Removal of copper ions from aqueous solution by the sodium salt of the maleic acid-allylpropionate-styrene terpolymer

Elchin Akperov, Oktay Akperov, Elnara Jafarova and Sabahiye Gafarova

ABSTRACT

The sodium salt of the maleic acid-allylpropionate-styrene terpolymer was used for recovery of copper ions from aqueous solution. Effects of contact time, sorbent weight and initial Cu$^{2+}$ ion concentrations on removal efficiency were tested. The maximum experimental sorption capacity of the sorbent for copper ions is 0.71 g g$^{-1}$. The sorption isotherm of copper ions onto a prepared polymer sorbent has been studied and the equilibrium data were analyzed using Langmuir and Freundlich isotherm models. The adsorption isotherm data showed that copper ions adsorption on the sorbent was better fitted to the Langmuir isotherm model. The Lagergren pseudo-first- and pseudo-second-order kinetic models were applied to examine the kinetics of the copper ions sorption by the synthesized sorbent. The kinetic data are best described by the pseudo-second-order model. The calculated value of the maximum sorption capacity by the pseudo-second-order equation (0.62 g g$^{-1}$) corresponds well with its experimentally found value (0.71 g g$^{-1}$). Considering the obtained kinetic data, and the Fourier transform infrared spectroscopy (FT-IR) and UV-vis spectra of the sorbent after the sorption, it is possible to come to the conclusion that during the sorption process Cu$^{2+}$ ions enter a complex with the carboxylic groups of the maleic acid units of the sorbent.

Key words | complexation, copper ions, isotherm, sorption, terpolymer

INTRODUCTION

Copper is a highly toxic heavy metal and at production and processing sites of copper ores the landscape, underground and surface waters are contaminated with compounds of copper that can do enormous harm to the environment. Accumulation of copper ions in natural objects can cause great ecological harm to living organisms. Many industries, such as metal finishing, electroplating, battery manufacturing, electric cable manufacturing, and steel and textile industries, release various concentrations of heavy metals like copper, cadmium, nickel and others into wastewater. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not degrade into harmless products. Therefore, every study carried out connected with the removal of heavy metal ions, including copper ions, from the water environment can contribute to finding solutions to the many practical problems in the field of environmental protection.

Many types of polymeric adsorbents have been developed and studied for the recovery and removal of copper ions from aqueous solutions (Wan Ngah et al. 2002; Kavaklı & Güven 2004; Zhongjin et al. 2008; Nacer et al. 2011). The complexation of natural or synthetic water-soluble polymers with adequate complexing ions is of great fundamental and practical interest. Such systems can find applications in a variety of fields including water treatment, ion-exchange resins (Rivas et al. 2003), biomedicine (Hatefi & Amsden 2002) and improved oil recovery (Cordova et al. 2008).

With recent rapid developments in technology, a great deal of attention has been paid to polymer materials, which can be used repeatedly as chelating resin and liquid membrane extractants for recovery of metals from impurities contained in systems (Saliba et al. 2000; Unuabonah et al. 2008; Qi et al. 2010). These polymers are capable of coordinating to different metal ions through reactive functional groups containing O, N, S, and P as donor atoms to form metal macromolecular complexes. The synthesis of metal macromolecular complexes containing nickel or rare earth metals with polymeric ligands, and their applications as florescent materials have been reported (Duan et al. 2006; Huang et al. 2007).
A new chelating polymer sorbent was synthesized through the copolymerization of styrene and maleic anhydride (MA) in the presence of divinylbenzene as a crosslinking agent, followed by hydrolysis (Roy et al. 2004). This newly developed chelating matrix has a high resin capacity for metal ions such as Cr, Fe, Ni, Cu and Pb. A chelating resin based on modified poly(styrene-alt-maleic anhydride) with 3-amino benzoic acid was synthesized (Hasanzadeh et al. 2013).

The adsorption behaviour of Fe(II), Cu(II), Zn(II) and Pb(II) ions was investigated using synthesized chelating resins at varying pH values, and the order of removal percentage changes was as follows: Fe(II) > Cu(II) > Zn(II) > Pb(II). In addition, the prepared resins were examined for removal of metal ions from industrial wastewater and were shown to have a very efficient adsorption in the case of Cu(II), Fe(II) and Pb(II). Chelating copolymers bearing carboxylic acid and/or carboxylate moieties based on ethyl methacrylate in the absence and in the presence of divinyl benzene as a crosslinked polymer were prepared via a new emulsion copolymerization route (El-Ghaffar and El-Hal 2015). The prepared chelating copolymers have been tested as adsorbents for various toxic heavy metal ions.

