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REMOVAL OF CR(VI) BY STABILIZED SOLVENT IMPREGNATED RESIN (SIR) PREPARED BY USING A HYDROPHILIC POLYMER ADSORBENT AND ALIQUAT 336.

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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[5,6].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 [7-11].

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. Thus, SIRs appear as alternative functional materials for removal of heavy metals from water. SIRs can have the advantages of both solvent extraction and ion exchange. They can be applied easily compared to solvent extraction systems due to mostly operational simplicity in fixed bed columns and easy recovery of loaded metal ions in the desorption step[12-17].

Preparation techniques and various applications of SIRs were reported in literature by Kabay et al.[18]. According to the literature, the SIRs containing Aliquat 336 were found to be highly effective for removal of Cr(VI) from aqueous solution. These SIRs were produced by a wet impregnation technique using hydrophobic styrene-divinylbenzene copolymer (Diaion HP-20) and hydrophilic methacryclic acid based polymer adsorbent (Diaion HP-2MG)[19].

Elsewhere, SIRs have been also prepared by impregnating Amberlite XAD-7 with Aliquat 336 as the extractant and acetone as the solvent by a wet impregnation technique for Cr(VI) removal[20].

It was reported that SIRs can be stabilized by coating the surface of a hydrophilic polymer, poly(vinylalcohol) (PVA) and chemical crosslinking using divinylsulphone[21]. According to the literature, the degree of crosslinking during stabilization by coating affects the kinetic and column performances of the resulting SIRs significantly from Cr(VI) separation[22-24]. Elsewhere, Hosseini-Bandegharaei et. al. studied the kinetics, equilibrium, and thermodynamic of Cr(VI) sorption by toluidine blue or-impregnated XAD-7 resin beads and its application for the treatment of wastewaters containing Cr(VI)[25]. Qureshia et al. studied the estimation of Cr(VI) sorption efficiency of novel regenerable c*p-tert*-butylcalix[8]areneoctamide impregnated Amberlite resin[26]. Yang et. al. studied the SIR prepared using ionic liquid Cyphos IL 104 for Cr(VI) removal[27].

Soylak et al. studied the biosorption of trac heavy metals on *Aspergillusfumigatus* immobilized Diaion HP-2MG resin prior to their spectroscopic analysis using AAS[28]. Chaedi et al. used the Diaion HP-2MG modified with 2-(2,6-dichlorobenzylideneamino) benzenethiol for metal ions determination[29]. Duran et al. studied the immobilization Anoxybacillusgonensis in HP-2MG for biosorption of heavy metals[30].

The aim of the current study is to prepare SIRs containing Aliquat 336 using hydrophilic polymer adsorbent Diaion HP-2MG resin and then stabilized by coating with PVA and crosslinked with divinylsulfone at different amounts to carry out the removal of Cr(VI) ions from aqueous solution. Thus, the kinetic behaviors of stabilized and unstabilized SIRs were evaluated using some mathematical model equations. Also, column performances of SIRs were compared.

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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 25ºC 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 25ºC for 24 h. After filtration and dried with air and then under vacuum, SIRs were added into Na_2CO_3 (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 25ºC. Finally, the coated SIRs were washed with deionized water and then air-dried with air and later in vacuum oven.

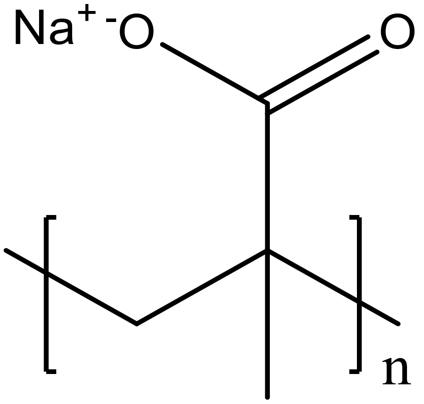

Figure 1. Structure of DiaionHP-2MG polymer adsorbent.

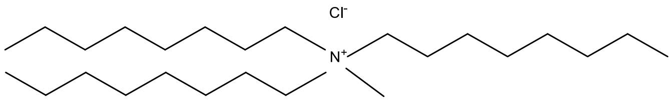

Figure 2. Structure of Aliquat336 (tricapril methyl ammonium chloride).

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 K_2CrO_4 (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 Guibal[33]. Some other results on the Cr(VI) removal by polymers and membranes at pH 4 have been also reported[34].

