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Chapter 8

The Use of Acrylic-Based Polymers in Environmental Remediation Studies

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Additional information is available at the end of the chapter

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Abstract

Heavy metals are not biodegradable and tend to accumulate in living organisms. Many heavy metal ions are known to be toxic or carcinogenic. Thus, removal of these toxic heavy metals from water is of crucial importance to protect the human population and the environment. In recent years, polymeric adsorbents have received considerable interest for heavy metal removal mainly due to important technological and scientific developments such as easy synthesis at controlled dimensions with variable functional groups, perfect mechanical rigidity, tunable surface chemistry, large surface area, pore size distribution, high uptake values and feasible regeneration under mild conditions. This chapter has attempted to present to the readers the widespread investigations of acrylic-based polymeric adsorbents so that the reader can get an idea about the various types and forms of polymeric materials used for the removal of heavy metals from water.

Keywords: acrylics, heavy metal, removal, adsorption, remediation

1. Introduction

Remediation of environmental sources is a very important concern for human beings since these are essential to sustain life [1]. The presence of heavy metal ions in the environment is becoming a serious threat to public health and the environment. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, chlor-alkali, radiator manufacturing, smelting, alloy industries and storage battery manufacture [2]. Most of the heavy metals are toxic, and therefore, their removal from environmental sources is very important [3]. Several methods can be used for the removal of metal ions from water including chemical precipitation, ion exchange, filtration, reverse osmosis,

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adsorption and membrane separation [4]. The advantages and the disadvantages of the various treatment processes used in heavy metal removal are given in **Table 1** [5].

By far, the most widely used method for removing heavy metals from solution is chemical precipitation. The soluble metal is converted into an insoluble precipitate (i.e. its hydroxide) by the increase in the pH of the solution. It is relatively simple and inexpensive to operate. The precipitates can be separated from the water by sedimentation or filtration. The treated water was then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulphide precipitation [5].

Ion exchange is another most widely used method for the removal of heavy metals from the solution [6]. The ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins.

Coagulation-flocculation can also be employed to treat water with heavy metals, wherein the coagulation process destabilises colloidal particles by adding a chemical agent (coagulant) and results in sedimentation [7]. Many coagulants are widely used in the conventional wastewater treatment processes such as aluminium, ferrous sulphate and ferric chloride, resulting in the effective removal of wastewater particulates and impurities by charge neutralisation of particles and by enmeshment of the impurities on the formed amorphous metal hydroxide precipitates. Coagulation is followed by flocculation of the unstable particles in order to increase their size and form into bulky floccules which can be settled out. Today, many kinds of flocculants, such as polyaluminium chloride, polyferric sulphate and polyacrylamide (PAM), are widely used in the treatment of waste water. However, it is nearly impracticable to remove heavy metals very well from waste water directly by these current flocculants.

Flotation is employed to separate solids or dispersed liquids from a liquid phase using bubble attachment [8]. Adsorptive bubble separation employs foaming to separate the metal impurities. Ion flotation, precipitate flotation and sorptive flotation are the main flotation process mechanisms for removal of metal ions from solution. Membrane filtration has received considerable attention for the treatment of inorganic effluent, since it is capable of removing not only suspended solid and organic compounds but also inorganic contaminants such as heavy metals.

Electrochemical methods involve the plating out of metal ions on a cathode surface and can recover metals in the elemental metal state. Electrochemical wastewater technologies involve relatively large capital investment and the expensive electricity supply. The cost factor prevents the usage of this method to be widely applied industrially [9].

Adsorption is now recognised as an effective and economic method for heavy metal wastewater treatment. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. Among these methods, adsorption via the use of adsorbent is one of the most effective methods since it is rapid, economic, effective and easy. In addition, the regeneration of the adsorbent with resultant economy of operation may be possible because adsorption is sometimes reversible [10].

Method	Advantages	Disadvantages
Chemical precipitation	Simple	Needs large amount of chemicals
	Inexpensive to operate	Excessive sludge production
	Convenient and safe	Sludge disposal cost
		High maintenance cost
		Slow metal precipitation
Ion exchange	High removal efficiency	Sensitive to the pH of the solution
	Fast kinetics	
	High treatment capacity	High initial cost
	High regeneration	High maintenance cost
Coagulation-flocculation	Bacterial inactivation capability	High chemical consumption
	Good sludge settling	High maintenance cost
	Good dewatering characteristics	High operation cost
		Increased sludge volume generation
Flotation	Removal of small particles	
	High selectivity to recover valuable ions	High maintenance cost
	Low retention time	High initial capital cost
	Production of more concentrated sludge	High operation cost
	High removal efficiency	
Membrane filtration	Low chemical consumption	Process complexity
	Low solid waste consumption	Limited use
	Small space requirement	High maintenance cost
	Possible to be metal selective	High initial capital cost
		High operation cost
Electrochemical treatment	Rapid	
	Less sludge production	High initial capital cost
	Less chemical use	High energy requirement
	Provide good reduction yields	Requires filtration for flocs
	Moderately metal selective	
Adsorption	High capacity	Performance depends on type of adsorbent
	Flexibility in design and operation	
	Fast kinetics	Chemical derivatization to improve sorption capacity
	Wide variety of target pollutant	

Table 1. Comparison of treatment processes used for heavy metal removal.

In recent years, polymeric adsorbents have received considerable interest for heavy metal removal mainly due to important properties such as easy synthesis at controlled dimensions with variable functional groups, perfect mechanical rigidity, tunable surface chemistry, large surface area, pore size distribution, high uptake values and feasible regeneration under mild conditions. These novel properties allow the polymeric adsorbent to be applied for use in drug delivery systems, optics and water treatment. These can also be incorporated with other particles making them extremely versatile [11].

2. Acrylic-based polymers

Acrylic monomers have been widely utilised for the preparation of polymeric materials that can be used as sorbents in environmental remediation studies due to their valuable characteristics such as water repellence, transparency and good film-forming ability. These have become more widely used in the last decades because they are also environmentally friendly, they offer easier clean-up, and, last but not least, their properties and application performance characteristics have been improved [12]. This section will explain the practical applications of polymeric adsorbents which are synthesised from their acrylic monomers for the removal of heavy metal ions in water.

2.1. Poly(acrylic acid) (PAAc)

Acrylic acid (AA), an important monomer of synthetic resins, is a versatile compound used in polymer synthesis. It has been widely used to fabricate a variety of functional materials, such as water-absorbent polymers, adhesives and textile-treatment agents and so on [13]. Radiation-induced graft polymerisation can be used to modify the polymers to introduce valuable properties to the synthesised materials. The technique is very advantageous over the conventional methods. For example, the chemical and photochemical grafting methods are simple and can be done without employing any additives or catalyst at any temperature [14].

Benamer et al. [15] have modified chitosan beads by a graft copolymerisation reaction of chitosan with AA by gamma radiation, and the removal of Cd and Pb ions from aqueous solutions was examined using the novel adsorbent. Raw chitosan beads were first modified by cross-linking with glutaraldehyde, and the radiation-induced grafting of AA onto the chitosan beads was performed using ^{60}Co gamma-source. The grafting rate of 81% was obtained at a dose rate of 20.64 Gy min^{-1}. The FTIR was used for the structural characterisation of the sorbent, and their swelling measurements were performed at different pH values. The adsorption experiments were carried out both with modified and unmodified chitosan beads for Cd(II) and Pb(II) ions, and it was found that the grafting of new groups increased the number of adsorption sites in chitosan, leading to the increase in adsorption capacity. The optimum pH for Cd(II) and Pb(II) uptake was between 4 and 7 using the synthesised adsorbent. The experimental kinetic data were found to have a better fit with pseudo-second-order reaction, and Langmuir isotherm model was found to be more suitable to represent the experimental equilibrium.

