Hexavalent chromium removal performance of anionic functionalized monolithic polymers: column adsorption, regeneration and modelling

Necla Barlik, Bülent Keskinler and M. Muhtar Kocakerim

ABSTRACT

Anionic functionalized monolithic macro-porous polymers were used for the removal of hexavalent chromium(VI) anions from aqueous solution in column experiments. At a flux of 1.0 cm min and 30 mg Cr(VI) L⁻¹ feed concentration, breakthrough capacity and apparent capacity were 0.066 g Cr(VI) g⁻¹ anionic monolith and 0.144 g Cr(VI) g⁻¹ anionic monolith, respectively. The degree of column utilization was found to lie in the range 41–46%. Two kinetic models, theoretical and Thomas models, were applied to experimental data to predict the breakthrough curves and to determine the characteristic parameters of the column useful for process design. The simulation of the whole breakthrough curve was effective with the models. At a flux of 1.0 cm min and 30 mg Cr(VI) L⁻¹ feed concentration, the dispersion coefficient and adsorption equilibrium constant (K) were 3.14 × 10⁻⁷ m s⁻¹ and 3,840, respectively. Also, Thomas model parameters k₁ (rate constant of adsorption) and qₑₘ (equilibrium solid-phase concentration of sorbed solute) were 1.08 × 10⁻³ L mg⁻¹ min⁻¹ and 0.124 g g⁻¹, respectively. After reaching equilibrium adsorption capacity, the monoliths were regenerated using 1 N HCl and were subsequently re-tested. It was found that the regeneration efficiency reduced from 98% after second usage to 97% after the third usage.

Key words | chromate removal, column adsorption, modelling, monolithic anion exchanger, regeneration

INTRODUCTION

Synthetic organic ion exchangers, commonly referred to as resins, and membranes consist of an elastic three-dimensional network of hydrocarbon chains which carry fixed ionic groups. There is no significant difference between ion exchange membranes and resins except for their mechanical and swelling properties. The membranes are in sheet form but the resins are in bead form (Escobar & Schafer 2014). Ionic groups such as −SO₃⁻, −COO⁻, −PO₃²⁻, −PO₃H⁻ and −C₆H₄O⁻, in their cationic forms, and −NH₃⁺, −NRH₂⁺, −NR₂H⁺, −NR₃⁺, −PR₃⁺ and −SR₂ in anionic forms are fixed within the matrix. The charge of the groups is balanced by mobile counter ions (Helfferich 1962; Xu 2005).

The first ion exchange resins having the form of beads were produced by Rohm & Haas Company in 1939 (Inoue et al. 2004), and the first ion exchange membranes were synthesized the 1920s (Xu 2005). Because the anionic or the cationic exchange resins and the membranes have an effective separation ability, they have attracted extensive attention in environmental pollutant treatment (Tchobanoglous et al. 2003; Basile & Pereira Nunes 2011). Moreover, these materials have been not only used for water engineering, but also applied extensively within medicine, inorganic analytical chemistry, and the food and chemical industry.

Because ion exchange resins and membranes have been used effectively in ion exchange columns and membrane processes for scientific or industrial purposes, their development and performances have been investigated by many researchers (Acton 2011; Tanaka 2003). PolyHIPE polymers, prepared through a high internal phase emulsion (HIPE) polymerization route, are a new class of cellular micro-porous materials (Barby & Haq 1985; Wakeman et al. 1998; Mercier et al. 2000; Akay et al. 2004; Barlik 2006). They are used either as monolithic micro-reactors or particulate form for chemical or biochemical conversions, or as absorbents as well as adsorbents or membranes or indeed...
as a combination of these three basic modes of operation (Barlık et al. 2015).

Hexavalent chromium (Cr(VI)) is commonly found in industrial sewage. The major anthropogenic sources of Cr(VI) are electronic, metallurgical, leather and textile industries. The effluent from these industries may contain Cr(VI) at varying concentrations up to hundreds of mg L⁻¹. The compounds of Cr(VI) are considered by the International Agency for Research on Cancer as a powerful carcinogenic agent that modifies DNA transcriptions (IARC undated). Additionally, the presence of chromium in water causes serious environmental problems. Among various treatment techniques available, the most commonly used ones are reduction and precipitation (Ruotolo & Gubulin 2009; Zafarani et al. 2014), bio-reduction (Chung et al. 2009; Thatoi et al. 2014), solvent extraction (Lee et al. 2009), membrane processes (Chen et al. 2009; Yoon et al. 2009), adsorption (Thanos et al. 2012; Solisio et al. 2013) and ion exchange (Marshall & Wartelle 2006; Campos et al. 2007; Shi et al. 2009).