The present study aimed to investigate the efficiency of the sodium salt of maleic acid-allylpropionate-styrene terpolymer as a sorbent for the removal of copper ions from aqueous solution. Experiments were conducted to investigate the effects of sorbent weight, contact time and initial copper ion concentrations on the removal efficiency of copper ions by the synthesized sorbent. Sorption equilibrium and kinetics were studied under the optimum sorption conditions. The Langmuir and Freundlich isotherms were applied to evaluate the adsorption properties in the batch experiments. In addition, the pseudo-first- and pseudo-second-order kinetic models were applied to examine the kinetics of the sorption process. Synthesis and research into the sorption properties of the studied polymer-sorbent for copper ions are executed for the first time and define the novelty of this work. The simplicity of the synthesis technique, the availability of the materials used and the high sorption properties display the originality and efficiency of the investigated polymer-sorbent for copper ion sorption from aqueous solutions.

**MATERIALS AND METHODS**

**Materials**

All chemicals used were analytical reagent grade. MA was purified before use by recrystallization from benzene and by sublimation under vacuum. Allylpropionate (AP) and styrene (St) were distilled before use and had the following characteristics: AP: b.p. 122–123 °C; St: b.p. 144–145 °C. Azobisisobutyronitrile (AIBN) was purified by recrystallisation from ethanol. A stock solution of Cu²⁺ ions was prepared by dissolving 25 g of CuSO₄·5H₂O in 1 L deionized water to obtain a concentration of Cu²⁺ ions of 0.2 mol L⁻¹ (12.8 g L⁻¹). The stock solution was diluted to obtain solutions with concentrations of Cu²⁺ in the range of 0.01–0.15 mol L⁻¹ (0.64–0.96 g L⁻¹). A 0.001 mol L⁻¹ xylenol-orange (3, 31-bis-di(carboxymethyl)amino methyl-O-cresolsulphophthaline) solution was prepared by dissolving 0.076 g of the reagent in 100 mL of deionized water. Buffer solutions of CH₃COOH/NH₄OH with a pH of 6 were used for formation of a Cu²⁺-xylenol-orange complex.

**Preparation of sorbent**

The sodium salt of maleic acid-allylpropionate-styrene terpolymer (SDS) was prepared in two steps (Figure 1). In the first step MA (4.9 g), AP (2.85 g, 3.0 mL), St (2.6 g, 2.85 mL) (molar ratio MA/AP/St = 2:1:1) and AIBN (0.1 g, 1.0%) were dissolved in butyl acetate (30 mL). After heating the mixture at 70 °C for 1 h, the obtained terpolymer MA, AP and St (TPL) was precipitated in ethanol or heptane and dried at 40 °C in the vacuum oven (78.5% yields) (Akperov et al. 2009). The monomer contents of TPL were determined by chemical analysis and ¹H NMR. It was established that the molar contents of MA, AP and St in the terpolymer were 51.5, 17.8 and 30.7 mol%, respectively. The intrinsic viscosity was 0.72 dL g⁻¹ (methyl ethyl ketone, 20 °C).

In the second step, a mixture of TPL (4.14 g) and sodium hydroxide (5% solution, 30 mL) was heated at 40–50 °C for
1 h. The obtained SDS was then precipitated in acetone, washed repeatedly with acetone and dried at 40 °C in the vacuum oven. The synthesized SDS was used as the sorbent for removal of copper ions from water solution.

Sorption experiments

Sorption of copper ions onto the synthesized sorbent was carried out using a batch experiment method. A volume of 40 mL of CuSO₄ solution of a certain concentration was placed in a 100 mL Erlenmeyer flask containing a sample of sorbent and was agitated in a temperature-controlled water bath to carry out the sorption experiment. At the end of the experiment the fulfilled sorbent (a sorbent complex with copper ions) was separated from the solution, and the residual copper ions in solution were evaluated by a photometric method. For this purpose 1 mL of the copper ion solution and 2 mL of the xylenol-orange solution were placed into a 25 mL graduated flask and were diluted with the buffer solution CH₃-COOH/NH₄OH. The optical density of the residual amount of copper ions was determined using a calibration curve.

