Review:

Possible removal of heavy metal and selective rare-earth ions by polymeric and nano-composite materials

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Abstract

Heavy metal contamination in aqueous environment from natural processes and human's activities including pesticides usage, mining, factories discharging and leaking irritation shows an extreme threat to environment and human health. The control of rising amount of heavy metal in environment not only requires critical observations at their original sources but also demands efficient removal methods. However, each conventional method is only suitable in a certain range of use. For example, inexpensive materials and convenient techniques are necessary for large scale heavy meal treatment, while high performance system to remove almost trace amount of heavy metals are critically required for drinking water treatment. On the other hands, heavy metal treatments must be applicable in some crucial environment conditions. Among solutions for environmental heavy metal control, polymeric materials have showed many advantages to enhance the performance of conventional heavy metal adsorbents. Possessing functional chemical moieties on their side chains and backbones, polymers can act as main metal ion adsorption component and/or effective supports for the adsorption property. In addition, the utilization of polymeric components can result in a low corrosion, selectivity, controllability, and recyclability of absorbents when operated in real environment conditions. This article summarizes the preparation techniques and desirable properties of polymer for removal of toxic heavy metal ion as well as the possibility of polymers in collecting some rare noble metal ions.

Keywords. Heavy metal ions, nano-composite, polymer.

1. INTRODUCTION

1.1. Heavy metals toxic effects

Heavy metals are found naturally in the earth surface, and are generally considered to be the metal elements whose density exceeds 5 g per cubic centimeter [1]. A large number of elements fall into this category, but the ones listed in Table 1 are those included in the WHO's list of ten chemical groups of major public health concern. Some toxic, semi-metallic elements, including arsenic and selenium are also listed in main toxicity group of heavy metal. They have been accumulated by the human activities and can enter plant, animal, and human tissues via inhalation, diet, and manual handling. Although some heavy metals are important in many biological process but the over uptake of heavy metal ions can cause serious cell and organs' defects. The toxic effects of arsenic, mercury, and lead were known from ancient era, but systematic recognition of their toxicity has just appeared from 19th century. Heavy metals can cause serious health defections, including reduced growth and development, cancer, organ damage, nervous system damage, and fatal cases when they tightly bind to and interfere with the functioning of vital cellular components. Exposure to some metals, such as mercury and lead, has been reported to cause development of autoimmunity, in which a person's immune system attacks its own nervous system [1, 2]. The exposure too many heavy metals can lead to extreme chronicle diseases such as rheumatoid arthritis, kidneys malfunctions, and damaging of the embryo. Long-term exposure to toxic heavy metals can have carcinogenic, central and peripheral nervous system and circulatory effects. Infants may receive higher doses of metals from food than adults by mean of intake dose per body weight. To repel bad effect of heavy metals to environment and health, many laws of controlling heavy metal discharge were applied in countries world-wide to minimize exposure to hazardous heavy metals and their derivatives. This includes limits on the types and concentration of heavy metals that may be present in the discharged wastewater, engine exhausted gas, and industrial

dust. The maximum contaminant level (MCL) standards, for those heavy metals, established by United States Environmental Protection Agency (USEPA) [2] are summarized in table 1.

Table 1: The MCL standards authorized for the most hazardous heavy metals by USEPA [2]

Heavy metal	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, human carcinogen	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	0.00003

Most heavy metals can easily be soluble to aquatic environment by dilution processes of industry, and can form many organo-complexes with other organic materials. Once they enter the food chain, large concentrations of heavy metals may accumulate in the organism and human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders [2]. Because of their long-term remaining in living organisms since absorbed, heavy metals are the most hazardous among the chemical waste of industries. Therefore, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment.

1.2. Toxic heavy metal sources

Heavy metal can be found widely on earth surface, some elements are rare to expose at outer rock layer, but some elements are abundant. The natural geological processes like earth quake, volcanic burst, erosion of surface and ground water can bring heavy metal from deeper ground layer to surface [1]. Recently, modern industries and mine exploring activities of human are more and more actively scattering the contamination of heavy metal to ecosystem than any times of civilizations. The industrial wastewater streams containing heavy metals are produced from different industries. For examples, electroplating and metal surface treatment processes generate significant quantities of wastewaters containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium) from a variety of applications. Another significant source of

heavy metals wastes results from printed circuit board (PCB) manufacturing. Other sources for the heavy metal wastes include: the wood processing industry where a chromated copper-arsenate wood treatment produces arsenic-containing wastes; inorganic pigment manufacturing produces pigments that contain chromium compounds and cadmium sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and ferro-cyanide. All of these industries generate large quantity of wastewaters, residues, and sludge that can be categorized as hazardous wastes requiring extensive waste treatment [1-3].

1.3. Conventional heavy metal treatment methods

The conventional processes for removing heavy metals from wastewater include many processes such as chemical precipitation, flotation, adsorption, ion exchange, and electrochemical deposition [1, 2]. These processes have significant disadvantages, which are, for instance, incomplete removal, high-energy requirements, and production of toxic sludge. Chemical precipitation is the most widely used for heavy metal removal from inorganic effluent. The conceptual mechanism of heavy metal removal by chemical precipitation is presented in Eq. 1 [4].

$$M^{2+} + 2(OH)^- \leftrightarrow M(OH)_2 \downarrow \qquad (1)$$
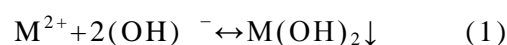
Where M^{2+} and OH^- represent the dissolved metal ions and the precipitant, respectively, while $M(OH)_2$ is the insoluble metal hydroxide.