In this study, we tested the performances of anionic functionalized monolithic macro-porous polyHIPE polymers prepared in our laboratory (Barlık et al. 2015) to remove hexavalent chromium (Cr(VI)) ions from aqueous solutions and we also tested regeneration of the polymers. The monoliths were prepared by polymerization of HIPE, and then the surface chemistry of them was modified by chloromethylation and amination to impart anionic functionality in the form of Cl⁻. The breakthrough curves obtained from the ion adsorption experiments were compared with those derived from the theoretical column model and Thomas model. Also, the parameters of the models were calculated.

**METHODS**

For ion adsorption tests, monolithic anion exchanger discs with 2.54 cm in diameter and 0.4 cm in height were used as the bed of exchange media. The anion exchanger discs were prepared in our laboratory. They were produced by bonding pyridine group to chloromethylated cross-linked styrene–divinyl benzene precursor. They had 90% of void volume with 12% degree of crosslinking. The chemical structure of the polymer with anionic functionality can be represented as (Scheme 1) (Barlık et al. 2015).

For the tests, the stock solution of chromate was prepared by dissolving in deionized water appropriate amounts of reagent grade K₂CrO₄, obtained from Merck. All tests were carried out at room temperature. The concentration of chromate ions was determined with a UV-160 Shimadzu spectrophotometer by measuring the absorbance of complex formed between 1,5-diphenylcarbazide and chromate (for all hexavalent chromium species) at 540 nm (APHA-AWWA-WEF 1998).

HCl, used for the regeneration of the polymer monoliths, and 1,5-diphenylcarbazide were reagent grade Merck products.

**Column experiments**

Fixed bed up-flow was conducted by a peristaltic pump at a constant flow rate of feed solution through the anion exchanger polymer monoliths (Figure 1). Feed concentration of 30, 50 and 100 mg L⁻¹ chromate (Run 1 to 3), and fluxes of 2.0 and 3.0 cm min⁻¹ (corresponding flows rates 10 mL min⁻¹, 15 mL min⁻¹, respectively) (Run 4 and 5) were chosen. The tests were carried out at initial pH 3.55 ± 0.05.

An apparatus made entirely from plastic components was used to house the monoliths of known dry mass. The concentration of the effluent was monitored with time, until it was the same as the feed concentration, and its concentration was analyzed, as described above, to yield output concentration breakthrough curves.

**Regeneration experiments**

1 N HCl was used as regenerate and experiments were performed in the fixed bed column test apparatus shown in
Figure 1. The adsorption (service) was in up-flow and regeneration was in down-flow. The operation was referred to as countercurrent ion exchange.

Feed concentration of 30 mg L$^{-1}$ chromate and flow rate of 10 mL min$^{-1}$ were chosen in adsorption experiments. Regenerate solution flowed down at 0.5 mL min$^{-1}$ (flux of 0.1 cm min). After service or regeneration the anion exchanger disc was washed with distilled water excessively. Service or regeneration was performed three times (Run 1S to 3S) or two times (Run 1R and 2R), respectively.

The results from the breakthrough experiments were integrated for the calculation of chromate adsorbed onto the monolith and these results were checked with the results obtained from elution studies. This information is important for the long-term use of these anionic monolithic polymers.

RESULT AND DISCUSSION

The chromate may be present in various forms such as HCrO$_4^-$, HCrO$_4^-$, CrO$_2^-^-$, HCr$_2$O$_7^-$ and Cr$_2$O$_7^{2-}$ in the aqueous solution as a function of pH. The predominant species of Cr(VI) is HCrO$_4^-$, in the aqueous phase at acidic pH, but CrO$_2^-^-$ is predominant at alkaline pH. The usual selectivity at neutral or alkaline pH of strong base anion exchangers is CrO$_2^-^-$ > HCrO$_4^-$, and at acidic pH there is a reversal in selectivity (Neagu et al. 2003).

Between the exchanger surface and chromate solutions can be expected to occur reactions given by Equations (1) and (2). Also, Equation (2) can be more predominant for the tests performed at pH 3.55 ± 0.05.

\[
2(R-\text{CH}_2\text{N}^+\text{Cl}^-) + \text{CrO}_4^{2-} \rightarrow (R-\text{CH}_2\text{N}^+)\text{CrO}_4^- + 2\text{Cl}^- \\
\text{(1)}
\]

\[
\text{R-CH}_2\text{N}^+\text{Cl}^- + \text{HCrO}_4^- \rightarrow \text{R-CH}_2\text{N}^+\text{HCrO}_4^- + \text{Cl}^- \\
\text{(2)}
\]

where R is resin group.

