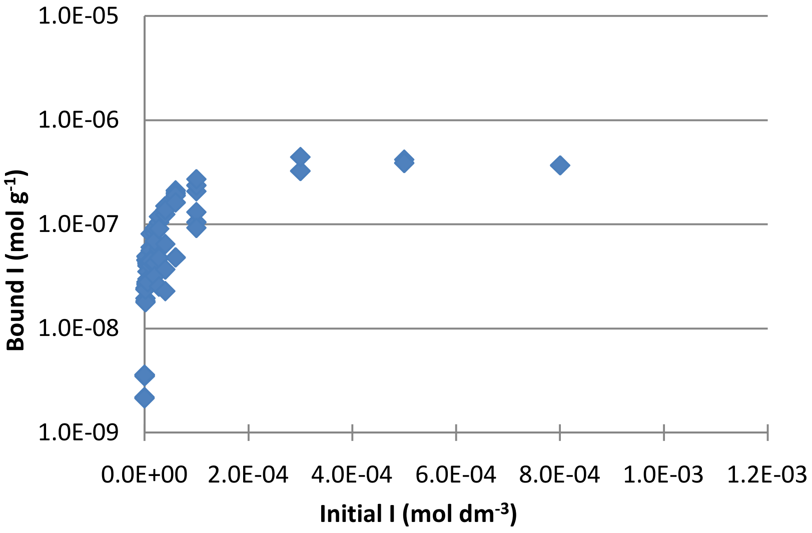


Figure 219. The iodide isotherm using increasing iodide concentrations in 31 cm^3 DI solutions in contact with 2 g of ST sludge using 1 week contact time.

5.3.2 Extraction of iodide from deionised water by ST columns

Several column experiments were carried out with deionised water. The ST columns (20 g – 75 g) were packed into Ø 2.6 cm glass columns and washed with deionised water for over 12 hours to remove soluble matter such as fulvic acid. The experiments were started by determining the porosities of the columns as described in Chapter 3 using tritiated water. An example graph on determination of porosity of a 20 g column is shown in Figure 220. The calculated porosities varied between 47.3 – 59.5%. After the measurements of the porosities, the columns were washed using deionised water to remove any trace of tritium. The iodide solutions (4.9 x 10^{-9} g dm^{-3} sodium iodide solution spiked with ^{125}I) were introduced into the columns and they were further washed using deionised water. A flow rate of 0.2 $cm^3\ min^{-1}$ was maintained throughout the experiments.

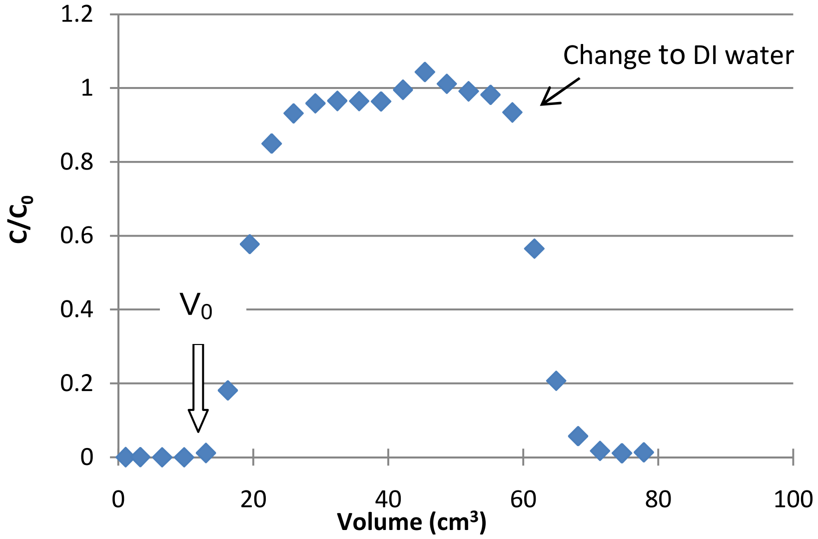


Figure 220. The C/C$_0$ results of ^{3}H plotted as function of solution pumped through the 20 g ST column. C is the specific activity of analyte coming through the column and C$_0$ is the specific activity entering the column. V$_0$ indicates the dead volume of the column.

The results from a 20 g ST column with introduction of 100 cm^3 of iodide solutions are shown in Figure 221. It can be concluded that ~20% of the iodide has been extracted by the ST sludge. The steep increase in extraction percentage after 100 cm^3 of solution has been introduced through the column shows the point when the solution was changed from iodide to deionised water. This rapid increase indicates strong extraction of iodide which cannot be released by deionised water.

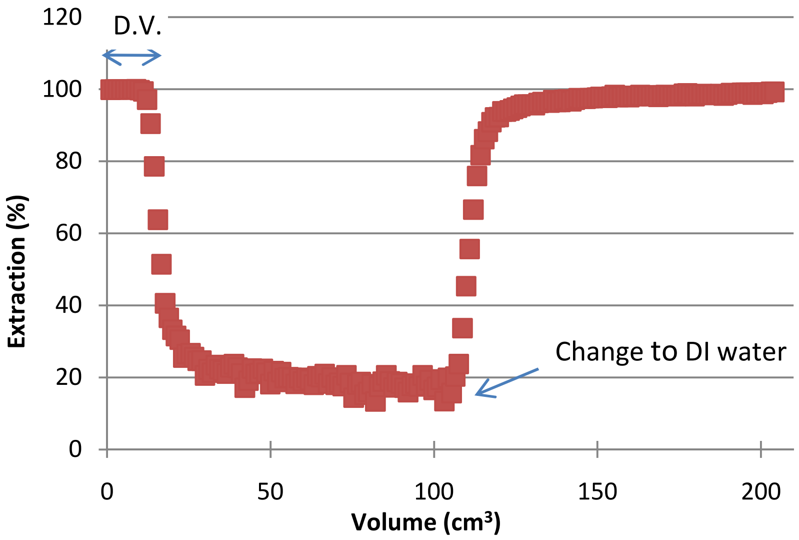


Figure 221. The extraction results for iodide from 100 cm^3 iodide solution in DI water (spiked with ^{125}I) by 20 g ST column. D.V. region is the dead volume of the column.

Another ST column was prepared similarly but with more than three times the amount of ST sludge (75 g). However, the results reveal (Figure 222) that the extraction percentage (20%) was not improved even when the amount of solid was increased from 20 g to 75 g. These results are in agreement with studies of Warwick *et al*. who observed that humic and fulvic materials can be labelled with iodine but the iodination process is slow without an oxidising agent [108]. Therefore, it can be concluded that since no significant difference on extraction percentage was observed when the amount of ST sludge was increased from 20 g to 75 g, the extraction of iodide by ST sludge is inefficient and a slow process.

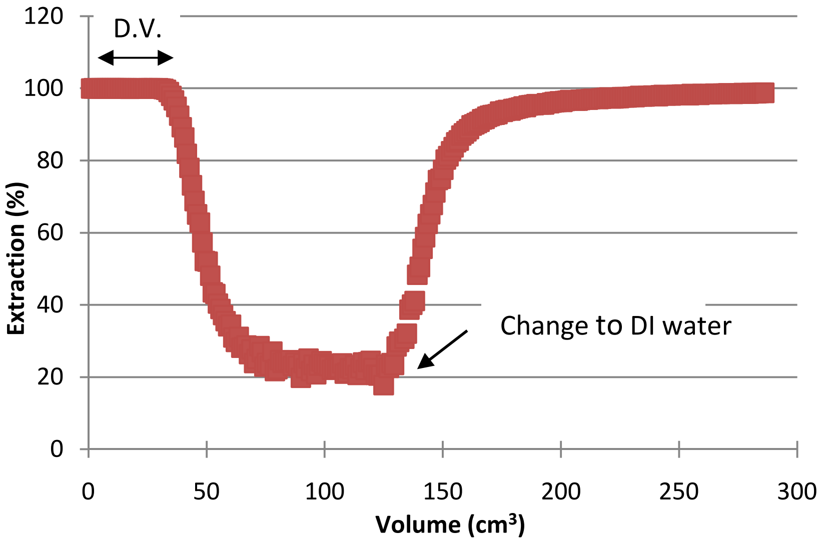


Figure 222. The extraction results for iodide from 100 cm^3 iodide solution in DI water (spiked with ^{125}I) by 75 g ST column. D.V. region is the dead volume of the column.

Following the previous experiments, the effect of contact time was studied by re-circulating 150 cm^3 of iodide solution through a 50 g ST column. The column was first washed with DI water for 24 h. When the iodide solution was re-circulated through the column with constant flow rate (0.2 cm^3 min^{-1}), samples were taken from the reservoir at different time intervals until a plateau in extraction percentage was reached after which the iodide solution in the reservoir was changed to deionised water.

The results for the 50 g ST column with re-circulation of the iodine containing solution are plotted in Figure 223. The results show that maximum extraction (80%) is reached after 7 days of re-circulation. On the seventh day the solution had been recycled 12 times through the column. On the 9th day of the experiment the solution in the reservoir was changed to DI water and re-circulation was continued for further 5 days. These results clearly exhibit the importance of contact time on the extraction of iodide from urine by ST sludge. The results also show that the extracted iodide was quickly released when washed with deionised water; after 5 days of re-circulation of deionised water all of the extracted iodide was released from the column. Therefore the uptake was reversible and this material can be re-generated. The capacity for regeneration increases the value of the ST sludge since it can be reused.

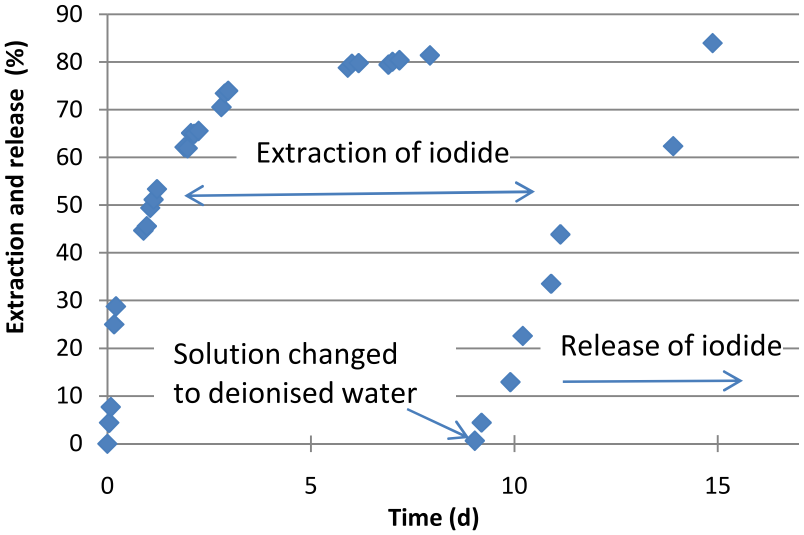


Figure 223. The extraction percentage results of iodide plotted as function of time in the re-circulated solutions through the 50 g ST column.

5.3.3 Column experiments in deionised water with oxidising agent Chloramine T

The iodination process of humic material is much faster when an oxidising agent is used [108]. Therefore, the final experiments using deionised water were carried out by adding oxidising agent Chloramine T into the iodide solution. 100 cm^3 of ^{125}I spiked iodide solutions (4.9 x 10^{-9} g dm^{-3} sodium iodide) with and without CT were introduced to 30 g ST columns. The columns were prewashed as in previous section. Figure 224 shows the extracted percentage of iodine species with and without CT, plotted against the volume of DI water. The results show that without oxidising agent CT the extraction of iodide is ~20% while with CT the extraction is ~100%. Therefore it can be concluded that the addition of CT significantly increases the extraction of iodine species from deionised water.

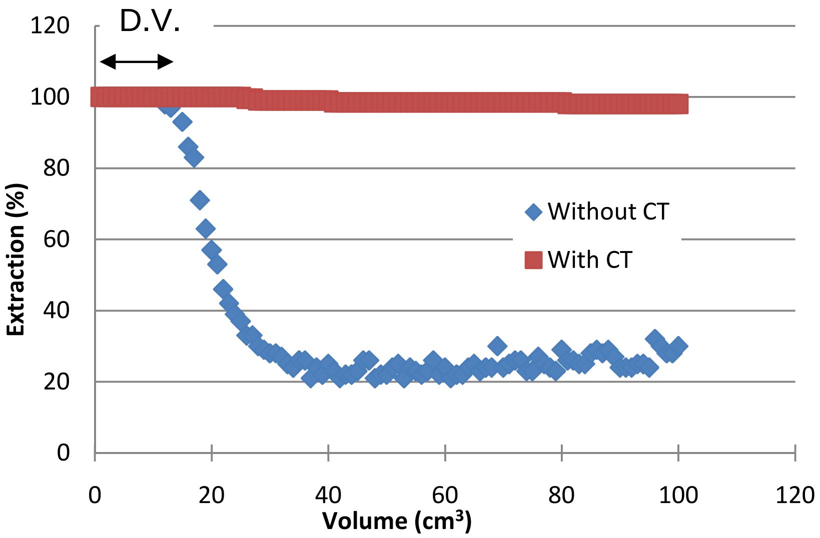


Figure 224. The extraction results for iodine species from 100 cm^3 iodide solution in DI water (spiked with ^{125}I) with and without Chloramine T (CT) by 30 g ST column. D.V. region is the dead volume of the column.