Adjustment of pH to the basic conditions (pH 9-11) is the major parameter that significantly improves heavy metal removal by chemical precipitation (Fig. 1). Lime (Ca(OH)$_2$ solution) and limestone (CaCO$_3$) are the most commonly employed precipitant agents due to their availability and low-cost in most countries [6]. Lime precipitation can be employed to effectively treat inorganic effluent with a metal concentration of higher than 1000 mg/L. Other advantages of using lime precipitation include the simplicity of the process, inexpensive equipment requirement, and convenient and safe operations. However, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are its excessive sludge production that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal [7]. With the use of large amount co-precipitation agents to treat mine discharge water, the recycling of rare noble metal amount in the sludge is more complicated or impossible in almost cases. Membrane separation has been increasingly recently used for the treatment of inorganic effluent due to its convenient operation. There are different types of membrane filtration such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) [2].
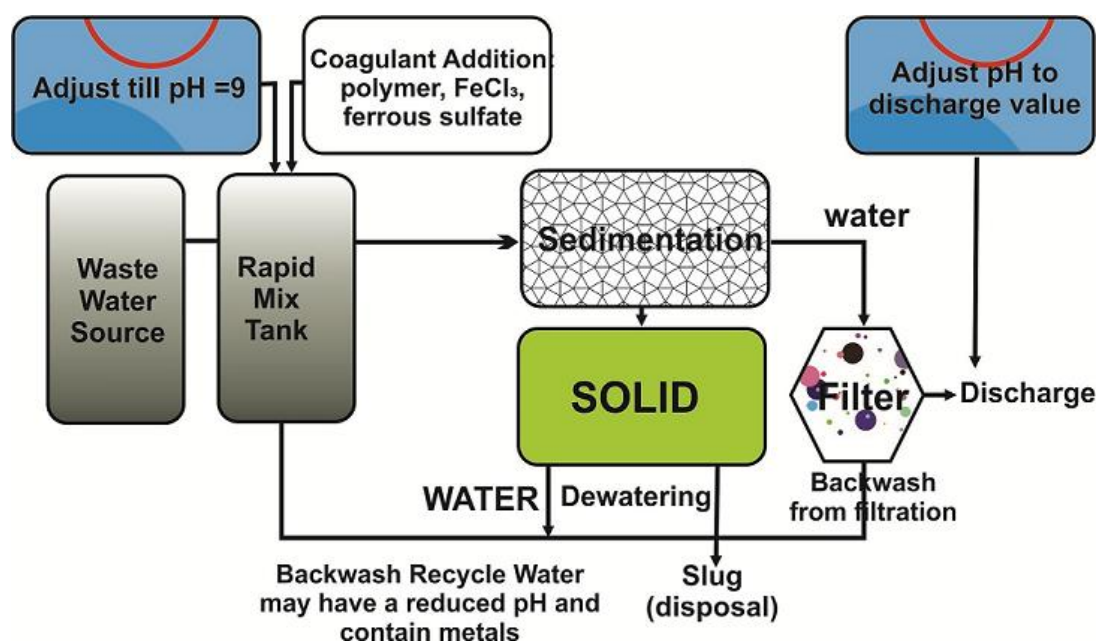

Figure 1: Processes of a conventional metals precipitation treatment plant [5]

Recently, numerous approaches have been studied for the development of cheaper and more effective solutions, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent. Electrotreatments such as electrodialysis [8] has also contributed to environmental protection. Photocatalytic process is an innovative and promising technique for efficient destruction of pollutants in water [9]. Adsorption has become one of the alternative treatments, in recent years, the search for low-cost adsorbents that have metal-binding capacities has intensified because they require lower operation energy but provide higher recyclability [10]. To date, the heavy metal adsorptive function has been developed for a wide range of materials including clays, minerals, polymeric materials of chemical or biological origin, industrial by-products, agricultural wastes, and chemically modified biomass [2].

1.4. Evaluation of conventional heavy metals removal methods

In general, physico-chemical treatments offer various advantages such as their rapid process, convenience in operation and manipulation. Unlike biological system, physico-chemical treatments can accommodate variable input loads and flow such as seasonal flows and complex discharge. However, the convenience of each method is outweighed by a number of drawbacks such as their high operational costs due to the chemicals used, high-energy

consumption and handling costs for sludge disposal. With reduced chemical costs (such as utilizing of low-cost adsorbents) and a feasible sludge disposal, physico-chemical treatments still stand as one of the most suitable treatments for inorganic effluent [2]. For instance, hydrometallurgy, a classical process to recover metals, is inhibited by the presence of organic compounds and a pre-treatment step, to remove or destroy organics, is generally required, pyro-metallurgy which is able to decontaminate systems from organic pollutants and recover metals suffers from lack of controllability, demanding extremely high temperatures. The photocatalytic methods to treat such complex systems can give more advanced results while consume photons from the UV-near visible region. These photo catalysts serve as electron relays, from the organic substrates to metal ions. Thus, they induce both degradation of organic pollutants and recovery of metals in one-pot systems, operable at traces of the target compounds (less than ppm). The advantages and disadvantages of each general method are listed in table 2.

Table 2: The main advantages and disadvantages of the various physico-chemical methods for heavy metals treatment in wastewater

No.	Treatment method	Advantages	Disadvantages
1	Chemical precipitation (Kurniawan et al., 2006)	Low-cost, simple operation	Sludge generation, extra operational cost for sludge disposal, co-precipitation of wanted noble metal ion
2	Adsorption by adsorbents (Babel and Kurniawan, 2003; and Aklil et al., 2004)	Low-cost, easy operating conditions, having wide pH range, high metal-binding capacities	Low selectivity, production of waste products
3	Membrane filtration (Kurniawan et al., 2006)	Small space requirement, low pressure, high separation selectivity	High operational cost due to membrane fouling
4	Electrodialysis (Mohammadi et al., 2005)	High separation selectivity	High operational cost due to membrane fouling and energy consumption
5	Photocatalysis (Barakat et al., 2004; and Kajitvichyanukula et al., 2005)	Removal of metals and organic pollutant simultaneously, less harmful by-products	Long operation time, limited applications

Among chemico-physical methods, the ones using adsorbent are desirable for low operating energy and recyclability. The main disadvantages of almost all adsorption methods are the low selectivity to the wide range of metal ion and complicated in material preparation. In wastewater containing heavy metals with other organic pollutants, the presence of one species usually impedes the removal of the other. Although many adsorbents can be employed for the treatment of inorganic effluent, we prefer the multifunctional materials which are not only suitable to apply on real environment condition but also satisfy demand of cost efficiency as well as the ease in manipulation. Overviewing through various innovative utilization of heavy metals ion removal materials in industrial wastewater treatments, irritation leaking treatments, and drinking water treatments, we highlight the application of polymeric and composite materials as absorbent supporters for heavy metals removal. The polymeric material can be produced both from chemical processes and/or extraction of biomass. Hydrophilic polymer can adsorb heavy metal ions as their functional groups allow ions to be hold inside their matrix. Besides, polymers' chemical moieties and physical properties can be conveniently altered by chemical techniques to enhanced adsorption properties. Through the structure manipulation, polymer matrix can support for metal ion absorbent in many ways as the mechanic holder, stabilizer, selective retender, and antioxidant. In this overview, we also describe the preparations as well as heavy-metal-adsorbing performances of this material class.

