KINETIC STUDIES ON SORPTION OF Ni(II) AND Cd(II) FROM CHLORIDE SOLUTIONS USING SELECTED ACIDIC CATION EXCHANGERS

Paulina OTREMBSKA, Jerzy GEGA

Czestochowa University of Technology, Department of Chemistry, 19 Armii Krajowej Str., 42-200 Czestochowa, Poland, e-mail: potrembska@wip.pcz.pl

Abstract: Sorption of nickel(II) and cadmium(II) ions from chloride solutions was tested. Three different strongly acidic cation exchangers, i.e. Lewatit MonoPlus SP 112, Amberlite 200C and Amberlyst 15, were used. Effects of phase contact time, pH and initial concentration of metal ions on equilibrium and kinetics of sorption by batch methods were studied. It was showed that sorption of Ni(II) and Cd(II) could be described by the pseudo-second order equation. Experimental results data were analyzed using the Langmuir and Freundlich isotherms. Sorption of Ni(II) and Cd(II) onto investigated resins followed the Langmuir isotherm.

Keywords: sorption, nickel, cadmium, adsorption kinetics, adsorption isotherm

Introduction

Increasing industrialization can lead to several environmental problems. Heavy metals like Cd, Ni, Cr, Cu, Pb can contaminate groundwater, surface water or sea. They are harmful to life and became a serious public health problem. Heavy metals are non-degradable substances, long standing, which can accumulate in the environment.

There are many different methods of removal and recovery of metal ions from water and wastewater. These methods include ion-exchange (Pehlivan and Altun, 2006; Gega and Otrembska, 2011), electrodepositon (Rudnik and Nikiel, 2007), precipitation (Lewis, 2010; Provazi et al., 2011), flocculation (Dabrowski et al., 2004; Kurniawan et al., 2006), sorption (Lazaridis, 2003; Srivastava et al., 2008; Kilyushik et al., 2011), solvent extraction (Gega et al., 2010; Rodrigues and Mansur, 2010; Clegg et al., 2011), reverse osmosis (Qin et al., 2004), electrodialysis (Marder et al., 2004) and membrane separation (Walkowiak et al., 2000; Gega et al., 2001; Pospiech and Walkowiak, 2007; Chaudhari and Murthy, 2010). Among these methods, the ion-
exchange is very popular and has been widely used for Ni(II) and Cd(II) removal (Dizge et al., 2009; Zainol and Nicol, 2009). It is based on replacement of ions between insoluble substance – ion exchange resin and aqueous phases. Resin releases ions like hydrogen or sodium to solution and binds metal ions without any structural change. After separation process attached heavy metals are recovered in a more concentrated form by elution with appropriate reagents. The physicochemical reaction which occur during nickel(II) and cadmium(II) removal can be presented as (Kurniawan et al., 2006):

\[
2\text{RSO}_3^-\cdots\text{Na}^+ + \text{M}^{2+} \rightarrow 2\text{RSO}_3^-\cdots\text{M}^{2+} + \text{Na}^+
\]

where \(\text{RSO}_3^-\) is the anionic group connected to the ion exchange resin, \(\text{M}^{2+}\) is Ni(II) or Cd(II) ion.

In recent years, a number of commercial resins such as Amberlite IRC-748 (Lin et al., 2008), Amberlite IR-120 (Demirbas et al., 2005), Lewatit CNP 80 (Demirbas et al., 2005), Purolite S930 (Deepatana and Valix, 2008) have been used to remove heavy metals from aqueous solutions. In comparison with other common methods, ion-exchange provides a lot of advantages. Wide application of this method was caused by invention and use of new organic and inorganic exchangers.

In this paper, the removal of Ni(II) and Cd(II) ions from chloride solutions using strongly acidic ion-exchange resins was investigated. The two main objectives of the study include: the study of the sorption mechanism of Ni(II) and Cd(II) ions on the resins under equilibrium conditions and the investigation of the kinetics characteristics. The effectiveness of sorption was studied as a function of pH, initial nickel(II) and cadmium(II) concentration and contact time in a batch system. The experimental results were fitted to the Langmuir and Freundlich adsorption isotherm models and were analyzed on the basis of Lagergren pseudo-first order and pseudo-second order equations.