González-Gómez et al. [16] have synthesised two new comb-type hydrogels using two monomers such as AA and 4-vinyl pyridine (4VP) by gamma radiation. The synthesised adsorbents were as follows: (a) Comb-type hydrogels of an AA network followed by grafting of 4VP (net-PAA)-g-4VP and comb-type hydrogels of an AA network grafted onto polypropylene (PP) followed by grafting of 4VP [net-(PP-g-AA)-g-4VP]. The ^{60}Co gamma source was used to synthesise the comb-type systems. The AA in synthesised comb-type hydrogels was capable of removing metals because the ions primarily interact with the carboxyl groups. Moreover, the amino groups in 4VP increased the stability constant and complexation bond strength between the metals and functional groups. The retention of Cu(II) and Zn(II) ions was evaluated by the new adsorbent, and a high adsorption capacity was found through the target ions. The quantification of the metal ions was performed with a colorimetric method using ultraviolet visible (UV-Vis) spectrophotometry. The net-(PP-g-AA)-g-4VP system exhibited better efficiency with Zn(II) ions (up to 90%), whereas the (net-PAA)-g-4VP system exhibited good efficiency for retaining both ions, with approximately 85–90% retention. The equilibrium adsorption capacities of Zn(II) ion were found to be 1086 and 480 mg g^{-1} for net-(PP-g-AA)-g-4VP and (net-PAA)-g-4VP, respectively, which were higher than some results reported in literature. Moreover, adsorption/desorption studies indicated that the regeneration of the adsorbent was possible by altering the pH of the solutions. Freundlich model was the best model to describe the adsorption process, indicating heterogeneous adsorption. In addition, the kinetic results agreed with pseudo-second-order reaction indicating that the retention process occurred by chemisorption.

Radiation-induced graft copolymerisation of AA, styrene (Sty) on poly(N-vinyl-2-pyrrolidon) (PVP), was realised by El-Mohdy et al. [17] to remove Co(II), Cu(II) and Fe(III) metal ions from aqueous solutions. In order to prepare the hydrogels, AA and Sty were mixed together with different monomer feed ratios (AAc:Sty) at room temperature. The PVP (50 wt%) was mixed with these compositions and then irradiated with ^{60}Co gamma rays at a dose rate of 6.13 kGy/h. The obtained hydrogel was washed with ethanol/water mixture to remove unreacted monomer components and then dried in vacuum oven at 40°C. The sulfonation (Sf) (to introduce sulfonic group onto the styrene benzene ring) and alkaline treatment (to convert –COOH group of AA into –COO) were applied in order to functionalise the hydrogels. The success of characterisation of the newly synthesised materials was confirmed using FTIR, UV, thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and X-ray diffraction (XRD) methods. The adsorption experiments of Co(II), Cu(II) and Fe(III) ions from aqueous solutions using the hydrogels were studied in terms of pH, temperature, initial metal concentration, contact time and polymer structure. The metal ion uptake efficiency of PVP/(AA-co-Sty) hydrogel was found to be in the following order: hydrogel treated with NaOH/Sf > hydrogel treated with NaOH > hydrogel treated with Sf > untreated hydrogel. The highest metal ion uptake was observed for Fe(III), and the lowest was observed for Cu(II). It was concluded that the hydrogels could be used as a potential adsorbent for the removal of target ions in environmental studies.

The poly(acrylic acid) (PAA), a polymer containing polar carboxylic functional groups in linear CH_2-CH_2 chain, has a great ability to form complexes with metal ions. It is pH sensitive and belongs to the class of commercial polymers produced on a large scale. It is widely used

in various industries, such as agriculture, medicine, etc., as pharmaceutical carriers, antifouling agents, flocculants and super absorbents [18].

Sezgin and Balkaya [19] have investigated the adsorption of Cu(II), Ni(II), Zn(II) and total Cr [Cr(III) and Cr(VI)] ions using polyacrylic acid hydrogel. The adsorbent was synthesised by free radical participation polymerisation of acrylic acid monomer in the presence of 1 mol% monomer cross-linker [N,N-methylenebisacrylamide (NMBA)], 1 mol% monomer initiator [potassium persulphate ($K_2S_2O_8$)] and an equal weight of accelerator [potassium bisulphite ($KHSO_3$)] under nitrogen atmosphere. The polymeric hydrogel was characterised by FTIR. The surface characteristics of the hydrogel were evaluated using a scanning electron microscopy/energy dispersive X-Ray (SEM/EDX) analysis. The effects of adsorbent amount, contact time and shaking speed were studied using a real wastewater sample. Among the kinetic models investigated, pseudo-second-order model was found to describe the adsorption process since the correlation coefficients of the model are high, and the calculated q_e (amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium) was in good agreement with the experimental ones. Moreover, a multiple diffusion model was determined to be effective in adsorption. Freundlich model was found to represent the adsorption data. Thermodynamic experiments have pointed out a spontaneous and exothermic behaviour. A comparison for the removal of the metal ions was performed for industrial wastewater (IWW) and synthetic wastewater (SWW) samples, and a higher adsorption capacity was found for SWW. According to the results presented in the manuscript, AA hydrogel was found to be as an effective material in order to remove target metal ions from wastewater samples.

The PAA hydrogel beads were also examined as a potential adsorbent for the removal of Pb(II)ion from waste water [20]. The batch-type adsorption was applied, and the effect of pH contact time and temperature was studied. The optimum pH value was found to be 6.3, and the adsorption of Pb(II) increased with increase in temperature and time. The maximum capacity was reached in 24 hours with 113.43 mg g^{-1} value. The adsorption kinetic data were described by the pseudo-first-order kinetic model, and the adsorption isotherm agreed well with the Langmuir model. Moreover, the adsorption process was stated to be spontaneous and endothermic.

Although PAA has a strong ability to form complexes with metal ions, the high water solubility of this polymer hinders its application to remove the metal ions from the aqueous solutions. To overcome these limitations, the polymer was modified with several functional groups or combined with various materials such as clay, chitosan, carbon nanotubes, etc. [21, 22].

A polyacrylic acid–organobentonite nanocomposite (PAA-Bent) was synthesised by the intercalation of cetyl trimethylammonium (CTA) surfactant and polyacrylic acid into the bentonite interlayer spaces. The XRD patterns and FTIR evidences of the novel adsorbent confirmed the success of the synthesis [23]. The newly synthesised material was applied for the removal of Pb(II) ions, and a removal efficiency of 99.6% was achieved by the nanocomposite with a 30-minute contact time for 7.5 g L^{-1} solid-to-liquid ratio and an initial metal concentration of 400 mg L^{-1} at 25°C. The maximum adsorption capacity of the adsorbent was 93 mg g^{-1} which was approximately twice as much as that of untreated Bent (52 mg g^{-1}). It was stated that the superior capacity and affinity of PAA-Bent nanocomposite towards Pb(II) were probably due to

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the complex formation between the polymer carboxyl groups and Pb(II) ions. The kinetics and thermodynamics of Pb(II) adsorption onto bentonite and PAAc-Bent adsorbent were also investigated by the same research group in another study [24]. Batch-type adsorption experiments were conducted at different times, Pb(II) concentrations and temperatures. A fast adsorption (≥99.4% adsorption in 30 min) was observed at low lead concentration due to high complexation affinity between metal ions and reactive functional groups on the surface of PAA-Bent. At higher lead concentrations, more Pb(II) ions were left unabsorbed in solution due to the saturation of binding sites so that the equilibrium time for Pb(II) adsorption by the PAA-Bent nanocomposite increased from ~30 to ~60 min. When the effect of temperature was examined, the adsorption of lead ions increased with increasing temperature both for Bent and PAA-Bent. The equilibrium studies showed that Pb(II) adsorption data on PAA-Bent followed the Langmuir model. The endothermic and spontaneous adsorption of Pb(II) ions for both Bent and PAA-Bent adsorbents was evaluated using thermodynamic studies. The adsorption kinetics of Pb onto PAA-Bent fitted better with the pseudo-second-order and pseudo-first-order kinetic models better than the Elovich and intraparticle diffusion models suggesting that chemi-adsorption controls the adsorption process. These results have indicated that PAA-Bent nanocomposite could be efficiently used as an adsorbent in lead removal studies from waste water.

