ABSTRACT

The solvent impregnated resin (SIR) was prepared by using Diaion HP-2MG as a hydrophilic polymer adsorbent and commercial Aliquat 336 as extractant for hexavalent chromium Cr(VI) removal from aqueous solution. The resulting SIRs were stabilized by coating using poly(vinyl alcohol) (PVA) and divinylsulfone as crosslinking reagent with different amounts.

In order to predict the mechanism involved in the adsorption process, several kinetic models were used. Among them, the sorption kinetics was usually described by pseudo-first or pseudo-second order models. The kinetic behavior of stabilized SIRs was investigated as a function of amount of crosslinking reagent by batch adsorption equilibrium. Uncoated resins exhibited a faster kinetics than coated ones. It was possible to improve the kinetic performance of crosslinked resins with conditioning by using NaOH-NaCl mixture. The breakthrough profiles of SIRs were also influenced by amount of crosslinking reagent.

Keywords: Ion exchange resins, solvent impregnated resin (SIR), Chromium, Adsorption.

INTRODUCTION

Industrial wastewaters are the important contaminating sources in pollution of the water environment. Industries that use large amounts of water for their processes have the potential to pollute waterways through the discharge of their wastewaters into streams, rivers, and nearby water sources. They include organic materials, pathogens, metals, salts, ammonia, pesticides, pharmaceuticals, endocrine disruptors, etc., and cause adverse impacts in the surrounding water resources[1]. Heavy metals can be introduced into rivers and other aquatic environments by natural and anthropogenic processes such as chemical leaching of bedrocks in drainage basins, discharge of urban runoff, domestic and industrial wastewater, mining and smelting operations, and combustion of fossil fuels, processing and manufacturing industries, and atmospheric deposition across the air–sea interface. The highest metal values are generally determined in urbanized and industrialized areas[2].

Chromium is a naturally occurring heavy metal that can exist in air, water, soil, and food. It is now considered as one of the major environmental pollutants due to its toxicity for ecological, nutritional, and environmental reasons. Chromium is added in the environment through various natural and anthropogenic activities and exists mainly in two forms as Cr(III) and Cr(VI). The Cr(VI) is considered to be more toxic than Cr(III) due to its high solubility and mobility. It is well reported that Cr(VI) is occupational carcinogen associated with lung, nasal and sinus cancers[3]. The maximum concentration permitted for chromium according to the World of Health Organization, WHO guidelines is 0.05 mg/L in water[4].

The common methods such as reduction–precipitation, solvent extraction, and adsorption/ion exchange have been used for recovery and removal of Cr(VI) from aqueous solutions. The disadvantage of reduction–precipitation method is large quantity of chemical consumption and generation of sludge which needs costly disposal procedure for landfill. The use of solvent extraction is also not effective for the separation of metal ions from dilute solutions because of the loss of extractant, third phase formation, and use of flammable diluents. Adsorption and ion exchange methods are effective for treatment of dilute metal solutions. On the other hand, the materials employed in adsorption and ion exchange processes have generally low adsorption capacities and they show less selectivity towards metal ions than solvent extraction method. Chelating ion exchange resins are highly selective but they are expensive and elution of metal ions from these resins are difficult[5]. Water-soluble polymers (WSP) in conjunction with ultrafiltration membranes are also good alternatives but they require an expensive operation system such as ultrafiltration to remove huge quantity of metal ions[6,7].

Solvent impregnated resins (SIRs) are macroporous resins impregnated with an extractant. In this approach, a liquid extractant is contained within the pores of adsorbent particles. Usually, the extractant is an organic liquid employed in solvent extraction process. Its function is to extract metal ions from a solution.
EXPERIMENTAL

Preparation of SIRs

Typical procedure involves immersing polymer adsorbent Diaion HP-2MG (Mitsubishi Chemical) (Fig. 1) in Aliquat 336 (Sigma-Aldrich) (Fig. 2) acetone solution (Merck) and shaking at 25°C for 24 h. The polymer beads were subsequently separated by filtration and several times washed with ultrapure water followed by air-drying.