Breakthrough behaviors

The breakthrough point (the time at which chromate concentration in the effluent reached 0.05*$C_0$) and bed exhaustion (the time at which chromate concentration in the effluent reached $C_0$) were used to evaluate the breakthrough curves. The capacities, utilized until breakthrough point and bed exhaustion, are called the ‘breakthrough’ capacity and the ‘apparent’ capacity, respectively.

Table 1 | Measured characteristics of column experiments and model parameter predictions

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Run 4</th>
<th>Run 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristics of column experiments</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flux (cm min$^{-1}$)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Influent concentration (mg L$^{-1}$)</td>
<td>30</td>
<td>50</td>
<td>100</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Breakthrough volume (L g$^{-1}$)</td>
<td>2.16</td>
<td>1.24</td>
<td>0.42</td>
<td>2.02</td>
<td>1.70</td>
</tr>
<tr>
<td>Apparent volume (L g$^{-1}$)</td>
<td>10.02</td>
<td>4.10</td>
<td>2.23</td>
<td>9.88</td>
<td>8.01</td>
</tr>
<tr>
<td>Breakthrough capacity *10$^{-3}$ (g g$^{-1}$)</td>
<td>66</td>
<td>58</td>
<td>46</td>
<td>63</td>
<td>54</td>
</tr>
<tr>
<td>Apparent capacity *10$^{-3}$ (g g$^{-1}$)</td>
<td>144</td>
<td>129</td>
<td>104</td>
<td>141</td>
<td>133</td>
</tr>
<tr>
<td>Degree of column utilization = breakthrough capacity/apparent capacity</td>
<td>0.46</td>
<td>0.45</td>
<td>0.44</td>
<td>0.45</td>
<td>0.41</td>
</tr>
</tbody>
</table>

**The theoretical column model**

\[
K \times 10^{-7} (m^2 s^{-1}) \\
D_L \times 10^{-7} (m^2 s^{-1}) \\
k_1 \times 10^{-3} (L mg^{-1} min^{-1}) \\
q_m \times 10^{-3} (g g^{-1}) \\
R^2 \\
\]

* *K* is the equilibrium constant for adsorption, $D_L$ is the longitudinal dispersion coefficient, $k_1$ is the rate constant of adsorption, $q_m$ is the equilibrium solid-phase concentration of sorbed solute and $R^2$ is the correlation coefficient for Equation (7).
For chromate, the breakthrough and the apparent capacities of the monoliths can be estimated from the effluent profiles by calculating the area between the S-curve and an axis representing the concentration of the outlet solution. Table 1 lists the capacities of the anion exchanger monoliths to remove chromate ions and the degrees of column utilization for all tests.

The maximum breakthrough and apparent capacities obtained from the tests were 66 mg g\(^{-1}\) and 144 mg g\(^{-1}\), respectively. At pH 4.00, Kabay et al. (2005) determined that these values for a strong base ion exchange resin, Amberlite IRA 904, were about 35 mg ml\(^{-1}\) and 41 mg ml\(^{-1}\), respectively. Wang et al. (2005) carried out Cr(VI) removal from aqueous solutions by using strong alkaline anion exchange fiber (SAAEF) as an absorbent. The maximum adsorption capacity of Cr(VI) by SAAEF was 201.2 mg g\(^{-1}\) at pH 2.00.

The mathematical models

Successful design of a column exchange process requires prediction of breakthrough curve and exchange capacity under given specific operating conditions. To model the breakthrough behavior of an exchange column, various simple mathematical models can be used (Helfferich 1962). These mathematical models, developed to predict the dynamic behavior of the column, must have suitable and logical numerical solutions and practical benefits (Hamdaoui 2009).

Performance of the monoliths as a fixed bed has been discussed using the following mathematical models.

Theoretical column model

Sherman (1962) obtained the following equation for the accumulation of solute on porous solid adsorbent:

\[
(D_M + D_L) \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} = \left(1 + \frac{(1 - \varepsilon)}{\varepsilon} K\right) \frac{\partial C}{\partial t} \tag{3}
\]

In the model development the following assumptions were made (i) axial dispersion coefficient remains constant, (ii) porosity and pore rate is uniform, (iii) radial dispersion does not occur, (iv) no stagnant zone in bed and (v) the particles are not porous.