2. UTILIZATION OF SYNTHETIC POLYMERIC MATERIALS AS HEAVY METAL ADSORBENTS

2.1. Artificially-crosslinked hydro-gels

The hydro-gels are crosslinked polymers, which contain several hydrophilic moieties, are capable of expanding their volumes due to their high swelling in water. Accordingly, they are widely used in the purification of wastewater. Various hydro-gels were synthesized and their adsorption behavior for heavy metals was investigated as for example Kesenci et al. (2002) prepared poly(ethyleneglycoldimetha-crylate-co-acrylamide) hydro-gel beads with the following metals in the order Pb(II) > Cd(II) > Hg(II) [11]; Essawy and Ibrahim (2004) studied poly(vinylpyrrolidone-co-methylacrylate) hydro-gel with Cu(II) > Ni(II) > Cd(II) [12] or Barakat and Sahiner (2008) synthesized poly(3-acrylamidopropyl)trimethyl ammonium chloride hydro-gels for As(V) removal [13, 14].
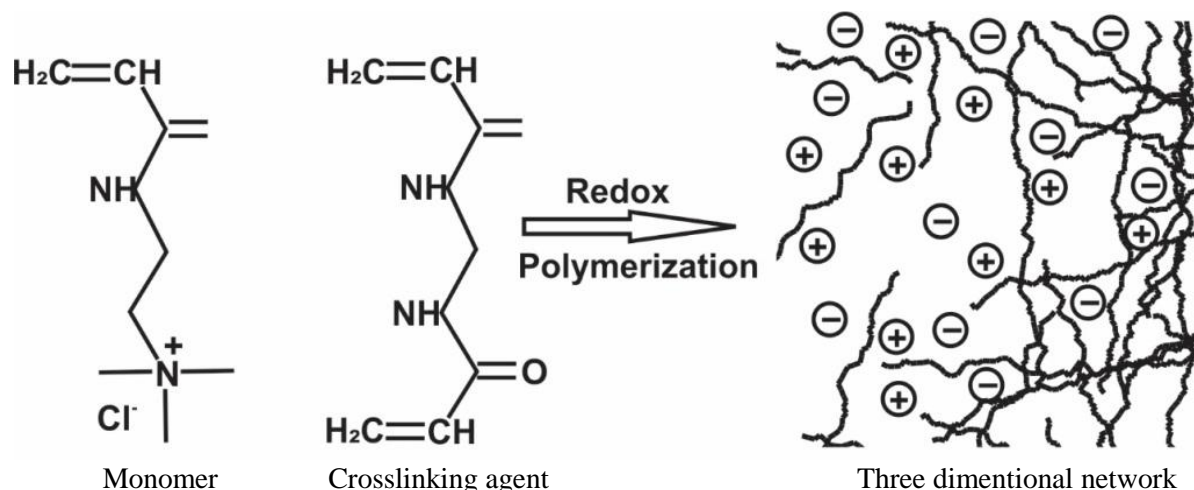

Figure 2: Three-dimensional network formation of cationic hydro-gel [13]

The removal is basically governed by the water diffusion into the hydro-gel, carrying the heavy metals inside especially in the absence of strongly binding sites. Maximum binding capacity increases in acid environment when pH is equal to 6.

Figure 2 shows the schematic representation of polymerization/crosslinking reaction that results in three-dimensional network formation of cationic hydro-gel, while the isothermal adsorption of As(V) onto the hydro-gel is shown in figure 3.
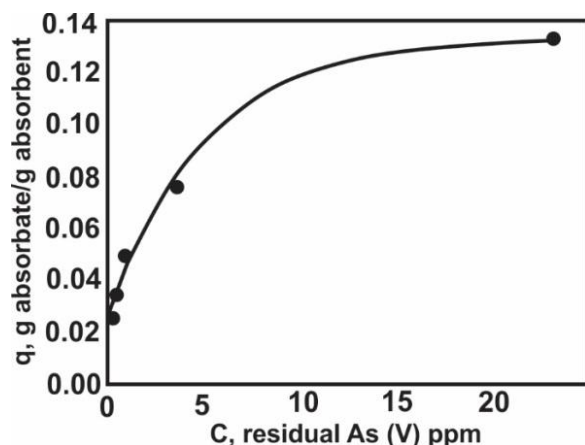

Figure 3: Adsorption of As (V) onto the hydro-gel of poly(vinylpyrrolidone-co-methylacrylate) [14]

2.2. Selective imprinted polymeric adsorbents

Molecularly Imprinted Polymerization (MIP) technique involves the process of binding templates molecules or ions in the polymer matrix during polymerization following by the removal of the template in post-polymerization to generate cavities.

The left cavities in polymer matrix have the complementary in morphology and chemical moieties with the templates therefore they act as the selective factors toward the predetermined molecules or ions of the template. Recently, molecular imprinting polymerization is recognized as a technique for ready preparation of polymeric materials containing recognition sites of predetermined specificity. The preparation conditions of metal ion-imprinted polymers should consider the nature of the polymer or monomer, metal ion concentration, polymer-monomer composition and degree of crosslinking, which may influence their affinity and selectivity towards metal ions were studied by in many researches. Fig. 4 describes the preparation and operation of imprinted polymeric adsorbent.