**Materials and methods**

**Ion-exchange resins**

Commercial strongly acidic cation (SAC) exchange resins: Lewatit MonoPlus SP 112 (Lanxess), Amberlite 200C, Amberlyst 15 (Rohm & Haas) in sodium form were used. The physical and chemical characteristic of the resins are given in Table 1. Wet forms of resins were used for experimental studies.

**Solution preparation and batch experiments**

Solutions of metal ions were prepared by dissolving an appropriate salt, i.e. nickel(II) chloride hexahydrate and cadmium(II) chloride hemipentahydrate in deionized water.
The pH was adjusted by the addition of appropriate volume of hydrochloric acid or sodium hydroxide solutions.

Table 1. Characteristics of main properties of strongly cation exchanging resins (based on information from manufacturers)

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Lewatit MonoPlus SP 112</th>
<th>Amberlite 200C</th>
<th>Amberlyst 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Structure</td>
<td>Macroporous</td>
<td>Macroporous</td>
<td>Macroporous</td>
</tr>
<tr>
<td>Matrix*</td>
<td>PS-DVB</td>
<td>S-DVB</td>
<td>S-DVB</td>
</tr>
<tr>
<td>Functional group</td>
<td>Sulfonic acid</td>
<td>Sulfonic acid</td>
<td>Sulfonic acid</td>
</tr>
<tr>
<td>Ionic form as shipped</td>
<td>Na⁺</td>
<td>Na⁺</td>
<td>H⁺</td>
</tr>
<tr>
<td>Total exchange capacity</td>
<td>1.7 val/dm³</td>
<td>≥1.7 val/dm³</td>
<td>5 val/kg</td>
</tr>
<tr>
<td>Moisture content</td>
<td>53–55%</td>
<td>46–52%</td>
<td>10%</td>
</tr>
<tr>
<td>Particle size</td>
<td>660 μm ±70 μm</td>
<td>600-850 μm</td>
<td>400–500 μm</td>
</tr>
<tr>
<td>Temperature limitations</td>
<td>1–120°C</td>
<td>1–135°C</td>
<td>1–120°C</td>
</tr>
</tbody>
</table>

* PS-DVB – polystyrene-divinylbenzene, S-DVB – styrene-divinylbenzene

The sorption of nickel(II) and cadmium(II) onto resins was carried out by means of the batch method. The amount of 2.5 g of wet resin was contacted with 25 cm³ of the corresponding equimolar Ni(II) and Cd(II) solution for 30 min using a laboratory shaker (WU-4, Premed). A mixture of the metal ions was used. Initial concentration of both ions was changed in the range from 0.1 mM to 100 mM. After shaking, the solution was separated from the resin by filtration, and concentration of ions was determined by atomic absorption spectrometry (SOLAAR 939) with an air/acetylene flame and the appropriate hollow cathode lamps.

**Data analysis**

The sorption ability of resins was estimated by means of recovery \( R(\%) \), the amount of ions sorbed at specific time \( t \), \( q_t \) (mg/g) and sorption capacity \( SC \) (mval/g) which were calculated as follows:

\[
R = \frac{c_0 - c_{eq}}{c_0} \times 100\% \tag{1}
\]

\[
q_t = \frac{c_0 - c_t}{w} V \tag{2}
\]

\[
SC = \frac{n_0 - n_{eq}}{m} \times 2 \tag{3}
\]

where \( c_0 \) and \( c_{eq} \) are initial and equilibrium concentrations of nickel(II) and cadmium(II) ions, (mg/dm³), \( V \) is the volume of the solutions (dm³), \( w \) is exchanger weight
(g), \( n_0 \) and \( n_{eq} \) are initial and equilibrium number of moles of metal ions (mole), \( m \) is amount of resin (g). Total SC was calculated as summarized sorption capacity for Ni(II) and for Cd(II).