Shirsath et al. [25] have prepared PAA hydrogel composite by incorporating kaoline (K) clay using ultrasound-induced polymerisation and conventional process. The utility of the synthesised hydrogels has been investigated for the removal of brilliant green (BG) dye. The PAA-K hydrogel was synthesised using AA (monomer), ammonium persulphate (initiator) and sodium dodecyl sulphate (surfactant). The morphology of PAA-K hydrogel was evaluated using FTIR and transmission electron microscope (TEM). The particle size of kaolin clay was measured from the TEM images and found to be in the range of 20–50 nm. The hydrogels were prepared using ultrasound-induced polymerisation and conventional process. The effect of different parameters (pH, temperature, initial dye concentration, quantity of hydrogel and clay content) on the extent of adsorption was examined in batch mode for the hydrogels that were prepared both by using ultrasound-induced polymerisation and conventional process. The concentration of BG dye was measured using UV-Vis spectrophotometer at 624 nm. Better results were obtained for the hydrogel prepared by ultrasound-assisted polymerisation process. The removal of BG dye was found to increase with an increase in pH (till the optimum value of 7), temperature, adsorbent and adsorbate concentrations as well as the kaolin clay content in the hydrogel. It has been observed that the maximum BG dye removal by PAA-K hydrogel was achieved for the initial dye concentration of 30 mg L^{-1} at a temperature of 35°C and pH 7. The pseudo-second-order kinetic model was found to fit the kinetic data. Both Freundlich and Langmuir adsorption isotherm models explained the experimental results satisfactorily. Moreover, the adsorption was spontaneous and endothermic in nature.

The removal of Co(II) from the aqueous solutions was investigated using PAA-grafted multiwall carbon nanotubes (MWCNTs) by Chen et al. [26]. Plasma techniques were applied to graft PAA onto the surface of MWCNTs to improve their dispersion property and adsorption capacity in the aqueous solutions. The characterisation of both raw MWCNT and MWCNT-g-PAA was performed using techniques such as FTIR, TGA, Raman spectroscopy, SEM and TEM. The microstructures of the raw MWCNTs and MWCNT-g-PAAc were observed by SEM

and TEM. An entangled and curled framework was noticed for both of the adsorbents with almost no differences in their surface. A more compact stacking morphology was observed for MWCNT-g-PAA due to the interactions of carboxylic acid groups on the surface of MWCNTs. A very thin layer of grafted PAA was coated on partial external walls of MWCNTs and was investigated with TEM images. The results of FTIR spectra of raw MWCNTs and MWCNT-g-PAA were compared, and MWCNT-g-PAA exhibited a relatively stronger broad peak around 3400 cm^{-1} due to the O–H stretching vibration, which suggests the existence of hydroxyl, the functional group from PAA and chemisorbed water. Moreover, peaks at 3430 cm^{-1} (—OH), 1680 cm^{-1} (C═O), 700 cm^{-1} (—CH_2—) and 1080 and 1200 cm^{-1} (C—O) suggest that PAA was successfully grafted on the surface of raw MWCNTs by the plasma-induced grafting method. The TGA curves have indicated that the carbon impurity (such as amorphous carbon) in MWCNTs used was negligible, and the weight percentage of grafted PAA on the surface of MWCNTs was estimated to be 4.4%. The adsorption capacity of both adsorbents towards Co(II) ions was investigated, and the adsorption parameters (shaking time, pH, ionic strength and temperature) were optimised. A pH-dependent and rapid adsorption was observed. The main adsorption mechanism for Co(II) adsorbed onto MWCNT-g-PAA was stated to be due to the complexation of Co(II) with carboxyl groups on the surface of MWCNT-g-PAA. The spontaneous and endothermic adsorption process was well described by the pseudo-second-order model. As a result, PAA was successfully grafted on the surface of raw MWCNTs and obviously enhanced its adsorption capacity for Co(II) which enables MWCNT-g-PAA as a promising adsorbent in water purification studies.

The effect of contact time, pH, foreign ions and PAA on oxidised MWCNT for the adsorption of Ni(II) was studied by Yang et al. [27]. The adsorbent characterisation was confirmed using FTIR. A rapid equilibration was achieved within 2 hours, and the experimental data were found to fit well by the pseudo-second-order model. The adsorption of Ni(II) on oxidised MWCNTs increased with increasing pH. A positive effect of PAA on Ni(II) adsorption was found at pH < 8, whereas a negative effect was observed at pH > 8. The effect of addition sequences of PAA/Ni(II) on the adsorption of Ni(II) to PAA-MWCNT hybrids was also studied. The results indicated that the adsorption of Ni(II) was influenced by the addition sequences obviously. The Ni(II) adsorption on oxidised MWCNTs was dependent on foreign ions at low pH values and independent of foreign ions at high pH values. The adsorption of Ni(II) on oxidised MWCNTs was stated to complicate and was attributed to surface complexation and ion exchange. The synthesised materials were found to be suitable adsorbents for the solidification and preconcentration of Ni(II) from aqueous solutions.

2.2. Polyacrylamide (PAM)

Polyacrylamide (PAM) is a water-soluble polymer, containing large number of amide groups as side groups, can be grafted onto various matrices and be used in environmental remediation studies as adsorbent [28].

Liu and Guo [29] have synthesised PAM-grafted attapulgite (ATP) nanofibrils by the surface-initiated atom transfer radical polymerisation of acrylamide from the modified surfaces of the fibrillar clays. The elemental analysis, FTIR, TGA and TEM were used to characterise

the synthesised adsorbent. The percentage of grafting (PG%) was calculated from the results of the elemental analysis, and polymerisation time has been found to increase PG%. The adsorption capacity of both bare ATP and PAM-ATP was evaluated both for mercury and dyes (methylene blue and methyl orange). It was evaluated that surface graft polymerisation of acrylamide enhanced the adsorption capacity towards mercury and methylene blue but not methyl orange.

Kaşgöz et al. [30] have modified PAM hydrogels by Mannich reaction using different amine compounds, namely, diethylenetriamine (DETA), ethylenediamine (EDA) and triethylenetetramine (TETA), and sulfomethylation reaction. The FTIR was used to characterise the adsorbents. Moreover, basic group content (BGC) and hydroxymethyl group content (HMG) and the equilibrium degree of swelling (EDS) were evaluated. These results indicated that the amine value (AV) of the adsorbents increased with time, temperature and amine amount. The adsorbents synthesised were used for the removal of Cu(II), Cd(II) and Pb(II) ions in competitive or non-competitive conditions, and the effect of pH and adsorption rate was investigated. It was observed that the removal capacities of the adsorbents changed mainly according to their AV, BGC and EDS. Moreover, the Mannich products were selective towards Cu(II) ion, and the sulfomethylation products were highly selective to Pb(II) ions. Furthermore, regeneration studies were performed to demonstrate the practical use of the adsorbents.

The hydroxamic acid–modified polyacrylamide/Fe_3O_4 adsorbent (M-PAM-HA) was synthesised by Zhao et al. by microemulsion polymerisation with acrylamide determined [31]. Its structure was characterised by various methods (XRD, FTIR, TGA, SEM, EDS, zeta potential), and its swelling and iron-leaching properties were also determined. Batch-type adsorption experiments were applied in order to investigate the removal efficiency of the adsorbent towards Cd(II), Pb(II), Co(II) and Ni(II) ions. The adsorption kinetic experiments revealed that the results are best correlated with the pseudo-second-order model indicating that the rate-controlling step was chemisorption. Moreover, the equilibrium data have shown that Sips isotherm model best fitted with the experimental results rather than Freundlich and Langmuir isotherm models. The adsorption mechanism was elucidated both with FTIR and theoretical calculations, and it was proposed that the carbonyl and hydroxyl groups formed stable five-membered ring chelates with divalent metal ions. Moreover, 0.1 M Na_2EDTA was found to regenerate the adsorbent efficiently which shows that the novel adsorbent has great potential in wastewater treatments.