5.4 Extraction of iodine species from synthetic urine by ST and CE sludge

The experiments were continued in synthetic urine which is a more complicated and a more realistic medium for this application. Similar batch and column experiments were carried out as those with deionised water, and the effect of addition of oxidising agent was also determined.

5.4.1 Extraction of iodide from synthetic urine by ST and CE sludges

Batch experiments were used to obtain the amount of ST and CE sludges needed to extract 22.6 MBq of iodide (4.9 x 10^{-9} g dm^{-3}) from synthetic urine.

Increasing amounts of ST and CE sludges (0.2, 0.7, 1.5 and 3 g) were placed in contact with 20 cm^3 of the spiked iodine solution, stirred for 24 h, filtered through 0.45 µm filter and the concentrations of radioactive iodide remaining in the solutions were measured using a gamma spectrometer.

The results in Figures 225 and 226 show almost three times as efficient extraction of iodide from synthetic urine by 3 g of CE sludge (~85%) compared to ST sludge (25-30%). These results are similar to the extraction results from deionised water in which 90-95% of iodide was extracted by 3 g of CE sludge and 15-20% by 3 g of ST sludge. The original data are shown in Appendix 5.

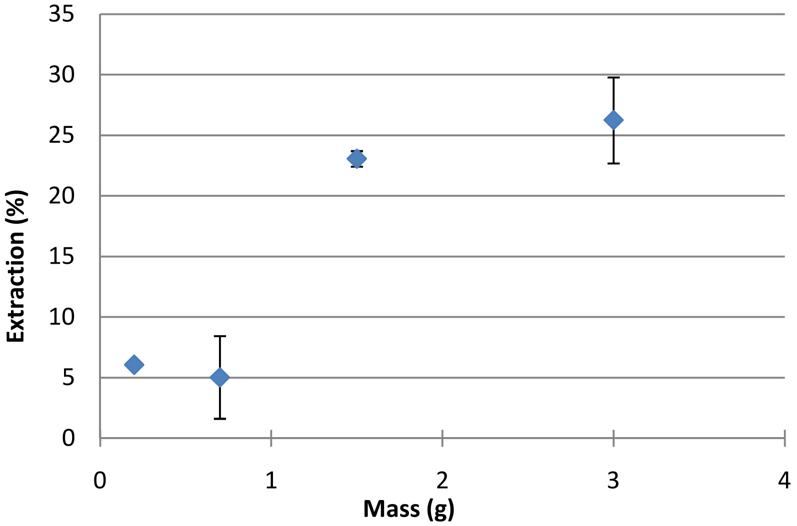


Figure 225. Extraction of iodide from synthetic urine by ST sludge using 24 h contact time.

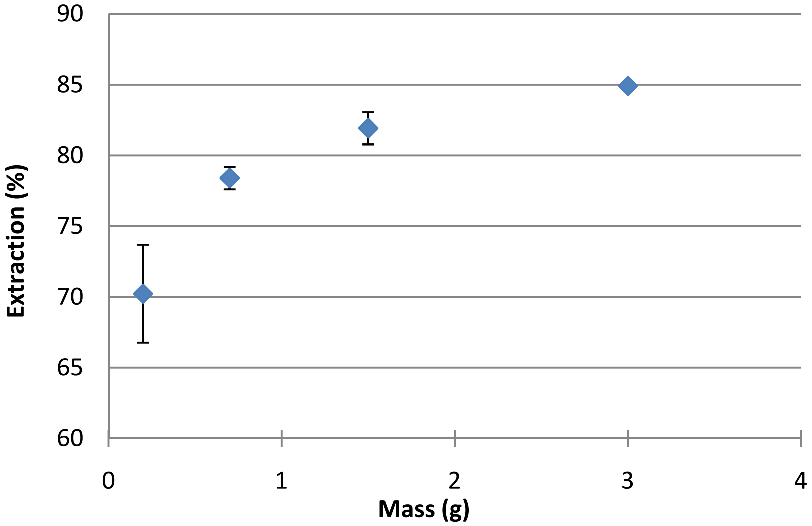


Figure 226. Extraction of iodide from synthetic urine by CE sludge using 24 h contact time.

5.4.2 Extraction of reactive iodine from synthetic urine by ST column

Extractions of reactive iodine from synthetic urine with oxidising agent Chloramine T were determined in a 30 g ST column. The column was pre-washed with deionised water prior to introduction of 100 cm^3 of synthetic urine spiked with stable iodide, ^{125}I, and CT.

Figure 227 shows the extracted percentage of reactive iodine plotted against the volume of synthetic urine pumped through the 30 g ST column. The results show efficient extraction since over 90% of iodine was extracted from the synthetic urine when iodide was oxidised to reactive iodine.

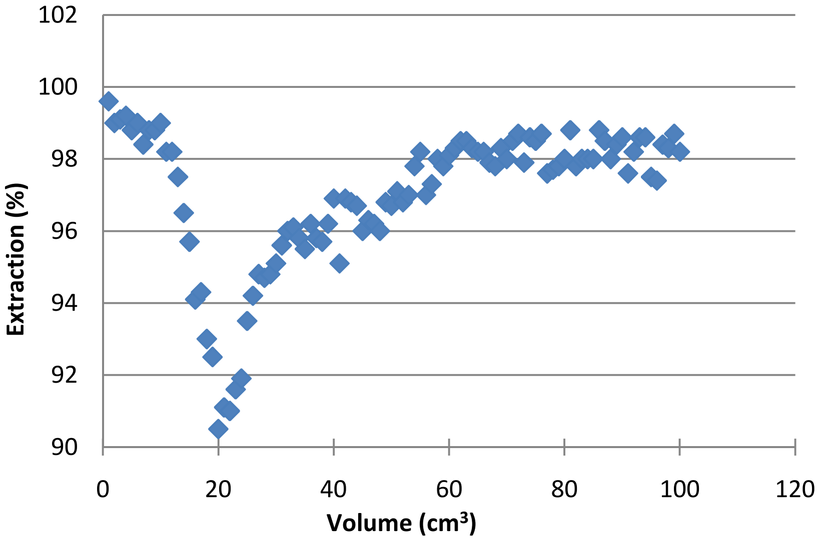


Figure 227. The extraction results for iodine species from 100 cm^3 iodide solution in synthetic urine (spiked with ^{125}I) with Chloroamine T by 30 g ST column.

5.5 Extraction of iodine species from urine by ST and CE sludges

The final experiments were carried out in real urine with and without oxidising agent. The urine samples were given by five 25-65 year old donors (A, B, C, D, and E). 200 cm^3 of urine was spiked with ^{125}I and sodium iodide to obtain minimum iodide concentration of 4.98×10^{-9} g dm^{-3} (equivalent to 22.6 MBq of ^{131}I). However, the added iodine concentration is negligible compared to iodine concentration naturally present in urine (100 to 200×10^{-6} g dm^{-3} [84]). The experiments were carried out in batches and columns with ST and CE sludges. Finally, the effect of a stronger oxidising agent than Chloramine T, potassium permanganate, was determined in batch studies.

5.5.1 Extraction of iodide from urine by ST and CE sludges

As in previous batch studies, 20 cm^3 of iodide spiked urine A was placed in contact with 0.2 g, 0.5 g and 1.0 g of ST and CE sludges. ^{125}I and sodium iodide were added to the urine to obtain a minimum amount of 4.9×10^{-9} g dm^{-3} of iodine. Samples were shaken for 1 h and 24 h and then filtered through 0.45 µm filter. The pH of the urine in 1h samples were 5.4 and in 24 h samples 5.9.

The extraction results of iodide from urine are shown in Figures 228 to 231. The results show that 1 g of ST sludge extracted ~30% of iodide using 1 h contact time and 30-40% using 24 h contact time. Similarly 1 g of CE sludge extracted 20-30% of iodide using 1 h contact time and ~35% using 24 h contact time. The results suggest that the extraction of iodide occurred within 1 h and an increase in contact time did not enhance the extraction process. In addition, the results show similar extractions of iodide for both of the sludges. The original data are shown in Appendix 5.

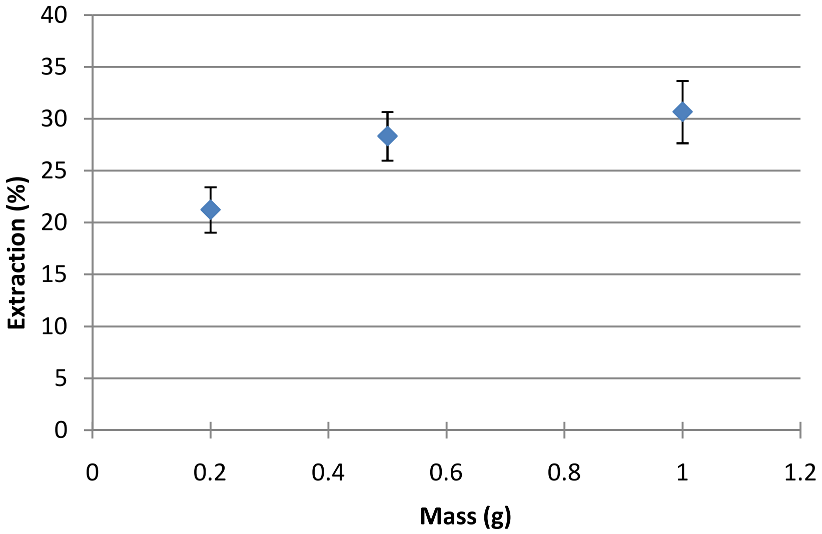


Figure 228. Extraction of iodide from urine A by increasing amount of ST sludge using 1 h contact time.

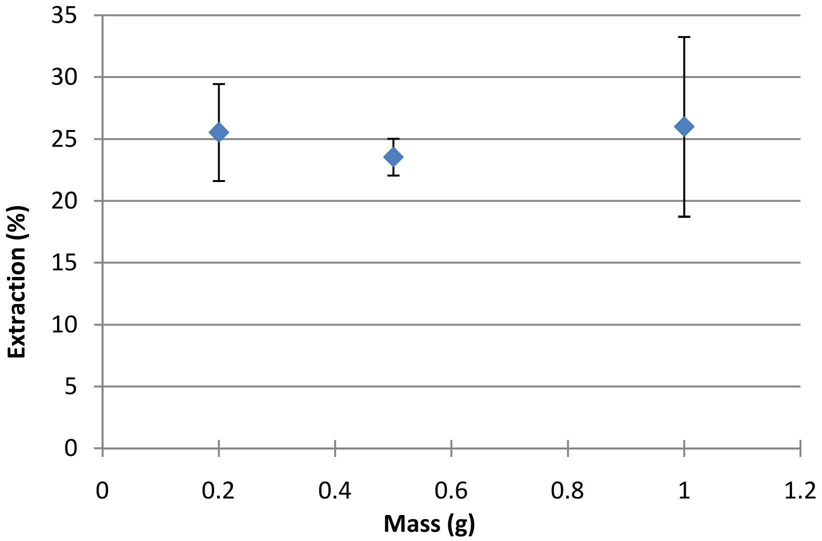


Figure 229. Extraction of iodide from urine A by increasing amount of CE sludge using 1 h contact time.

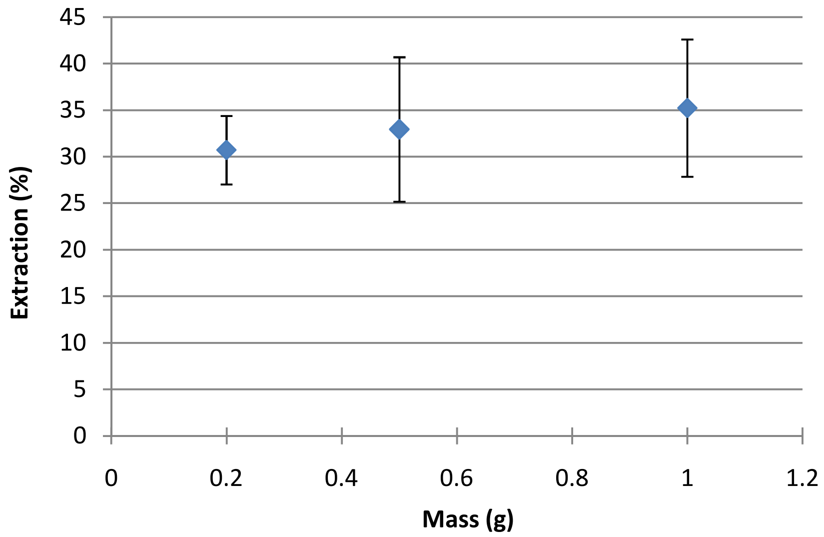


Figure 230. Extraction of iodide from urine A by increasing amount of ST sludge using 24 h contact time.