In Equation (3), \(D_M\) is the molecular dispersion coefficient (m\(^2\) s\(^{-1}\)), \(D_L\) is the longitudinal dispersion coefficient (m\(^2\) s\(^{-1}\)), \(C\) is the effluent concentration (mg L\(^{-1}\)), \(\varepsilon\) is porosity of the bed, \(K\) is an equilibrium constant for adsorption, \(z\) is the distance variable in the direction of flow (m), \(t\) is time (s) and \(u\) is average pore velocity in axial direction (m s\(^{-1}\)).

The molecular dispersion coefficient, \(D_M\), corrects for the tortuous path through the bed of packed solids and the longitudinal dispersion coefficient, \(D_L\), is due to the flow pattern in the bed of packed solids. \(D_M\) is small compared to \(D_L\) for very low flow rates. Also, \(u\) can be calculated, as \(u = q/Ae\). In this relationship \(q\) is flow rate (m\(^3\) s\(^{-1}\)) and \(A\) is the cross-sectional area of the bed (m\(^2\)). Then, Equation (3) could be rearranged as follows:

\[
D_L \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} = \frac{1}{K} \frac{\partial C}{\partial t} \tag{4}
\]

where

\[
\lambda = \frac{\varepsilon}{\varepsilon + K(1 - \varepsilon)}
\]

The solution of Equation (4) with the following initial and boundary conditions is shown in Equation (5):

\[
t = 0 \quad z \geq 0 \quad C = 0
\]

\[
t > 0 \quad z = 0 \quad C = C_0
\]

\[
z = \infty \quad C = 0
\]

\[
\frac{C}{C_0} = 1 - \frac{1}{2} \left[\text{erfc}\left(\frac{R_1}{2\sqrt{R_S}}\right) + \exp\left(\frac{1}{S}\right)\text{erfc}\left(\frac{1 + R_i}{2\sqrt{R_S}}\right)\right] \tag{5}
\]

where

\[
R = ut/z \quad \text{and} \quad S = D_L/uz
\]

The theoretical effective concentration \((c/c_0)\) values can be calculated by choosing the dispersion coefficient and adsorption equilibrium constant. The least square was used to estimate the constants \(D_L\) and \(K\) by minimizing the error function \(F\) defined as:

\[
F = \sum_{i=1}^{np} \left[\frac{(C/C_0)_{\text{exp}} - (C/C_0)_{\text{model}}}{2}\right]^2 \tag{6}
\]

A MATLAB code was developed to estimate values of \(D_L\) and \(K\) and to calculate theoretic effective concentration...
Then experimental and theoretic effective concentration profiles were plotted as Figure 2. The values of $D_L$ and $K$ are listed in Table 1.

The breakthrough curves of column tests of different influent concentrations (Runs 1 to 3) can be found in Figure 2(a)–2(c). This figure shows that the breakthrough time generally occurred faster with higher influent concentrations. The breakthrough and apparent capacities decreased when the influent concentrations increased from 50 to 100 mg L$^{-1}$ (Table 1). This indicates that the
anionic monolithic bed was saturated faster by chromate at higher concentrations due to higher chromate loading rates. The apparent capacity and breakthrough capacity of these experiments are all between 0.104 to 0.144 g Cr(VI) g\(^{-1}\) anionic monolith and 0.46 to 0.66 g Cr(VI) g\(^{-1}\) anionic monolith, respectively. It seems that the degree of column utilization is not very sensitive to variations in influent concentrations.

The effect of flux on the capacities was investigated using tests Run 1, Run 4, and Run 5 (Figure 2(a), 2(d), and 2(e)). The breakthrough time and the treated volume of water decreased with the rise in flux (Figure 2 and Table 1). As reported in Table 1, the apparent capacity obtained from these experiments was in the range of 0.133 to 0.144 g Cr(VI) g\(^{-1}\) anionic monolith as flux decreased from 3 to 1 cm min.

Table 1 shows that the estimated values of \(D_L\) for fluxes and influent concentrations change from \(3.14 \times 10^{-7}\) to \(2.91 \times 10^{-7}\) m\(^2\) s\(^{-1}\) and from \(4.04 \times 10^{-7}\) to \(3.14 \times 10^{-7}\) m\(^2\) s\(^{-1}\), respectively. \(K\) decreases when the influent concentrations increase but it remains nearly constant when the flux changes from 1 to 5 cm min. It can be deduced that flux has a negligible effect on \(D_L\) and \(K\).