In a study by Yavuz et al. [32], polyacrylamide was grafted onto cross-linked poly(4-vinyl pyridine) (P4-VP-g-PAm) and used only for the purpose of mercury removal from water samples at mg L^{-1} concentration levels. Yayayürük et al. [33] have used the same adsorbent, for the first time, for the selective preconcentration of Hg(II) prior to cold-vapour atomic-fluorescence measurements, and separate determinations of Hg(II) and MeHg(I) at the trace level were performed at a ng L^{-1} level. In addition, adsorption isotherms were studied, and the affinity of the adsorbent to several metal ions, such as Pb(II), Zn(II), Cu(II), Cd(II) and Fe(III), was investigated. The developed method was also applied to the determination of Hg(II) and MeHg(I) in sea water and estuarine water. The high uptake capacity of the adsorbent allowed the quantitative retention of Hg(II) in water samples, which is very important in Hg-polluted matrices.

2.3. Poly(glycidyl methacrylate) (PGMA)

The use of poly(glycidyl methacrylate) (GMA) has become very attractive as an adsorbent in environmental remediation studies during the last years because of its high tensile strength, porous structure and resistance to acid and alkaline media. Moreover, GMA can be readily modified by chemical reaction and grafting. The GMA functional group can be easily transformed into urea, pyrazole, amines, iminodiacetic, pyridine groups, etc. due to the epoxy group in GMA molecule [34].

Nastasovic et al. [35] have synthesised macroporous cross-linked poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) and poly(GMA-co-EGDMA) with different porosities by suspension copolymerisation and functionalised with ethylene diamine and diethylene triamine. These have elucidated the kinetics of the adsorbents towards hexavalent chromium [Cr(VI)] under both competitive and non-competitive conditions. The competitive kinetics was studied with several multicomponent solutions. A very fast Cr(VI) uptake was observed in non-competitive conditions due to the amino groups present at the adsorbent's surface. It was found that the adsorption of Cr(VI) was much slower from their binary solutions than from single-component solution. This situation was pronounced due to competition of the metals for the active sites of the adsorbents. The pseudo-second-order model was determined to best fit with adsorption data meaning that adsorption depends both on the properties of the metal and the adsorbent. Nastasovic et al. [36] have also functionalised macroporous poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) (PGME) by reacting the pendant epoxy groups with diethylene triamine (PGME-10/12-DETA) and investigated the adsorption mechanism of the adsorbent towards Cu(II), Cd(II) and Pb(II) ions in aqueous solution. The FTIR, X-ray photoelectron spectroscopy (XPS), SEM-EDX and atomic force microscopy (AFM) were used to elucidate the adsorption mechanism before and after interaction of PGME-10/12-DETA with the target ions. The XPS and FTIR analyses suggest that complexation through the formation of metal–O and metal–N bonds with the -OH, -NH and $-NH_2$ groups as the possible mechanism of Cu(II), Cd(II) and Pb(II) adsorption on sample PGME-10/12-DETA. The AFM images indicate that the metal adsorption induces change in the size and morphology of the amino-functionalised PGME. The time required to reach 50% of the total adsorption capacity was 5 min for all the investigated metal ions. Already after 30 min, PGME-10/12-DETA attained approximately 90%, and after 180 min, 95% of metal ions with maximal capacity was adsorbed. The pseudo-first-order, pseudo-second-order and surface reaction-based kinetic models were fitted to the experimental data, and the pseudo-second-order model was found to describe adsorption kinetics for all metal ions.

A magnetic glycidyl methacrylate resin was synthesised by Elwakeel et al. [37] for the removal of Hg(II) in industrial waste water. The adsorbent was synthesised by coating a magnetite core with glycidyl methacrylate–based polymer. Further, it was grafted with diethylene triamine (DETA). The characterisation methods (SEM, SEM-EDX, FTIR, BET and TEM) used indicated the successful synthesis of the polymer. The absence of coercivity and remanence in vibrating sample magnetometry (VSM) analysis confirmed that the material has super paramagnetic properties. The effects of pH, counter ions, adsorbent amount and the temperature were investigated. Moreover, reaction kinetics and adsorption isotherms were studied.

The maximum adsorption capacity was obtained at a pH of ~4. The adsorption kinetics and isotherms were best fitted with the pseudo-second-order model and Langmuir equation, respectively. Thermodynamic studies indicated that adsorption of Hg(II) by the adsorbent is exothermic and spontaneous with increased randomness. The desorption from the adsorbent was realised with KI or KI-thiourea mixture, and at least four cycles of adsorption/desorption were obtained with the proposed adsorbent. Two industrial effluents were used for the removal of Hg(II), and satisfactory results were obtained.

In a recent work by Şenkal and Bıçak, glycidyl methacrylate (GMA)-methyl methacrylate (MMA)-divinylbenzene (DVB) terpolymer having diethylenetriamine tetra acetic acid (DTTA) as a functional group was synthesised and used for the efficient removal of Ca(II) and Mg(II) ions from water [38]. The cross-linked terpolymer beads were prepared by suspension polymerisation of GMA (0.4 mol), MMA (0.5 mol) and DVB (0.1 mol) mixture and have been modified through epoxy functional groups in two steps: (i) by treating with excess of diethylene triamine (DETA) and (ii) by subsequent reaction with potassium chloroacetate. The resulting polymer possesses DTTA functional groups (with a degree of functionalisation, DF: 1.70 mmol g^{-1}). The polymeric adsorbent was separated into different particular sizes within the range of 125–250 μm by steel sieves prior to use. This novel adsorbent was also used for the removal of Hg(II) and Cu(II) ions in aqueous solution. In order to clarify the adsorption process with the novel adsorbent, the effect of pH, contact time and adsorbent amount was elucidated. The adsorption process was then investigated in terms of Langmuir and Freundlich isotherms to characterise the uptake of target ions by the adsorbent. In addition, the affinity of the adsorbent to several metal ions was investigated. The developed method was also applied to the determination of Hg(II) and Cu(II) in water samples. According to the obtained results, the polymeric adsorbent was proposed as a promising adsorbent for the removal of target ions in contaminated water [39, 40].

2.4. Poly(methyl methacrylate)

Poly(methyl methacrylate) (PMMA) is an important member in the family of poly(acrylic ester(s)). It was found to have widespread use due to its desirable properties such as good solvent resistance, excellent optical transparency, low cost and good flexibility [41].

Al-Muhtaseb et al. [42] have evaluated the adsorption potential of PMMA to remove phenol from water. The PMMA was polymerised using atom transfer radical polymerisation (ATRP) technique. The percentage conversion of the methyl methacrylate monomer was determined by weighing the dried polymer. Both ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of the adsorbent were recorded. Moreover, FTIR spectra of the adsorbent were taken before and after adsorption with phenol to check the functional groups of the materials. Batch-type adsorption was applied at various temperatures (25–55°C), initial phenol concentrations (10–90 mg L^{-1}) and contact times (15 min to 4.5 hours). Phenol adsorption was found to increase with increase in contact time and initial phenol concentration. The data were best correlated with the pseudo-second-order kinetic model. From the intraparticle diffusion and Boyd models, the adsorption of phenol on PMMA was shown to be governed by film diffusion. Both Freundlich and Redlich-Peterson isotherm models were found to describe the

adsorption data. Thermodynamic parameters indicated that the adsorption process is exothermic and spontaneous in nature and higher ambient temperature results in more favourable adsorption [42].