The vacuum drying (room temperature, overnight) completed the preparation procedure. The surface of SIRs was coated for a protective layer by immersing the SIRs in a solution of PVA (Merck) and KCl solution (Merck) and stirred at 25°C for 24 h. After filtration and dried with air and then under vacuum, SIRs were added into Na2CO3 (Merck) solution of 1 mol/L and stirred for 1 h, and then different amounts of divinylsulphone (Sigma-Aldrich) as crosslinking reagent are added into this mixture and stirred for 24 h at 25°C. Finally, the coated SIRs were washed with deionized water and then air-dried with air and later in vacuum oven.

![Figure 1. Structure of DiaionHP-2MG polymer adsorbent.](image1)

![Figure 2. Structure of Aliquat336 (tricapril methyl ammonium chloride).](image2)

Cr(VI) Adsorption Tests

Sorption performances of SIRs prepared were examined using batch and column sorption methods. For batch sorption tests, various amounts of SIRs (10, 25, 50, 100, 150, and 200 mg) were contacted with 25 mL of Cr(VI) solution (20 mg/L, pH 4) for kinetic studies. 1.5 g of SIR was contacted with 750 mL of Cr(VI) containing solution (20 mg/L) and stirred at 250 rpm.

For the column mode operation, a 0.5 mL of wet SIR was packed into a column having an internal diameter (ID) of 0.7 cm. A Cr(VI) solution prepared from K2Cr2O7 (Merck) of 20 mg/L (pH 4.0) was passed through the column at Scan Velocity (SV) 15 h⁻¹. The pH of the solution as pH 4.0 was selected according to the results obtained by Kabay et al. [19] and also determined by Vincent and Guibat [31]. Some other results on the Cr(VI) removal by polymers and membranes at pH 4 have been also reported [32].

The column elution of Cr(VI) from the resin was performed with a mixture of 1 M NaOH (J.T. Baker, 97%) and 1 M NaCl solutions (Riedel, 99.8%) at a space velocity (SV) 5 h⁻¹.

The analyses of Cr(VI) was carried out by a Varian 10 Plus model Atomic Absorption Spectrometer, AAS.

Kinetic Study

In order to predict the mechanism involved in the adsorption process, several kinetic models were used. Among them, the sorption kinetics was usually described by pseudo-first or pseudo-second order kinetic model equations [13].

The sorption kinetics following the pseudo-first-order is given by Eq. 1:

\[
\frac{dq}{dt} = k_1(q_e - q_t)
\]

\(q_t\): Amount of adsorbed species (mg/g) at ant time t.

\(q_e\): Amount of adsorbed species (mg/g) at equilibrium time.

\(k_1\): Adsorption rate constant (min⁻¹).

Integrating Eq. (1) with respect to boundary conditions:

\[
\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t
\]

Adsorption rate constant \(k_1\) (min⁻¹) can be calculated from the plot of \(\log(q_e - q_t)\) versus time.

The kinetic data can be analyzed by means of pseudo-second-order kinetics using Eq.2:

\[
\frac{dq}{dt} = k_2(q_e - q_t)^2
\]

\(k_2\): Pseudo-second-order rate constant (g/mg min)

\(q_t\): Amount of adsorbed species (mg/g) at ant time t

\(q_e\): Amount of adsorbed species (mg/g) at equilibrium time. Varying the variables in Eq. (3) one gets

\[
\frac{dq}{(q_e - q_t)^2} = k_2 dt
\]

and integrating Eq. (4) for the boundary conditions:

\[
t = 0\ to\ t = t, \ and\ q = 0 \ and\ q = q_e, \ one\ obtains\ the\ final\ form
\]

\[
\frac{t}{q_e} = \frac{1}{k_2q_t^2} + \frac{1}{q_e}t
\]

A plot \(t/q\) versus \(t\) gives the value of the constants \(k_2\) (g/mg min). It is possible to calculate \(q_e\) (mg/g).

The ion exchange between the counterion in the solution and the exchangeable ion on the active site of the resin takes place in a heterogeneous process. Mass transfer models are based on the following steps in the process [32]:

a) Transport of the exchanging ions from bulk solution to the outer surface of the resin particle,

b) Diffusion through a film/boundary layer at the external surface of the particle,

c) Pore diffusion of the ions to the active sites,

d) Actual exchange process (chemical reaction),

e) Pore diffusion of the ions outward through the particle from the active sites,

f) Back diffusion through the film/boundary layer at the particle surface, and

g) Transport of the exchanged ions from the external surface of the resin particle to the bulk solution.
The overall rate of ion exchange process is determined by the relative rates of these steps. Usually, the resistance in the bulk solution (a and g) is easily controlled and negligible. The kinetic studies on ion exchange separation consider only three resistances; therefore, the exchange rate can be controlled by film diffusion (b and f), particle diffusion (c and e), and chemical reaction (d).