The interesting results of imprinted binary polymer system are their selectivity toward

multivalent metal ions such as Co^{2+}, Ni^{2+}, Cu^{2+} and Pb^{2+}. Msagati et al. (2014) summarized metal ion-imprinted polymerization of some common industrial polymers like poly (vinyl alcohol) (PVA), polyacrylamide (PAAc), polypropylene and their binary system of high hydrophobicity linker such as 2-Acrylamido-2-methyl propane sulfonic acid (AMPS). In these polymerizations, Acrylic acid (AAc) and Acrylamide (AAm) monomers were

prepared in presence of metal ions and N, N'-methylene bisacrylamidecross-linker. The affinity of PVA towards Co or Ni was enhanced by mixing it with AAc, AAm and AMPS. Such affinity was improved in the order PVA/AAm < PVA/AAc < PVA/AMPS. Co- or Ni-imprinted PVA/AAc has a great affinity towards Co rather than Ni, when these metal ions exist in a mixture.
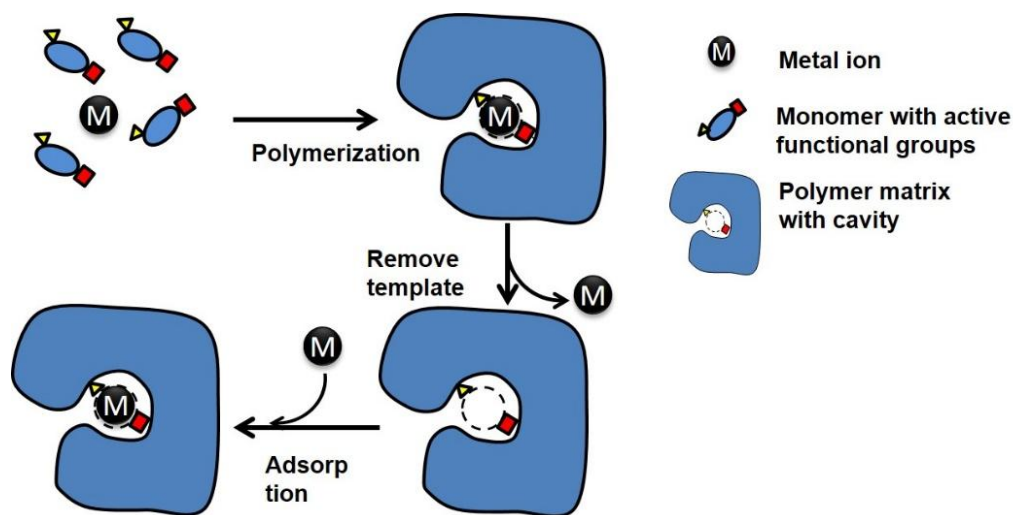

Figure 4: Preparation and operation of imprinted polymeric adsorbent [15]

2.3. Hydrophilic surface on polymeric supporter by radiation induced grafting

Radiation-induced grafting is a powerful technique for the preparation of novel materials based on easily available and low cost synthetic and natural polymers. Radiation provides a highly advantageous means of grafting. A large concentration of free radicals is produced in the irradiated material without the use of chemical initiators and these radicals undergo reaction with a monomer of choice to produce macromolecular chains that are covalently bound to the irradiated specimen. The materials to be developed by radiation-induced grafting include special adsorbents and membranes for use in environmental and industrial applications.

Grafting is used in situations where the requirements for bulk properties and surface properties cannot be readily met using a single polymeric material. Different geometries, including films, powders and macroscopic objects, have had surface grafted layers attached in this way. Direct radiation grafting technique used to graft for several plastic polymers such as epoxies, nylons, polyvinyl

alcohol, polyethylene, polypropylene (etc.) was made for supporting heavy metals removal [16-18]. Ether rings and amine rings, which can form specific chelation with metal ions, are often employed to conjugate with a polymer substrate. Fig. 5 demonstrates a conjugation process to introduce ether rings onto polymeric fiber surface through radiation-induced activation step.

The grafting of glycidyl methacrylate (GMA) monomer containing epoxy ring was performed onto polypropylene (PP) fiber by Abdel-Rehim et al. [16]. The ring opening of the epoxy ring in (GMA) by different amino groups was performed to introduce various chelating agents on to polypropylene surface. The characterization and some selected properties of the prepared grafted fibers were studied and accordingly the possibility of its practical use for water treatment from iron and manganese metals was investigated. Besides, the synthesis of highly selected polymers prepared from Poly (vinyl alcohol) (PVA), 2-Acrylamido-2-methyl propane sulfonic acid (AMPS) and grafted with Acrylic acid (AAc) or Acrylamide (AAm) monomers using γ-rays as initiator and their characteristics as well as were studied; the possibility of their applications in

the selective removal of some heavy metals were investigated. A great ability to recover the metal ions such as: Ni^{+2}, Co^{+2}, Cu^{+2} and Cr^{+3} from their solutions by prepared grafted hydro-gel was reported. It was found that AMPS content in the graft copolymers is the main effective parameter for the selectivity of the copolymer towards metal ions. The higher the AMPS content the higher the selectivity towards Co and Ni ions.