The column elution of Cr(VI) from the resin was performed with a mixture of 1 M NaOH (J.T. Baker, 97%) and1 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 [31].

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

$$\frac{dq}{dt} = k_1(q_e - q_t) \qquad (1)$$

q_t: Amount of adsorbed species (mg/g) at ant tine 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:

$q = 0$ at $t = 0$, and $q = q_t$ at $t = t$ it is obtained

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} \qquad (2)$$

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:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \qquad (3)$$

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

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

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

$$\frac{dq}{(q_e - q_t)^2} = k_2 dt \qquad (4)$$

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

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \qquad (5)$$

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 1. Diffusional and reaction kinetic models[32].

Method	Equation	Rate controlling step
ISV	$-\ln(1-x)=kt$ Where $k=3DC/r_0\delta Cr$	Film diffusion
	$-\ln(1-x^2)=k_{li}t$ Where $k=D_r\pi^2/r_0^2$	Particle diffusion
UCM	$X=\left(\frac{3C_{A_0}K_{MA}}{ar_0C_{S_0}}\right)t$	Liquid film
	$3-3(1-x)^{2/3}-2x=\left(\frac{6D_{CR}C_{A_0}}{ar_0^2C_{S_0}}\right)t$	Reacted layer
	$1-(1-x)^{1/3}=\left(\frac{k_SC_{A_0}}{r_0}\right)t$	Chemical reaction

RESULTS AND DISCUSION

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.

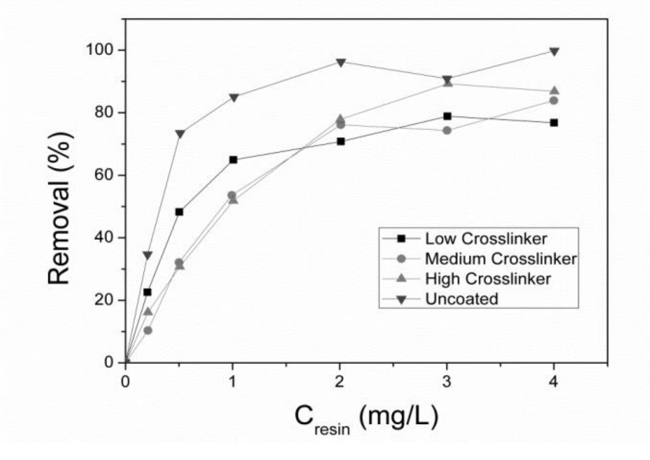

Figure 3. Effect of crosslinking degree during preparation of coated SIRs on batch removal of Cr(VI).

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.

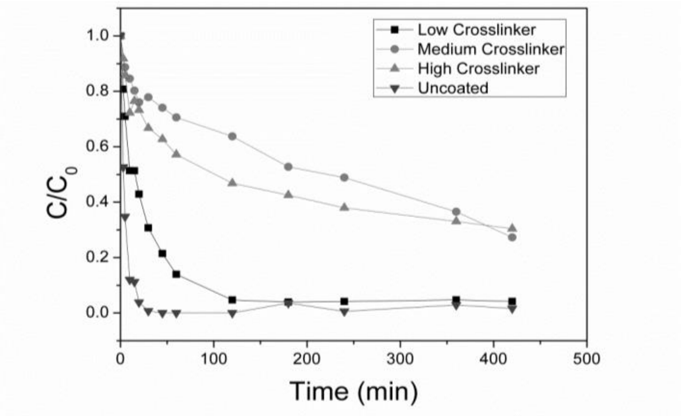

Figure 4. Effect of crosslinking degree on kinetic profiles of SIRs for Cr(VI) removal.

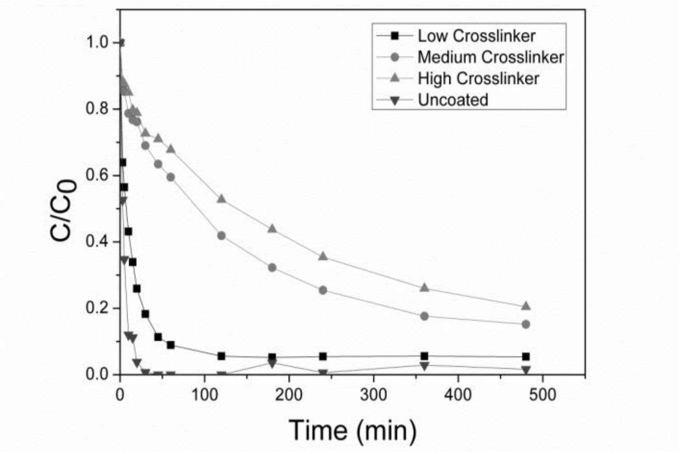

Figure 5. Effect of conditioning by a mixture of NaOH-NaCl solution on kinetic profiles of SIRs

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).