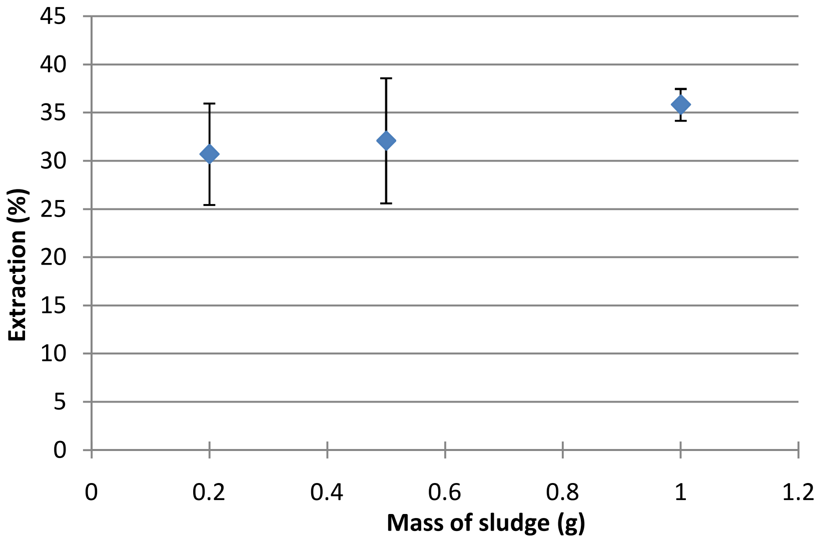


Figure 231. Extraction of iodide from urine A by increasing amount of CE sludge using 24 h contact time.

5.5.2 Extraction of reactive iodine from urine using ST sludge in the presence of an oxidising agent

The effect of oxidising agent CT was determined in urine samples from 4 different donors (A-D). Increasing amounts of ST and CE sludges (0.2, 0.5 and 1 g) were placed in contact with 20 cm^3 of the spiked iodine solution into which CT had been added (1 g into 200 cm^3 of urine). The mixtures were stirred for 1 h after which the samples were filtered through a 0.45 µm filter and the concentrations of iodine species remaining in solution were measured by gamma spectrometry.

The results were non-conclusive; in Urine D the addition of CT increased the extraction percentage (Figure 232), in Urine B the addition of CT decreased the extraction percentage (Figure 233), and in Urine A there was no significant difference in extraction percentages with and without CT (Figure 234). In addition, the extraction was negligible in Urine C with and without CT.

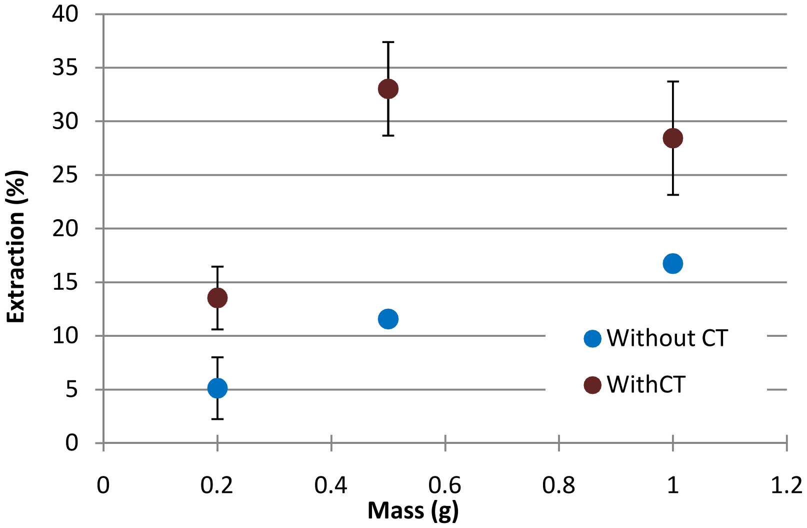


Figure 232. Extraction of iodine species from urine D by increasing amount of ST sludge using 1 h contact time.

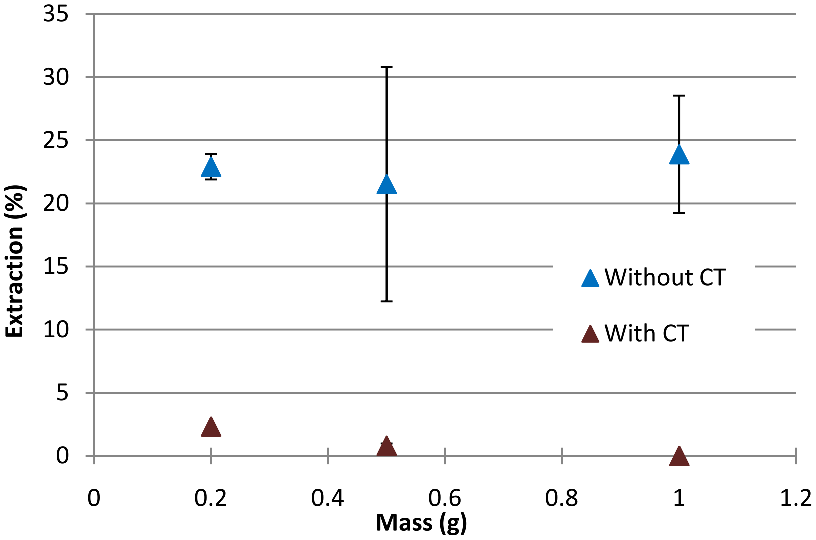


Figure 233. Extraction of iodine species from urine B by increasing amount of ST sludge using 1 h contact time.

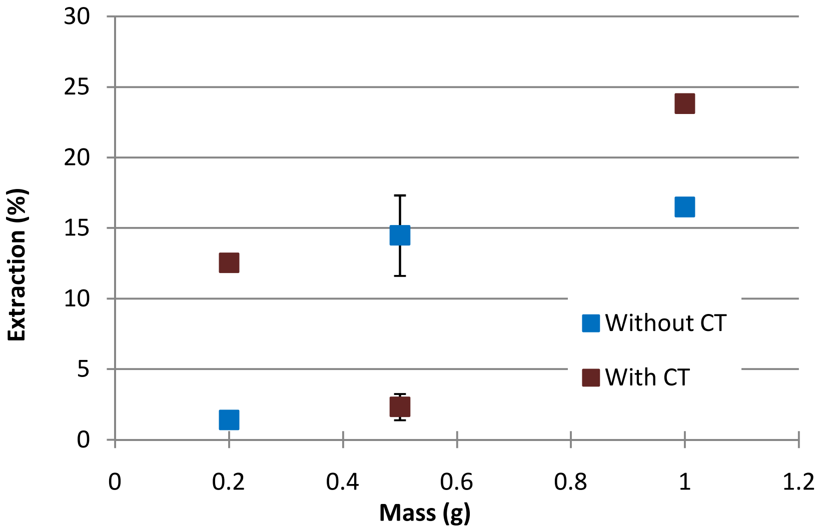


Figure 234. Extraction of iodine species from urine A by increasing amount of ST sludge using 1 h contact time.

Table 59 summarises the extraction results for 1 g of ST sludge. The results show clearly that in some cases the addition of CT has increased the extraction of iodine species from 17% to 28%, but in some cases decreased from 24% to negligible. The most likely explanation for the differences in the extraction results is the complexity of the urine composition and the difference between the urine samples. Since the volume and content of the urine depend on what has been eaten, drunk and produced by metabolism, the composition of urine varies enormously [117]. In addition, the metabolic end products, such as urea or uric acid [117], can consume the oxidative power of CT or reduce oxidised reactive iodine back to iodide. The results also show that the pH of the urine samples was controlled by the composition of urine.

Table 59. The initial and final pH and average extraction percentages of iodine species from urine samples from 4 donors in contact with 1 g of ST sludge with and without CT using 1 h contact time

ID	*Initial pH*	*Final pH with CT*	*Extr. % with CT*	*Final pH without CT*	*Extr. % without CT*
A, female	6.1	6.0	24	5.8	17
B, female	5.7	5.6	negligible	5.3	24
C, female	6.7	6.6	5	6.5	negligible
D, male	7.8	6.3	28	7.0	17

5.5.3 Extraction of iodine species from urine by ST columns

Two column experiments with and without CT were carried out by packing 150 g of ST sludge into 2.6 cm Ø glass columns. The columns were washed with DI water prior to porosity experiments, as explained in Chapter 3, and introduction of urine A spiked with ^{125}I and sodium iodide (4.9×10^{-9} g dm^{-3}). The flow rates were 0.2 cm^3 min^{-1}. 1 g of CT was added to 1000 cm^3 of urine A when experiments were carried out with oxidising agent. The first column (with CT) had porosity of 53.6% and the second column (without CT) porosity of 53.1%. The pH of the urine were 5.4 (with CT) and 4.0 (without CT).

The results of the two 150 g columns are presented in Figure 235. The results show that addition of CT has not had a significant effect on the extraction since only 20% of reactive iodine was extracted by the ST column. The fluctuation of the line during the CT experiments after 500 cm^3 is due to partial blocking of the column.

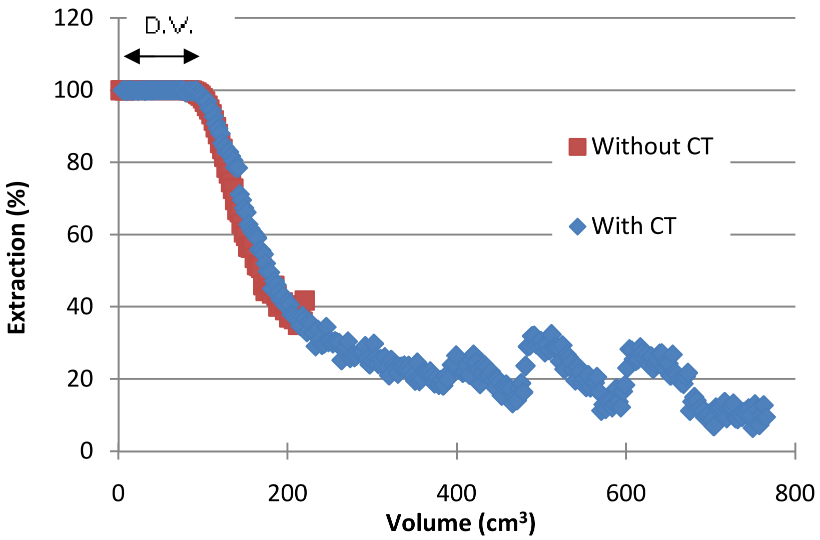


Figure 235. Extraction of iodine species from urine A by 150 g ST sludge with and without CT. D.V. region is the dead volume of the column.

Column experiments with and without CT in urine D were also carried out using 30 g of ST sludge. The results of the two columns are presented in Figure 236 and it can be seen that addition of CT has increased the extraction percentage from nearly zero to about 20%. Therefore, it can be concluded that, as in batch experiments, the composition of the urine has played an important role in the extraction processes. Also amount of reducing agents, such as urea and uric acid, in the urine inhibits the oxidising power of the CT.

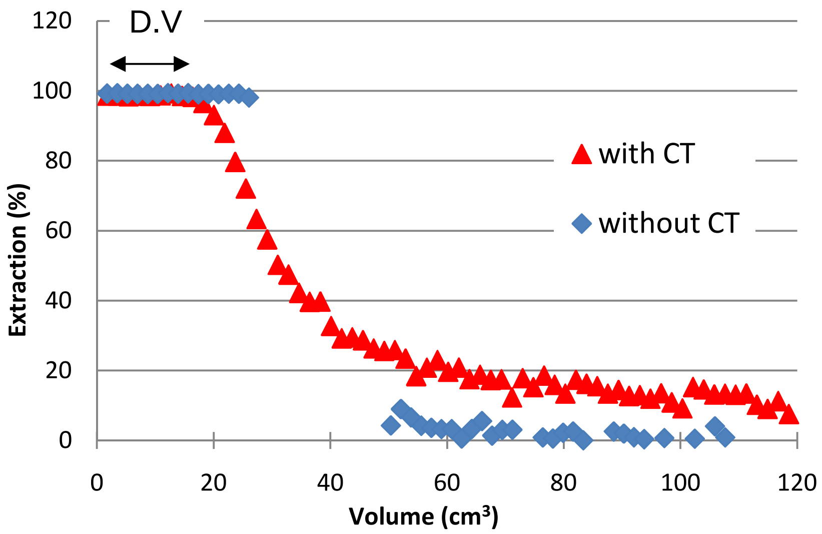


Figure 236. Extraction of iodine species from urine D by 30 g ST sludge with and without CT. D.V. region is the dead volume of the column.

5.5.4 Extraction of iodine species from urine by CE columns

Column experiments with and without CT using CE sludge were carried out as mentioned in previous section by packing 150 g of CE sludge into 2.6 cm Ø glass columns. The columns were washed with DI water prior to porosity experiments after which the porosity experiments were carried out. The flow rates were 0.2 cm^3 min^{-1}. Urine A was spiked with ^{125}I and sodium iodide (4.9 x 10^{-9} g dm^{-3}). 1 g of CT was added to 1000 cm^3 of urine A when experiments were carried out with oxidising agent. The first column had porosity of 33.3% (with CT) and the second column porosity of 42.2% (without CT). The pH of the urine was 6.3 (with CT) and 7.2 (without CT).

The results of the two 150 g CE columns are presented in Figure 237 and it can be seen that addition of CT has increased the extraction percentage from ~30% to ~50%. Therefore, the oxidation of iodine has significantly improved the extraction percentage.