Preparation of a novel adsorbent by grafting amino-terminated hyper-branched polymer to abundantly available cotton fibers and the adsorption of heavy metal ions from aqueous solution was reported by Chen et al. 2011 [17]. The amino-terminated hyper-branched polymer was grafted to the oxidized cotton fibers, and the adsorbent with amino-terminated hyper-branched polymer was successfully obtained. The grooves on the surface of the grafted cotton fiber were filled with amino-terminated hyper-branched polymer. The adsorption experiments show that the adsorption amount of Cu^{2+} and Pb^{2+} was up to 16.1 mg/g and 13.4 mg/g with the metal ion concentration of 319.5 ppm and 315.9 ppm, respectively. When the dosage of adsorbent was 1.5 g in 100 mL metal ion solution, the adsorption rate of Cu^{2+} and Pb^{2+}reached 73.5 wt. % and 71.2 wt.%, respectively. The use of the adsorbent for the removal of metal ions is considered to be efficient and have great potential for practical.
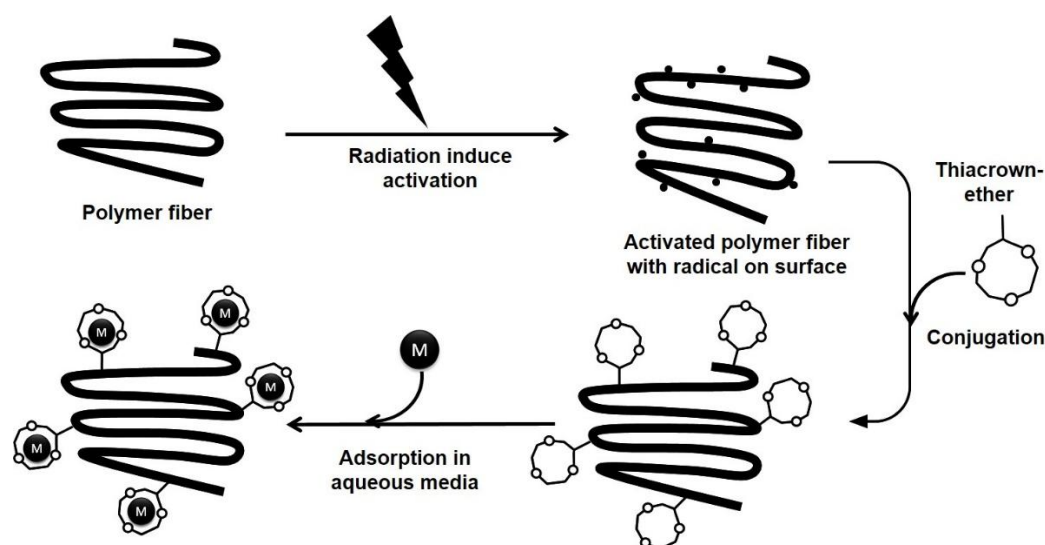

Figure 5: Preparation of thiacrown-grafting polymer through a radiation induced activation and its selective adsorption toward metal ions

Synthetic fibers such as nylon-6, polyesters, woven and knitted fabrics have excellent tensile strength owing to their high molecular-weight and crystallinity. Those fibers are often used for textile according to high durability and surface ratio. However, synthetic fabrics' surface shows very less hydrophylicity due to their high crystallinity, making them less active in aqueous environment. By grafting with suitable hydrophilic materials, the textile fabrics can be converted to good metal ion adsorbents. For this purpose, modified Nylon-6, polyester woven and knitted fabrics were prepared by means of coating their surface with a layer of aqueous solution of carboxymethyl cellulose (CMC) and acrylic acid (AAc) under cross-linking induced by electron beam [18]. Sayeda M. Ibrahim (2010) described the effect of AAc concentration on the hydrophilic properties of the coated fabrics. The modified materials showed a considerable enhancement in water uptake for nylon-6, followed by polyester woven and polyester knitted fabrics. The performances of the modified textile fabrics were evaluated in terms of the recovery of Cu^{+2} and Cr^{+3} from aqueous solution. It was found that there is a marked increase in the recovery of metal ions when both the immersion time and concentration of AAc are increased. The results obtained showed that there is a good possibility of using such modified textile fabrics for the removal of some heavy metals, such as Cu and Cr.

2.4. Bio- and chemically modified bio-polymers

Biopolymers are industrially attractive because they are, capable of lowering transition metal ion concentrations to sub-part per billion concentrations, widely available, and environmentally safe. Another attractive feature of biopolymers is that they possess

a vast number of different functional groups, such as hydroxyl, sulphonyl and amine, which can increase the efficiency of metal ion uptake and the maximum chemical loading possibility. Massively produced from agriculture and aquaculture wastes, polysaccharides-based-materials are very suitable for heavy wastewater metals treatment in developing countries. In Vietnam, several research group have focus on modification of waste products such as crustacean shells (Trung X. Nguyen et al., 2007), plant cobs (Thieng H. Le et al., 2010), and seed peels (Hung T. Le et al., 2008), for highly efficient heavy metal adsorbents [19-22]. There are two main ways for preparation of adsorbents containing polysaccharide derivatives: (a) crosslinking reactions between the hydroxyl or amino groups of the chains with a coupling agent to form water-insoluble crosslinked networks (gels); (b) immobilization of polysaccharides on insoluble supports by coupling or grafting reactions in order to give hybrid or composite materials, [19-30]. Modification and utilization of biomass-polysaccharide-derivatives were also studied by many researchers in several past decades:

- Chitosan - $(C_6H_{13}O_5N)_n$ is a macromolecule of an N-glucosamine. Containing N-glucosamine units, which are powerful chelating agents, the whole molecule of chitosan interacts very efficiently with transition metal ions [23]. Chitosan can be extracted from crab and shrimp shell wastes; therefore, its adsorptive functionality toward metal ion is intensively studied with expectation of applying for large scale water treatment in countries with high developed fishing and aqua-culture industries.

The sorption mechanisms of amino-polysaccharide-based-materials like chitosan are more complicated as compared with the conventional adsorbents because they implicate the presence of different interactions. For example, metal complexation by chitosan may involve two different mechanisms (chelation versus ion exchange) depending on the pH since this parameter may affect the protonation of the macromolecule. Chitosan is characterized by its high percentage of nitrogen, present in the form of amine groups that are responsible for metal ion binding through chelation mechanisms. Amine sites are the main reactive groups for metal ions though hydroxyl groups, especially in the C-3 position, and they may contribute to adsorption. However, chitosan is also a cationic polymer and its pKa ranges from 6.2 to 7. Thereby, in acidic solutions it is protonated and possesses electrostatic properties. Thus, it is also

possible to adsorb metal ions through anion exchange mechanisms [24].

Chitosan modified with conjugation of thia-crown ethers were prepared by immobilizing the ligands into sol–gel matrix [33]. The competitive sorption characteristics of a mixture of Zn(II), Cd(II), Co(II), Mn(II), Cu(II), Ni(II), and Ag(I) were studied. The results revealed that the thia-crown ethers exhibit highest selectivity toward Ag(I). The modification of Chitosan by polyamide to enhance and for selective separation of heavy metal ions was reported by N. Li, R. Bai (2006). Research of electro-optic analyses indicated that the adsorption of metal ions on chitosan beads was mainly attributed to the amine groups of chitosan, the novel amine-shielded cross-linking method preserved most of the amine groups from being consumed by the cross-linking process and hence improved the adsorption capacity of the cross-linked chitosan beads [25, 28-40].

