Heavy and toxic metal uptake by mesoporous hypercrosslinked SMA beads: Isotherms and kinetics

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Abstract Hypercrosslinked styrene-maleic acid copolymer beads were used for the removal of metal ions from mimicked industrial effluents. The polymer was characterized by SEM which revealed the presence of a porous network. Carboxyl acid groups of the polymer were identified as active sites for metal uptake. Highly porous surface enhanced metal ion uptake was achieved through a physicochemical process. Equilibrium sorption of metal ions was best described by the Freundlich and Temkin model with $R^2 > 0.99$. Adsorption followed pseudo first and pseudo second order reaction kinetics. Intraparticle diffusion model suggested a three step equilibrium. Desorption was a fast process with $\approx 90\%$ in 60 min.

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1. Introduction

In recent years we have experienced an increasing awareness about water pollution and its far reaching effects have prompted concerted efforts toward pollution abatement (Dönmmez et al., 1999). Rapid industrialization has seriously contributed to the release of toxic heavy metals in water streams. Mining, electroplating, metal processing, textile and battery manufacturing industries are the main sources of heavy metal contamination (Babel and Opiso, 2007; Nwuche and Ugoji, 2008). These activities pollute water streams especially rivers and make them lose their potential value and beneficial uses (Celik and Demirbas, 2005; Demirbas et al., 2005; Kadirvelu et al., 2001). Contamination of aqueous environments by heavy metals and dyes is a worldwide environmental problem due to their toxic effects and accumulation through the food chain (Kapoor et al., 1999; Perez-Rama et al., 2002; Sternberg and Dorn, 2002). Among these heavy metal ions, the ions of Cd, Zn, Hg, Pb, Cr, Cu, As etc. have gained importance due to their highly toxic nature even at very low concentrations. High concentration of heavy metals in the environment can be detrimental to a variety of living species. Excessive ingestion of these metals by humans can cause accumulative poisoning, cancer, nervous system damage and ultimately death (Corapcioglu and Huang, 1987; Issabayeva et al., 2007). Heavy metals cannot be metabolized and bioaccumulate in the body...
of organisms. These toxic metals can move through the biological chain thereby reaching the human being and leading to chronic and acute ailments. Heavy metal toxicity can result in damaged or reduced mental and central nervous functions, lower energy levels and damage to the blood composition, lungs, kidneys, liver and organs (Volesky and Holan, 1995; Zulkaln et al., 2006). Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts and chocolate. The potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paper and paper board mills, wood pulp production and the fertilizer industry (Nuhoglu and Oguz, 2003; Wan Ngah et al., 2002; Ozsoy and Kumbur, 2006). Excessive intake of copper results in accumulation in the liver, leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, and central nervous problems followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney, hemorrhysis, liver and kidney damage, irritation of upper respiratory tract, gastrointestinal disturbance, and diarrhea. It is also toxic to aquatic organisms even at very small concentrations in natural water (Ozsoy and Kumbur, 2006). Zinc is biologically essential but an overdose can lead to depression, lethargy, and neurologic signs such as seizures and ataxia and increased thirst (Kurniawan et al., 2006). Zinc is harmful for both irrigational and industrial applications. Zinc is introduced into water from metal mining, melting, plating, pesticides, oil-based paint pigments, alloy processing and sewage sludge. The most common adverse health effect of nickel in humans is an allergic reaction; large amounts of nickel can cause lung and nasal sinus cancers. Nickel (Ni) may be found in wastewater discharged from mining, electroplating, pigments and ceramic industries, and battery and accumulator manufacturing (Parab et al., 2006). Nickel is toxic to a variety of aquatic organisms, even at very low concentrations. The most common adverse health effect of nickel in humans is an allergic reaction; large amounts of nickel can cause lung and nasal sinus cancers. Impact of Ni can be manifested in chronic toxicity, dermatitis, nausea, chronic asthma abdominal cramps, diarrhea, vertigo and lassitude but acute toxicity is not typical (Borbely and Nagy, 2009). Nickel is also toxic, especially to activated sludge bacteria. The presence of Ni(II) is detrimental to the operation of anaerobic digesters used in wastewater treatment plants. Thus removal of trace amounts of heavy metal ions from wastewater and drinking water is of great importance due to its high toxicity (Abdel-Ghani and Elchaghaby, 2007; Abdel-Ghani et al., 2009; Resmi et al., 2010).