**Thomas model**

The main advantages of the Thomas model (Thomas 1948) are its simplicity and reasonable accuracy in predicting the breakthrough curves under various operating conditions. In most instances the equation which represents the macroscopic model is written as (Inglezakis & Poulopoulos 2006):

\[
\ln\left(\frac{C}{C_0} - 1\right) = -k_1 q_m M \frac{Q}{Q} - k_1 C_0 t
\]  

where \(C\) is the effluent concentration (mg L\(^{-1}\)), \(C_0\) is the influent concentration (mg L\(^{-1}\)), \(k_1\) the rate constant of adsorption (L mg\(^{-1}\) h\(^{-1}\)), \(q_m\) the equilibrium solid-phase concentration of sorbed solute (gram of solute per gram of adsorbent), \(M\) the mass of adsorbent (g), \(Q\) the flow rate (L h\(^{-1}\)) and \(t\) is the time (h).

The parameters \(k_1\) and \(q_m\) can be determined by plotting \(\ln(C/C_0) - 1\) against \(t\) using the observed data. Figure 3 shows the plot \(\ln(C/(C_0-C))\) versus \(t\) for Run 1 to 5. The values of \(k_1\) and \(q_m\) are listed in Table 1. The linear regression coefficients (\(R^2\)) of the Thomas model graph are in the range from 0.97 to 0.78. However, it is visible from the shape of the curve (Figure 3) that the relationship is
not linear. Using the estimated parameters, the breakthrough curves for the Run 1 to 5 could be reconstructed for Cr(VI) adsorption as Figure 2.

Regeneration performances

The anionic monolith was subsequently regenerated using 1 N HCl solution. The adsorption (service) and the regeneration were repeated three and two times, respectively. A reversal of the reactions given in Equations (1) and (2) can be expected for the regeneration.

The typical profiles of the service were tested using 30 mg Cr(VI) L\(^{-1}\) and 2.0 cm min of flux, are shown in Figure 4(a). Figure 4(b) shows elution curves for chromate during regeneration of exhausted the monolith using 1 N HCl.

Regeneration efficiency is defined as the ratio of the total equivalents of ions removed from a resin to the total equivalents of ions present in the volume of regenerant used (Benefield et al. 1982). For both regenerations, the volume of HCl solution passed through the bed were almost equal and the efficiency of regeneration was decreased by only 1%. The regeneration and services parameters for the monolith are given in Table 2.

### CONCLUSIONS

Hexavalent Cr(VI) removal from aqueous solutions in a continuous system was studied using the anionic functionalized monolithic polymers previously synthesized in our laboratory.

- It has been the first study to describe column adsorption of Cr(VI) onto the anionic functionalized monolithic polyHIPE polymers. The experiments showed that it is possible to remove the Cr(VI) ions from aqueous medium through sorption onto the monoliths.
- The anionic functionalized monolithic polymers have been demonstrated as an effective adsorbent. Also, depending on the column operating conditions, higher removal efficiencies can be achieved.
- The variations in flow rate had a negligible effect on the total Cr(VI) adsorption capacity. However, the capacity of monoliths was influenced by feed concentration. Moreover, the dispersion coefficient and equilibrium constants for adsorption were influenced by the feed concentration.
- Regeneration tests with HCl showed that the monoliths can have desorption capacity. It was found that the regeneration efficiency reduced from 98% after second usage to 97% after the third usage. They have potential for the treatment of industrial effluents. The concentrated chromate solutions arising from the elution of the monoliths can be used for industrial plating in the raw form, or as an anti-corrosion agent in a cooling tower by converting to sodium chromate form (Terry 2004).
- Two different models, used widely in the laboratory scale, were applied to experimental data obtained from a continuous system using fixed columns to predict the breakthrough curves and to determine the column kinetic parameters. The model parameters were determined successfully. \(D_L\) was increased with an increase in influent concentration but decreased dramatically with an increase in flux. However, the opposite trends were observed for \(K\).
- These models have given good approximations to experimental behavior. The simulations of the breakthrough curves are compatible with the theoretical column model and the Thomas model, but the theoretical column model is better. They can be used for convenient representation of the column ion adsorption process under the present experimental conditions.

### ACKNOWLEDGEMENT

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### REFERENCES

Acton, Q. 2011 Ion Exchange Resins: Advances in Research and Application. Scholarly Editions, Atlanta, GA, USA.


Association/American Water Works Association/Water Environment Federation, Washington, DC.


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