For these purposes, chitosan matrixes were often manipulated by several cross-linking methods which resulted in hydrogel beads with different swelling degree. The hydrogels were often prepared by the cross-linking with other polymeric substrates like ethylene glycol diglycidyl ether (EGDE) via amine-coupling, then the surfaces of chitosan beads were functionalized by grafting with a hydrophilic species via surface-initiated atom transfer radical polymerization (ATRP) method [40]. It was found that chitosan beads were effective in heavy metal adsorption, the conventional cross-linking method improved the acidic stability of the beads but reduced their adsorption capacity, and the novel amine-shielded cross-linking method retained the good adsorption capacity while it improved the acidic stability of the beads. The grafting of polyacrylamide on chitosan beads not only enhanced the adsorption capacity but also provided the beads with excellent selectivity for mercury over lead ions. Amide groups from the polyacrylamide grafted on the chitosan beads increased the adsorption capacity and also made possible selective adsorption of mercury ions because the amide groups can form covalent bonds with mercury ions.

Sacrans are anionic megamolecules having extremely high molecular weights (*Mw*: 1.6×10^7). Kaneko and Okajima (2009) have described the new megamolecule family "sacrans" extracted from microbial species *Aphanothece* sp found in an isolated Japanese hot-spring. This type of megamolecular polysaccharides is the exo-secreted to protect cells of the microorganisms which inhabit

at some extreme conditions such as high acidity, high toxicity and high temperature. This biopolymer family is composed of various partial structures such as continuous and combination structures of uronic acids and hexoses. Highly swollen sacran gels (swelling degree: 700-800 times of dry weight) were prepared by chemical cross-linking with diamines such as L-lysine. Sacran derivatives gels shrank and clouded in aqueous solutions of In and Gadolinium (Gd) ions and showed more than 100 times adsorption ratios of these metal ions compared with non-cross-linked sacran presumably by lowering distance between uronic acid units [26, 27].

Poly(alginate) (PAL) is a natural hydrophilic colloidal polysaccharide with an abundance of free carboxyl and hydroxyl groups distributed along its backbone. PAL is generally isolated from brown seaweeds and bacteria [28]. Because of its excellent gelation properties, PAL has been widely used in the separation of metal ions from solution [29, 30]. Other advantages of PAL include its stability, good biodegradability and non-toxicity. Interestingly, the gel particles can be formed when meeting the divalent metal ion (Ca^{2+}, Ba^{2+}), which makes the separation of PAL more easy. However, the dense poly(alginate) particles have low adsorption efficiency. Poly-γ-glutamate (PGA) is a natural macromolecular polymer that is synthesized by several gram-positive bacteria from the genus *Bacillus*. PGA has unique physicochemical properties, such as film-forming ability, water-retention capacity, plasticity, and biodegradability [31, 32]. PGA has been widely used in the fields of pharmaceutical manufacturing, food processing, cosmetics production, protection of plant seeds, and water treatment. PGA is an anionic polypeptide produced via the polymerization of glutamates via γ-amide linkages [26]. Each monomer contains a carboxyl group that can chelate with rare earth ions, resulting in the adsorption of REE ions on PGA. However, because of the water solubility a stabilizer should be used to realize the recovery and separation of PGA-REEs from the liquid. Through doping sodium alginate (SA) with poly-γ-glutamate (PGA), an immobilized gel particle material was produced. The composite exhibited excellent capacity for adsorbing rare earth elements (REEs). The amount of La^{3+} adsorbed on the SA-PGA gel particles reached approximately 163.93 mg/g compared to the 81.97 mg/g adsorbed on SA alone [33].

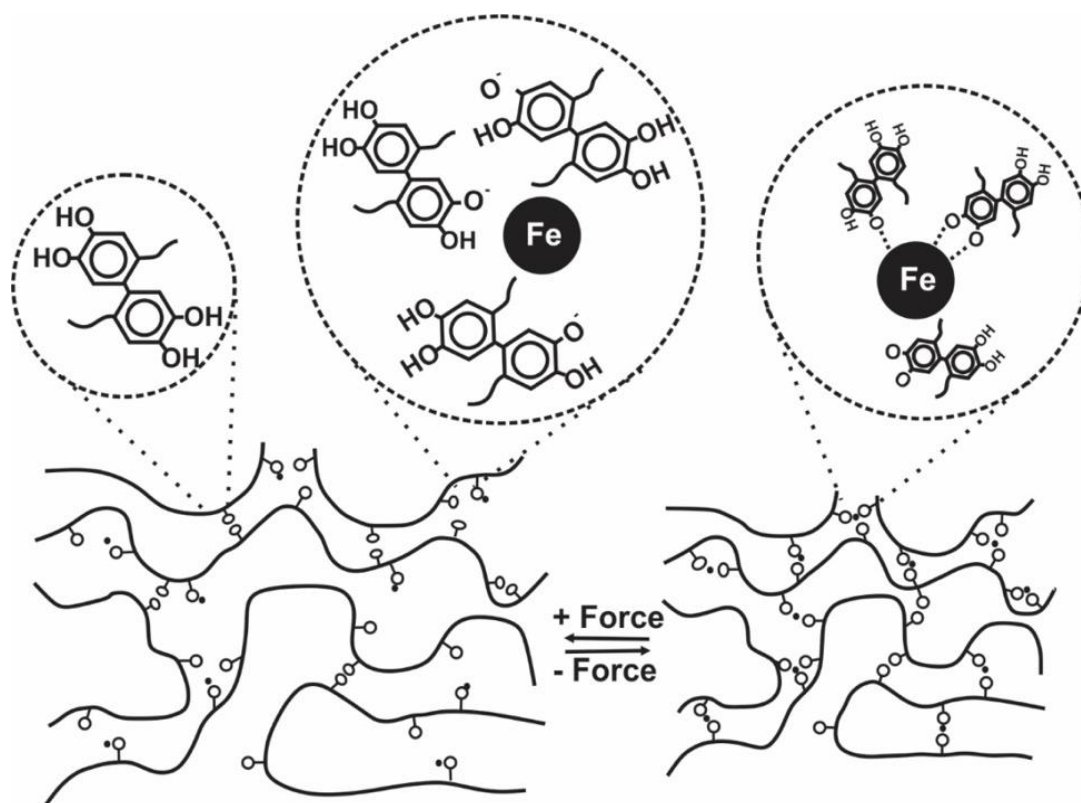*Figure 6:* Adsorption of catechol toward Fe^{+3} [34]