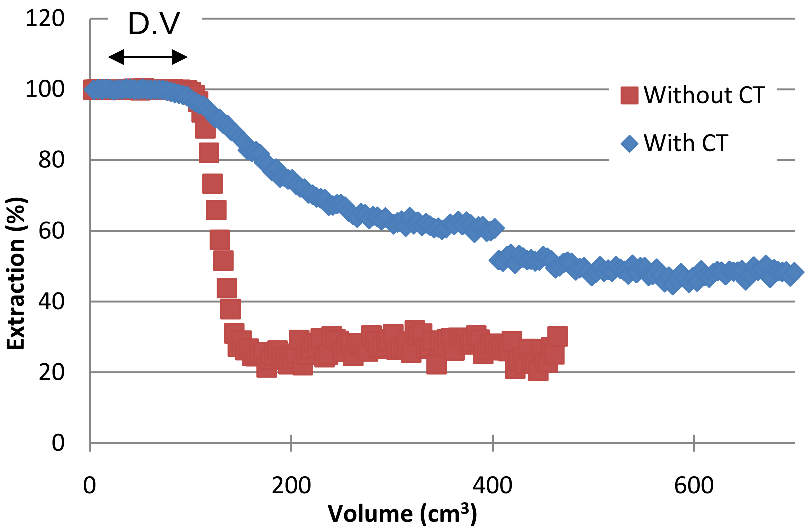


Figure 237. Extraction of iodine species from urine A by 150 g CE sludge with and without CT. D.V. region is the dead volume of the column.

5.5.5 Extraction of iodine species from urine by ST and CE sludges using a stronger oxidising agent

Urine contains reducing compounds, such as urea and uric acid, which may overpower the oxidising capacity of Chloramine T and cause only partial oxidation. Thus the effect of an even stronger oxidising agent, potassium permanganate, was investigated. Increasing amounts of ST and CE sludges (0.2, 0.7, 1.5 and 3 g) were placed in contact with 20 cm^3 of the spiked urine. The mixtures were stirred for 24 h after which the samples were filtered through 0.45 µm filter and the concentrations of iodine species remaining in the solutions were measured using gamma spectrometry.

The results of iodine species extraction when potassium permanganate was used as an oxidiser are shown in Figures 238 and 239. The results show that 3 g of ST sludge can extract 20-25% of iodine from 20 cm^3 urine solution whereas the same result for CE sludge is 40-45%. The original data are shown in Appendix 5.

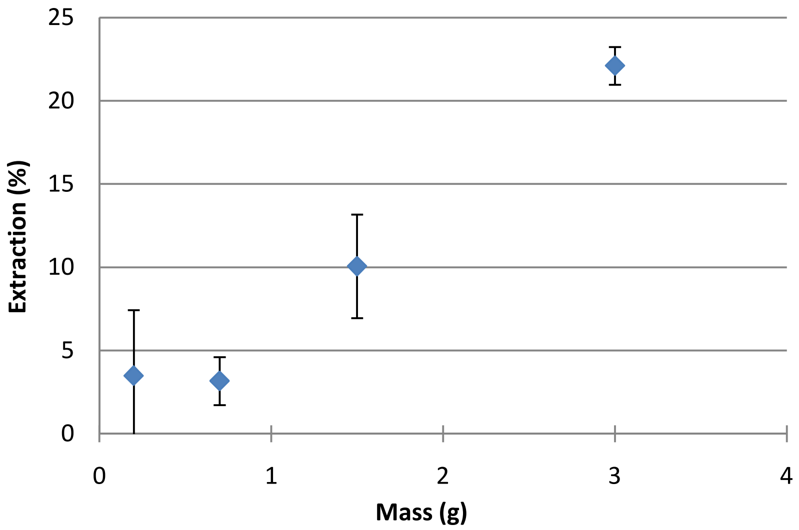


Figure 238. Extraction of iodine species from urine by ST sludge using potassium permanganate as an oxidising agent and 24 hours contact time.

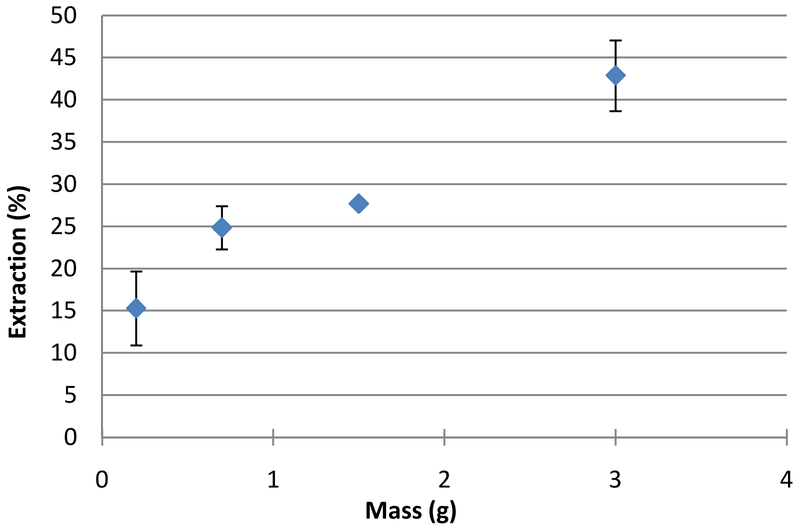


Figure 239. Extraction of iodine species from urine by CE sludge using potassium permanganate as an oxidising agent and 24 hours contact time.

5.6 Summary

5.6.1 Extraction of iodine species from deionised water, synthetic urine and urine by ST and CE sludge batches

Table 60 shows the masses of ST and CE sludges with their corresponding extraction percentages for iodine species from 20 cm^3 of deionised water, synthetic urine and urine containing at least 4.9 x 10^{-9} g dm^{-3} iodide. The results show that 3 g of ST and CE sludge exhibited similar extraction for iodide from deionised water (15-20% and 90-95%, respectively) and from synthetic urine (25-30% and ~85%, respectively) when the suspensions were mixed for 24 hours. However, the corresponding results in urine A showed that 1 g of ST extracted 30-40% of iodide. This result is surprising since the matrix of urine is much more complicated than that of deionised water or synthetic urine and still extraction percentages are similar. In the 1 g CE sludge samples with 24 hours contact time, the extraction percentage for iodide from urine A was ~35%.

The presence and absence of Chloramine T did not exhibit conclusive extraction results from urines A-D. In some cases, the extraction was increased in the presence of the oxidiser and decreased in others. The addition of potassium permanganate into urine A had only little effect on the extraction percentage since 1 g of ST sludge could extract 30-40% of iodine species from untreated urine A whereas 3 g of ST sludge could extract 20-25% of iodine species from potassium permanganate treated urine A. In addition, ~35% of iodine species were extracted from untreated urine A by 1 g of CE sludge where as 3 g of CE sludge could extract 40-45% of iodine species from potassium permanganate treated urine A.

Table 60. Summary of the extraction percentages of iodine species from 20 cm^3 deionised, synthetic urine and urine samples using 1 h and 24 h contact times

Sludge	***Solution***	***Contact time (h)***	***Mass (g)***	***Extraction (%)***
ST	DI	24	3	15-20
CE	DI	24	3	90-95
ST	Synthetic urine	24	3	25-30
CE	Synthetic urine	24	3	~85
ST	Urine A	1	1	~30
CE	Urine A	1	1	20-30
ST	Urine A	24	1	30-40
CE	Urine A	24	1	~35
ST	Urine A-C with CT	1	1	Negligible to 28.4
ST	Urine A-C	1	1	Negligible to 23.9
ST	Urine A with $KMnO_4$	24	3	20-25
CE	Urine A with $KMnO_4$	24	3	40-45

5.6.2 Extraction of iodine species from deionised water, synthetic urine and urine by ST and CE columns

The column experiments showed 20% extraction of iodide from deionised water by ST sludge without oxidising agent Chloramine T. The maximum extraction percentage was 20% even when the amount of sludge was increased from 20 g to 75 g. These results were in a good agreement with studies of Warwick *et al*. who observed radiolabelling of humic substances by iodine to be a slow process [108]. The importance of contact time was observed in the column study in which the iodide solution was re-circulated through the 50 g ST column. The results showed that 80% extraction was reached within 7 days. However, 7 days treatment time is almost as long as the half-life of ^{131}I (8.0

days), and therefore re-circulation of the solution through a column is not preferable solution to carry out the extraction of iodine species. The addition of oxidising agent Chloramine T had a positive effect on the extraction of reactive iodine since it increased the extraction in deionised water from 20% to 100% by the ST column. Similar extraction behaviour (>90%) was also observed in synthetic urine in the presence of the oxidiser. In addition, ST sludge can be re-generated which enhances its usability and therefore its commercial value.

When the extraction experiments were carried out in urine, the results revealed that in one case the addition of oxidising agent Chloramine T did not have significant effect on the extraction of iodine species by ST sludge whereas in other case it increased the extraction percentage from nearly zero to about 20%. The effect of oxidiser was clearer in the CE columns in which the extraction percentage was increased from 30% to 50% by addition of CT. There are several aspects that can influence the extraction of iodine species in the absence and presence of Chloramine T;

i) Loss of oxidising power of Chloramine T i.e. aging of the oxidising agent. However, the loss of oxidising power of CT is an unlike reason since all the experiments were carried out with recently purchased Chloramine T.

ii) Presence of reducing agents, such as urea or uric acid, in urine. The reducing agents can exhaust the oxidising power of the oxidising agent or reduce the oxidised iodine species. This hypothesis could be tested by addition of increasing amount of CT in contact with constant amount of ST/CE sludge and urine. As the amount of CT increases, the extraction percentage should increase until a plateau is reached. Similar studies in deionised water could be used as a reference. If the extraction maximums reach the same level, it could be concluded that the reducing agents in the urine play a significant role in the extraction process and their effect can be overcome by addition of higher amounts of oxidiser.

iii) Presence of significant amount of chlorine which can be oxidised instead of iodine. Chlorine is a major component of urine [117] and is also a halogen and therefore they can behave similarly. This hypothesis could be tested by addition of increasing amount of NaCl in contact with constant amount of ST/CE sludges and Chloramine T. If increasing amount of NaCl decreases the extraction percentage, it could be concluded that chlorine has a significant effect on the extraction process. Presence of chlorine can also be a reason for low extraction without oxidiser because it is anion and competes for same extraction sites as iodide. This hypothesis could be tested as mentioned above but without the presence of Chloramine T. Also naturally present iodine in urine (100-200 µg dm^{-3}) occupies extraction sites.

iv) Reducing power of dissolved organic matter. Studies in Chapter 2 showed solubility of both ST and CE sludges and therefore, dissolved organic matter can potentially act as a reducing agent.

v) Iodine interacts with some component in the urine and remains in the solution. Iodine is also masked by the component and cannot be oxidised.

5.7 Conclusions

In general, CE sludge exhibited better extraction performance than ST sludge throughout the investigations on extraction of iodine species from deionised water, synthetic urine and urine. The ST column experiments showed that even addition of oxidising agent did not increase the extraction percentage from 20%. However, oxidation of iodide to reactive iodine increased the extraction percentage from 30% to 50% by CE sludge. When the results from the column studies in urine are interpreted in the light of the previous summary, it can be said that it is hard or even impossible to make final conclusions without further studies. Nevertheless, it can be stated that the composition of the urine may have a significant effect on the extraction of iodine species due to the presence of reducing agents (urea and uric acid) and competing anions (chlorine and naturally present iodine). However, batch studies using a stronger oxidising agent (potassium permanganate) than CT did not significantly increase the extraction percentage suggesting that presence of reducing agents is not of a major concern. The solubility of the sludge can also play a role in the extraction since dissolved organic matter can reduce oxidised iodine to iodide and therefore decrease the extraction. In addition, dissolved organic matter can extract iodine species but act as a carrier through the column. The significance of dissolved organic matter can be a major reason for lower extraction by ST sludge since it exhibited higher solubility in Chapter 2 which could explain the lower extraction performance compared to CE sludge.

CHAPTER 6

CONCLUSIONS AND DISCUSSION

CHAPTER 6 – CONCLUSIONS AND DISCUSSION

Industrial activities and accidental releases have introduced a large amount of inorganic and organic contaminants to the environment, and therefore contamination of soils, sediments and surface and groundwater are a global concern. Even though more attention has been directed towards the protection of nature, the legacy of previous activities is still present. In addition, accidental releases are almost daily phenomena. Therefore, remediation of contaminants and especially prevention of contaminant releases are crucial in protection of the environment and consequently humans and animals.

Humic substances are capable of interacting with metals in number of ways; they form soluble complexes and cause precipitation via reduction, adsorption, ion exchange and other sorption processes. Carboxylic and phenolic functional groups present in the humic substances are responsible for the majority of metal binding. Bonding mechanisms for organic chemicals by humic substances include ion exchange, hydrogen bonding, and coordination through an attached metal ion (ligand exchange). Also sorption can occur by physical adsorption (van der Waals forces) on a surface or by partitioning into hydrophobic media or both. In this study, the ability of humic substances to interact strongly with metals and organic pollutants was investigated in the remediation of diverse contaminants. The aim was to investigate the suitability of the Severn Trent sludge (ST) and Ukrainian sediment (CE) as remediation materials (both are rich in humic substances) in two environmental applications (**Chapters 3 and 4**) and in one pharmaceutical application (**Chapter 5**).