The kinetic data could be evaluated using diffusion model equations based on Unreacted Core Model (UCM) and Infinite Solution Volume (ISV) models (Table 1).

<table>
<thead>
<tr>
<th>Method</th>
<th>Equation</th>
<th>Rate controlling step</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISV</td>
<td>[-\ln(1-x) = kt] Where ( k = \frac{3DC}{r_0\delta Cr}]</td>
<td>Film diffusion</td>
</tr>
<tr>
<td></td>
<td>[-\ln(1-x^2) = k_{lt}t] Where ( k = \frac{D_r\pi^2}{r_0^2}]</td>
<td>Particle diffusion</td>
</tr>
<tr>
<td>UCM</td>
<td>[X = \left(\frac{3C_A0K_{MA}a}{ar_0C_s0}\right)^t]</td>
<td>Liquid film</td>
</tr>
<tr>
<td></td>
<td>[3 - 3(1 - x)^{1/3} = 2x] Where ( k = \frac{6DC_A0C_s0}{ar_0C_s0}]</td>
<td>Reacted layer</td>
</tr>
<tr>
<td></td>
<td>[1 - (1 - x)^{1/3} = \left(\frac{kSC_A0}{r_0}\right)^t]</td>
<td>Chemical reaction</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

**Batchwise removal of Cr(VI) by SIRs**

As shown in Fig. 3, removal of Cr(VI) by uncoated SIRs was higher than those coated SIRs. When the degree of crosslinking increased, it was not easy to get a high percent removal of Cr(VI) especially with low amounts of SIRs.

**Figure 3.** Effect of crosslinking degree during preparation of coated SIRs on batch removal of Cr(VI).

Fig. 4 shows the kinetic profiles of uncoated and coated SIRs. By increasing the degree of crosslinking, the kinetic performance of SIRs declined. For coated-unconditioned SIRs we observed that uncoated and low crosslinked SIRs reach the equilibrium in 100 min. Similar results were found in the literature by Kabay et. al.\[18, 22\]. Following conditioning of SIRs using a solution of NaOH-NaCl mixture, kinetic performance of SIRs improved greatly due to the improvement on the surface morphology of SIRs as seen in Fig. 5. Uncoated and low crosslinked coated-conditioned SIRs reach the equilibrium in 50 min. The same behavior was observed by Kabay et al.\[22\]. This demonstrated again that is important to enhance the Cr(VI) removal capacity of SIRs by a conditioning process with 1M NaOH-1M NaCl mixed solution.

**Figure 4.** Effect of crosslinking degree on kinetic profiles of SIRs for Cr(VI) removal.

**Figure 5.** Effect of conditioning by a mixture of NaOH-NaCl solution on kinetic profiles of SIRs

**Table 2.** Evaluation of kinetic data for coated unconditioned SIRs using conventional (pseudo-first and pseudo-second orders), diffusional, and reaction model equations (unconditioned SIRs).

<table>
<thead>
<tr>
<th>Model</th>
<th>LC*</th>
<th>MC*</th>
<th>HC*</th>
</tr>
</thead>
<tbody>
<tr>
<td>First order</td>
<td>0.9705</td>
<td>0.9705</td>
<td>0.9532</td>
</tr>
<tr>
<td>Second order</td>
<td>0.9400</td>
<td>0.9400</td>
<td>0.9946</td>
</tr>
<tr>
<td>ISV</td>
<td>f(x)=(-\ln(1-x))</td>
<td>0.9705</td>
<td>0.9705</td>
</tr>
<tr>
<td></td>
<td>f(x)=(-\ln(1-x^2))</td>
<td>0.9491</td>
<td>0.9491</td>
</tr>
<tr>
<td></td>
<td>f(x)=x</td>
<td>0.9491</td>
<td>0.9491</td>
</tr>
<tr>
<td>UCM</td>
<td>f(x)=3(3(1-x)^{2/3})</td>
<td>0.9608</td>
<td>0.9608</td>
</tr>
<tr>
<td></td>
<td>f(x)=1((1-x)^{1/3})</td>
<td>0.9677</td>
<td>0.9677</td>
</tr>
</tbody>
</table>