Catechol is polyphenol polymer, rich in mussel species with chemical interactions that vary widely over the pH range. Barrett et al. described how pH influences the mechanical performance of materials

formed by reacting synthetic catechol polymers with Fe^{3+}. Processing Fe^{3+}-catechol polymer materials through a mussel-mimetic acidic-to-alkaline pH change leads to mechanically tough materials based on a covalent network fortified by sacrificial Fe^{3+}-catechol coordination bonds. These findings offer the first direct evidence of Fe^{3+}-induced covalent cross-linking of catechol polymers, reveal additional insight into the pH dependence and mechanical role of Fe^{3+}-catechol interactions in mussel byssi, and illustrate the wide range of physical properties accessible in synthetic materials through mimicry of mussel-protein chemistry and processing. This discovery revealed that selective adsorption of tri valences heavy metal ions on polyphenolic gel polymers can be driven by only adjusting pH [34]

2.5. Selective adsorption of bio polymer-inorganic composite

Beside the chemical modification, the cooperation of inorganic components like micro silica beads, nano clay, and metal oxides can also bring about many specific effect to enhance adsorptive properties of biopolymer matrix. The composites consisting of inorganic-organic components not only exhibit the functionalities of each component but also show new physico-chemical properties resulted by the nano-scale interaction between components' surface. Following composites of such material are selected as the highly selective adsorbent for collecting of noble metal ion as well as heavy metal remediation's.

2.6. DNA-polyamide-silica membrane

DNAs are outstanding candidates for selective accumulation of rare earth metal and heavy metal ions as they contain several multifunctional and repeating chemical moieties on backbone [35]. A DNA-inorganic hybrid film (DNA film) was prepared by mixing DNA and a silane coupling reagent, bis (trimethoxysilylpropyl)amine by Yamada and Abe (2014). This DNA film can accumulate heavy metal ions in aqueous solution. The accumulation of rare earth metal and heavy metal ions using DNA-inorganic hybrid-immobilized glass beads (DNA beads), which were prepared by coating the DNA-inorganic hybrid onto glass beads were demonstrated in the research. When these DNA beads were placed in an aqueous solution of metal ions and incubated for 24 h (batch method), the DNA beads selectively accumulated

heavy metal and rare earth metal ions. The maximum-accumulated amounts of Cu^{2+}, Cd^{2+}, In^{3+}, and La^{3+} were ~1.2, 0.94, 1.6 and 1.3 μmol, respectively, for 1 mg of DNA (3.0 μmol of nucleotide). The molar ratio of DNA to a metal ion was nucleotide: metal ion = 1:0.5. Accumulation of metal ions is performed by a prepared DNA-bead column (DNA column). DNA column effectively accumulated the heavy metal and rare earth metal ions. The DNA column can be recycled simply by washing with an EDTA solution.

2.7. Chitosan-silica beads

Recently other modified chitosan beads were proposed for diffusion of metal ions through crosslinked chitosan membranes [36]. The excellent saturation sorption capacity for Cu(II) with the crosslinked chitosan beads was achieved at pH 5 forming new hybrid materials that adsorb transition metal ions by immobilizing chitosan on the surface of non-porous glass beads. Column chromatography on the resulting glass beads revealed that they have strong affinities to Cu(II), Fe(III) and Cd(II) [32]. There was proposed the use of chitosan derivatives containing crown ether. The materials, with high adsorption capacity for Pb(II), Cr(III), Cd(II) and Hg(II), can be regenerated and their selectivity properties were better than crosslinked chitosan without crown ether [37-39].

2.8. Sacran-clay nano composites

As mentioned previously, sacran is an anionic megamolecular polysaccharide extracted from the cyanobacterium Aphanothece sacrum by Kaneko et al. [41]. Assemble of sepiolite, a fibrous hydrated magnesium silicate, in sacran matrix for the selective uptake of neodymium Sacran, is an interesting functional clay-based bionanocomposites due to its colloidal and metal complexing properties. The bionanocomposite showed some of their special features. Owing the well-known adsorption properties of sepiolite and the ability of sacran to complex rare earth and heavy metal ions, sacran–sepiolite can act as adsorbents of lanthanide ions. Sacran–sepiolite materials show a reasonable selectivity to Nd^{3+} ions over of Ce^{3+}, Eu^{3+} and Gd^{3+} ions.

The assembly of sepiolite within sacran matrix also enhanced mechanic properties of sacran. Sacran–sepiolite films show tensile moduli about twice that of pure sacran films, and improved

resistance and integrity in aqueous solutions. In addition, the selectivity of material was explained by changing of sacran matrix conformation to crystalline domains when anchored by clay bars. Materials prepared from concentrated sacran solutions were rearranged to form liquid crystals by clay bars, and involved remarkable synergistic effect on the retention of Nd^{3+} ions.