The extraction behaviour of any material is closely linked to its composition, therefore detailed characterisation of the extraction materials were carried out (**Chapter 2**). Both of the materials are rich in organic matter (ST 49.5% and CE 82.7%) with high aromaticity. The main constituents in the inorganic fraction were iron hydroxide in ST and quartz and calcite in CE. The natural pH of the ST sludge in aqueous solution was pH 4-5. The buffering capacity was derived from leaching iron which hydrolyses water and produces H^+. The buffering capacity of CE sludge towards pH 7-8 was initiated by dissolving calcite and formation of OH^-. The solubility of humic substances showed higher solubility by the ST sludge compared to the CE sludge. It was estimated, that in long term experiments, the mass loss of 10% per year by ST sludge may prevent its use. The corresponding mass loss of CE sludge was insignificant with release of less than 1% in a year. However, it was concluded that both of the sludges had potential to be efficient remediation materials due to their organic content, aromaticity, porosity, and buffering behaviour, if the solubility of the ST sludge could be overcome or if it were not of major concern. Significant release of iron from ST sludge was observed and therefore, the use of ST sludge as landfill should be re-considered.

It was demonstrated in **Chapter 3** that release of iron from ST sludge prevented its use as a remediation material for arsenic, iron, and uranium from industrial effluents. However, the CE sludge exhibited excellent extraction capacities for all three elements under investigation. The arsenic removal occurred via ion exchange most likely by carboxylic functional groups present in the organic matter of the CE sludge. Iron was removed from the solution via precipitation as hydroxide whereas the extraction of uranium (uranyl ion) occurred most likely via complexation with carboxylate groups acting as bidentate ligands. In addition, the natural buffering capacity of CE sludge increased the pH towards 8 even in the strongly acidic effluents with pH 3.

The data produced in Chapter 3 can be used in the evaluation on the technical and economical performance of the CE sludge on an industrial scale. According to the maximum extraction results, one tonne of CE sludge could remove iron from 2.9 million litres or uranium from 633 million litres of un-treated plant P effluent. The same amount of CE sludge could remove arsenic from 193 million litres, iron from 0.44 million litres or uranium from 2 billion litres of un-treated plant R effluent. However, these results were calculated for extraction of a single element at a time assuming no competition by other elements present in the effluents. These results also present total extraction of the element of interest from the effluent even though the limit for arsenic for example in drinking water is 10 µg dm^{-3}, for uranium 15 µg dm^{-3} and for iron 200 µg dm^{-3} [119, 120]. Mining activities in 13 working pits in the St Austell China Clay region produce around 2 million tonnes of refined kaolin per year and over 20 million tonnes of waste including both solid and liquid waste [53]. Therefore, one working pit produces about 1.54 million kilograms of waste. If 10% of the waste is in liquid form (1 kg of waste equals to 1 dm^3 of waste), all iron could be extracted by ~50 tonnes of CE or all uranium by less than a tonne from the un-treated plant P effluent. Less than a tonne of CE sludge could extract all arsenic and uranium from the un-treated plant R effluent whereas one of the major metals, iron, would require ~350 tonnes of CE sludge. These estimations show that the amount of waste containing arsenic, iron and uranium produced in a year could be significantly reduced. However, these results are predictions and field studies are required to obtain more realistic results.

The relationship between solubility of an organic compound and extraction capacity into ST and CE sludges was investigated in **Chapter 4**. The results showed clear correlation between the hydrophilicities and extraction capacities of chlorinated anilines and phenols whereas the hydrophobicities of the chlorinated benzenes were clearly linked with their extraction capacities by ST and CE sludges. The results were explained by the presence the polar NH_2 groups in anilines and OH groups in phenols and their capability to form hydrogen linked bonds with the polar O- and N- containing functional groups in the sludges. The lower polarity of NO_2 groups in chlorinated nitrobenzenes caused nonpolar behaviour resulting in partitioning to the ST and CE sludges. Detailed information on the mechanisms of binding of chlorinated anilines, phenols and benzenes could be investigated using techniques such as NMR, ESR, and FT-IR.

It was explained in **Chapter 5** that oxidation of iodide to reactive iodine showed increased extraction from deionised water and synthetic urine. However, the extractions of iodine species from urine in the presence and absence of oxidising agent were more complicated. It was suggested that the composition of the urine (presence of reducing agents, such as urea and uric acid, and competing anions, such as chlorine) and release of humic substances from the sludges were the main reasons for lowered extraction capacities. The solubility of the sludges, especially of ST sludge, was concluded to play a major role in the extraction since dissolved organic matter can reduce oxidised reactive iodine to iodide and therefore decrease extraction efficiency.

Based on the results in previous chapters, the major conclusions of the work herein are that the remediation materials under investigation, namely ST and CE sludges;

i) Showed interesting results on the extraction of iodine species from urine. Even though the extraction percentages from urine were not as promising as from deionised water and synthetic urine, scientific interest was raised and more investigations on the effect of composition of the urine and solubility of the sludges on the extraction of iodine species are recommended.

ii) Showed similar and excellent performance on extraction of chlorinated anilines, phenols and benzenes. However, further studies on permeability and solubility are recommended prior to field studies for ST and CE sludges as reactive materials in permeable reactive barriers.

iii) The release of iron from ST sludge inhibited its usage as remediation material for arsenic, iron and uranium from industrial effluents whereas CE sludge showed excellent performance. The extractions were both rapid and efficient. The overall conclusion in this application is that the performance of CE sludge to remediate contaminants from industrial effluents is ready to be tested in a field study.

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Personal development training record

Date and Location	Title	Training type	Duration (d)
21st Nov 2007, Manchester, UK	Actinide materials	Seminar	1
30th Jan 2008, Loughborough, UK	Plagiarism, Citation and managing your references	Workshop	0.5
25th to 26th Feb 2008, London, UK	NORM waste	Conference	2
23rd to 25th June, 2008, Liskaerd, UK	Contamination mapping of a industrial plant	Fieldtrip	3
6th to 7th Oct, 2008, Barcelona, Spain	FUNMIG	Training	2
11th Nov 2008, Loughborough, UK	RSC- Production, use and disposal of isotopes in nuclear medicine	Seminar	1
17th to 18th Nov 2008, Loughborough, UK	NDA Research and development strategy workshop	Workshop	2
4th Dec 2008, Loughborough, UK	Teaching Skills – Preparing to teach	Training	1
11th Dec 2008, Loughborough, UK	Teaching skills – Promoting learning	Training	1
15th Dec 2008, Loughborough, UK	Teaching skills – Supervising practical activities	Training	1
6th to 8th April 2009, Liverpool, UK	29th Co-ordinating group on Environmental Radioactivity	Conference; presentation (Appendix 6)	2.5

Personal development training record (cont.)

Date and Location	Title	Training type	Duration (d)
3rd to 7th Aug, 2009, Glascow, UK	42nd IUPAC, Chemical solutions	Congress	2
6th Oct 2009, London, UK	RCG –Radioactivity and law	Seminar	1
2nd Dec 2009, Manchester, UK	RCG-Chemistry of geological disposal	Seminar	1
18th to 23rd April, 2010, Marianske Lazne, Czech republic	Radiochemical conference	Conference; poster and flash presentation (Appendix 6)	4
27th June to 2nd July 2010, Tenerife, Spain	15th International humic substance society's meeting	Conference; presentation and poster (Appendix 6)	5
14th to 17th Sep 2010, Chester, UK	11th International Symposium on Environmental radiochemical analysis	Conference; presentation (Appendix 6)	3

Appendix 1 – Chapter 2 - Characterisation of remediation materials

1.1 Iron content in ST and CE sludges

Sample	Sample into furnace (g)	Ash (g)	Fe in ash (g)	Fe in ash (%)	Fe in sludge (%)
ST	2.0052	0.6079	0.4180	68.7	20.8
ST	2.0013	0.6074	0.5292	87.1	26.4
ST	2.0034	0.6107	0.4151	68.0	20.7
CE	5.0525	2.9782	0.0430	1.4	0.9
CE	5.0469	2.8061	0.0583	2.1	1.2
CE	5.0637	2.914	0.0432	1.5	0.9

1.2 CEC of ST and CE sludges

Sample	Mass (g)	pH	Abs 472	CEC (UV)	Co (g dm^{-3})	CEC (ICP)
Co sol		5.07	0.9165		1.088	
ST 1	2.002	4.3	0.8673		1.017	7.224
ST 2	2.0005	4.65	0.8339	9.010	0.984	10.586
ST 3	2.0005	4.84	0.8141	11.170	1.084	
CE 4	1.9995	7.73	0.7279	20.583	0.856	23.550
CE 5	2.0002	7.72	0.7242	20.980	0.846	24.602
CE 6	1.9993	7.78	0.7304	20.313	0.847	24.524

Appendix 1 – Chapter 2 - Characterisation of remediation materials (cont.)

1.3 Buffering capacity of ST and CE sludges

ST sets	**HNO_3 volume (cm^3)**	**pH**	**ST sets**	**NaOH volume (cm^3)**	**pH**
1	0	5.15	4	0	5.37
	1.09	2.17		0.05	8.65
	1.78	2		0.12	10.32
	2.29	1.92		0.19	11
	3.47	1.78		0.99	12
	5.21	1.65	5	0	5.14
	7.99	1.51		0.04	9.91
	25.15	1.21		0.1	10.99
	25.2	1.1		0.72	12.01
	28.19	1	6	0	5.16
2	0	5.56		0.09	10.26
	0.12	3.53		0.18	10.95
	0.19	2.98		0.3	11.26
	2.22	2.01		0.92	12.02
	25.01	1.17			
	31.14	1			
3	0	5.58			
	0.05	3.51			
	0.21	2.98			
	2.53	1.99			
	32.01	1.01			

Appendix 1 – Chapter 2 - Characterisation of remediation materials (cont.)

CE sets	HNO3 volume (cm^3)	pH	CE sets	NaOH volume (cm^3)	pH
7	0	8.14	10	0	7.97
	0.04	6.37		0.03	10.95
	0.25	3.22		0.11	11.4
	0.37	2.97		0.59	11.99
	2.23	1.97	11	0	7.98
	39.42	1		0.1	10.98
8	0	8.23		0.13	11.38
	0.01	6.73		1.09	12
	0.12	5.78	12	0	8.13
	0.22	4.48		0.02	11.07
	0.31	3.32		0.12	11.43
	0.41	3.02		0.63	12.11
	2.34	2.01			
	43.21	1			
9	0	8.27			
	0.09	6.26			
	0.18	5.56			
	0.32	3.1			
	0.41	2.92			
	2.39	1.99			
	38.19	1			

DI sets	HNO3 volume (cm^3)	pH	DI sets	NaOH volume (cm^3)	pH
13	0	5.64	14	0	6.72
	0.05	3.06		0.03	11.05
	1.79	2		0.15	11.37
	44.13	1.01		0.7	12.02

Appendix 2 – Chapter 3 - Extraction of arsenic, iron and uranium from industrial effluents

2.1 Extraction of As, Fe and U from electrolyte

1 h isotherm			**24 h isotherm**	
As free (mol dm^{-3})	**As bound (mol g^{-1})**		**As free (mol dm^{-3})**	**As bound (mol g^{-1})**
2.55E-07	3.75E-08		2.40E-07	3.89E-08
3.50E-07	2.81E-08		2.59E-07	3.61E-08
2.49E-07	3.82E-08		3.11E-07	6.99E-08
3.48E-07	1.76E-08		3.26E-07	6.84E-08
3.22E-07	2.02E-08		2.75E-07	7.36E-08
3.24E-07	1.99E-08		5.51E-07	1.26E-07
5.28E-07	3.85E-08		5.57E-07	1.26E-07
5.53E-07	3.60E-08		5.56E-07	1.26E-07
5.00E-07	4.14E-08		8.01E-07	1.69E-07
1.11E-06	6.13E-08		7.93E-07	1.70E-07
1.08E-06	6.41E-08		8.14E-07	1.67E-07
1.10E-06	6.25E-08		2.20E-03	1.86E-05
1.49E-06	7.70E-08		2.20E-03	1.82E-05
1.49E-06	7.65E-08		2.20E-03	1.87E-05
1.50E-06	7.55E-08		1.62E-03	1.26E-05
2.57E-05	3.00E-07		1.64E-03	1.10E-05
2.48E-05	3.87E-07		1.65E-03	9.76E-06
2.49E-05	3.78E-07		7.36E-04	6.56E-06
2.53E-04	2.65E-06		7.32E-04	7.04E-06
2.49E-04	3.04E-06		7.43E-04	5.93E-06
2.52E-04	2.78E-06		2.33E-04	4.67E-06
7.27E-04	7.49E-06		2.35E-04	4.51E-06
7.31E-04	7.17E-06		2.36E-04	4.40E-06
7.26E-04	7.59E-06		2.02E-05	8.52E-07
1.61E-03	1.39E-05		1.90E-05	9.61E-07
1.61E-03	1.32E-05		2.02E-05	8.49E-07
1.62E-03	1.27E-05		6.65E-03	3.11E-06
2.21E-03	1.78E-05		6.58E-03	9.34E-06
2.22E-03	1.63E-05		6.61E-03	7.05E-06
2.21E-03	1.77E-05		1.00E-02	4.81E-06
1.32E-02	3.48E-05		9.96E-03	1.36E-05
1.33E-02	2.13E-05		1.34E-02	1.66E-05
1.63E-02	1.11E-04		1.34E-02	1.49E-05
1.66E-02	7.75E-05			
1.59E-02	1.53E-04			

Appendix 2 – Chapter 3 - Extraction of arsenic, iron and uranium from industrial effluents (cont.)