Current methods for wastewater treatment include precipitation, coagulation/flotation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, biological process, chemical reactions, adsorption and ion exchange. But the selection of the wastewater treatment method is based on the concentration of waste and the cost of treatment. However, these processes have significant disadvantages such as incomplete metal removal, particularly at low concentrations and high operational costs (Cochrane et al., 2006). Cost-effective treatment technologies, therefore, are needed to meet these requirements. Out of the several physicochemical processes for the removal and recovery of metal ions from effluents, adsorption is the most effective one (Nyholm et al., 1992; Mavros et al., 1994; Ghosh and Bhattacharyya, 2002). The important aspect of the adsorption process is easy regeneration ability and less operational cost, simple design, easy operation and free or less generation of toxic substances (Khan et al., 2008). Adsorption techniques have proven successful in removing colored organic species and the choice of the adsorbent is one of the key factors determining the effectiveness of any adsorption process. The adsorption process at solid/liquid interface has been extensively employed for several reasons, mainly due to its efficiency and economy (Namasivayam et al., 2003; Gürses et al., 2006). Physical adsorption because of its low cost, high efficiency, easy handling, wide variety of adsorbents and high stabilities toward the adsorbents, has become the most widely used methods for the elimination of dye from wastewater.

Porous materials such as clay (Jaber et al., 2005), activated carbon (Zhu et al., 2009), zeolites (Wingenfelder et al., 2009) and biomass (Deng and Ting, 2005) are usually used as toxic metal ion adsorbents because of their high surface area, large pore volume, and the presence of exchangeable ions presenting themselves as good candidates for adsorbents. For better adsorption performance, the pore size of a porous adsorbent should match the adsorbates atomic/molecular size (Yang, 2003). Compared to traditional microporous adsorbents such as activated carbons and zeolites, organic porous polymers possess various advantages like pore size tuning (Jiang et al., 2007, 2008). Introduction of a specific surface functionality can introduce a wide variety of synthetic strategies and enhance adsorption properties (Karbarz et al., 2010). Further these polymers can be replicated from well-defined monomers and optimized conditions (Carrington et al., 2007; Balaji et al., 2006; Adnan, 2001). These advantages render microporous polymers to be potential and possibly superior candidates for the removal of toxic metal ions from wastewater. Hypercrosslinked polymers represent a class of predominantly microporous organic materials that can exhibit high surface area (Tsyrupa et al., 2003) and are also being evaluated as potential candidates for hydrogen and methane storage (Wood et al., 2007, 2008; Lee et al., 2006). Macroporous or mesoporous analogous materials have been widely reported as adsorbents for organic/gas adsorbates and commercial microporous hypercrosslinked polymers with the functional group as a strong acid cation-exchange resin which has accelerated the development of several important technologies such as purification, removal of hazardous organic materials and so on.

In the present study, the equilibrium adsorption of Cu(II), Ni(II), Zn(II) and Co(II) ions onto hypercrosslinked styrene-maleic acid copolymer (SMA) beads from mimicked wastewater systems was investigated. The influence of experimental conditions such as pH, adsorbent dose, initial metal and ion concentration was investigated. The Langmuir, Freundlich, Temkin and D–R equations were used to fit the equilibrium isotherm. Adsorption rates were determined quantitatively and compared by the first and second-order kinetic models. The mechanism and thermodynamics of adsorption were also studied. This information can be useful for system design in the industrial waste water treatment plants.

