KINETIC AND THERMODYNAMIC PROCESSES ON WEAK ACID RESINS IN METALS REMOVAL FROM WASTEWATER

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Abstract.
The chemical and metallurgical industries are the main producers of metal-bearing liquid effluents that due to the toxic character of many of the metals contained in them need to be treated before the final discharge. The removal of Cr⁶⁺ from aqueous solution by an ion-exchange resin is described. Ion-exchange resins Purolite A 500 shows a remarkable increase in sorption capacity for Cr⁶⁺, compared to other resins. The sorption process, which is pH dependent shows the maximum removal of Cr⁶⁺ in the pH range 1–5 for an initial Cr⁶⁺ concentration of 1 g/L. The sorption of Cr⁶⁺ on these cation exchange resins follows first-order reversible kinetics and pseudo-first-order kinetics.

Key words: ion-exchange; heavy metals; liquid effluents; environment, Cr⁶⁺

Introduction
Chromium, occurring as Cr³⁺ or Cr⁶⁺ in the environment, is an important material resource, an essential micronutrient or toxic contaminant too. Cr³⁺ is necessary for the normal development of human and animal organisms but Cr⁶⁺ activates teratogenic processes, disturbs DNA synthesis and can give rise to mutagenous changes leading to malignant tumours (Cavaco et al., 2009). Natural sources of chromium include weathered rocks, volcanic exhalations and biogeochemical processes and, in the man-polluted environment, mainly waste after processing and utilization of chromium compounds. Chromium is an important and widely used element in industry. The hexavalent and trivalent chromium are often present in electroplating wastewater. Other sources of chromium pollution are leather tanning, textile, metal processing, paint and pigments, dyeing and steel fabrication. To remove toxic chromium compounds from sewages several methods are used such as: precipitation, coagulation, solvent extraction and various kinds of membrane processes, ion flotation, adsorption and ion-exchange (Dąbrowski et al., 2004). The maximum limit in drinking water is of 0.05 mg/L. The drinking groundwater chromium content ranges on the average from 0.07 to 2 mg/L.

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0.02 mg/L is accepted as the permissible content of chromium in groundwater. The daily dose taken by the adult can be of 50-200 mg/day (or 60-290 mg/day). Cr$_{3+}$ cation predominates in most tissues except the liver. Chromium is associated with nucleic acids and it may be concentrated in liver cells. It plays an important role in the metabolism of glucose, certain proteins and fats, is part of enzymes and stimulates the activity of others. All chromium compounds without chromate are rapidly cleared from the blood. Chromium also accumulates in the liver and kidneys. High concentrations of chromium, observed in the lungs of people exposed to this metal, indicate that at least part of chromium is stored in this organ in the form of insoluble compounds.

The binding of chromium with the elements of blood and transport of chromium by blood depends mainly on its valence. Hexavalent chromium readily crosses the membranes of red blood cells and after reduction to trivalent chromium is bound to hemoglobin. The reduction of hexavalent to trivalent chromium, occurring within cells, considered as the activation of the carcinogenic chromium, increases because of the probability of interaction of trivalent chromium with the DNA.

Among various techniques, the adsorption is the most promising technique to remove and eliminate Cr$_{6+}$ from drinking water. Some of the conventional techniques for metals removal from industrial wastewater include chemical precipitation, adsorption, solvent extraction, membrane separation, ion-exchange, electrolytic techniques, coagulation/flotation, sedimentation, filtration, membrane process, biological process and chemical reaction (Asgari et al., 2008; Gode and Pehlivan, 2003). Sorption operations, including adsorption and ion-exchange are a potential alternative water and wastewater treatment. In an adsorption process, atoms or ions (adsorbate) in a fluid phase diffuse to the surface of a solid (adsorbent), where they are bound with the solid surface or are held there by weak intermolecular forces (Kocaoba and Akcin, 2002). A number of investigators have studied the removal of metal ions namely cadmium, cobalt, zinc, silver, copper, mercury, chromium and lead from aqueous solution using different adsorbents (Anderson, 1997; Boddu et al., 2003; Lee et al., 2003; Park et al., 2008; Verma et al., 2006). However, the improved sorption capacity of ion exchange resins may have advantages over such non-specific adsorbents and so the ion-exchange resins present great potential for the heavy metals removal from water and industrial wastewater. Rengaraj and co-workers reported on the removal of heavy metals from water and nuclear power plant coolant water using ion exchange resins (Alonso, 1999; Boddu et al., 2003; Dupont and Guillon, 2003; Gandhi et al., 2010; Mahvi et al., 2010; Rivero et al., 2004; Sengupta, 1995; Verma et al., 2006).
In the present study, the anion exchange resin A 500 was used for the removal of \( \text{Cr}^{6+} \) from an aqueous solution. The main objective of this study was to investigate the kinetic parameters of this ion-exchange resin. In addition, the parameters that influence the process, such as initial \( \text{Cr}^{6+} \) concentration, contact time, pH, and kinetic studies were also investigated.