1 h isotherm			**24 h isotherm**	
Fe free (mol dm^{-3})	**Fe bound (mol g^{-1})**		**Fe free (mol dm^{-3})**	**Fe bound (mol g^{-1})**
1.83E-02	1.17E-03		1.49E-02	1.51E-03
2.13E-02	8.71E-04		1.63E-02	1.37E-03
2.27E-02	7.25E-04		2.10E-02	9.05E-04
7.23E-04	4.28E-04		2.96E-05	4.97E-04
1.89E-03	3.11E-04		2.39E-05	4.97E-04
2.75E-03	2.25E-04		1.59E-05	4.98E-04
3.57E-02	1.43E-03		3.72E-02	1.28E-03
3.49E-02	1.51E-03		3.41E-02	1.59E-03
3.55E-02	1.44E-03		3.44E-02	1.56E-03
1.65E-06	2.98E-05		5.41E-03	4.60E-04
1.65E-06	2.98E-05		4.60E-03	5.39E-04
2.05E-06	2.97E-05		4.53E-03	5.47E-04
1.40E-06	4.99E-05		4.12E-06	2.96E-05
2.46E-06	4.96E-05		4.94E-06	2.95E-05
1.56E-06	4.98E-05		3.87E-06	2.96E-05
2.32E-06	6.97E-05		2.45E-06	4.99E-05
2.20E-06	7.00E-05		3.46E-06	4.98E-05
2.87E-06	6.96E-05		2.78E-06	4.97E-05
7.06E-05	9.28E-05		2.03E-06	6.98E-05
6.69E-05	9.32E-05		1.32E-06	6.97E-05
6.23E-05	9.37E-05		1.80E-06	6.99E-05
3.61E-06	9.64E-06		8.87E-07	1.00E-04
6.04E-06	9.38E-06		8.35E-07	1.00E-04
4.62E-06	9.54E-06		1.77E-06	9.99E-05
2.69E-06	7.30E-07		5.16E-06	9.48E-06
2.83E-06	7.17E-07		5.17E-06	9.49E-06
2.56E-06	7.46E-07		3.98E-06	9.62E-06
			3.58E-06	6.44E-07
			2.97E-06	7.02E-07
			5.77E-06	4.22E-07

Appendix 2 – Chapter 3 - Extraction of arsenic, iron and uranium from industrial effluents (cont.)

1h isotherm			**24 h isotherm**	
U Free (mol dm^{-3})	**U Bound (mol g^{-1})**		**U Free (mol dm^{-3})**	**U Bound (mol g^{-1})**
2.16E-06	3.94E-07		2.91E-06	2.89E-07
2.18E-06	3.91E-07		2.86E-06	2.94E-07
2.11E-06	3.98E-07		2.60E-06	3.20E-07
1.47E-05	6.35E-06		1.06E-05	7.07E-06
1.52E-05	6.29E-06		1.26E-05	6.87E-06
1.53E-05	6.28E-06		1.45E-05	6.68E-06
1.90E-04	6.76E-05		3.67E-04	5.04E-05
2.10E-04	6.55E-05		3.77E-04	4.94E-05
2.13E-04	6.53E-05		3.61E-04	5.10E-05
1.92E-03	1.21E-04		1.76E-04	2.92E-04
1.94E-03	1.19E-04		2.21E-04	2.88E-04
1.92E-03	1.21E-04		1.84E-04	2.92E-04
3.69E-03	1.48E-04		1.73E-03	3.54E-04
3.96E-03	1.20E-04		1.86E-03	3.41E-04
3.91E-03	1.26E-04		1.99E-03	3.28E-04
6.90E-03	1.57E-04		4.77E-03	3.71E-04
6.79E-03	1.75E-04		4.92E-03	3.57E-04
6.88E-03	1.65E-04		5.12E-03	3.37E-04

Appendix 2 – Chapter 3 - Extraction of arsenic, iron and uranium from industrial effluents (cont.)

2.2 Extraction of As, Fe and U from un-treated plant P effluent

As Free (mol dm^{-3})	**As Bound (mol g^{-1})**	**Fe free (mol dm^{-3})**	**Fe bound (mol g^{-1})**	**U free (mol dm^{-3})**	**U bound (mol g^{-1})**
1.26E-03	7.75E-06	2.27E-04	4.09E-04	1.99E-03	2.24E-04
1.25E-03	8.36E-06	8.61E-05	4.23E-04	1.82E-03	2.41E-04
1.25E-03	8.63E-06	2.27E-04	4.09E-04	1.91E-03	2.32E-04
2.45E-03	1.83E-05	8.61E-05	4.23E-04	1.02E-02	1.44E-04
2.45E-03	1.83E-05	4.45E-04	3.87E-04	9.83E-03	1.83E-04
6.36E-03	2.75E-05	3.36E-02	4.06E-04	1.02E-02	1.41E-04
6.42E-03	2.22E-05	3.55E-02	2.16E-04	1.35E-04	2.57E-05
1.27E-02	4.42E-05	3.71E-02	4.93E-05	1.31E-04	2.61E-05
1.26E-02	4.88E-05	9.29E-06	1.14E-06	1.32E-04	2.60E-05
1.27E-02	3.99E-05	6.89E-06	1.39E-10	2.31E-04	5.94E-05
3.88E-02	2.37E-04	8.47E-06	1.23E-06	2.23E-04	6.04E-05
3.90E-02	2.19E-04	6.38E-06	1.31E-04	2.18E-04	6.08E-05
6.99E-02	5.47E-04	6.05E-06	1.31E-04	4.59E-04	1.61E-04
7.01E-02	5.29E-04	7.23E-06	1.31E-04	4.83E-04	1.58E-04
6.98E-02	5.55E-04	6.64E-06	2.69E-04	5.11E-04	1.56E-04
		9.48E-06	2.68E-04	5.68E-03	2.87E-04
		5.02E-06	2.70E-04	6.18E-03	2.37E-04
		1.84E-04	6.51E-04	5.96E-03	2.59E-04
		1.46E-04	6.54E-04		
		1.85E-04	6.51E-04		

2.3 Extraction of As, Fe and U from treated plant P effluent

As free (mol dm^{-3})	**As bound (mol g^{-1})**	**Fe free (mol dm^{-3})**	**Fe bound (mol g^{-1})**	**U free (mol dm^{-3})**	**U bound (mol g^{-1})**
7.44E-03	1.02E-04	1.60E-05	1.02E-04	4.97E-04	9.18E-06
8.01E-02	1.12E-04	9.02E-06	1.03E-04	4.90E-04	9.94E-06
8.01E-02	1.17E-04	8.88E-06	1.03E-04	5.07E-04	8.30E-06
5.78E-03	4.99E-05	3.64E-06	3.26E-04	1.36E-03	9.56E-05
5.74E-03	5.39E-05	2.90E-06	3.27E-04	1.34E-03	9.76E-05
2.78E-03	2.18E-05	2.50E-06	3.27E-04	1.31E-03	1.00E-04
2.77E-03	2.26E-05	2.93E-05	3.30E-03	1.40E-03	4.22E-04
2.74E-03	2.58E-05	2.08E-05	3.30E-03	1.41E-03	4.21E-04
2.79E-02	1.18E-04	3.14E-05	3.29E-03	1.36E-03	4.26E-04
2.82E-02	9.11E-05			2.01E-03	7.81E-04
2.83E-02	8.52E-05			2.22E-03	7.61E-04
				2.08E-03	7.76E-04

Appendix 2 – Chapter 3 - Extraction of arsenic, iron and uranium from industrial effluents (cont.)

2.4 Extraction of As, Fe and U from un-treated plant R effluent

As free (mol dm^{-3})	**As bound (mol g^{-1})**	**Fe free (mol dm^{-3})**	**Fe bound (mol g^{-1})**	**U free (mol dm^{-3})**	**U bound (mol g^{-1})**
1.62E-03	7.44E-06	1.53E-03	3.64E-04	4.96E-08	5.30E-08
1.63E-03	6.79E-06	1.23E-03	3.93E-04	5.20E-08	5.27E-08
1.65E-03	4.95E-06	1.23E-03	3.94E-04	5.17E-08	5.27E-08
7.28E-03	3.75E-05	2.92E-03	5.69E-04	6.09E-07	1.49E-07
7.30E-03	3.57E-05	2.95E-03	5.66E-04	5.67E-07	1.53E-07
7.28E-03	3.73E-05	2.92E-03	5.69E-04	5.67E-07	1.53E-07
1.29E-02	1.45E-04	1.06E-02	4.52E-04	2.26E-06	1.97E-07
1.28E-02	1.56E-04	1.06E-02	4.60E-04	2.26E-06	1.96E-07
1.36E-02	7.52E-05	1.05E-02	4.66E-04	2.26E-06	1.97E-07
4.26E-02	3.32E-04	2.77E-05	1.31E-04	6.80E-03	1.32E-04
4.24E-02	3.48E-04	1.13E-04	1.12E-04	6.85E-03	1.28E-04
4.25E-02	3.45E-04	1.48E-04	1.08E-04	6.79E-03	1.33E-04
6.93E-02	2.89E-04	9.77E-06	1.23E-04	1.04E-02	1.83E-04
6.84E-02	3.86E-04	5.25E-03	4.48E-04	1.10E-02	1.29E-04
6.88E-02	3.44E-04	4.80E-03	4.93E-04	9.36E-03	2.90E-04
		4.37E-03	5.35E-04	4.71E-03	1.70E-04
				4.52E-03	1.90E-04
				4.94E-03	1.48E-04

Appendix 3 – Chapter 4 - Extraction of organic contaminants

Guidance on the groundwater regulations 1998 [5]
List of substances recommended to be confirmed as List 1

Aldrin
Atrazine
Azinphos methyl
Azinphos-ethyl
Bromoxynil (as Bromoxynil-phenol)
Bromoxynil octanoate
Cadmium
2-Chloroaniline
Chlorobenzene
Chlordane
Chloro-2,4-dinitrobenzene
Chlorfenvinphos
4-Chloro-3-methylphenol
(IPBC)
Chloro-2-nitrobenzene
Chloro-3-nitrobenzene
Chloro-4-nitrobenzene
2-Chlorophenol
Chlorothalonil
2-Chlorotoluene
α-Chlorotoluene
Chlorpyrifos
Coumaphos
Cypermethrin
DDT
Demeton
Diazinon
Dibutyl bis(oxylauroyl)tin
Dichlofluanid
Dichloroaniline
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Dichloronitrobenzene (all isomers)
2,4-Dichlorophenol
1,3-Dichloropropene
Dichlorprop
Dichlorvos
Dicofol
Dieldrin
Dimethoate
Diuron
Endosulfan
Endrin
Fenitrothion
Fenthion
Heptachlor
Hexachlorobenzene
Hexachlorobutadiene (HCBD)
Hexachlorocyclohexane
Hexachloroethane
Hexachloronorbornadiene
Hexaconazole
3-Iodo-2-proponyl n-butyl carbamate
Linuron
Malathion
Mercury
Mevinphos
Oxydemeton-methyl
Parathion
Parathion-methyl
Pentachlorobenzene
Pentachloroethane
Pentachlorophenol (PCP)
Permethrin
Propanil
Simazine
Tetrabutyltin
1,2,4,5-Tetrachlorobenzene
Tetrachloroethylene
Triazophos
Tributyl tin oxide (TBTO)
Tributyl-phosphate
Trichlorfon
1,2,4-Trichlorobenzene
Trichloroethylene
Trichlorophenol (all isomers)
Trifluralin
Triphenyl tin oxide (TPTO)
Triphenyl-phosphate

Appendix 4 – Chapter 4 - Extraction of organic contaminants

4.1 Extraction of chlorinated anilines

Mass of ST sludge	2-chloroaniline (1d)	2-chloroaniline (1w)
0.2		
0.2	12.2	
0.2	13.4	
0.5	27.1	39.6
0.5	32.5	37.3
0.5	31.5	42.3
0.7	38.7	46.4
0.7	41.6	50.5
0.7	41.9	52.2
1	48.3	60.3
1	52.1	62.4
1	52.7	62.2
Mass of ST sludge	**2,3-dichloroaniline (1 d)**	**2,3-dichloroaniline (1 w)**
0.2	11.0	
0.2	14.9	
0.2	22.6	
0.5	29.4	22.7
0.5	27.3	12.1
0.5	30.7	
0.7	31.4	35.2
0.7	32.5	25.8
0.7	29.1	22.8
1	40.3	41.6
1	28.4	37.7
1	35.1	32.0

Appendix 4 – Chapter 4 - Extraction of organic contaminants (cont.)

Mass of CE sludge	**2-chloroaniline (1d)**	**2-chloroaniline (1 w)**
0.2	23.3	51.9
0.2	32.8	51.1
0.2	28.4	53.9
0.5	37.3	60.4
0.5	40.2	59.0
0.5	41.4	60.1
0.7	43.0	65.5
0.7	45.6	63.1
0.7	47.4	64.6
1		71.0
1	63.4	70.0
1	61.7	68.5
Mass of CE sludge	**2,3-dichloroaniline (1 d)**	**2,3-dichloroaniline (1 w)**
0.2	23.2	
0.2	23.4	36.6
0.2	10.8	28.0
0.5	42.0	54.9
0.5	28.1	50.4
0.5	18.5	49.8
0.7	37.7	68.3
0.7	39.3	62.2
0.7	37.0	65.1
1	39.7	75.2
1	38.5	70.1
1	48.8	74.3

Appendix 4 – Chapter 4 - Extraction of organic contaminants (cont.)