Results and discussion

Effect of pH and initial metal ions concentration on Ni(II) and Cd(II) sorption from aqueous solution

The pH of solution is a significant factor which controls the surface charge of the adsorbent and ionization of the adsorbate in solution (Dizge et al., 2009). The influence of pH on the sorption of nickel(II) and cadmium(II) from chloride solution was investigated in the range of 0 to 5 and is shown in Fig. 1. The results indicate that very high recovery were obtained for all resins. Recovery factor was the lowest at pH = 0 and almost 100%, at pH = 2 and higher for both ions, separation of these ions was not possible. At pH = 0 some differences between sorption of Ni\(^{2+}\) and Cd\(^{2+}\) were observed, what indicate possibilities of separation of both metal ions. Sorption at pH above 5 was not carried out to avoid any possible interference from metal precipitation in solution.

![Figure 1](image_url)

Fig. 1. Recovery of Ni(II) and Cd(II) as a function of pH in ion-exchange processes.
Initial concentration of ions: 10 mM, volume: 25 cm\(^3\), pH = 0–5, amount of resin: 2.5 g, time: 30 min

Ion exchange is an equilibrium reaction that is dependent on the ionic concentrations of various ions both inside and outside of resin bead. Effect of initial concentration of Ni(II) and Cd(II) ions in aqueous solution on their sorption have been also studied. The results are presented in Fig. 2. The amount of adsorbed metal ions is dependent on the initial metal ion concentration. The calculated values of sorption capacity (SC) show that the best results are obtained for Lewatit MonoPlus SP 112: (1.70 mval/g), and for Amberlite 200C (1.64 mval/g), the lowest for Amberlyst 15 (0.97 mval/g).
Effect of agitation time on Ni(II) and Cd(II) sorption from chloride solution

Effect of agitation time on nickel(II) and cadmium(II) sorption on investigated ion-exchange resins has been studied. Figure 3 demonstrates that the amount of the adsorbed metal ions onto SAC exchange resins increases with time. The sorption of Ni(II) and Cd(II) was rapid for the first 5 min and equilibrium was reached after 20 min. Therefore, the period of 30 min was considered as the optimum time for all experiments presented in the paper.
Fig. 3. Kinetic studies of Ni\(^{2+}\) and Cd\(^{2+}\) sorption process on (a) Amberlite 200C, (b) Lewatit MonoPlus SP 112, (c) Amberlyst 15 at pH = 1. Experimental conditions – see Fig. 1.

Kinetic modeling

There are two very important factors decisive for resins application in metal ion sorption: sorbate–sorbent interaction and experimental conditions. In ion exchange, the moving of ions is controlled by either intraparticle diffusion or boundary layer diffusion. The process of removing ions with and ion-exchange resin is followed by metal ions transfer from the bulk of the solution to a liquid thin layer which surrounds each resin particle, followed by diffusion of ions through liquid thin layer to the resin surface, thereafter intraparticle diffusion of ions through resin channels proceed then cationic exchange occurs (Hamdaoui, 2009; Plazinski et al., 2009). In some cases the first step can be neglected in controlling the overall sorption rate, e.g. in very fast mechanical mixing of sorbate–sorbent system. The most popular equations used in analysis of experimental results are the pseudo-first and pseudo-second order kinetic equations.

Pseudo-first order model

At the end of 19\(^{th}\) century, Lagergren presented an empirical rate equation for adsorption of oxalic and malonic acid onto charcoal. It was the pseudo-first order kinetic equation which is called also the Lagergren equation and has been one of the most
Kinetic studies on sorption of Ni(II) and Cd(II) from chloride solutions...

often used kinetic equations to date. In the paper published by Lagergren the pseudo-first order kinetic equation was expressed as:

$$\frac{dx}{dt} = k(X - x)$$ \hspace{1cm} (4)

where $X$ and $x$ (mg/g) are the adsorption capacity at equilibrium and at time $t$ and $k$(1/min) is the rate constant of the pseudo-first order kinetic equation (Yuh-Shan, 2004). Today, the most popular form of this kinetic equation is:

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303} t$$ \hspace{1cm} (5)

where $q_e$ is the amount of metal ions adsorbed per unit weight of adsorbent at equilibrium (mg/g), $q_t$ is the amount of metal ions (mg/g) adsorbed at specific time $t$ and $k_1$ (1/min) is the rate constant. The value of $k_1$ (1/min) was calculated from the slopes of the linear plot of $\lg(q_e - q_t)$ versus $t$. The higher $k_1$ parameters indicate obtaining the equilibrium in shorter time.