2. Materials and methods

2.1. Materials

Styrene (Merk, India) and divinylbenzene (Sigma Aldrich 80%, India) were purified with 1N NaOH prior to use. Azob-
The adsorption of Zn(II) was carried out by agitating 30 ml of 200 mg/L, 250 mg/L and 500 mg/L of Zn(II) with 0.5 g SMA each for 5, 15, 30, 45, 60, 75, 90 and 120 min at the end of set time duration, 1 ml of supernatant solution was used to detect the concentration of the metal ions remaining in the solution. The effect of solution pH on adsorption was observed for a batch of 0.5 g SMA in 30 ml of 100 mg/L Zn(II) solution. The amount of SMA beads was also varied (0.2, 0.5 and 1.0 g) for a fixed metal ion concentration of 250 mg/L for 120 min to obtain another set of data. The concentration of the metal ions was evaluated by titrating the fixed amount of Zn(II) solution at a specific time interval against standard EDTA solution (Wan Ngah et al., 2002). For Cu(II), Co(II) and Ni(II), adsorption was determined spectrophotometrically at 720, 510 and 660 nm for Cu(II), Co(II) and Ni(II), respectively using SMA samples in contact with 20 ml of metal ion solution for 120 min. Absorbance was noted at regular time intervals of 15 min. Adsorption isotherm is the plot of equilibrium adsorption capacity (qe) versus equilibrium concentration of the residual metal ions in the solution (Ce). The equilibrium adsorption capacity was calculated using the following equation:

\[ q_e = \frac{(C_0 - C_e)V}{M} \]  

where \( q_e \) (mg/g) is the equilibrium adsorption capacity, \( C_0 \) and \( C_e \) are initial and equilibrium concentrations (mg/L) of metal ions in solution, \( V(L) \) is volume of the solution and \( M(g) \) is the weight of the adsorbent.

2.3. Characterization

The crosslinked porous SMA beads synthesized by suspension polymerization were characterized by Fourier Transform Infrared spectroscopy (FTIR) Perkin Elmer 1600 spectrophotometer and the surface morphology was observed through JEOL ASM 6360A scanning electron microscope. The concentrations of the metal ions were checked using Systronic 166 UV–Visible Spectrophotometer.

2.4. Metal ion solutions

Single metal ion stock solutions (2000 mg L\(^{-1}\)) were prepared by dissolving the metal salts in 1000 ml of distilled water. The various concentrations were then obtained by diluting the stock solution with deionized water.

2.5. Batch adsorption experiments

The crosslinked styrene-maleic acid copolymer beads were synthesized by a suspension polymerization technique using free radical initiator (Mathew and Deb, 1996). The crosslinked styrene-maleic acid copolymer beads were synthesized as reported in our previous publication (Gonte et al., 2012). Briefly, to a homogeneous solution of monomers (styrene and maleic anhydride), crosslinker (DVB) in MIBK was added to the aqueous salt solution with insitu formed magnesium hydroxide. The mixture was stirred at 800 rpm to obtain uniform sized (200–400 \( \mu \)m diameter) spherical beads of crosslinked styrene-maleic anhydride which were further hydrolyzed to produce crosslinked styrene-maleic acid (SMA) copolymer beads. The beads were then water soxhlated and finally acetone soxhlated and dried under vacuum at 50 °C to constant weight.

2.6. Equilibrium isotherms

Adsorption isotherm studies were conducted at a constant temperature of 303 K using 0.5 g SMA beads in contact with 20 ml of metal ion solution for 120 min. Absorbance was noted at regular time intervals of 15 min. Adsorption isotherms are plots of equilibrium adsorption capacity (qe) versus equilibrium concentration of the residual metal ions in the solution (Ce). The equilibrium adsorption capacity was calculated using the following equation:

\[ q_e = \frac{(C_0 - C_e)V}{M} \]  

where \( q_e \) (mg/g) is the equilibrium adsorption capacity, \( C_0 \) and \( C_e \) are initial and equilibrium concentrations (mg/L) of metal ions in solution, \( V(L) \) is volume of the solution and \( M(g) \) is the weight of the adsorbent.