4.2 Extraction of chlorinated phenols

Mass of ST sludge	2-chlorophenol (1 d)	2-chlorophenol (1 w)
0.2	17.5	
0.2	38.2	64.8
0.2	11.9	67.9
0.5	49.9	78.1
0.5		79.8
0.5		
0.7	81.8	
0.7	85.6	85.3
0.7	85.6	73.4
1	80.3	87.9
1	84.6	86.7
1	86.4	
Mass of ST sludge	**2,3,5-trichlorophenol (1d)**	**2,3,5-trichlorophenol (1w)**
0.2		
0.2		
0.2	31.7	70.9
0.5	44.5	85.9
0.5	48.6	83.3
0.5	56.3	77.4
0.7	66.7	88.1
0.7	66.6	85.0
0.7	63.5	83.9
1	70.7	93.6
1	72.6	87.9
1	73.9	90.0

Appendix 4 – Chapter 4 - Extraction of organic contaminants (cont.)

Mass of ST sludge	**2,3,4-trichloro-phenol (1d)**	**2,3,4-trichloro-phenol (1w)**	**2,4-dichloro-phenol (1d)**	**2,4-dichloro-phenol (1w)**
0.2			27.3	
0.2			27.1	
0.2	15.8		32.7	
0.5	43.2	60.5	31.0	4.9
0.5	25.2	48.7	30.4	
0.5			36.5	
0.7	41.3		32.1	
0.7	46.1		34.7	
0.7	34.6		37.7	
1			37.2	10.7
1			37.3	8.9
1				
1.5		81.9		
1.5		78.2		
1.5		75.6		
2.5		100		53.0
2.5		100		43.6
2.5		100		47.9

Mass of ST sludge	**3,4,5-trichlorophenol (1 d)**	**3,4,5-trichlorophenol (1 w)**	**4-chloro-c-3-methylphenol (1 w)**
0.2	44.1	62.3	
0.2	50.8	50.6	
0.2	57.1		14.3
0.5			31.6
0.5	59.6	66.0	25.7
0.5		62.8	18.9
0.7	71.9	77.0	31.8
0.7	53.5	69.4	
0.7	53.2	63.5	37.3
1	65.0	77.5	37.3
1	51.9	70.2	37.0
1	60.7	72.0	38.0

Appendix 4 – Chapter 4 - Extraction of organic contaminants (cont.)

Mass of CE sludge	4-chloro-3-methyl-phenol (1 d)	4-chloro-3-methyl-phenol (1 w)	2,3,5-trichloro-phenol (1 d)	2,3,5-trichloro-phenol (1 w)
0.2	7.9		5.3	8.0
0.2	6.1	49.8		
0.2	7.9			
0.5			14.0	
0.5	22.3	52.3	19.8	
0.5	18.7	40.0	18.0	
0.7	17.5	48.3		29.4
0.7	20.1	48.8		22.4
0.7	24.4	54.5		20.5
1	24.6	68.4	50.7	35.5
1	30.0	66.5	45.3	40.2
1	33.3	61.8	46.3	39.7

Mass of CE sludge	3,4,5-trichloro-phenol (1 d)	3,4,5-trichloro-phenol (1 w)	2,3,4-trichloro-phenol (1 d)	2,3,4-trichloro-phenol (1 w)
0.2	71.3			55.0
0.2	65.4	23.0	4.3	30.0
0.2	69.2	18.0	1.2	31.3
0.5	79.1	58.4	34.6	65.7
0.5	94.5	49.1	28.4	57.9
0.5	90.9	45.5	27.1	51.9
0.7	91.0	70.0		71.2
0.7	98.7	59.7	36.5	66.2
0.7	97.2	62.1		70.1
1			61.2	84.9
1			75.3	80.9
1			56.5	81.3

Appendix 4 – Chapter 4 - Extraction of organic contaminants (cont.)

Mass of CE sludge	**2,4-dichlorophenol (1 d)**	**2,4-dichlorophenol (1 d)**
0.2	22.3	13.8
0.2	12.7	5.7
0.2	12.8	2.4
0.5	20.8	26.3
0.5	20.5	26.3
0.5	23.0	23.7
0.7	32.6	47.3
0.7	33.8	38.9
0.7	32.0	41.3
1	43.6	53.7
1	39.8	55.7
1	43.3	56.6

4.3 Extraction of chlorinated benzenes

Mass of ST sludge	**Chloro-2,4-dinitro-benzene (1 d)**	**Chloro-2,4-dinitro-benzene (1 w)**	**Chloro-4-nitro-benzene (1 d)**	**Chloro-4-nitro-benzene (1 d)**
0.2			48.6	19.7
0.2	1.5		51.4	46.6
0.2	7.7	51.3	57.0	49.5
0.5	10.4	59.4	60.5	67.1
0.5	9.3	57.4	59.7	60.1
0.5	7.7	61.1	66.2	47.8
0.7	14.3	65.1	70.8	
0.7	20.8	71.9	73.7	
0.7	22.9	71.7	75.0	
1	28.7	67.9	76.7	100
1	28.4		82.4	100
1	32.5		81.6	100

Appendix 4 – Chapter 4 - Extraction of organic contaminants (cont.)

Mass of ST sludge	**Chloro-2-nitro-benzene (1d)**	**Chloro-2-nitro-benzene (1 w)**	**2,4-dichloronitro-benzene (1 d)**	**2,4-dichloronitro-benzene (1 w)**
0.2			0.5	35.0
0.2			9.6	36.1
0.2				
0.5	86.4		75.6	35.4
0.5	78.5		61.4	52.2
0.5	80.3		61.6	38.6
0.7	88.8		65.9	
0.7	82.5		67.7	54.3
0.7	85.7		68.5	43.2
1	89.9		73.0	56.4
1	90.2		100.0	
1	90.0		94.6	
4		100		
4		100		
4		100		
2.5		86.8		
2.5		86.4		
2.5		90.6		
1		77.7		
1		67.2		
1		67.8		

Mass of CE sludge	**Chloro-2,4-dinitro-benzene (1d)**	**Chloro-2,4-dinitro-benzene (1d)**	**2,4-dichloronitro-benzene (1 d)**	**2,4-dichloronitro-benzene (1 w)**
0.2	57.8	9.1		
0.2	61.3	13.0		43.7
0.2	64.2	17.2		39.9
0.5	66.7	28.4		76.5
0.5	68.0	26.6	24.1	61.5
0.5	68.6	30.8	31.5	63.3
0.7	71.1	38.5	39.9	80.0
0.7	72.2	41.2	37.5	68.6
0.7	72.6	45.0	41.7	65.7
1	75.0	49.3	54.3	86.0
1	75.3	48.3	55.6	79.4
1	76.5	46.8	56.2	81.5

Appendix 4 – Chapter 4 - Extraction of organic contaminants (cont.)

Mass of CE sludge	**Chloro-4-nitro-benzene (1d)**	**Chloro-4-nitro-benzene (1w)**	**Chloro-2-nitro-benzene (1 d)**	**Chloro-2-nitro-benzene (1 w)**	**1,2-dichloro-benzene (1 d)**
0.2			4.9		38.9
0.2	8.1	15.0		28.2	23.6
0.2	7.4	15.7	1.5	27.5	23.2
0.5	12.0	28.9	23.6	46.9	40.6
0.5	12.5	28.0	24.3		31.4
0.5	26.0	24.0	14.3	34.4	29.7
0.7	21.4	37.8	32.9	46.4	
0.7	33.4	29.7	21.3	46.7	
0.7	28.9	35.8	12.8	45.5	
1	26.2	51.0	44.9	47.2	48.0
1	44.1	45.3	36.5	39.2	53.4
1		44.1	34.9	39.7	50.2

Appendix 5 – Chapter 5 - Extraction of iodine species from urine

5.1 Extraction of iodine species from deionised water

Solution	Mass of ST sludge (g)	Extraction (%)	Mass of CE sludge (g)	Extraction (%)
DI	0.2003	4.6	0.1997	80.5
DI	0.1996	4.6	0.1996	75.4
DI	0.6997	9.7	0.1995	77.8
DI	1.5003	5.6	0.6997	84.1
DI	1.5002	11.2	0.7003	81.2
DI	1.4999	8.0	0.7005	85.1
DI	2.9994	21.6	1.5004	90.5
DI	2.9995	15.6	1.4995	89.2
DI	3	14.9	1.5001	89.2
DI			2.9999	92.9
DI			3.0001	92.6
DI			3	91.7

5.2 Extraction of iodine species from synthetic urine

Mass of ST sludge(g)	Extraction (%)	Mass of CE sludge (g)	Extraction (%)
0.1997	6.1	0.1995	73.1
0.7	6.9	0.1995	66.4
0.7001	1.1	0.1997	71.3
0.7	7.0	0.6997	79.3
1.5005	23.5	0.6996	78.3
		0.7005	77.7
1.5003	22.6	1.4998	80.6
3.0004	23.1	1.5002	82.3
3.0003	25.5	1.4997	82.8
3.0004	30.1	2.9996	85.2
		3	84.6
		3.0002	84.9

Appendix 5 – Chapter 5 - Extraction of iodine species from urine (cont.)

5.3 Extraction of iodine species from urine

Sludge	Contact time	Mass (g)	Sorption (%)	Contact time	Mass (g)	Sorption (%)
ST	1h	0.1999	21.3	24 h	0.2	29.2
ST	1h	0.2	23.4	24 h	0.1998	34.9
ST	1h	0.2	19.0	24 h	0.2002	28.1
ST	1h	0.5	30.5	24 h	0.4999	31.3
ST	1h	0.5001	28.7	24 h	0.5002	26.1
ST	1h	0.5002	25.8	24 h	0.5002	41.4
ST	1h	1	30.6	24 h	0.9999	27.3
ST	1h	1.0002	27.7	24 h	0.9998	41.9
ST	1h	1.0002	33.7	24 h	1.0002	36.6
CE	1h	0.2	26.7	24 h	0.1998	33.3
CE	1h	0.1998	28.7	24 h	0.2002	34.2
CE	1h	0.2	21.2	24 h	0.2	24.6
CE	1h	0.502	25.3	24 h	0.5001	25.7
CE	1h	0.4999	22.6	24 h	0.4999	38.7
CE	1h	0.5001	22.8	24 h	0.5001	31.9
CE	1h	1	20.9	24 h	0.9999	37.0
CE	1h	1	31.1	24 h	0.9999	34.7

Sludge	Solution	Mass (g)	Extr (%)	Sludge	Mass (g)	Extr %
ST	Urine + $KMnO_4$	0.1998	6.3	CE	0.1997	20.1
ST	Urine + $KMnO_4$	0.2004	0.7	CE	0.2002	14.3
ST	Urine + $KMnO_4$	0.6998	4.6	CE	0.1999	11.5
ST	Urine + $KMnO_4$	0.6997	1.8	CE	1.4996	27.8
ST	Urine + $KMnO_4$	0.7004	3.1	CE	1.5001	27.6
ST	Urine + $KMnO_4$	1.4997	10.5	CE	2.9999	41.5
ST	Urine + $KMnO_4$	1.4998	12.9	CE	3.0003	47.6
ST	Urine + $KMnO_4$	1.5	6.7	CE	2.9998	39.5
ST	Urine + $KMnO_4$	3.0001	23.4	CE		
ST	Urine + $KMnO_4$	2.9995	21.5	CE		
ST	Urine + $KMnO_4$	2.9996	21.4	CE		

Appendix 6 – Abstracts – 28th Co-ordinating group on Environmental Radioactivity, 2008

Using Natural Organic Matter as a Permeable Reactive Barrier

Anumaija Leskinen and Peter Warwick
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Natural organic matter (NOM) is produced in the environment from the decomposition of plants and animals and consists primarily of humic (HA) and fulvic acids (FA). A working definition of NOM is that humic acid is soluble above pH 2 but insoluble below it and fulvic acid is soluble across the whole pH range. Because their origins vary and they decompose with time, their structure can not be described as a unique structure.

A Permeable Reactive Barrier (PRB) is an *in situ* method to remediate contaminated groundwater. As groundwater flows through it, the barrier extracts contaminants, or at least reduces their concentration. This method has lower cost than the traditional pump-and-treat methods. Different materials have been used as the reactive matter such as activated carbon and zero-valent iron.

Natural organic matter could be a good reactive material, because it is widely available and cheap, but first it has to fulfil three qualifications. Firstly, it has to be permeable, because groundwater has to be able to flow through it. Secondly, it has to have extracting properties. Thirdly, it has to be insoluble, because even though it might be porous and a good extractor, it could release the captured contaminants as it dissolves.

Studies of NOM porosity have been investigated on the laboratory scale and it has been shown to be porous. Further studies will be carried out to determine how the porosity changes with pressure, because certainly the porosity will not be the same in the upper part and lower part of the PRB.

NOM has been shown to efficiently extract metals such as nickel, cadmium, and zinc. NOM also extracts bromine. The extraction efficiency of NOM for organic pollutants and some radionuclides will be examined.

Appendix 6 – Abstracts (cont.) – 29th Co-ordinating group on Environmental Radioactivity, 2009

Using Natural Organic Matter as a Remediation material

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Department of Chemistry
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Using natural organic matter as a remediation material is under investigation. Natural organic matter (NOM) is produced in the environment from the decomposition of plants and animals and consists primarily of humic (HA), fulvic acids (FA), and humin.