3. ABILITY AND APPLICABILITY OF POLYMERIC ADSORBENT FOR COLLECTING NOBLE METAL ELEMENTS

As mentioned in the section above, polymeric adsorbent showed specificity in adsorption of heavy metal ions. The selectivity of polymer matrix depended on their contained chemical moiety such as, amino groups, hydroxyl groups, phenol groups, amide groups, etc. However, the number of functional group distributing on the polymer main chain as well as the interaction between chains can affect the selectivity of polymer matrix greatly toward metal ions by their size, number of charges

and retention behavior. Most of the hydro-gels become gellated when adsorbing multivalences metal ion by means of temporary metal-ion-induced crosslinking between polymer chains. Catechol and sacran showed the high selectivity toward tri-valences metal ion like Nd^{3+}, As^{3+}, Fe^{3+} whereas, the rest polymer material does not show a clear selectivity. The artificial modification of polymer matrix such as radiation induced graft polymer surface and molecular imprinted polymers exhibit very high selectivity. The nano-composite of sacran shows extremely high selectivity to Nd^{3+} because their network only allows the retention of Nd^{3+} inside the matrix when the crystallized regions of sacran are defined by ordering layer of sepiolite clay bars. The DNAs-silica composite has the outstanding adsorption and selectivity as the DNA chain contains specific sequence to each metal ion. Employing the high selectivity of polymeric matrix, we expect the effective method to collect some noble rare-earth metal. The adsorption ability of some representative polymeric adsorbent is listed in table 3.
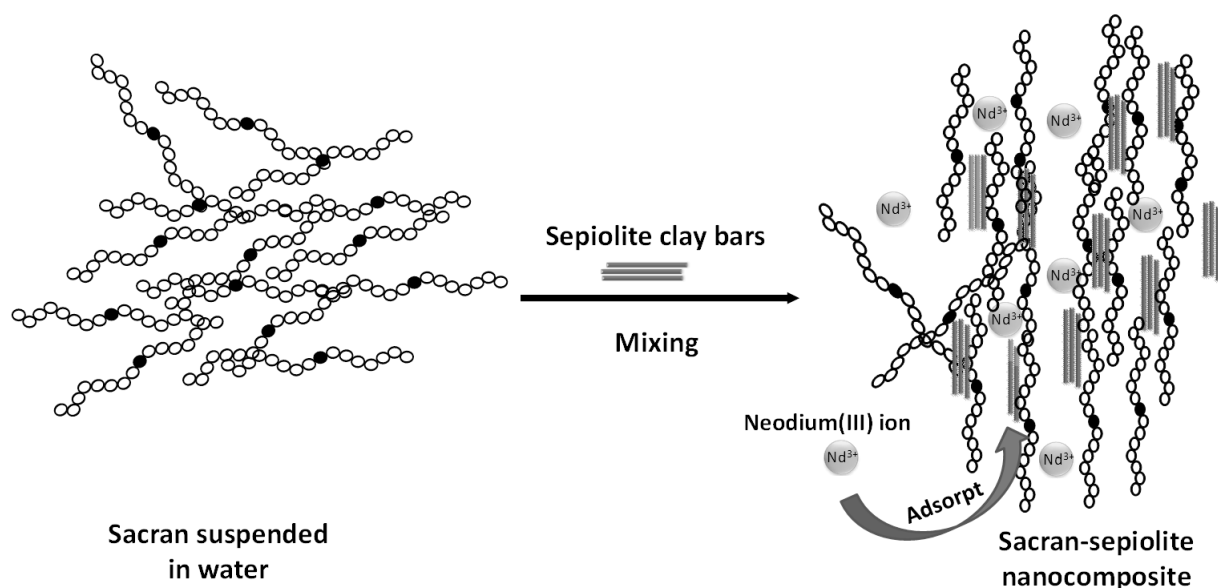

Figure 7: Demonstration of sacran hydro-gel matrix supported by sepiolite clay [41]

4. CONCLUSION

Over the reported results by many researchers, polymeric materials and their composites showed a wide range of chemo-physical properties and performed as the excellent candidates for heavy metal ions remover. The properties of polymeric material are especially diverse by mean of their

structures, chemical moieties and probabilities to be manipulated by chemical techniques. Some class of polymer can be explored from natural by living activities of organism, meaning that the material produced from them are biologically recyclable. With the reduction of chemicals today, using of polymeric materials for large scale heavy metal treatment in water are extremely reasonable because polymer structure can help the absorbent materials to be stabilized in crucial environment conditions. The

support polymer matrix also provides selectivity property for adsorbent materials and brings about the benefit of noble metal ions collecting, such as rare-earth metal, for advanced industries.

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Table 3: Maximum adsorption ability of several prepared polymeric adsorbents to various metal ions

Material	Preparation	Adsorption ability (mg/g)											
		Nd^{3+}	OL(*)	Cd^{2+}	Cu^{2+}	Hg^{2+}	As^{5+}	Pb^{2+}	Ni^{2+}	Cr^{3+}	Mn^{3+}	Co^{3+}	Fe^{3+}
Poly(ethyleneglycoldimethacrylate-co-acrylamide) [11]	Crosslinked gel	-	-	34		90	-	351	-	-	-	-	-
Poly(3-acrylamidopropyl) trimethyl ammonium chloride [13]	Crosslinked gel	-	-	-	-	-	33	-	-	-	-	-	-
poly(vinylpyrrolidone-co-methylacrylate) [12]	Crosslinked gel	-	-	-	4	-	-	-	11	11	-	-	-
Poly(amino-co-polysaccharide) [15]	RG (**)	-	-	-	30	-	-	-	35	-	-	40	-
Hydrophilic textile fibers [17]	RG	-	-	-	16	-	-	12	-	-	-	-	-
GMA/AAc, AMPS, AAM [18]	RG	-	-		5	-	-	-	31	12	35	43	74
Amino-grafted cotton [16]	RG	-	-		26	-	-	-	28	-	-	25	32
Catechol [28]	Bio-/extracted	-	-			-	-	-	-	-	-	-	>10³
Cross linked-chitosan [1]	Bio-/extracted	-	-	150	164	-	230	-	-	-	-	-	-
Poly(alginate)-co- poly(-γ-glutamate) [27]	Bio-/extracted	-	163	-	-	-	-	-	-	-	-	-	-
Crosslinked starch gel [1]	modified-bio	-	-	-	135	-	-	433	-	-	-	-	-
Alumina chitosan [1]	Bio-composite	-	-	-	200	-	-	-	-	-	-	-	-
Sacran/sepiolite [35]	Bio-composite	2x10³	170	-	-	-	-	-	-	-	-	-	-
DNA/Silica gel bead [36]	Bio-composite		182	105	76	-	-	-	-	-	-	-	-

(*) refer to other Lanthanide ions; (**) refer to Radiation-induced grafting method; (+) refer to molecular-imprinted polymerization