Although PMMA is non-toxic, easy to obtain, cheap and being insoluble in water, its brittle texture and low thermal and mechanical stability are the disadvantages of this material. To overcome these drawbacks, several chemicals such as mesoporous silica or carbon were added to the polymer matrix that will result in an increase both in thermal and mechanical behaviour and its physical performance. Salisu et al. [43] have synthesised a novel adsorbent, sodium alginate-graft-poly(methyl methacrylate) (Alg-g-PMMA) in the form of calcium cross-linked beads and utilised for the removal of Pb(II) in aqueous solution. The beads were formed using a simple encapsulation method that enables the ionic interactions between glutaronate blocks of the graft copolymer and calcium ions. The FTIR, SEM and particle size analyser were used to characterise the adsorbents. The beads owing a spherical shape, rough surface and porosity having a mean size of ~1.2 mm were obtained. The adsorption process was found to depend on the initial pH and Pb(II) concentration. The optimum pH for the adsorption of the metal ions was found to be 4.0. The Langmuir model was found to describe the adsorption data with a maximum adsorption capacity of 526 mg g^{-1}. Moreover, the adsorption followed a pseudo-second-order kinetic model. HNO_3 (0.1 M) was used in the regeneration studies. The results showed that the material proved to be excellent in the removal of the Pb(II) ions after nine cycles with no significant loss of adsorption capacity.

The oxidative-free radical-graft copolymerisation reaction was applied in order to synthesise a novel adsorbent, poly(methyl methacrylate)-grafted alginate/Fe_3O_4 nanocomposite for the removal of Pb(II) ions in aqueous solution [44]. The FTIR, XRD, SEM, TEM, TGA and DSC were employed to characterise the adsorbent. The adsorption feasibility of the adsorbent towards Pb(II) and Cu(II) ions was investigated in terms of pH, contact time, initial metal concentration and adsorbent dose. The adsorption of Pb(II) and Cu(II) was found to be pH dependent, and a pH 5 was found to be optimum for both of the metal ions. An increase was observed in the adsorption capacity of the adsorbent as the metal concentrations increase. This was due to the electrostatic interactions between metal ions and adsorbent, which involves active sites of progressively lower affinity for the heavy metal ions up to the saturation point. Moreover, the amount of metal ions was adsorbed rapidly at the initial stages of the adsorption process due to the availability of binding sites of the adsorbent, but as time went by, the adsorption slowed down before reaching equilibrium at about 180 min. The adsorption capacity of the adsorbent was increased with increasing the temperature indicating an endothermic nature of the adsorbent. The pseudo-first-order and pseudo-second-order Elovich and Weber-Morris intraparticle diffusion models were investigated to elucidate the adsorption kinetics, and the data were best described with the pseudo-second-order kinetic model. The experimental data were also investigated using Langmuir, Freundlich, Sips and Temkin models, and the data were best followed by the Freundlich model. The desorption of Pb(II) and Cu(II) was carried out by using 0.1 M HCl solution. The comparison of the adsorbent was done with some studies in literature, and it was found that the adsorbent exhibited a very good adsorption capacity towards Pb(II) and Cu(II). Therefore, the present adsorbent can be utilised for successful removal of these metal ions from industrial wastewater samples.

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The poly(ethylene imine) (PEI)-immobilised PMMA microspheres were synthesised by Duru et al. [45] by suspension polymerisation and subsequent modifications. The SEM and elemental analysis were performed to characterise the adsorbent. The free amine content of the PEI-immobilised PMMA microspheres was determined by potentiometric titration. The extent of removal of copper, cadmium and lead ions was evaluated with different initial amounts of metal ions (50–600 mg L^{-1}) and at several pH values (3.0–7.0). The adsorption of heavy metal ions on the unmodified PMMA microspheres was very low. But, PEI-immobilised PMMA microspheres exhibited a higher adsorption capacity due to the presence of the metal-chelating ligand PEI on the surface of the adsorbent. The adsorption capacities increased with increasing pH, and an optimum pH value of 5.5 for Cu(II) and Pb(II) and 6.0 for Cd(II) was evaluated. The affinity order of adsorption was Cd(II) > Cu(II) > Pb(II). The experimental data were found to be consistent with the Langmuir model.

2.5. Poly(n-butyl acrylate) (PBA)

Poly(n-butyl acrylate) can also be used in adsorption studies since its homopolymer had a low glass transition temperature and hydrophobic characteristics. These two important properties make it to be tailored to several materials (e.g. chitosan and zeolite), and thereby, the mechanical properties and water resistance properties will be improved in the final product [46].

Kumar et al. [47] have applied a novel microwave-assisted method for the preparation of n-butyl acrylate–grafted chitosan and used it as an adsorbent in Cr(VI) removal studies. Three minutes of irradiation time was applied to prepare the adsorbent. The analysis of chromium was performed spectrophotometrically at 540 nm by complexation of Cr(VI) with diphenylcarbazide. The surface characterisations of the adsorbent and the mechanism of the adsorption process were achieved using techniques, namely, FTIR, XRD and SEM/EDS. Moreover, XPS spectra of the n-butyl acrylate-grafted chitosan before and after adsorption with Cr(VI) were assessed. It was evaluated that the adsorption mechanism involved the electrostatic interaction between hydrochromate anion and the amino hydroxyl groups of the adsorbent. An effective adsorption was achieved at a pH of 3.5 with 25 mL of 20 mg L^{-1} Cr(VI) solution. The Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Elovich and Redlich isotherms were studied in detail. A Langmuir adsorption capacity of 17.15 mg g^{-1} was attained, and the negative entropy change obtained in the study was due to the decrease in randomness at adsorbent-solution interface. The pseudo-second-order kinetics and spontaneous exothermic adsorption process were evaluated in the study. The quantitative desorption of chromium was achieved with ammonium hydroxide. Finally, n-butyl acrylate-grafted chitosan was proposed as a promising adsorbent in chromium removal in real samples.

The Cr(VI) removal was also studied using chitosan-g-poly(butyl acrylate)/silica gel (Cs-g-PBA/SG) nanocomposite in aqueous solution. The modification of chitosan was achieved by graft copolymerisation with butyl acrylate, and glutaraldehyde cross-linked silica gel/chitosan-g-poly(butyl acrylate) nanocomposite was synthesised by sol-gel method. The particle size of the prepared Cs-g-PBA/SG nanocomposite was found to be 615.1 nm. The BET-specific surface area and average pore radius were determined by BET experiment and found to be 95.9044 m^2 g^{-1} and 1.7787 nm, respectively. The FTIR spectrum of bare Cs-g-PBA copolymer

and Cs-g-PBA/SG nanocomposite before and after chromium adsorption was studied to analyse the reaction routes of the modification and adsorption process. The surface morphology of the Cs-g-PBA/SG nanocomposites obtained with SEM indicated that the nanocomposite was composed of particles of different shapes and sizes. The surface characterisation methods appeared to indicate that chromium ions were adsorbed via binding to the abundant –OH, –NH and C═O sites available in the composite prepared using sol-gel process which offered the possibility to tailor silica porosity and modulate the diffusion properties of the composites. Batch-type experiments were also conducted to investigate the effect of contact tine, adsorbent dose and pH, and the optimum values were found to be 120 min, 4 g and 7.0, respectively. The Langmuir model agreed well with the experimental data with a maximum adsorption capacity of 55.71 mg g^{-1}. Moreover, the kinetic data followed pseudo-second-order model. The authors have concluded that Cs-g-PBA/SG nanocomposite is an excellent adsorbent for Cr(VI) removal from waste water [48].

Nithya and Sudha have also synthesised chitosan-g-poly(butyl acrylate)/bentonite nanocomposite and used for the removal of Cr(VI) and Pb(II) ions from tannery industrial waste water. The samples collected were also analysed for total hardness, turbidity, total solids, total dissolved solids, total suspended solids, chemical oxygen demand, biochemical oxygen demand, salinity and electrical conductivity. Batch-type adsorption experiments were conducted, and the influence of different experimental parameters on adsorption, such as pH (2–8), contact time (1–6 hours) and adsorbent amount (1–6 g), was evaluated. The maximum removal percentage (97.81%) of Cr(VI) in the tannery industrial waste water was found at an optimum adsorbent dosage of 5 g, contact time of 4 hours and pH of 3. Therefore, chitosan-g-poly(butyl acrylate)/bentonite nanocomposite was proposed as a promising adsorbent for target ions removal [49].