2.7. Kinetic studies

Kinetic experiments were conducted by using a known weight of SMA dosage and different initial metal ion concentrations. The samples at different time intervals (0–120 min) were taken and centrifuged. Suitable aliquots were analyzed for the presence of metal ions concentration and recorded. The rate constants were calculated by using the conventional rate expression. The amount of metal ion sorbed, \( q_t \), was calculated from

\[ q_t = \frac{(C_0 - C_t)V}{M} \]  

where \( q_t \) (mg/g) is the equilibrium adsorption capacity.

2.8. Desorption experiments

The reusability of the SMA beads was tested by treating the metal ion adsorbed beads with 1 M HCl solution. Desorption ratio was calculated from the equation:

\[ \text{Desorption ratio} = \frac{\text{amount of metal ions desorbed to the desorbing media}}{\text{amount of metal ions adsorbed onto SMA beads}} \times 100 \]  

3. Results and discussion

The crosslinked styrene-maleic acid copolymer beads were synthesized as reported in our previous publication (Mathew and Deb, 1996). The SEM micrograph as shown in Fig. 1a confirms the spherical shape of the beads and reveals the uniform smooth surface of the polymer beads. However, the magnified SEM image reflects the presence of a microporous network structure with the presence of a micro void and a micro fissure (Fig. 1b). IR spectrum of the crosslinked SMA copolymer, exhibits a characteristic peak at 1710 cm\(^{-1}\) related to stretching frequency of the carboxyl group confirming the conversion of maleic anhydride to maleic acid as shown in Fig. 1c.

The presence of microporous surface and active carboxylic groups in the polymer is assumed to exhibit enhanced adsorption of metal ions. The uptake of the metal ions from the aqueous solution is possible by two ways – (a) adsorption of the metal ions into the pores and (b) complex formation of the metal ions with the acid function group of the polymer. The schematic representation for adsorption of metal ions is shown in Fig. 2a.
The affinity of carboxyl group toward metal ions is high as compared to hydrogen bonding interactions. The presence of metal ions in the polymer matrix was noted by a change in the color of the beads from colorless to the color of the respective metal ion (Fig. 2b) and confirmed from the EDX spectra.

3.1. Effect of pH on adsorption of metal ions by SMA

The removal of metal ions from aqueous solutions by adsorption was found to be dependent on the solution pH. Adsorption of Cu(II), Co(II), Zn(II) and Ni(II) ions was observed to increase with increase in pH from 4 to 7 as shown in Fig. 3a. The decrease in the adsorption below pH 6 can be explained by the fact that at pH below 6, the $\text{H}_3\text{O}^+$ ions present in the aqueous solutions compete with the free metal ions for the active sites with carboxylic groups. The carboxyl groups get protonated which blocks the site for adsorption and further the steric hindrance created by the protonation of acid decreases the metal ion uptake. The increase in the adsorption efficiency of the SMA with increase in pH from 4 to 7 was observed in the case of all four metal ions, which suggests that the mechanism of uptake is the same in all cases.

3.2. Effect of sorbent dose on dye adsorption

It was observed that adsorption increases with increase in SMA dose from 0.1 to 1.0 g (Fig. 3b). Further increase in sorbent dose showed no significant increase in the adsorption of metal ions. Removal of metal ions increases with increased adsorbent dosage due to increase in active sites.

3.3. Effect of initial dye concentrations

The effect of metal ion concentration on the adsorption efficiency of SMA beads is shown in Fig. 3c. It was observed that adsorption decreases with increase in the initial metal ion concentration. As a rule, increasing the initial metal ion concentration results in an increase in the adsorption capacity because it provides a driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phase. However, the sorption efficiency decreases since the adsorbent has a limited number of active sites, which saturates at a certain concentration. This indicates that the adsorption capacity will increase with the increase of initial concentration mainly due to the rise in the mass transfer from the concentration gradient. However, the concentration will inversely impact on the adsorption efficiency because of the limited adsorption sites available for the uptake of metal ions.