**Pseudo-second order model**

The pseudo-second order model was proposed by Blanchard et al. (1984) to describe the kinetics of heavy metal ions removal by natural zeolites. This model is usually associated with the situation when the rate of direct adsorption/desorption process controls the overall sorption kinetics. The most frequently used form of the pseudo-second order equation is the one presented by Ho (Ho et al., 1996; Ho and McKay, 1999):

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t$$ \hspace{1cm} (6)

where $k_2$ (g/(mg·min)) is the rate constant and can be determined from the plot of $t/q_t$ versus $t$. The initial sorption rate, $h$ (mg/(g·min)), can be calculated by using following formula:

$$h = k_2q_e^2.$$ \hspace{1cm} (7)

**Kinetic analysis**

The results which were subjected to the kinetic analysis were obtained by batch method and presented in Table 2. It was presented that correlation coefficient values of the pseudo-second order kinetic equation were higher than those of the pseudo-first order kinetic equation. Comparison of $q_e$ values from kinetic equations and experimental results was done. The $q_e$ values calculated from the pseudo-first order kinetic equation were meaningfully different than calculated from experiments as opposed to the $q_e$
values calculated from the pseudo-second order kinetic equation. Based on the agreement of the calculated \( q_e \) values with the experimental and high correlation coefficients sorption of nickel(II) and cadmium(II) on the SAC resins presented in this work was best described by the pseudo-second order kinetic equation. As it was showed in Table 2 the highest initial sorption rate was for Lewatit MonoPlus SP 112. It was possible to order the SAC resins with the \( h \) value decreasing: Lewatit MonoPlus SP 112 > Amberlite 200C > Amberlyst 15.

**Isotherm modeling**

In order to supply information about surface properties, resin affinities for Ni(II) and Cd(II) equilibrium isotherm equations are used. In this study the equilibrium isotherms are described by the Langmuir and Freundlich equations. Linear regression was used to determine the best fitting isotherm.

The best known and most widely applied adsorption isotherm is the Langmuir equation. The linearized Langmuir isotherm equation is:

\[
\frac{c_e}{q_e} = \frac{1}{Q_0 b} + \frac{c_e}{Q_0}
\]

where \( c_e \) is the equilibrium concentration of metal ions (mg/dm\(^3\)), \( q_e \) is the amount of metal ions adsorbed per unit mass of adsorbent at equilibrium (mg/g), \( Q_0 \) (mg/g) and \( b \) (dm\(^3\)/mg) are the Langmuir constants related with the monolayer sorption capacity and the free energy of sorption and can be calculated from the plot \( c_e/q_e \) versus \( c_e \).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Resin</th>
<th>Experimental</th>
<th>Calculated from kinetic equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( q_e )</td>
<td>Pseudo-first order</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(II)</td>
<td>Lewatit MonoPlus SP112</td>
<td>5.10</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>Amberlite 200C</td>
<td>4.93</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>Amberlyst 15</td>
<td>5.06</td>
<td>2.02</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>Lewatit MonoPlusSP112</td>
<td>10.26</td>
<td>3.94</td>
</tr>
<tr>
<td></td>
<td>Amberlite 200C</td>
<td>10.17</td>
<td>5.00</td>
</tr>
<tr>
<td></td>
<td>Amberlyst 15</td>
<td>10.48</td>
<td>5.57</td>
</tr>
</tbody>
</table>

\( q_e \) (mg/g); \( k_1 \) (1/min); \( k_2 \) (g/(mg·min)); \( h \) (mg/(g·min))

The dimensionless constant separation factor \( (R_L) \) was also calculated. The \( R_L \) parameter is defined as:

\[
R_L = \frac{1}{1 + bc_0}
\]
where $c_0$ is the initial concentration of the adsorbate (mg/dm$^3$). The value of $R_L$ indicates the shape of the isotherm: $R_L > 1$ – unfavorable, $R_L = 1$ – linear, $0 < R_L < 1$ – favorable, $R_L = 0$ – irreversible (Bulut et al., 2008; Wołowicz and Hubicki, 2011).