Two environmental materials are being tested; both of which are readily available:
i) Material A. 68% of the material is organic including 19% of humic acid, 27% of fulvic acid and 21% of humin. 32% of the material is inorganic including 23% of iron.
ii) Material B. Majority of the material is inorganic (57%). The organic part of the material (43%) consists of fulvic acid (27%), humin (13%) and humic acid (3%).
The humin fraction of these two materials can also contain humic acid that has been immobilised by sorption to clays or minerals.

The materials has been tested for three applications;
i) *Extraction of organic compounds in permeable reactive barriers*
A permeable reactive barrier (PRB) is an *in situ* method to remediate contaminated groundwater. As groundwater flows through it, the barrier extracts contaminants, or at least reduces their concentration.

ii) *Extraction of iodide from urine*
^{131}I may be given to patients with thyroid problems for diagnosis or treatment. About 30% of the activity (2-3 GBq) is excreted in urine during the first day after administration. In some parts of Europe, the radioactive urine is collected in tanks in the hospital and the objective of this of this investigation is to determine whether the radioactive iodine can be extracted from the urine and thereby concentrated in a smaller volume of solid.

iii) Extraction of iron and other contaminants from industrial effluents
In China Clay plants, the initially brown coloured china clay (colour caused by Fe^{3+}) is converted to white China Clay by addition of acid and a reducing agent to reduce Fe^{3+} to soluble Fe^{2+}. In this process, other contaminants such as uranium are also extracted from the clay. The contaminants are removed from the effluent by iron precipitation and the treatment significantly increases the iron content of the effluent and thus causes problems in the environment. This investigation attempts to use solid natural organic material to remove iron and other contaminants.

Appendix 6 – Abstracts (cont.) – 16th Radiochemical conference 2010

Using Natural Organic Matter as a Remediation Material in Environmental Applications

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Natural organic matter (NOM) is being characterised and investigated for use as a remediation material in various applications.
Two readily available environmental materials are being tested:

iii) Material A. 68% by weight of the material is organic including 19% -humic acid, 28% fulvic acid and 21% humin. 32% of the material is inorganic, containing 23% iron.

iv) Material B. 57% by weight of the material is inorganic, 3% is humic acid, 27% is fulvic acid and 13% is humin. The humin fraction of these two materials may contain humic acid that has been immobilised by clays or other minerals.

The materials have been tested in three applications;

iv) *As a permeable reactive barrier*
A permeable reactive barrier is a passive, *in situ* method that is used to remediate contaminated groundwater. As groundwater flows through it, the barrier extracts contaminants, significantly reducing their concentration. Both materials are capable of extracting metals and organic pollutants from groundwater

v) *Extraction of iodine from urine*
^{131}I may be given to patients with thyroid problems for diagnosis or treatment. About 30% of the activity (2-3 GBq) is excreted in urine during the first day after administration. In some parts of Europe, the radioactive urine is collected in tanks at the hospital. The objective of this investigation is to determine whether the radioiodine can be extracted from urine and concentrated in a smaller volume of solid.

vi) Extraction of iron and other contaminants from industrial effluents
During the production of kaolinite or China Clay, brown discoloration caused by Fe^{3+}-containing impurities is removed by the addition of acid and a reducing agent, forming soluble Fe^{2+}. The latter is then removed from the effluent by precipitation with NaOH and flocculants. This study investigates the use of solid NOM to bind iron and co-contaminants directly, avoiding the need for alkali addition and precipitation of large quantities of slurry.

Acknowledgements. Anumaija Leskinen thanks Loughborough University and Enterpris Ltd for financial support.

Appendix 6 – Abstracts (cont.) – 15th International humic substance society's meeting, 2010

Extraction of arsenic, iron and uranium from industrial effluents by natural organic matter

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1. Introduction

Purified kaolin (China Clay) is used extensively in the paper, ceramics, paint, and rubber industries. When freshly mined, China Clay is coloured cream through yellow to brown owing to the presence of impurities, primarily iron oxides, which affect its usefulness as an industrial coating and hence its commercial value [1,2]. Treatment to remove coloration by acidification and reduction of Fe(III) to Fe(II) can also release contaminants such as arsenic and uranium into aqueous effluents. Conventionally, re-oxidation and iron hydroxide precipitation is used to lower the concentration of contaminants in effluents to acceptable levels. However, the resultant sludge has to be disposed of, typically to lagoons. The objective of this investigation is to assess the viability of using natural organic matter (NOM) as an alternative to iron precipitation as a method for removing arsenic, iron, and uranium on the industrial scale.

2. Materials and Methods

The chemistry, mineralogy and particle size distribution of the selected NOM has been characterised in detail [3]. Samples of industrial effluent were collected over a one year period and analysed by ICP-OES and ICP-MS. The average pH of the effluents was 2.7 ± 0.2 and they contained 24 - 132 µg dm^{-3} arsenic, 65.4 – 75.8 mg dm^{-3} iron and 18.6 – 18.8 µg dm^{-3} uranium. The kinetics of extraction was determined by placing 0.5g, 1.0g or 10.0g of NOM in contact with 100 cm^3 of solution. The mixtures were constantly stirred before sampling for analysis after intervals from 1 – 60 min (0.2 µm filter). The maximum extraction capacity (mol g^{-1}) for each contaminant was measured by placing 0.2 g of NOM in contact with 20 cm^3 of solution containing varying concentrations of arsenic, iron or uranium. After 24 hours, the concentration of each contaminant remaining in solution was measured. The ionic strength of the effluent was determined and thereafter control experiments were repeated using arsenic, iron and uranium in 0.1 mol dm^{-3} sodium nitrate solution.

The possibility of using NOM in a dynamic flow system was investigated by conducting a column experiment in which 50g of NOM was placed into a glass column (2.6 cm diameter) and 100 cm^3 of effluent were pumped through the column with a flow rate of 0.2 cm^3 min^{-1}. The output from the column was fraction collected and the arsenic (ICP-OES), iron (ICP-OES) and uranium (ICP-OES or ICP-MS) concentrations were measured in each fraction.

3. Results and Discussion

The kinetic experiments showed that arsenic (100% within 20 min) and uranium (100% within 30 min) were quickly bound to NOM. The kinetic results for iron are shown in Figure 1. Within 60 minutes, the extraction of iron reached 100% in samples containing 1:10 and 1:100 solid liquid ratios. However, only 40% of iron was extracted in 60 minutes from samples with a solid to liquid ratio of 1:200.

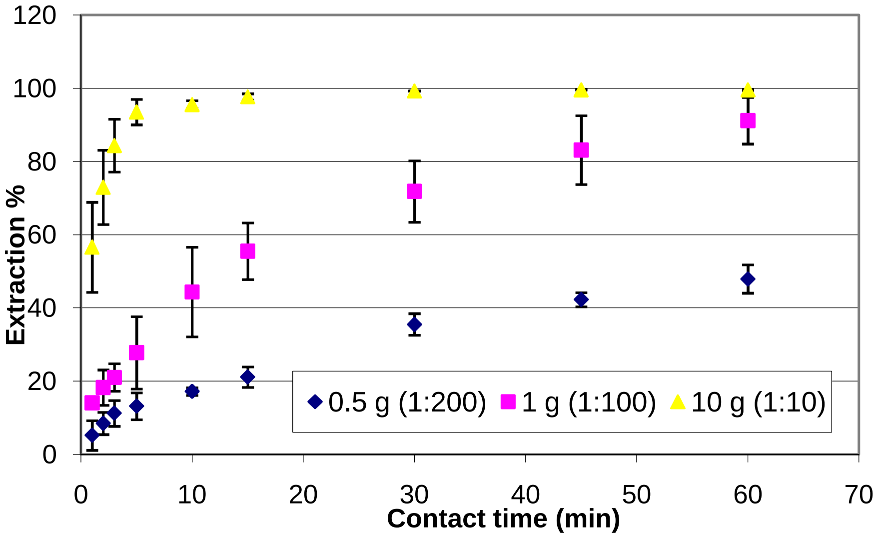

Figure 1 Extraction of iron from effluent by NOM. 100 cm^3 of industrial effluent was placed in contact with 0.5 g, 1 g and 10 g of NOM giving solid: liquid ratios of 1:200, 1:100 and 1:10, respectively.

The extraction capacities of the NOM in electrolyte and industrial effluent are shown in Table 1. It should be noted that the value for arsenic extraction is lower than the actual value for the NOM extraction capacity because saturation of the NOM was not achieved.

Table 1. Arsenic, iron and uranium extraction capacities of NOM in electrolyte and industrial effluent

Solution	*Arsenic (mol g^{-1})*	*Iron (mol g^{-1})*	*Uranium (mol g^{-1})*
0.1 mol dm^{-3} $NaNO_3$	1.2E-05	5.2E-04	1.4E-04
Industrial effluent	≥ 3.4E-04	5.1E-04	1.8E-04

The results of the column experiment are shown in Figure 2. The extraction of arsenic and iron was greater than 99% and greater than 90% for uranium.

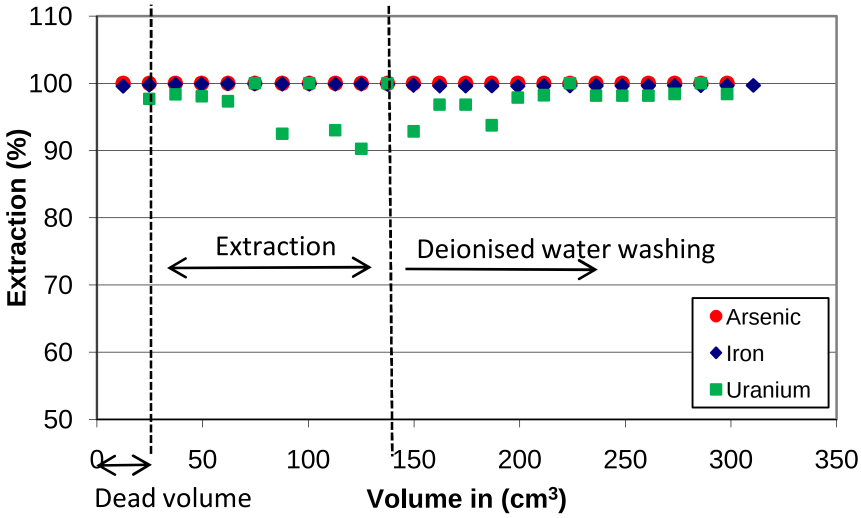

Figure 2. Extraction of arsenic, iron, and uranium from industrial effluent by 50 g NOM column.

4. Conclusions

Batch and column experiments have shown that the NOM used in the experiments described above has potential for industrial use in effluent clean up even where the effluent is strongly acidic. This is unusual and appears to be a specific property of the source material. Similar experiments using other sources of humic matter were ineffective in removing metals below pH4.

Acknowledgements

Anumaija Leskinen would like to thank Loughborough University and Enterpris Ltd for financial support.

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Preferred presentation form: ***Oral***

Appendix 6 – Abstracts (cont.) – 11th International Symposium on Environmental radiochemical analysis, 2010

Maximum extraction capacities of arsenic, iron and uranium from industrial effluents by natural organic matter

Anumaija Leskinen[a*], *David Read*[a,b], *Peter Warwick*[a]

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The presence of impurities, mainly iron oxides, can cause undesired coloration in China Clay. This coloration can be removed by acidification and reduction of Fe(III) to Fe(II). However, the treatment can also release contaminants such as arsenic and uranium into aqueous effluents. Hence, treatment with natural organic matter (NOM) could be an alternative treatment and replace commonly used iron precipitation method. The objective of this investigation is to determine the maximum extraction capacities (mol g^{-1}) for arsenic, iron and uranium using NOM.

Samples of industrial effluent were collected over one year period and characterised by ICP-OES and ICP-MS. The average pH of the effluents was 2.7 ± 0.2 and they contained 24 - 132 µg dm^{-3} arsenic, 65.4 – 75.8 mg dm^{-3} iron and 18.6 – 18.8 µg dm^{-3} uranium. The experiments were carried by placing 0.2 g of NOM in contact with 20 cm^3 of effluent containing varying concentrations of arsenic, iron or uranium. After 24 hours, the concentration of each contaminant remaining in solution was measured. The ionic strength of the effluent was determined and thereafter control experiments were repeated using arsenic, iron and uranium in sodium nitrate solution of equivalent ionic strength (0.1 mol dm^{-3}). The reversibility of extractions was determined by replacing the solution with electrolyte after the NOM had been saturated with each analyte and measuring each contaminant released in solution.

The results are shown in Table 1. It should be noted that the value for arsenic extraction shown is lower than the actual value for the NOM because saturation of the NOM was not achieved. Arsenic was reversibly bound to NOM whereas iron and uranium were irreversibly bound. The results showed efficient extraction of arsenic, iron and uranium and thus the NOM has potential for industrial use in effluent clean up even when the effluent is strongly acidic. Similar experiments using other sources of humic matter were ineffective in removing metals below pH 4.

Table 1. Arsenic, iron and uranium extraction capacities of NOM in electrolyte and industrial effluent

Solution	*Arsenic (mol g^{-1})*	*Iron (mol g^{-1})*	*Uranium (mol g^{-1})*
0.1 mol dm^{-3} $NaNO_3$	1.2E-05	5.2E-04	1.4E-04
Industrial effluent	≥ 3.4E-04	5.1E-04	1.8E-04