3.4. Isotherm studies

Adsorption isotherm studies are important to determine the efficiency of adsorption. The adsorption isotherm indicates how the adsorption molecules distribute between the liquid
phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. There are several isotherm equations available for analyzing experimental adsorption equilibrium data. Several adsorption isotherms originally used for gas phase adsorption are available and readily adopted to correlate adsorption equilibria in heavy metal adsorption. Some well-known ones are the Freundlich, Langmuir, Temkin, Redlich–Paterson and Sips equations (Febrianto et al., 2009). In this study, the equilibrium experimental data for adsorbed metal ions onto crosslinked SMA copolymer beads were analyzed using the Langmuir, Freundlich and Temkin models. The isotherm constants for the three models were obtained by linear regression methods and are presented in Table 1. These isotherms are as follows:

### 3.4.1. Langmuir isotherm model

The Langmuir model assumes that a monomolecular layer is formed when adsorption takes place without any interaction between the adsorbed molecules (Aksu, 2002). The Langmuir model can be represented as:

\[
q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e}
\]

where \( q_e \) is the equilibrium concentration (mg/l), \( q \) the amount of metal ion sorbed (mg/g), \( q_{\text{max}} \) is \( q_e \) for a complete monolayer (mg/g), \( K_L \) is a constant related to the affinity of the binding sites (l/mg). The linearized form of the Langmuir equation is:

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}} K_L} + \frac{C_e}{q_{\text{max}}}
\]

The experimental data were plotted as \( C_e/q_e \) versus \( C_e \) and are shown in Fig. 4a. The values of Langmuir constants \( q_{\text{max}} \) and \( K_L \) were obtained by the linear regression method which exhibited high correlation with Langmuir model within the studied temperature range.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, \( R_L \) which is defined by Hall et al. (1996) as:

\[
R_L = \frac{1}{1 + K_L C_0}
\]

where \( K_L \) (l/mg) is the Langmuir constant and \( C_0 \) (mg/l) is the initial concentration. The value of \( R_L \) provides information as to whether the adsorption is irreversible \((R_L = 0)\), favorable \((0 < R_L < 1)\), linear favorable \((R_L = 1)\) or unfavorable \((R_L > 1)\). The \( R_L \) values obtained are greater than zero and less than unity and the regression coefficient values of 0.99, indicate favorable adsorption of metal ions.

### 3.4.2. Freundlich isotherm model

The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces and the adsorption capacity is related to the concentration of metal ions at equilibrium. This isotherm model is defined by the equation (Li et al., 2005) below:

\[
q_e = K_F C_e^n
\]

where \( q_e \) and \( C_e \) are the equilibrium concentrations of metal ions in adsorbed (mg/g) and liquid phases (mg/l), respectively. \( K_F \) and \( n \) are the Freundlich constants which are related to adsorption capacity and intensity, respectively. This equation can be written in the linear form given below:
The experimental data plotted with $\ln q_e$ versus $\ln C_e$ are shown in Fig. 4b. To determine the maximum sorption capacity, it is necessary to operate with constant initial concentration $C_0$ and variable weights of sorbent, thus $\ln q_m$ is the extrapolated value of $\ln q$ for $C=C_0$. According to Halsey (Li et al., 2005):