2.6. Poly(2-hydroxyethyl methacrylate) (PHEMA)

2-Hydroxyethyl methacrylate (HEMA) is an important functional monomer which is widely used in the manufacture of soft contact lenses. Although PHEMA homopolymer was hydrophilic and has a high degree of hydration, it is not water soluble [50]. Poly(2-hydroxyethyl methacrylate) (PHEMA) is a biocompatible polymer, which is sensitive to pH and temperature and swells in water to form hydrogel. It has been used in dentistry, ophthalmic, scaffold, drug delivery and neutral tissue engineering [51].

Kharismadewi et al. [51] have synthesised graphene oxide-poly(2-hydroxyethyl methacrylate) composite (GO-PHEMA) by dispersion polymerisation in supercritical CO_2 and used for the removal of methylene blue (MB) in aqueous solutions. For this purpose, graphite was oxidised to GO using the modified Hummer's method to have the functional groups of epoxides, hydroxyls and carboxylic acids. The epoxide and hydroxyl groups were located on the GO surface, whereas carboxylic acid was located near the edges. From the –OH group, modification occurred, where silane coupling agent, 3-(trimethoxysilyl)propyl methacrylate (MPTMS), reacted to produce the vinyl groups as the tail of GO. After modification with MPTMS, GO-MPTMS was polymerised with HEMA monomer by dispersion polymerisation in supercritical CO_2 using 2,2′-azobisisobutyronitrile as the initiator. The GO-PHEMA composite as

an adsorbent formed a gel in an aqueous solution that provides benefit in the separation of adsorbent. The FTIR, TGA, SEM and XPS were used to confirm the existence of the grafted polymer onto the GO. The composite exhibited an improved thermal loss temperature and a decelerated decomposition rate than GO and GO-MPTMS. The adsorption behaviour of the adsorbent was investigated for the removal of MB from the aqueous solution as a function of the adsorbent concentration, contact time, pH and initial dye concentration. It was evaluated that 99.8% of MB was removed by the adsorbent under the optimum conditions (adsorbent dosage of 15 mg at pH 7, a contact time of 45 min and an initial dye concentration of 10 mg L^{-1} at 25°C). The stability investigation showed that the composite still can remove 81.9% of MB from the solution after six cycles. The adsorption isotherm parameters were fitted well with the Freundlich adsorption isotherm owing a R^2 value of 0.975 and the maximum predicted adsorption capacities of 39.41 mg g^{-1} at 25°C. The adsorption kinetic studies showed that the adsorption behaviour followed a pseudo-second-order model. Furthermore, the thermodynamic studies showed that the adsorption process of MB onto the adsorbent was spontaneous and endothermic in nature with the highest adsorption efficiency observed at 45°C.

Denizli et al. [52] have synthesised poly(hydroxyethyl methacrylate-N-methacryloyl-(L)-glutamic acid) [poly(HEMA-MAGA)] beads by suspension polymerisation for the removal of lead ions. Copolymer MAGA acted as the metal-complexing ligand and polymerised with HEMA. Therefore, the need for the leakage of metal complexing ligand was not necessary. The adsorbent was characterised with FTIR and ^{1}H NMR. The surface area of the poly(HEMA-MAGA) beads was measured by the BET method. The water uptake ratio, elemental analysis and surface morphology of the beads were also evaluated. Batch-type adsorption was used for the removal of Pb(II) ions, and the effect of pH (2.0–7.0) and initial ion concentration (10–500 mg L^{-1}) were determined. Sixty minutes was found to be enough to reach equilibrium. The adsorption of Pb(II) ions increased with increasing pH and reached to a plateau value at a pH of 5.0. It was evaluated that incorporation of MAGA into the polymer structure increased the lead adsorption capacity, ca. tenfold. The adsorption capacities of the poly(HEMA-MAGA) beads for Cd(II), Pb(II) and Hg(II) from synthetic waste water were determined, and the affinity order of adsorption was found as Cd(II) > Pb(II) > Hg(II). The consecutive adsorption and elution cycles indicated the feasibility of repeated use meaning that the newly synthesised beads have a great potential for industrial heavy metal removal applications.

2.7. Polyacrylonitrile (PAN)

Polymers based on acrylonitrile (AN) are easy to prepare and present a reactive pendant cyano group, which can be modified by introducing new functional groups by nucleophilic addition and cycloaddition reactions. In general, AN polymers and copolymers for adsorbent are synthesised through suspension polymerisation to give spherical beads which can be readily handled. The porous-chelating resins can adsorb metal ions more efficiently because the existence of pores would provide convenient diffusion channels for metal ions into the interior of the resins when they are used in adsorption of metal ions in aqueous solution [53].

Godjevargova et al. [54] have synthesised five types of adsorbents from polyacrylonitrile (PAN) by varying its concentration and the composition of the coagulation bath, aiming to

achieve different porous structures in the modified adsorbents. The SEM analysis was applied to identify the porous structure of the adsorbents, and specific area, pore volume and pore radius were determined using a porosimeter. The sodium hydroxide and hydroxylamine were used to modify the adsorbents in order to introduce amidoxime and carboxylic groups into the adsorbent. The ability of the modified adsorbents through Cu(II), Ni(II), Zn(II) and Pb(II) ions was determined, and the highest adsorption with respect to all metal ions was achieved at pH values of 3–4. In addition, a rapid (20 min) metal uptake took place in all cases studied. The order of metal uptake for all types of PAN adsorbents was determined as Cu(II) > Ni(II) > Zn(II) > Pb(II). The EDTA was found to desorb the metal ions from the adsorbents. As a result, it was found that the synthesised adsorbents have good adsorption characteristics and are good candidates for the removal of Cu(II), Ni(II), Zn(II) and Pb (II) ions from aqueous solution.

Amine-containing resins based on PAN were synthesised through chemical modifications of PAN with diethylene triamine (DETA) by Kiani et al. [55]. The modified PAN resins (PAN-DETA50 and PAN-DETA150) were used as adsorbent for the removal of Hg(II), Fe(III), Pb(II), Ag(I) and Zn(II) from aqueous solution. The FTIR, SEM and TGA were used to study the surface morphology of the adsorbents. Moreover, the amine content of the resins was determined by titration. The TGA and FTIR spectroscopy study on metal-resin complexes showed the presence of metal ions in PAN-DETA complexes. The SEM micrographs clarified that there are no drastic differences in morphology of resins when compared with unmodified PAN (except PAN-DETA-Zn). The adsorption behaviour of the resins studied for all metal ions confirmed that they have acceptable adsorption capacities. In addition, the adsorption of metal ions was examined under different pH conditions, and it was seen that adsorption was increased with increasing pH values [55].

3. Conclusions

The rise in industrial, medical, technological and domestic activities has led to huge increases in the levels of heavy metals which have serious impacts on both human health and environment. Therefore, the demand for reducing the effects of potential pollutants has increased throughout the world by improving existing techniques and introducing novel adsorbent materials. The preparation of such materials which can remove toxic heavy metals from aqueous media is still a continuing objective of environmental remediation efforts, particularly where there is a need to enhance the adsorption capacity and metal ion specificity. Recently, researchers have focused on polymeric adsorbents for separation and purification purposes due to their valuable advantages such as relatively easy regeneration, perfect mechanical rigidity, vast surface area, adjustable surface chemistry, simple processing and possibility to shape them into most suitable form (e.g. sheets, beads and membranes). This chapter highlighted the practical applications of acrylic-based polymers for the removal of heavy metals ions in water. In summary, it was clearly seen that there is still a need to develop new adsorbents for the removal of heavy metals to introduce simple, rapid and quantitative methods that can be applied in environmental remediation studies.