The Freundlich isotherm is used to describe the adsorption characteristics of the resin used in solutions. It is given in linear form by:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln c_e$$

(10)

where $k_F$ is the Freundlich constant connected with the sorption capacity of adsorbent (mg/g), $1/n$ is the Freundlich constant connected with the sorbent surface heterogeneity: $1/n = 0$ – irreversible, $0 < 1/n < 1$ – favorable, $1/n > 1$ – unfavorable. Freundlich constants were calculated from the plot of $\ln q_e$ versus $\ln c_e$.

The Langmuir and Freundlich isotherm parameters values obtained for all resins are shown in Table 3. The values of determination coefficient of the Langmuir isotherm are higher than those calculated from Freundlich isotherm. This means that the Langmuir isotherm represents a better fit of the experimental data than the other one. The sorption data obtained for Lewatit MonoPlus SP 112 was compared with the course of the Langmuir and Freundlich isotherms and the results are shown in Fig. 4.

![Fig. 4. Fitting of Freundlich and Langmuir isotherms to the experimental data obtained for the Lewatit MonoPlus SP 112: a) cadmium(II), b) nickel(II)](image)

The Freundlich constant $1/n$ for all three resins was less than unity which means that the sorption of Ni(II) and Cd(II) ions is favorable. The Langmuir isotherm was found to be fitted with the determination coefficient in range of 0.992 to 0.999. The maximum monolayer capacity $Q_0$ was the highest for Amberlite 200C and it was 34.20 mg/g for Ni(II) and 39.47 mg/g for Cd(II). The $R_L$ values (equilibrium parameter) for both ions were found to be in the range from 0 to 1 for all resins. It confirmed that the sorption of nickel(II) and cadmium(II) was favorable.
Table 3. Adsorption isotherm parameters for adsorption of Ni(II) and Cd(II) on SAC resins

<table>
<thead>
<tr>
<th>Ion</th>
<th>Resin</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$Q_0$</td>
<td>$b \cdot 10^3$</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>Lewatit MonoPlus SP112</td>
<td>33.73</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>Amberlite 200C</td>
<td>34.20</td>
<td>6.56</td>
</tr>
<tr>
<td></td>
<td>Amberlyst 15</td>
<td>29.57</td>
<td>9.18</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>Lewatit MonoPlus SP112</td>
<td>35.20</td>
<td>2.83</td>
</tr>
<tr>
<td></td>
<td>Amberlite 200C</td>
<td>39.47</td>
<td>2.17</td>
</tr>
<tr>
<td></td>
<td>Amberlyst 15</td>
<td>28.10</td>
<td>5.50</td>
</tr>
</tbody>
</table>

$Q_0$ (mg/g); $b$ (dm$^3$/mg); $k_F$ (mg/g)

Conclusions

In this study, the potential of SAC exchange resins for nickel(II) and cadmium(II) sorption from chloride solutions was investigated. The amount of the adsorbed metal ions onto SAC exchange resins increases with time. The sorption process is fast. The experimental results show that 30 min is enough to reach the equilibrium. The amount of adsorbed ions is dependent on the initial metal ion concentration. The biggest sorption capacity (SC) was obtained for Lewatit MonoPlus SP 112: (1.70 mval/g), and for Amberlite 200C (1.64 mval/g), the lowest for Amberlyst 15 (0.97 mval/g). The main factor governing the effectiveness of sorption and separation of Ni(II) and Cd(II) is concentration of H$^+$ in solution. To obtain separation of Ni(II) and Cd(II) appropriate pH of initial solution should be used (Gega and Otrembska, 2012). The recovery was the lowest at pH = 0, higher at pH = 1 and almost 100% at pH = 2 and higher for both ions. It was found that Ni(II) and Cd(II) sorption on Lewatit MonoPlus SP 112, Amberlite 200C and Amberlyst 15 was very well described by the Langmuir isotherm (monolayer model). The kinetics of adsorption of metal ions onto SAC resins was studied by using pseudo-first and pseudo-second order equations. For studied system, the pseudo-second order kinetic model showed the best correlation with the experimental data.

References


ZAINOL Z., NICOL M.J., 2009. **Comparative study of chelating ion exchange resins for the recovery of nickel and cobalt from laterite leach tailings.** Hydrometallurgy 96(4): 283–287.