Adsorption of Co(II) from the simulated solution by zeolite NaX derived from rice husk ash

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ABSTRACT

The adsorption of Co(II) from the simulated solution was investigated using zeolite NaX derived from rice husk ash as an alternative adsorbent. The adsorption behavior of Co(II) depended strongly on the equilibrium pH, Co (II) concentration, zeolite NaX dosage, and reaction time. The high adsorption efficiency of Co(II) by zeolite NaX was obtained under the conditions: pH 3.0, 100 mg/L of Co(II), 5 g/L of zeolite NaX, and a reaction time of 75 min. The loading behavior of Co(II) onto the zeolite NaX was well-fitted to the Freundlich adsorption isotherm and the Co(II) loading capacity by zeolite NaX was around 38 mg/g. The obtained results indicate that synthesized zeolite NaX from rice husk ash is a potential adsorbent to remove cobalt from waste solutions due to its high adsorption.

Keywords

Adsorption, cobalt, loading capacity, zeolite NaX

1. INTRODUCTION

Cobalt, a metal is used in various fields such as catalysts, colors/pigments, hard materials carbides/diamond tooling, chemical applications, and batteries (Nguyen et al., 2013). In lithium-ion batteries, cobalt can account for a fifth of the material in a lithium-ion cathode (Hannan et al., 2018). The role of cobalt in these batteries is a stabilizing effect and prevents cathode corrosion. The growth in the use of lithium-ion batteries released a great number of spent lithium-ion batteries which cause serious environmental problems (Zhu et al., 2012). Due to environmental concerns and the demand for lithium and cobalt in industry, spent lithium-ion batteries have been recognized as a secondary source for the recovery of these metals (Zhu et al., 2012; Wang et al., 2016; Golmohammadzadeh et al., 2017; Nguyen & Lee, 2018; Quintero-Almanza et al., 2019; Hong & Nhung, 2020). Hydrometallurgical processes containing leaching and solution purification were commonly investigated for the recovery of cobalt (Co) and lithium (Li) from the spent lithium-ion batteries in many past studies (Nguyen & Lee, 2018). To recover Co(II) and Li(I), inorganic acids such as HCl and H₂SO₄ were commonly used as leachants to dissolve all these metals from the spent lithium-ion batteries. After dissolving Co(II) and Li(I), solvent extraction or ion exchange was used to separate and recover these metals from the acid leaching solutions (Nguyen & Lee, 2018). Since Co(II) and Li(I) existed as cationic species so solvent extraction with cationic extractants, such as PC88A (2-ethylhexyl phosphonic acid-mono-2-ethylhexyl ester), D2EHPA (di-2-ethylhexyl
phosphoric acid), and Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid) was recommended to extract Co(II) over Li(I) and other metals from acid leaching solutions (Pranolo et al., 2010; Chen et al., 2015; Swain et al., 2015; Nguyen & Lee, 2018; Quintero-Almanza et al., 2019). High extraction efficiency of Co(II) was obtained by these solvent extraction systems; however the high co-extraction of these metals and the small amount of Co(II) in the lithium solutions were the main disadvantages of solvent extraction processes (Nguyen & Lee, 2018). Therefore, ion exchange with commercial cationic resins can be used as a second separation step to remove impurities in the recovery process of Co(II) and Li(I) (Pranolo et al., 2010).

In the ion exchange, commercial resins such as Lewatit MonoPlus SP 112, Dowex M4195®, Amberlite IRC748®, Ionac SR-5®, and Purolite S930® have been used to remove Co(II) from moderate acid solutions (Mendes & Martins, 2004; Aşçı & Kaya, 2013). Although high adsorption efficiency of Co(II) by these resins was obtained, the high cost of commercial resins has limited their application for removing cobalt from waste solutions. Therefore, synthesized absorbents consisting of various activated carbons which contain phenolic, carboxyl, and carbonyl groups for promoting the adsorption of metal ions have been used to adsorb Co(II) from different solutions (Sulaymon et al., 2009; Osinśka, 2016; Ramos et al., 2016; Bernábé et al., 2019; Getasew et al., 2020). Osinśka (2016) showed that carbon gels can absorb Cu(II), Co(II), Pb(II), and Ni(II) from the simulated solutions, which can be apply to remove contaminants from wastewater. The adsorption of Co(II) and other metals were also investigated by activated carbon (Sulaymon et al., 2009; Bernábé et al., 2019; Getasew et al., 2020). The loading capacity of carbon gels and activated carbon for Co(II) was typically lower than 10 mg/g. A carboxylate-functionalized sugarcane bagasse (SPA) was synthesized to remove Co(II), Cu(II), and Ni(II) from their single solution (Ramos et al., 2016). The loading capacity of SPA for Co(II), Cu(II), and Ni(II) was found to be 0.561, 0.935, and 0.932 mmol/g, respectively. Although synthesized absorbents can remove Co(II), the synthesis of absorbents with green methods and enhancement of their loading capacity for Co(II) still remain great challenges in the adsorption process. Thus, the synthesis of new absorbents with green processes and economic efficiency requires more attention to remove cobalt as well as other metals from wastewater in developing countries.