$$\ln q_e = 1/n \ln C_e + \ln K_F$$

The linear plot of $\ln q_e$ versus $\ln C_e$ gives slope of value $1/n$ and an intercept $\ln K_F$. When $C_e$ equals unity $\ln K_F$ is equal to $\ln q_e$. In the other case, when $1/n = 1$, the $K_F$ value depends on the units in which $q_e$ and $C_e$ are expressed. A favorable adsorption tends to give Freundlich constant $n$ a value between 1 and 10. Larger value of $n$ (smaller value of $1/n$) implies strong interaction between sorbent and metal ions while $1/n$ equal to 1 indicates linear adsorption leading to identical adsorption energies for all the sites. It can be observed from Table 1 that for all the metal ions, the value of $n$ is positive. The order of interactions was noted to be Co(II) > Ni(II) > Zn(II) > Cu(II). The regression coefficients were also greater than 0.99 for all metal ions clearly indicating that the equilibrium adsorption isotherm can be very well described by the Freundlich model.

### Table 1 Equilibrium adsorption isotherm parameters.

<table>
<thead>
<tr>
<th></th>
<th>Cu(II)</th>
<th>Co(II)</th>
<th>Ni(II)</th>
<th>Zn(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Freundlich isotherm</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>1.71</td>
<td>2.56</td>
<td>1.95</td>
<td>1.86</td>
</tr>
<tr>
<td>$K_F$</td>
<td>0.383</td>
<td>1.029</td>
<td>0.490</td>
<td>0.543</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9939</td>
<td>0.9792</td>
<td>0.9972</td>
<td>0.9994</td>
</tr>
<tr>
<td>$q_{\max}$</td>
<td>14.45</td>
<td>11.61</td>
<td>11.86</td>
<td>15.13</td>
</tr>
<tr>
<td><strong>Langmuir isotherm</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_L (10^{-3})$</td>
<td>4.93</td>
<td>11.51</td>
<td>6.12</td>
<td>5.64</td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.288</td>
<td>0.148</td>
<td>0.246</td>
<td>0.261</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9755</td>
<td>0.9798</td>
<td>0.9896</td>
<td>0.9548</td>
</tr>
<tr>
<td>$q_{\max}$</td>
<td>17.45</td>
<td>12.07</td>
<td>13.92</td>
<td>17.36</td>
</tr>
<tr>
<td><strong>Temkin isotherm</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_T$</td>
<td>0.094</td>
<td>0.040</td>
<td>0.047</td>
<td>0.044</td>
</tr>
<tr>
<td>$b_T$</td>
<td>887.14</td>
<td>604.35</td>
<td>735.90</td>
<td>594.95</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9743</td>
<td>0.9896</td>
<td>0.9936</td>
<td>0.9760</td>
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</table>

The linear plot of $\ln q_e$ versus $\ln C_e$ gives slope of value $1/n$ and an intercept $\ln K_F$. The linear adsorption leading to identical adsorption energies for all the sites. It can be observed from Table 1 that for all the metal ions, the value of $n$ is positive. The order of interactions was noted to be Co(II) > Ni(II) > Zn(II) > Cu(II). The regression coefficients were also greater than 0.99 for all metal ions clearly indicating that the equilibrium adsorption isotherm can be very well described by the Freundlich model.

3.4.3. Temkin isotherm model

Temkin’s isotherm, considers the effects of the heat of adsorption that decreases linearly with coverage of the adsorbate and adsorbent interactions (Djeribi and Hamdaoui, 2008). The Temkin’s isotherm has been used in the form as follows:
where $R$ is gas constant $8.314 \times 10^{-3}$ kJ mol$^{-1}$ K$^{-1}$, $T$ is absolute temperature K, $b_T$ is the Temkin’s constant related to the heat of adsorption (kJ mol$^{-1}$) and $a_T$ is the equilibrium binding constant corresponding to the maximum binding energy (l/g). The liner plots of $q_e$ versus log $C_e$ enable to determine the constant $a_T$ and $b_T$ (Fig. 4c). The Temkin’s constant given in Table 1 clearly suggests that the adsorption involves chemisorption and physisorption of the metal ions rather than an ion exchange mechanism. The Temkin’s isotherm gives a satisfactory linear fit data with all the metal ions.