*LC: Low Crosslinked, MC: Medium Crosslinked and HC: High Crosslinked.
According to Table 2, SIRs coated using low and medium amounts of crosslinker follow a kinetic mechanism of pseudo-first order although the kinetic data of highly crosslinked SIRs obey well to pseudo-second order kinetics model. In terms of the diffusion and reaction models, the rate is controlled by film diffusion for SIRs coated using low and medium amounts of crosslinker and by particle diffusion for SIRs coated using high amount of crosslinker. When evaluated kinetic data using UCM model equations, it was seen that chemical reaction was rate controlling step for low and medium crosslinked SIRs while particle diffusion in the case of highly crosslinked SIRs.

Table 3. Evaluation of kinetic data for coated SIRs conditioned with a solution of NaOH-NaCl mixture using conventional (pseudo-first and pseudo-second orders), diffusional, and reaction model equations.

<table>
<thead>
<tr>
<th>Model</th>
<th>LC*</th>
<th>MC*</th>
<th>HC*</th>
</tr>
</thead>
<tbody>
<tr>
<td>First order</td>
<td>0.9909</td>
<td>0.9909</td>
<td>0.9898</td>
</tr>
<tr>
<td>Second order</td>
<td>0.9735</td>
<td>0.9735</td>
<td>0.9708</td>
</tr>
<tr>
<td>ISV</td>
<td>f(x)=-ln(1-x)</td>
<td>0.9909</td>
<td>0.9909</td>
</tr>
<tr>
<td></td>
<td>f(x)=-ln(x^2)</td>
<td>0.9724</td>
<td>0.9724</td>
</tr>
<tr>
<td>UCM</td>
<td>f(x)=3-3(1-x)^{0.5}</td>
<td>0.9958</td>
<td>0.9958</td>
</tr>
<tr>
<td></td>
<td>f(x)=1-(1-x)^{0.5}</td>
<td>0.9800</td>
<td>0.9800</td>
</tr>
</tbody>
</table>

*LC: Low Crosslinked, MC: Medium Crosslinked

Removal of Cr(VI) by SIRs by column method

A comparative column study for removal of Cr(VI) was performed using low and medium crosslinked coated conditioned SIRs. The breakthrough profiles of SIRs are shown in Figure 6. The column study data are summarized in Table 4.

![Figure 6](image)

Table 4. Column data for SIRs (coated conditioned).

<table>
<thead>
<tr>
<th>Column data</th>
<th>LC*</th>
<th>MC*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Breakthrough Point (BV)</td>
<td>281</td>
<td>260</td>
</tr>
<tr>
<td>Breakthrough Point Cr(VI) Concentration (mg/L)</td>
<td>1.49</td>
<td>1.82</td>
</tr>
<tr>
<td>Breakthrough Capacity (mg Cr(VI)/L-resin)</td>
<td>4.85</td>
<td>4.52</td>
</tr>
<tr>
<td>Total Capacity (mg Cr(VI)/L-resin)</td>
<td>8.00</td>
<td>7.30</td>
</tr>
<tr>
<td>Column Utilization (%)</td>
<td>60.5</td>
<td>69.8</td>
</tr>
<tr>
<td>Elution Efficiency (%)</td>
<td>74.4</td>
<td>69.9</td>
</tr>
</tbody>
</table>

*LC: Low Crosslinked, MC: Medium Crosslinked

CONCLUSIONS

Aliquat 336 containing SIRs were prepared by using a hydrophilic polymer matrix Diaion HP-2MG. Chemical stabilization of prepared SIRs through coating and crosslinking were performed to eliminate the possible leakage of extractant from the polymer adsorbent. On the other hand, degree of crosslinking influenced the kinetic performance of SIRs greatly. Conditioning with a solution of NaOH-NaCl mixture was helpful to improve the kinetics for especially highly crosslinked SIRs. It is possible to remove Cr(VI) ions from aqueous solution by continuous method with coated-conditioned SIRs.

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