Rice husk ash (RHA), an agricultural waste, was commonly used to synthesize zeolite, silica, and cordierite because of its high content of silica (Sembiring et al., 2016; Santana Costa & Paranhos, 2018; Tran-Nguyen et al., 2021). Zeolites are also known as adsorbents of heavy metals so that the synthesis of zeolites from RHA not only solves environmental pollution caused by RHA, but also offers new absorbents to remove metals from industrial wastewater (Zanin et al., 2017; Holub et al., 2018; Elboughdiri, 2020; Tran-Nguyen et al., 2021). Therefore, a simple and cheaper process for the synthesis of zeolite NaX was developed using RHA without any pretreatment in the previous study (Tran-Nguyen et al., 2021). To investigate the removal efficiency of metals by synthesized zeolite NaX, the adsorption behavior of Co(II) by the zeolite NaX from simulated solutions was carried out. Various parameters including equilibrium pH value, the concentration of metal, zeolite dose, and time reaction are investigated. The loading capacity of the synthesized zeolite NaX for Co(II) was also investigated and compared in this work.

2. MATERIALS AND METHODS

2.1. Chemicals and reagents

A simulated solution containing Co(II) was prepared by dissolving CoCl2.6H2O (Sigma-Aldrich Co.) in distilled water. The acidity of the solution was adjusted using NaOH or HCl (Sigma-Aldrich) solution. Acetone (Sigma-Aldrich), and potassium thiocyanate (KSCN, Sigma-Aldrich) were used for preparing the standard and sample solution to measure cobalt concentration by ultraviolet spectrophotometer (UV-Vis).

| Table 1. Optimum synthesis condition and characteristic of zeolite NaX used in this study (Tran-Nguyen et al., 2021) |
|---------------------------------------------------------------|---------|-----------------|
| Synthesis conditions                                         | Surface area (m²/g) | Pore diameter (Å) |
| SiO₂/Al₂O₃ : 4                                               | 388.41  | 12.37           |
| Na₂O/Al₂O₃ : 10                                              |          |                 |
| Reaction time: 4 h                                           |          |                 |
| Reaction temperature: 90℃                                    |          |                 |

Zeolite NaX was synthesized directly using rice husk ash without any pretreatment (Tran-Nguyen et al., 2021). The optimum synthesis conditions and characteristics of zeolite NaX are shown in Table 1.
2.2. Adsorption procedure

Batch adsorption experiments were carried out by placing the desired amount of adsorbent into 20 mL of the simulated solution. Different factors affecting adsorption were pH value (2.5-4.0), metal ion concentration (50-300 mg/L), zeolite NaX dosage (1-10 g/L), and reaction time (30-120 min) were studied to find the optimum conditions for the adsorption of Co(II). All samples were shaken with Phoenix instrument linear shaker (RS-LS 20) for a specific time. After filtering the adsorbent by filter paper, the cobalt concentration in the solutions before and after adsorption was measured by UV-Vis (Jasco 730, Japan). The concentration of metal up-taken onto adsorbent was obtained by mass balance. Two replicate experiments were carried out simultaneously in each set of the experiment and the errors associated with the adsorption percentages varied within ± 5%. The adsorption percentage of metals by adsorbent was calculated by the following equation:

\[
\text{Adsorption percentage} = \frac{C_o - C_e}{C_o} \times 100
\]

where \(C_o\) and \(C_e\) were the concentration of metal in the solution before and after adsorption, respectively.

The loading capacity experiments were conducted by contacting 0.5 g of zeolite NaX with 50 mL of fresh Co(II) solution several times until the number of metal ions adsorbed onto the zeolite NaX surface became constant. In these experiments, the concentration of cobalt was kept at 100 mg/L and solution pH was adjusted to 3.0. Each sample was shaken for 75 min at room temperature. The cumulative amount of the metal loaded onto the zeolite NaX was then calculated by the difference in the concentration of metal in the solution after each stage of contact.