The sorption degree (%) and sorption capacity (g g⁻¹) of the sorbent have been calculated using the following equations:

\[
\text{Sorption degree} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100\% \tag{1}
\]

\[
\text{Sorption capacity} = \left( \frac{C_0 - C_e}{m_{\text{sorb}}} \right) \times \frac{V_{\text{sol}}}{m_{\text{sorb}}} \tag{2}
\]

where \(C_0\) and \(C_e\) (g L⁻¹) are initial and equilibrium concentrations of copper ions solutions, respectively, \(V_{\text{sol}}\) (L) is the volume of the copper ions solution submitted to sorption, and \(m_{\text{sorb}}\) (g) is the weight of the sorbent. The Fourier transform infrared spectroscopy (FT-IR) spectrum of the sorbent after sorption was recorded in the range 4,000–500 cm⁻¹ using a Varian 3600 FT-IR spectrometer. A photocalorimeter (model KFK-3M, Russia) was used to determine the concentration of Cu²⁺ ions after sorption at 490 nm. The UV-vis spectrum was measured on a UV-visible SPECORD 220 PLUS in the range 190–1,100 nm. A pH meter (model pH-600-AQ, Romania) was used for pH measurements.

RESULTS AND DISCUSSION

Effect of sorbent weight

The effect of adsorbent weight on the copper ions sorption process has been investigated (initial concentration of copper ions 0.025 mmol L⁻¹, pH 6, time 180 min, 20 °C). The result shows that, the removal efficiency increases with increasing sorbent weight. The increase of the sorbent weight from 0.04 up to 0.20 g causes an increase in the sorption degree of copper ions from 14.4 up to 71.2% (Table 1).

The sorption degree increased with the increasing sorbent weight up to 0.12–0.15 g, beyond which it attained an almost constant value (65.6–69.7%). Hence, a sorbent amount equal to 0.12 g is optimum at an initial concentration of copper ions equal to 1.6 g L⁻¹. Therefore, in further experiments 0.12 g of sorbent was used.

Effect of contact time

The effect of contact time on copper ion sorption by sorbent (initial concentration of copper ions 1.6 g L⁻¹, pH 6, sorbent weight 0.12 g, volume of solution of copper ions 0.04 L) has been investigated at different contact times varying between 30 and 210 min at 20 °C (Table 2).

The sorption degree increased with increasing contact time up to 150–180 min, beyond which it attained an almost constant value (65.6–69.7%). Therefore, the contact time equal to 150–180 min was considered to be sufficient for sorption of copper ions onto sorbent and has been used for all experiments.

Table 1 | Effect of sorbent mass on sorption degree (pH 6, initial concentration of copper ions 1.6 g L⁻¹, volume of solution 0.04 L, 20 °C, 180 min)

<table>
<thead>
<tr>
<th>Mass of sorbent, (m_{\text{sorb}}), (g)</th>
<th>0.04</th>
<th>0.06</th>
<th>0.08</th>
<th>0.10</th>
<th>0.12</th>
<th>0.15</th>
<th>0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption degree, (R), %</td>
<td>14.4</td>
<td>36.9</td>
<td>49.0</td>
<td>60.0</td>
<td>69.7</td>
<td>70.3</td>
<td>71.2</td>
</tr>
</tbody>
</table>

Table 2 | Effect of time on sorption degree (pH 6, initial concentration of copper ion 1.6 g L⁻¹, volume of solution 0.04 L, mass of sorbent 0.12 g, 20 °C)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>30</th>
<th>60</th>
<th>90</th>
<th>120</th>
<th>150</th>
<th>180</th>
<th>210</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption degree, (R), %</td>
<td>24.0</td>
<td>37.1</td>
<td>49.0</td>
<td>60.0</td>
<td>65.6</td>
<td>69.7</td>
<td>70.1</td>
</tr>
</tbody>
</table>
Effect of initial copper ions concentration and sorption isotherm of sorbent