The application of ion-exchange is an attractive method to remove heavy metal contaminants. Nowadays, chelating resins are increasingly used in the removal of metal ions due to their high adsorption capacities, selectivity and durability (Alonso, 1999; Ahmaruzzaman and Sharma, 2005; Yang and Al-Duri, 2005; Ortiz et al., 2003). It obtained very good results in the sorption and separation of traces and milligram amounts of \( \text{Cr}^{6+} \) complexes using chelating ion-exchangers. These resins are polymers with the functional groups able to form complexes with selected ions. In contrast to the conventional ion-exchange resins, chelating resins combine with ion-exchange and complex formation and hence can exhibit high selectivity for some ions or groups of ions, providing a wide range of practical use and industrial applications both in hydrometallurgy and analytical chemistry. The properties of chelating ion-exchangers depend on the type of functional groups, though to a lesser extent on grain size and physical properties. Rivero et al. (2004) studied the \( \text{Cr}^{6+} \) removal from wastewater using Lewatit FO36, an anion –exchanger. The ion-exchange resins are used in their entire range to improve water quality, depending on the types and concentrations of the impurities. The selective resins were deemed major options for wastewater treatment. Traces of environmentally harmful substances accumulate on the Lewatit FO36 ion-exchange resins and are thereby removed from the wastewater. They can be used for the elimination or separation of heavy metals from aqueous solutions, accumulation and recovery of heavy metals, removal of heavy metals from water and process water. Lewatit FO36 has high exchange capacity, very good chemical, mechanical and thermal stability, good ion-exchange kinetics make it suitable for the treatment of electroplating rinse waters. Gel resins usually have higher efficiencies and cost less (Rivero et al., 2004).

**Experimental**

\( \text{Cr}^{6+} \) can exist in several forms such as \( \text{Cr}_2\text{O}_7^{2-} \), \( \text{HCrO}_4^- \), \( \text{HCrO}_7^- \) and \( \text{CrO}_4^{2-} \) and the relative abundance of particular complex depends on the concentration of the chromium ion and the pH of the solution. In the concentration range and pH of the work the main species of \( \text{Cr}^{6+} \) is \( \text{HCrO}_4^- \), as shown in Fig 1.
Fig. 1. Predominance diagram showing the relative distribution of different \( \text{Cr}^{6+} \) species in water as a function of pH and total \( \text{Cr}^{6+} \) concentration (Rivero et al., 2004)

The following anion-exchange resin A 500 Purolite was used in this study for the removal of \( \text{Cr}^{6+} \) from wastewater. Purolite A500 is a macroporous type I strong basic anion-exchanger having quaternary ammonium groups. The characteristic properties of this ion-exchanger used are presented in Table 1.