Figure 4  Isotherms (a) Langmuir; (b) Freundlich (c) Temkin.

### Table 2  Kinetic parameters.

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Metal ion conc. (mg/l)</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
<th>Intraparticle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$K_1$ (min$^{-1}$)</td>
<td>$q_e$ (mg/g)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>200</td>
<td>0.022</td>
<td>4.52</td>
<td>0.9783</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.025</td>
<td>6.43</td>
<td>0.9917</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.017</td>
<td>10.66</td>
<td>0.9865</td>
</tr>
<tr>
<td>Co(II)</td>
<td>200</td>
<td>0.010</td>
<td>5.43</td>
<td>0.9783</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0.014</td>
<td>6.33</td>
<td>0.9888</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>0.010</td>
<td>10.28</td>
<td>0.9940</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>200</td>
<td>0.011</td>
<td>4.80</td>
<td>0.9857</td>
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<td></td>
<td>250</td>
<td>0.025</td>
<td>6.69</td>
<td>0.9765</td>
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<tr>
<td></td>
<td>500</td>
<td>0.026</td>
<td>10.16</td>
<td>0.9836</td>
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<tr>
<td>Zn(II)</td>
<td>200</td>
<td>0.231</td>
<td>4.59</td>
<td>0.9863</td>
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<td></td>
<td>250</td>
<td>0.017</td>
<td>5.12</td>
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<tr>
<td></td>
<td>500</td>
<td>0.049</td>
<td>11.62</td>
<td>0.9817</td>
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</table>
3.5. Kinetics

To investigate the mechanism of adsorption and its potential rate-controlling steps that include mass transport and chemical reaction processes, kinetic models have been exploited to analyze the experimental data. In addition, information on the kinetics of metal uptake is required to select the optimum condition for full scale batch metal removal processes.

3.5.1. Pseudo first order kinetic model

Lagergren showed that the rate of adsorption of the solute on the adsorbent is based on the adsorption capacity and followed by a pseudo first order equation which is often used to estimate the $k_a$ considered as mass transfer coefficient in the design calculations. The pseudo first-order rate equation is given as:

$$\log\left(\frac{q_e}{q_t}\right) = \log\frac{q_e}{C_0} - k_{12}t$$

where $q_e$ and $q_t$ are the amounts of adsorbed metal ions on the adsorbent at equilibrium and at time $t$, respectively (mg/g), and $k_1$ is the first-order adsorption rate constant (min$^{-1}$). The plot of $\log(q_e - q_t)$ versus $t$ gives a straight line and the pseudo first-order rate constant can be calculated from the slope value. The calculated results of the pseudo first-order rate equation are given in Table 2. The correlation coefficient values (0.99) obtained by this method shows good quality of linearization. The $q_e$ values acquired are in good agreement with the experimental values. Thus the adsorption mechanism suggested can be classified as first-order.

3.5.2. Pseudo-second order kinetic model

The pseudo-second order reaction is greatly influenced by the amount of metal on the adsorbent’s surface and the amount of metal adsorbed at equilibrium. The rate is directly proportional to the number of active surface sites (Rengaraj et al., 2004). The pseudo-second order equation is given as:

$$t/q_t = 1/k_2q_e + \frac{1}{q_e}t$$

where $k_2$ is the second-order adsorption rate constant (g mg$^{-1}$ min$^{-1}$), and $q_e$ is the adsorption capacity calculated by the pseudo-second-order kinetic model (mg/g). The constant $k_2$ is used to calculate the initial sorption rate $h$ (mg/(g min)), at $t \to 0$ as follows:

$$h = k_2q_e$$

The application of the pseudo second order kinetics by plotting $t/q_t$ versus $t$ yielded the second order rate constant $k_2$. The kinetic parameters calculated are shown in Table 2. The calculated $q_e$ values agreed very well with the experimental values.