		LC*	MC*	HC*
	Model	**R^2**	**R^2**	**R^2**
	First order	0.9705	0.9705	0.9532
	Second order	0.9400	0.9400	0.9946
ISV	f(x)=-ln(1-x)	0.9705	0.9705	0.9532
	$f(x)=-\ln(1-x^2)$	0.9491	0.9491	0.9910
	f(x)=x	0.9491	0.9491	0.7546
UCM	$f(x)= 3-3(1-x)^{2/3-2x}$	0.9608	0.9608	0.9783
	$f(x)= 1-(1-x)^{1/3}$	0.9677	0.9677	0.9002

*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.

	Model	LC* R^2	MC* R^2	HC* R^2
	First order	0.9909	0.9909	0.9898
	Second order	0.9735	0.9735	0.9708
ISV	$f(x)=-\ln(1-x)$	0.9909	0.9909	0.9898
	$f(x)=-\ln(1-x^2)$	0.9724	0.9724	0.9971
UCM	$f(x)=x$	0.8264	0.8264	0.8817
	$f(x)= 3-3(1-x)^{2/3-2x}$	0.9958	0.9958	0.9980
	$f(x)= 1-(1-x)^{1/3}$	0.9800	0.9800	0.9657

*LC: Low Crosslinked, MC: Medium Crosslinked and HC: High Crosslinked

Some changes were obtained in the results of kinetic evaluation, especially in the case of highly crosslinked SIRs after conditioning with a solution of NaOH-NaCl mixture prior to kinetic tests (Table 3). The Low, Medium and High crosslinked coated-conditioned SIRs follow a kinetic model of pseudo-first order. For diffusion and reaction models, the rate is controlled by film diffusion for low and medium crosslinked coated-conditioned SIRs while by particle diffusion for high crosslinked coated-conditioned SIRs. The kinetic data evaluated by UCM model equations demonstrated that the particle diffusion was the rate controlling step for low, medium, and high crosslinked coated-conditioned SIRs.

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.

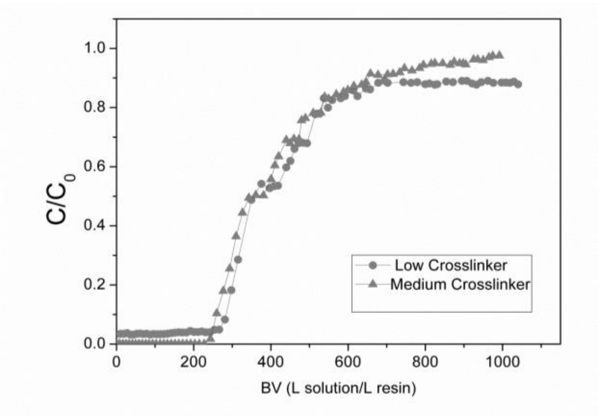

Figure 6. Breakthrough profiles of coated conditioned SIRs for Cr(VI) removal

As shown in Fig. 6, the breakthrough started earlier to some extent with the increase of crosslinking due to the difficulty in interaction of Cr(VI) ions and the functional groups of the SIR. A similar behavior was observed in by Sengupta and Clifford [35].The column utilization is increased with an increase in the amount of crosslinker reagent for HP-2MG resin, but breaktrough point (BV), breaktrough capacity, total capacity, and elution efficiency decreased with an increase of crosslinker. In general, a better column performance was achieved by low crosslinked SIR. Similar behavior was reported in the literature[19, 23, 24] .

Since the column tests were performed with small amount of SIR (0.5 mL), the chanelling effect was observed especially in case of medium crosslinked SIRs due to irregularity in particle size and bed packing. This should be overcome by using larger volumes of SIR in column study with a good packing efficiency.

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

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

*LC: Low Crosslinked, MC: MediumCrosslinked

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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