**Table 1.** The characteristic properties of ion-exchanger (Technical Data Sheet Purolite A500)

<table>
<thead>
<tr>
<th>Property</th>
<th><em>Ion-exchange resin type Purolite A500</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer structure</td>
<td>macroporous polystyrene crosslinked with divinylbenzene</td>
</tr>
<tr>
<td>Physical form and appearance</td>
<td>Faint light yellow spherical beads</td>
</tr>
<tr>
<td>Functional groups</td>
<td>Type I Quaternary ammonium R-N(CH(_3))(_3)OH</td>
</tr>
<tr>
<td>Ionic form as shipped</td>
<td>Cl(^-)</td>
</tr>
<tr>
<td>Particle size range</td>
<td>0.3 – 1.2 mm</td>
</tr>
<tr>
<td>Moisture retention</td>
<td>53 – 58%</td>
</tr>
<tr>
<td>Uniformity coefficient</td>
<td>1.7</td>
</tr>
<tr>
<td>Total exchange capacity</td>
<td>1.15 eq/L</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.08</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>100ºC</td>
</tr>
</tbody>
</table>
Figure 2 (a and b) depicts FTIR spectra of fresh A500 resin and chromium treated A500 resin respectively. The broad band at 3440 cm$^{-1}$ indicates the presence of $\text{–OH}$ and $\text{–NH}$ stretching vibrations. The band at 2924 cm$^{-1}$ indicates the $\text{–CH}$ stretching vibration in $\text{–CH}$ and $\text{–CH}_2$. A band at 1635 cm$^{-1}$ corresponds to $\text{–NH}$ bending vibration in $\text{–NH}_2$ and 1065 cm$^{-1}$ indicates the presence of $\text{–CO}$ stretching vibration in $\text{–COH}$. The band at 1079 cm$^{-1}$, 1052, 862 cm$^{-1}$ suggesting that $\text{N}$-methyl glucamine present in the A500 resin and in chromium sorbed A500 resin these bands become broad and shifted to lower frequencies which confirms that chromium sorption has occurred on the A500 resin. The new band at 906 cm$^{-1}$ indicates the $\text{Cr} = \text{O}$ bonds of chromate anion confirming the sorption of $\text{Cr}^{6+}$ onto the A500 resin. The new band at 540 cm$^{-1}$ indicates the presence of $\text{Cr(OH)}_3$ in the chromium treated A500 resin (Mahvi et al., 2010).

All the chemicals used were of analytical grade and were produced by Merk, Germany. A stock solution of 1 g/L of $\text{Cr}^{6+}$ was prepared by dissolving 14.13 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 1000 mL distilled water. This solution was diluted as required to obtain standard solution containing 0.1 – 1.0 g/L of $\text{Cr}^{6+}$.

Kinetic studies were carried out with different initial concentrations of $\text{Cr}^{6+}$ while maintaining the resin dosage at a constant level. In batch experiments, 100 mL of sample solution and ion-exchanger (1.0 g) were put into a conical flask and shaken at different time intervals using a laboratory shaker. These experiments indicated that no adsorption by the container walls was detectable. In the kinetic study, aqueous solutions containing 0.1, 0.4, 0.6, 0.8 and 1.0 g/L were used. 100
mL of solution were contacted with $1 \pm 2 \cdot 10^{-4}$ g of resin, in batch system, at contact times of 2, 4, 6, 8, 10, 15, 20, and 30 minutes. The shaking speed was of 200 rpm to maintain resin particles in suspension. The influence of the pH was studied on a resin saturated with Cl as exchange ion, at pH values of $1.0 \pm 0.05$, $2.0 \pm 0.05$, $3.0 \pm 0.05$ and $5 \pm 0.2$, at temperature of $20 \pm 1^\circ$C. Temperature control was done by using an incubator FOC 225E –Velp Scientifica. Cr$^{6+}$ concentration in aqueous phase was determined by the colorimetric method based on diphenyl-carbazyde as colour reagent, using a spectrophotometer model CINTRA 5. The experiments were conducted in three parallel series.

To describe the ion exchange equilibrium, it was presumed that it can be mathematically described as adsorption equilibrium. Adsorption isotherms were drawn up with different initial concentrations varying from 0.1g/L to 1.0 g/L of metal ions while keeping the constant amount of resins at room temperature 20$^\circ$C. The equilibrium between the solid and liquid phases was modelled by the Langmuir and Freundlich equations as it follows.

**Results and discussion**

In this paper, the ion-exchange kinetics was studied by recording variation in time of Cr$^{6+}$ concentration in aqueous phase. In this way, integral kinetic curves concentration vs. time $C(t)$ were drawn. To determine variation in time of chromium concentration in resin, a mass balance equation was used (Ahmaruzzaman and Sharma, 2005). (Eq. 1), where: $V$ is volume of aqueous phase (mL); $C_i$ is Cr$^{6+}$ concentration in aqueous phase before phase contact (mg/L); $C_e$ is Cr$^{6+}$ concentration in aqueous phase at equilibrium (mg/L); $q$ is Cr$^{6+}$ concentration in resin at equilibrium (mg/kg); $m$ is resin mass (g).

$$q = \frac{V \cdot (C_i - C_e)}{m}$$  \hspace{1cm} (1)

The study of ion-exchange in order to characterise the process from the kinetic point of view comprises the curves obtained using the experimental apparatus described above. The process efficiency is controlled by the kinetics of adsorption and hence the several kinetic models are available to predict the mechanism involved in the sorption process. Among these models, there are pseudo-first-order, pseudo-second-order and interparticle diffusion, rate equation (Boddu et al., 2003).