The metal uptake mechanism depends on the initial heavy metal concentration. At low concentrations, the metal ions were adsorbed at specific sites, whereas with increasing metal ion concentration, the specific sites were saturated and exchange sites were filled (Patel et al. 2007). With increasing metal ion concentration the equilibrium ion concentration and adsorption capacity of the sorbent increases. However, with increasing equilibrium ion concentration the adsorption capacity of the sorbent also increases. Copper ions sorption by synthesized sorbent was studied at initial copper ions concentrations ranging from 0.64 up to 9.6 g L\(^{-1}\). The results show that the copper ions sorption onto sorbent were strongly affected by the initial copper ions concentration, and with increasing initial copper ions concentration the degree of sorption decreases (Figure 2). This is because with increasing metal ion concentration, the specific sites of a sorbent are saturated and exchange sites are filled.

The equilibrium sorption capacity of the sorbent was calculated for the initial copper ions concentration range between 0.64 and 9.6 g L\(^{-1}\) at 20 °C and pH 6, for 180 min contact time. The experimental results show that the sorption capacity of the sorbent increases rapidly with the increase in the equilibrium concentration of copper ions (Figure 3). When the copper ion concentration reached a certain level, the rate of increase in the adsorption capacity slowed down and it came close to a constant value. It can be concluded that the experimental maximum sorption capacity \((q_{\text{exp}})\) of the sorbent in the equilibrium conditions is 0.71 g g\(^{-1}\).

**Langmuir and Freundlich models**

The Langmuir and Freundlich equations are the most commonly used calculation formulae for experimental data of liquid phase adsorption if the sorption of the solvent is neglected. The Langmuir isotherm describes monolayer adsorption based on the assumption that all the adsorption sites have equal adsorbate affinity and that adsorption at one site does not affect adsorption at an adjacent site. The Langmuir isotherm is given below:

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

(3)

where \(C_e\) is the equilibrium concentration (g L\(^{-1}\)), \(q_e\) is the amount adsorbed at equilibrium (g g\(^{-1}\)), \(q_{\text{max}}\) is the monolayer adsorption capacity (g g\(^{-1}\)) and \(K_L\) is the Langmuir equilibrium constant (L g\(^{-1}\)). The Freundlich isotherm equation considers heterogeneous surfaces and is based on the idea that the adsorption depends on the energy of the adsorption sites. The Freundlich isotherm can be written as:

\[
\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e
\]

(4)

where \(K_F\) is the Freundlich constant and \(1/n\) is the heterogeneity factor.

The obtained experimental equilibrium data were fitted to the Langmuir and Freundlich isotherm models. The linear curve of specific sorption \((C_e/q_e)\) versus equilibrium concentration of copper ions in solution \((C_e)\), and the logarithmic curve of the equilibrium adsorption capacity \((\log q_e)\) and equilibrium concentration \((\log C_e)\) are given in Figures 4 and 5, respectively.
The Langmuir and Freundlich isotherm constants were calculated from the slope and intercept of the plots, and are given in Table 3. The correlation coefficient ($R^2 = 0.9996$) of the adsorption isotherm data showed that copper ions adsorption on sorbent was better fitted to the Langmuir isotherm model.

The obtained values of the Langmuir equation parameters specify a high enough sorption activity of the synthesized sorbent for copper ions. The high value of $K_L$ (2.05 L g$^{-1}$) is most likely to be connected with the strong attraction for copper ions on the sorbent surface owing to the chemical interaction of copper ions with functional groups of the sorbent chelate center. In addition, calculated ($q_{max}$) and experimental ($q_{exp}$) maximum sorption capacity values (0.75 and 0.71 g g$^{-1}$, respectively) practically do not differ.

**Sorption kinetics**

Kinetic studies were carried out under the optimized conditions from 0 up to 270 min. Linear forms of the Lagergren pseudo-first-order and pseudo-second-order kinetic models (Bagherifam et al. 2010) fit the experimental data for the sorption of copper ions by the synthesized sorbent. The pseudo-first-order kinetic model can be expressed as:

$$\log(Q_e - Q_t) = \log Q_e - 0.434 k_1 t$$  \hspace{1cm} (5)

where $Q_t$ and $Q_e$ are the amounts of copper ions adsorbed at time $t$ (min) and at equilibrium (g g$^{-1}$), respectively, and $k_1$ is the rate constant of the pseudo-first-order adsorption process (min$^{-1}$).