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References

[1] Gupta VK, Gupta M, Sharma S. Process development for the removal of lead and chromium from aqueous solution using red mud—An aluminum industry waste. Water Research. 2001;**35**(5):1125-1134. DOI: 10.1016/S0043-1354(00)00389-4

[2] Hegazi HA. Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. HBRC Journal. 2013;**9**:276-282. DOI: 10.1016/j.hbrcj.2013.08.004

[3] Barakat MA. New trends in removing heavy metals from industrial wastewater. Arabian Journal of Chemistry. 2011;**4**:361-377. DOI: 10.1016/j.arabjc.2010.07.019

[4] Fu F, Wang Q. Removal of heavy metal ions from wastewaters: A review. Journal of Environmental Management. 2011;**92**:407-418. DOI: 10.1016/j.jenvman.2010.11.011

[5] O'Connell DW, Birkinshaw C, O'Dwyer TF. Heavy metal adsorbents prepared from the modification of cellulose: A review. Bioresource Technology. 2008;**99**:6709-6724. DOI: 10.1016/j.biortech.2008.01.036

[6] Shukla A, Zhang YH, Dubey P, Margrave JL, Shukla SS. The role of sawdust in the removal of unwanted materials from water. Journal of Hazardous Materials. 2002;**95**(1-2): 137-152. DOI: 10.1016/S0304-3894(02)00089-4

[7] Charerntanyarak L. Heavy metals removal by chemical coagulation and precipitation. Water Science and Technology. 1999;**39**:135-138. DOI: 10.1016/S0273-1223(99)00304-2

[8] Rubio J, Souza ML, Smith RW. Overview of flotation as a wastewater treatment technique. Minerals Engineering. 2002;**15**(3):139-155. DOI: 10.1016/S0892-6875(01)00216-3

[9] Chen GH. Electrochemical technologies in wastewater treatment. Separation and Purification Technology. 2004;**38**:11-41. DOI: 10.1016/j.seppur.2003.10.006

[10] Babel S, Kurniawan TA. Low-cost adsorbents for heavy metals uptake from contaminated water: A review. Journal of Hazardous Materials. 2003;**97**:219-243. DOI: 10.1016/S0304-3894(02)00263-7

[11] Reddy BSR, Kulasekaran S, Reddy CR, Rajadurai S, Joseph KT, Santappa M. Treatment and disposal of tannery effluents by polymeric scavengers. Leather Science. 1977;**24**:378-383

[12] Choung JH, Lee YW, Choi DK. Adsorption equilibria of toluene on polymeric adsorbents. Journal of Chemical Engineering Data. 2001;**46**(4):954-958. DOI: 10.1021/je000282i

[13] Zhang X, Lin L, Zhang T, Liu H, Zhang X. Catalytic dehydration of lactic acid to acrylic acid over modified ZSM-5 catalysts. Chemical Engineering Journal. 2016;**284**:934-941. DOI: 10.1016/j.cej.2015.09.03

[14] Nasefa MM, Hegazy EA. Preparation and applications of ion exchange membranes by radiation-induced graft copolymerization of polar monomers onto non-polar films. Progress in Polymer Science. 2004;**29**:499-561. DOI: 10.1016/j.progpolymsci.2004.01.003

[15] Benamer S, Mahlous M, Tahtat D, Nacer-Khodja A, Arabi M, Lounici H, Mameri N. Radiation synthesis of chitosan beads grafted with acrylic acid for metal ions sorption. Radiation Physics and Chemistry. 2011;**80**:1391-1397. DOI: 10.1016/j.radphyschem.2011.06.013

[16] González-Gómez R, Ortega A, Lazo LM, Burillo G. Retention of heavy metal ions on comb-type hydrogels based on acrylic acid and 4-vinylpyridine synthesized by gamma radiation. Radiation Physics and Chemistry. 2014;**102**:117-123. DOI: 10.1016/j.radphyschem.2014.04.026

[17] El-Mohdy HLA, Hegazy EA, El-Nesr EM, El-Wahab MA. Metal sorption behavior of poly(N-vinyl-2-pyrrolidone)/(acrylic acid-co-styrene) hydrogels synthesized by gamma radiation. Journal of Environmental Chemical Engineering. 2013;**1**:328-338. DOI: 10.1016/j.jece.2013.05.013

[18] Wang B, Wang YP, Zhou P, Liu ZQ, Luo SZ, Chu W, Guo Z. Formation of poly(acrylic acid)/alumina composite via in situ polymerization of acrylic acid adsorbed within oxide pores. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2017;**514**:168-177. DOI: 10.1016/j.colsurfa.2016.11.051

[19] Sezgin N, Balkaya N. Adsorption of heavy metals from industrial wastewater by using polyacrylic acid hydrogel. Desalination and Water Treatment. 2016;**57**:2466-2480. DOI: 10.1080/19443994.2015.1030453

[20] Mouayad QAA, Nagam SAA, Ahmed MAA. Evaluation of poly acrylic acid(PAA) hydrogel beads as adsorbent for the removal of lead(II) ion from water. Journal of Al-Nahrain University. 2013;**16**(3):30-39

[21] Marcelo GV, Antonio GBP, André RF, Antônio CNA, Francisco HAR. Methylene blue adsorption on chitosan-g-poly(acrylic acid)/rice husk ash superabsorbent composite: Kinetics, equilibrium, and thermodynamics. Water, Air, & Soil Pollution. 2017;**228**:1-14. DOI: 10.1007/s11270-016-3185-4

[22] Liu Y, Wang W, Wang A. Adsorption of lead ions from aqueous solution by using carboxymethyl cellulose-*g*-poly (acrylic acid)/attapulgite hydrogel composites. Desalination. 2010;**259**(15):258-264. DOI: 10.1016/j.desal.2010.03.039

[23] Rafiei HR, Shirvani M, Ogunseitan OA. Removal of lead from aqueous solutions by a poly(acrylic acid)/bentonite nanocomposite. Applied Water Science. 2016;**6**:331-338. DOI: 10.1007/s13201-014-0228-0

[24] Rafiei HR, Shirvani M, Ogunseitan OA. Kinetics and thermodynamics of Pb sorption onto bentonite and poly(acrylic acid)/bentonite hybrid sorbent. Desalination and Water Treatment. 2016;**57**:22467-22479. DOI: 10.1080/19443994.2015.1130655

[25] Shirsath SR, Patil AP, Patil R, Naik JB, Gogate PR, Sonawane SH. Removal of brilliant green from wastewater using conventional and ultrasonically prepared poly(acrylic acid) hydrogel loaded with kaolin clay: A comparative study. Ultrasonics Sonochemistry. 2013;**20**:914-923. DOI: 10.1016/j.ultsonch.2012.11.010

[26] Chen H, Li J, Shao D, Ren X, Wang X. Poly(acrylic acid) grafted multiwall carbon nanotubes by plasma techniques for Co(II) removal from aqueous solution. Chemical Engineering Journal. 2012;**210**:475-481. DOI: 10.1016/j.cej.2012.08.082

[27] Yang S, Li J, Shao D, Hu J, Wang X. Adsorption of Ni(II) on oxidized multi-walled carbon nanotubes: Effect of contact time, pH, foreign ions and PAA. Journal of Hazardous Materials. 2009;**166**:109-116. DOI: 10.1016/j.jhazmat.2008.11.003

[28] Manju GN, Krishnan KA, Vinod VP, Anirudhan TS. An investigation into the sorption of heavy metals from wastewaters by polyacrylamide-grafted iron(III) oxide. Journal of Hazardous Materials. 2002;**91**:221-228. DOI: 10.1016/S0304-3894(01)00392-2

[29] Liu P, Guo J. Polyacrylamide grafted attapulgite (PAM-ATP) via surface-initiated atom transfer radical polymerization (SI-ATRP) for removal of Hg(II) ion and dyes. Colloids and Surfaces A: Physicochemical Engineering Aspects. 2006;**282-283**:498-503. DOI: 10.1016/j.colsurfa.2006.02.052

[30] Kaşgöz H, Özgümüş S, Orbay M. Modified polyacrylamide hydrogels and their application in removal of heavy metal ions. Polymer. 2003;**44**:1785-1793. DOI: 10.1016/S0032-3861(03)00033-8

[31] Zhao F, Tang WZ, Zhao D, Meng Y, Yin D, Sillanpää M. Adsorption kinetics, isotherms and mechanisms of Cd(II), Pb(II), Co(II) and Ni(II) by a modified magnetic polyacrylamide microcomposite adsorbent. Journal of Water Process Engineering. 2014;**4**:47-57. DOI: 10.1016/j.jwpe.2014.09.003