Figure 5  Pseudo first order kinetic model (a) Cu(II); (b) Ni(II); (c) Co(II); (d) Zn(II).
data and the correlation coefficient gave best fit linearized plots. Thus experiment results support the assumption behind the model that the rate limiting step in the adsorption of heavy metals are chemisorptions involving valence forces through the sharing or exchange of electrons between adsorbent and metal ions.

3.5.3. Adsorption mechanism

The prediction of the rate-limiting step is an important factor to be considered in the adsorption process (Rengaraj et al., 2004). It is governed by the adsorption mechanism, which is generally required for the design mechanism. For a solid–liquid sorption process, the solute transfer is usually characterized by external mass transfer (boundary layer diffusion), or intraparticle diffusion, or both. The most commonly used technique for identifying the mechanism involved in the adsorption process is by fitting and intraparticle diffusion plot. According to Weber and Morris (Sarkar et al., 2003), an intraparticle diffusion coefficient $K_{int}$ is given by the equation

$$q_t = K_{int} t^{1/2}$$

(16)

where $K_{int}$ is the intra-particle diffusion rate constant (mg g$^{-1}$ min$^{-0.5}$). The plot of $q_t$ versus $t^{0.5}$ at different initial solution concentrations gives the value of $K_{int}$ and may present multi-linearity which indicates two or more steps occurring in the adsorption process. The first sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage where the intraparticle diffusion rate is controlled. The third is the final equilibrium stage where intraparticle diffusion starts to slow down due to extremely low solute concentration in the solution. The parameters calculated are given in Table 2. The intraparticle diffusion rate was obtained from the slope of the gentle-sloped portion. The value of $K_{int}$ was higher at the higher concentrations. The multi-stepped adsorption observed for all the metal ions and best fitting obtained for the experimental data with high regression coefficient values indicates that intraparticle diffusion might play a significant role in the adsorption of metal ions onto porous SMA beads. The pseudo first order kinetic model, pseudo second order kinetic model and intraparticle diffusion model are shown in Figs. 5–7.

3.6. Desorption studies

Desorption of Cu(II), Ni(II) and Co(II) ions from the cross-linked SMA beads was achieved using 1 M HCl solution. Complete desorption of the metal ions occurred in less than
1 hr. Rapid desorption (~80%) was noted in 10 min. The results are shown in Fig. 8. It can be clearly noted that desorption of Cu(II) ions occurs to its maximum of 97% within 15 min after which no further desorption occurred. Desorption of Ni(II) and Co(II) reached its maximum within 30 min. Thus the results show that the crosslinked SMA copolymer beads can be successfully regenerated and its reapplication for the uptake of metal ions from aqueous solution is possible.

4. Conclusions

The present studies focus on use of microporous crosslinked copolymer beads for the adsorption of metal ions from aqueous solutions. Adsorption was found to be pH dependent with maximum adsorption at pH 6.7. Fast adsorption is observed for Cu(II), Co(II), Ni(II) and Zn(II) which suggests the adsorbent to be used effectively for continuous flow water systems. Carboxylic groups present in the polymer matrix were found to be the active sites of metal adsorption. Adsorption was enhanced due to presence of micropores, voids and fissures. The development of well defined flow lines in the polymer was observed to induce capillary action in the matrix. Equilibrium isotherms were attempted with three different models, among which Freundlich and Temkin models are in good agreement with the experimental data with high correlation coefficient values. Kinetic data suggest that the mechanism of metal uptake is dominated initially by pseudo first order kinetics followed by pseudo second order kinetic mechanisms. The
intraparticle diffusion model suggested multilinearity with a three step adsorption suggesting the attainment of an equilibrium state. The result proves that the adsorption of metal ions occurs by a physicochemical process rather than an ion exchange mechanism. Fast desorption of metal ions was achieved in 1 M HCl solution. The results thus indicate that crosslinked SMA copolymer beads can prove to be potential candidates for the treatment of industrial waste water.

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References