The process efficiency is controlled by the kinetics of adsorption and hence several kinetic models are available in order to predict the mechanism involved in the sorption process. Among these models, Lagergren’s rate equation appears to be one solute from a liquid solution (Yang and Al-Duri, 2005).

Pseudo-first-order (Eq. 2):
\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t 
\]

(2)

Pseudo-second-order (Eq. 3):

\[
\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}
\]

(3)

The interparticle diffusion model has been applied to various adsorption systems and was found to account for adsorption systems (Eq. 4) (Yang and Al-Duri, 2005).

\[
q_t = k_p t^{0.5}
\]

(4)

Samples were taken after 2.5, 5, 10, 20 and 30 minutes, the results of the experiments are presented in Figs. 2-5. The curves reveal that the ion-exchange rate is higher using Purolite A500, with a higher exchange capacity.

Fig. 2. Rate of sorption in resin vs. retention time at pH =1

Fig. 3. Rate of sorption in resin vs. retention time at pH =2
Figures 2-5 show the different variations of Cr$^{6+}$ concentration in time. The results showed that Cr$^{6+}$ removal was more than 95.6% at a contact time of 30 min. These diagrams depict the effect of pH on chromium removal. The maximum efficiency of chromium removal is at pH = 1. The result shows that the increasing the value of pH in wastewater sample, the extent of removal increases.

The pH of the solution plays a very important role in the chromium sorption. The amount of retained chromium is the highest at pH 1.0, for a solution containing 1 g/L of Cr$^{6+}$. The amount of the retained chromium decreases rapidly when the pH is increased above 5 due to the formation of a chromium precipitate at higher pH values. For the ion-exchange resins, the sorption at pH above 5 shows a decreasing trend because of the formation of hydroxyl complexes of chromium, Cr(OH)$_3$ (Mahvi et al., 2010; Ortiz et al., 2003).

The similar behaviour between the two samples in terms of kinetics in the first 5 minutes of the ion-exchange process is probably due to the fact that the ion-exchange process is controlled by internal diffusion. Several kinetic models including pseudo first order, pseudo second order and pore diffusion were used for the simulation of the experimental data. The kinetic parameters calculated from equations 2-5 for the adsorption of Cr$^{6+}$ are given in Table 2. The pseudo second order and pore diffusion models successfully fit the adsorption kinetic.


Table 2. Kinetic model parameters for the adsorption of Cr\(^{6+}\) on A500

<table>
<thead>
<tr>
<th>Kinetic model parameters</th>
<th>Temperature, 20°C</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>A 500</td>
</tr>
<tr>
<td>Pseudo first order</td>
<td></td>
</tr>
<tr>
<td>(k_1)</td>
<td>0.033</td>
</tr>
<tr>
<td>(r^2)</td>
<td>0.999</td>
</tr>
<tr>
<td>Pseudo second order</td>
<td></td>
</tr>
<tr>
<td>(k_2)</td>
<td>0.235</td>
</tr>
<tr>
<td>(r^2)</td>
<td>0.986</td>
</tr>
<tr>
<td>Pore diffusion</td>
<td></td>
</tr>
<tr>
<td>(k_p)</td>
<td>5.949</td>
</tr>
<tr>
<td>(r^2)</td>
<td>0.991</td>
</tr>
</tbody>
</table>

Pseudo first order adsorption kinetic model experiments were also directed in an attempt to understand the kinetics of Cr\(^{6+}\) removal by the A500 Purolite resins. It is a well-established fact that the sorption of ions in an aqueous system follows reversible pseudo first order kinetics, when a single species is considered on a homogeneous surface. The kinetics of sorption describing the solute uptake rate which, in turn, governs the residence time of the sorption reaction is one of the important characteristics that define the sorption efficiency.

Sorption involves the transfer and resulting equilibrium distribution of one or more solutes between a fluid phase and solid particles. The design of this kind of system requires: first, knowledge of the sorption equilibrium that can be obtained from experimental data. It is also important to determine the working capacity of an ion-exchanger. Secondly, as these operations usually take place in fixed beds, some knowledge of how transitions travel through a bed is required. This introduces both time and space into the analysis. Methods for analyzing fixed bed transitions go from the local equilibrium theory, based only on stoichiometric factors, to full rate modelling where mass transfer resistances are incorporated.