The pseudo-second-order kinetic equation is presented as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$$  \hspace{1cm} (6)

where $Q_t$ and $Q_e$ are the amounts of copper ions sorbed at time $t$ (min) and at equilibrium (g g$^{-1}$), and $k_2$ is the pseudo-second-order equilibrium rate constant (g g$^{-1}$ min$^{-1}$).

The slope and intercept of plots of $\log(Q_e - Q_t)$ versus $t$ were used to determine the pseudo-first-order rate constant $k_1$ and equilibrium adsorption capacity $Q_e$ (Figure 6). The plot of $t/Q_t$ versus $t$ gives a linear relationship, and $k_2$ and $Q_e$ can be calculated from the slope and intercept of the line (Figure 7). In Table 4, the kinetic rate constants $k_1$ and $k_2$, values of experimental $Q_e$ and calculated $Q_e$ for the sorbent and correlation coefficients ($R^2$) are illustrated. According to these results, the kinetic data are well described using the pseudo-second-order kinetic equation. From the obtained results it can be concluded that the pseudo-second-order equation provides the best correlation coefficient (0.9567) and conformity between calculated and experimental values. The kinetic data are well described using the pseudo-second-order kinetic equation.
(0.62 g g⁻¹) and experimental (0.71 g g⁻¹) $q_e$ values, suggesting that chemisorption is a defining stage in the copper ions adsorption process on a synthesized sorbent.

**Spectrophotometric investigation of the sorbent after sorption**

For identification of the possible mechanism of the copper ions sorption process, the sorbent was characterized using FT-IR and UV-vis spectra (Figures 8 and 9, respectively) after sorption.

The absorption bands at 1,540 and 1,559 cm⁻¹ were assigned to the asymmetric vibration absorption of the carboxylate (COO⁻) groups (Bellamy 1975). It is possible to believe that copper ions enter into a complex with two carboxylic groups of the maleic acid units of the sorbent. The absorption band in the region of 1,653 cm⁻¹ is attributed to the –OH bending mode of adsorbed water, and the broad band centred near 3,420 cm⁻¹ is attributed to the –OH stretching band for connected water, which indicates the presence of water molecules in this complex. A complexation of copper ions with carboxyl containing polymers, including copolymers of maleic acid has been reported (Rivas et al. 2001, 2002; Oikonomou et al. 2008). It is noted that Cu²⁺ ions can form mononuclear and binuclear complexes with maleic acid copolymers depending on the hydrophobic or hydrophilic degree of the monomers, and the absorption of binuclear complexes is observed in the region 350–370 nm (Oikonomou et al. 2008). In our case absorption is observed...
in the range 480–490 nm (Figure 9), that specifies formation of a mononuclear complex of the copper ions with two carboxylic groups of the maleic acid units and water molecules (Figure 10). Considering the obtained kinetic data and the FT-IR and UV-vis spectra of the sorbent after the sorption, it is possible to come to the conclusion that during the sorption process Cu$^{2+}$ ions enter a complex with the carboxylic groups of the maleic acid units of the sorbent. One of the most probable variants of the complex is illustrated above (Figure 10), but other variants of interaction are not excluded.

**CONCLUSIONS**

The sodium salt of the maleic acid-allylpropionate-styrene terpolymer has been used for the removal of copper ions from aqueous solution. Effects of contact time, sorbent weight and initial concentration of copper ions on removal efficiency were tested and optimum conditions were evaluated. Optimum parameters for sorption are contact time 150–180 min, sorbent weight 0.12 g, copper ions initial concentration 1.6 g L$^{-1}$ and temperature 20 °C. The experimentally sorbed amount of copper ions at equilibrium is 0.71 g g$^{-1}$. Kinetic studies showed that the experimentally obtained data fitted well to the Lagergren pseudo-second-order model. Considering the obtained kinetic data and FT-IR and UV-vis spectra of the sorbent after sorption, it is possible to come to the conclusion that Cu$^{2+}$ ions enter a complex with two carboxylic groups of the maleic acid units of the sorbent in the sorption process. The experimentally obtained data allow the conclusion that prepared sorbent can be used for the removal of copper ions from aqueous solutions.

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