[32] Yavuz E, Senkal BF, Bicak N, Poly(acrylamide) grafts on spherical polyvinyl pyridine resin for removal of mercury from aqueous solutions. Reactive & Functional Polymers. 2005;**65**:121-125. DOI: 10.1016/j.reactfunctpolym.2004.12.006

[33] Yayayürük O, Henden E, Bicak N, Determination of mercury(II) in the presence of methylmercury after preconcentration using poly(acrylamide) grafted onto cross-linked poly(4-vinyl pyridine): Application to mercury speciation. Analytical Sciences. 2011;**27**(8):833-838. DOI: 10.2116/analsci.27.833

[34] Suárez E, Paredes B, Rubiera F, Rendueles M, Villa-Garcia MA, Diaz JM. Functionalized glycidyl methacrylate based polymers as stationary phases for protein retention. Separation and Purification Technology. 2002;**27**:1-10. DOI: 10.1016/S1383-5866(01)00163-0

[35] Nastasovic AB, Ekmescic BM, Sandic ZP, Ran–delovic DV, Mozetic M, Vesel A, Onjia AE. Mechanism of Cu(II), Cd(II) and Pb(II) ions sorption from aqueous solutions by macroporous poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate). Applied Surface Science. 2016;**385**:605-615. DOI: 10.1016/j.apsusc.2016.05.165

[36] Nastasovic A, Sandic Z, Surucic L, Maksin D, Jakovljevic D, Onjia A. Kinetics of hexavalent chromium sorption on amino-functionalized macroporous glycidyl methacrylate copolymer. Journal of Hazardous Materials. 2009;**171**:153-159. DOI: 10.1016/j.jhazmat.2009.05.116

[37] Elwakeel KZ, Guibal E. Potential use of magnetic glycidyl methacrylate resin as a mercury sorbent: From basic study to the application to wastewater treatment. Journal of Environmental Chemical Engineering. 2016;**4**:3632-3645. DOI: 10.1016/j.jece.2016.08.001

[38] Şenkal BF, Biçak N. Glycidyl methacrylate based polymer resins with diethylene triamine tetra acetic acid functions for efficient removal of Ca(II) and Mg(II). Reactive and Functional Polymers. 2001;**49**(2):151-157. DOI: 10.1016/s1381-5148(01)00075-x

[39] Yayayürük O, Yayayürük AE, Removal of Cu(II) from water samples using glycidyl methacrylate-based polymer functionalized with diethylenetriamine tetraacetic acid: Investigation of adsorption characteristics. Water, Air & Soil Pollution. 2016;**227**:244-256. DOI: 10.1007/s11270-016-2943-7

[40] Yayayürük O, Yayayürük AE, Karagöz B, Bıçak N. Preconcentration of mercury(II) from waters using glycidyl methacrylate-methyl methacrylate-divinyl benzene terpolymer with diethylenetriamine tetra acetic acid functions prior to inductively coupled plasma mass spectrometric determination. Desalination and Water Treatment. 2016;**57**:27834-27842. DOI: 10.1080/19443994.2016.1178176

[41] Cifçi C, Durmaz O. Removal of heavy metal ions from aqueous solutions by poly(methyl m ethacrylate-co-ethyl acrylate) and poly(methyl methacrylate-co-buthyl m ethacrylate) membranes. Desalination and Water Treatment. 2011;**28**:255-259. DOI: 10/5004/dwt.2011.2174

[42] Al-Muhtaseb AH, Ibrahim KA, Albadarin AB, Ali-khashman O, Walker GM, Ahmad MNM. Remediation of phenol-contaminated water by adsorption using poly(methyl methacrylate) (PMMA). Chemical Engineering Journal. 2011;**168**:691-699. DOI: 10.1016/j.cej.2011.01.057

[43] Salisu A, Sanagi MM, Naim AA, Ibrahim WAW, Karim KJA. Removal of lead ions from aqueous solutions using sodium alginate-graft-poly(methyl methacrylate) beads. Desalination and Water Treatment. 2016;**57**:15353-15361. DOI: 10.1080/19443994.2015.1071685

[44] Mittal A, Ahmad R, Hasan I. Poly (methyl methacrylate)-grafted alginate/Fe3O4 nanocomposite: synthesis and its application for the removal of heavy metal ions. Desalination and Water Treatment. 2016;**57**:19820-19833. DOI: 10.1080/19443994.2015.1104726

[45] Duru PE, Bektaş S, Genç Ö, Patir S, Denizli A. Adsorption of heavy metal ions on poly(ethylene imine)-immobilized poly(methyl methacrylate) microspheres. Journal of Applied Polymer Science. 2001;**81**:197-205. DOI: 10.1002/app.1429

[46] Anbinder P, Macchi C, Amalvy J, Somoza A. Chitosan-graft-poly(n-butyl acrylate) copolymer: Synthesis and characterization of a natural/synthetic hybrid material. Carbohydrate Polymers. 2016;**145**:86-94. DOI: 10.1016/j.carbpol.2016.02.072

[47] Kumar ASK, Kumar CU, Rajesh V, Rajesh N. Microwave assisted preparation of n-butyl-acrylate grafted chitosanand its application for Cr(VI) adsorption. International Journal of Biological Macromolecules. 2014;**66**:135-143. DOI: 10.1016/j.ijbiomac.2014.02.007

[48] Nithya R, Gomathi T, Sudha PN, Venkatesan J, Anil S, Kim S. Removal of Cr(VI) from aqueous solution using chitosan-g-poly(butylacrylate)/silica gel nanocomposite. International Journal of Biological Macromolecules. 2016;**87**:545-554. DOI: 10.1016/j.ijbiomac.2016.02.076

[49] Nithya R, Sudha PN. Removal of heavy metals from tannery effluent using chitosan-g-poly(butylacrylate)/bentonite nanocomposite as an adsorbent. Textiles and Clothing Sustainability. 2016;**2**(7):1-8. DOI: 10.1186/s40689-016-0018-1

[50] Robinson KL, Khan MA, de Paz Banesez MV, Wang XS, Armes SP. Controlled polymerization of 2-hydroxyethyl methacrylate by ATRP at ambient temperature. Macromolecules. 2001;**34**:3155-3158. DOI: 10.1021/ma0019611

[51] Kharismadewi D, Haldorai Y, Nguyen VH, Tuma D, Shim JJ. Synthesis of graphene oxide-poly(2-hydroxyethyl methacrylate) composite by dispersion polymerization in supercritical CO2: Adsorption behavior for the removal of organic dye. Composite Interfaces. 2016;**23**(7):719-739. DOI: 10.1080/09276440.2016.1169707

[52] Denizli A, Garipcan B, Karabakan A, Senöz H. Synthesis and characterization of poly(hydroxyethyl methacrylate-N-methacryloyl-(l)-glutamic acid) copolymer beads for removal of lead ions. Materials Science and Engineering C. 2005;**25**:448-454. DOI: 10.1016/j.msec.2004.12.001

[53] Liu X, Chen H, Wang C, Qu R, Ji C, Sun C, Zhang Y. Synthesis of porous acrylonitrile/methyl acrylate copolymer beads by suspended emulsion polymerization and their adsorption properties after amidoximation. Journal of Hazardous Materials. 2010;**175**:1014-1021. DOI: 10.1016/j.jhazmat.2009.10.111

[54] Godjevargova T, Simeonova A, Dimov A. Adsorption of heavy metal ions from aqueous solutions by porous polyacrylonitrile beads. Journal of Applied Polymer Science. 2002;**83**:3036-3044. DOI: 10.1002/app.2334

[55] Kiani GR, Sheikhloie H, Arsalani N. Heavy metal ion removal from aqueous solutions by functionalized polyacrylonitrile. Desalination. 2011;**269**:266-270. DOI: 10.1016/j.desal.2010.11.012

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