The equilibrium between Cr\(^{6+}\) in the solution and in the anion exchanger A500, in the Cl\(^-\) form, is described by Eq. 5. The equilibrium normally cannot be described by a simple binary approach but anion exchanging resins in acidic pH are very highly selective for chromate. The Langmuir equation was applicable to the homogeneous adsorption system, while the Freundlich equation was the non-empirical one employed to describe the heterogeneous systems and was not restricted to the formation of the monolayer. The well-known Langmuir equation was represented as given by Eq. (5), where: \(q_e\) is the equilibrium Cr\(^{6+}\) ions concentration on the ion-exchanger, (mg/g); \(C_e\) is the equilibrium Cr\(^{6+}\) ions concentration in solution (mg/L); \(q_m\) is the monolayer capacity of ion-exchanger (mg/g); \(b\) is the Langmuir adsorption constant (L/g) related to the free energy of adsorption.
The values of $q_m$ and $b$ were calculated from the slope and the intercept of the linear plots $C/q_e$ vs. $C_e$. On the other hand, the Freundlich equation was represented by Eq. (6), where: $K_f$ and $1/n$ are the Freundlich constants corresponding to the adsorption capacity and the adsorption intensity.

$$q_e = K_f \cdot C_e^{(1/n)}$$  \hspace{1cm} (6)
Table 3. Both isotherms can be classified as favourable (concave downward) which means that a considerable amount of solute can be achieved in the solid although there is a low concentration in the fluid phase. Besides, the value of n of the Freundlich isotherm lies between 1 and 10, which also indicates favourable adsorption. The values of the parameters reported in Table 3 show that the best fitting of the experimental data was obtained with the Freundlich equation with fitting parameters that fall in the range reported in the literature. However, there is insufficient improvement to discard the simplicity of the chemical equilibrium constant approach.

Table 3. Parameters of Langmuir and Freundlich equations and chemical equilibrium

| pH | Langmuir | | Freundlich | | |
|----|----------|----------|----------------|----------|
|    | a, mmole/g | b, L/m mole | K, mmole/g | n | R² |
| 1  | 2.398 | 4.799 | 0.880 | 1.803 | 5.155 | 0.996 |
| 3  | 2.134 | 4.644 | 0.866 | 1.800 | 5.078 | 0.990 |
| 5  | 2.188 | 4.664 | 0.802 | 1.788 | 5.021 | 0.960 |

Conclusions

In the present study, the removal of Cr⁶⁺ using A500 Purolite was found to be effective. The experimental results indicated that A500 can be successfully used for the adsorption of Cr⁶⁺ from aqueous solutions using a batch system. The results herein indicate that ion-exchange resins can efficiently remove traces of Cr⁶⁺ present in aqueous solutions.

The adsorption of Cr⁶⁺ on ion exchange resins followed intraparticle diffusion process. We conclude that ion-exchange resins could be exploited for applications in the tertiary level treatment of drinking water as well as industrial effluents. The kinetic data would be useful for the design and built wastewater treatment plants.

The use of the resin A500 led to viable results for the treatment of groundwater polluted/contaminated with Cr⁶⁺. The equilibrium between the resin and the liquid phases was also properly described by the empirical Freundlich isotherm.

Ion-exchange of the Cr⁶⁺ is dependent on the initial concentrations of the adsorbate, contact time and pH level. Experimental parameters must be optimally selected to obtain the highest possible removal of Cr⁶⁺ from aqueous solutions using A500. The amount of Cr⁶⁺ ions adsorbed per unit mass of A500 increased with the initial chromium concentration as expected. To reach the plateau values that represent the saturation of the active groups which are available for interaction with Cr⁶⁺ ions on the resin.
The equilibrium data well followed the linear Langmuir and Freundlich models. The adsorption of the $\text{Cr}^{6+}$ ion is pH dependent. The results obtained from the effect of pH on the adsorption capacity of the A500 indicated that the maximum ion-exchange was obtained at pH 1 for resin. The total ion-exchange capacities for $\text{Cr}^{6+}$ ions are in the range of 0.12–0.55 mmole/g for A 500.

Acknowledgements

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