2.3. Method for measuring cobalt concentration

Our preliminary experiments indicated that cobalt concentrations can be determined by UV-Vis through the formation of cobalt complexes, \(\text{K}_2[\text{Co(SCN)}_4]\) in the mixture of HCl, acetone, and potassium thiocyanate solution. The conditions for the formation of \(\text{K}_2[\text{Co(SCN)}_4]\) were 0.5 M HCl, 50% v/v acetone, and 10 % wt KSCN. The UV-Vis spectrum of \(\text{K}_2[\text{Co(SCN)}_4]\) was illustrated in Figure 1. The adsorption peaks of \(\text{K}_2[\text{Co(SCN)}_4]\) were observed at wavelengths of 488 and 623 nm. Since the maximum adsorption of \(\text{K}_2[\text{Co(SCN)}_4]\) was obtained at 623 nm, this wavelength was selected to determine cobalt concentration in the present work.

To measure cobalt concentration in the solutions, cobalt standard solutions and calibration curve for Co(II) by UV-Vis were carried out by preparing a series of 20 mL cobalt standard solutions containing 0-40 mg/L Co(II) in 0.5 M HCl, 50% v/v acetone, and 10 % wt KSCN. All samples were measured at \(\lambda = 623\) nm. The calibration curve of \(\text{K}_2[\text{Co(SCN)}_4]\) by UV-Vis is shown in Figure 2. The obtained linear regression equation of cobalt was \(A = 0.0382 \times C + 0.042\) (\(R^2 = 0.998\)), where \(A\) and \(C\) were absorbance and metal concentration, respectively. The standard error of this method was 0.79.

All samples were measured three times and the average was obtained as the final results.

![Figure 1. UV-Vis spectrum of \(\text{K}_2[\text{Co(SCN)}_4]\) complex in the mixture of HCl, acetone, and KSCN solution](image1)

![Figure 2. Calibration curve for \(\text{K}_2[\text{Co(SCN)}_4]\) complex by UV-Vis at the wavelength of 623 nm](image2)

3. RESULTS AND DISCUSSION

3.1. Effect of pH

Since synthesized zeolite NaX can be dissolved in the solution at pH <2.0, the effect of pH value on the adsorption of Co(II) was studied in the solution pH
range from 2.5 to 4.0. The concentration of Co (II) and zeolite NaX were kept at 50 mg/L and 2.5 g/L, respectively. The mixtures of adsorbent and Co(II) solution were shaken for 30 min. The obtained results are shown in Figure 3. The adsorption percentage of Co(II) by zeolite NaX increased from 39.6% to 52.5% with an increase in pH value from 2.5 to 3.0. When the solution pH was higher than 3.0, the adsorption behavior of Co(II) remained unchanged. Cationic species of Co(II), namely Co$^{2+}$ and CoCl$^+$, were formed in the pH value of 2.5–4.0 (Oh & Lee, 2005), which can be adsorbed by cationic resin, zeolite NaX. This is a reason why Co(II) can load onto zeolite NaX in our experimental conditions. According to Figure 3, the pH value of 3.0 was chosen for further experiments due to the high adsorption efficiency of Co(II).

![Figure 3. Effect of pH on the adsorption percentage of Co(II) using zeolite NaX. Co(II) concentration of 50 mg/L, pH: 2.5-4.0; Zeolite NaX: 2.5 g/L; Time: 30 min](image)

3.2. Effect of Co(II) concentration

The effect of cobalt concentration on the adsorption percentage of Co(II) by zeolite NaX was studied in the range of 50–300 mg/L. The pH value of these solutions was controlled at 3.0 and the concentration of zeolite NaX was additionally fixed at 2.5 g/L. The mixture solutions were stirred for 30 min. Figure 4 shows the variation adsorption percentage of Co(II) with the variation of cobalt concentration. The adsorption percentage of Co(II) decreased from 57% to 40% with an increase of Co(II) concentration from 50 to 200 mg/L and then remained unchanged with further increases in Co(II) concentrations. The decrease in the adsorption percentage of Co(II) at a high concentration of Co(II) might be related to the fraction of cationic species of Co(II) in the solution (Oh & Lee, 2005). Since the concentration of Co(II) in some real waste solutions is very low (Hong & Nhung, 2020), the solution containing 100 mg/L of Co(II) at pH 3.0 was chosen for further experiments.

![Figure 4. Effect of Co(II) concentration on the adsorption percentage of Co(II) using zeolite NaX. Co(II) concentration of 50-300 mg/L, pH 3.0; Zeolite NaX: 2.5 g/L; Time: 30 min](image)

3.3. Effect of zeolite NaX dosage

Using the above-mentioned solution conditions, the simulated solution containing 100 mg/L of Co(II) at pH 3.0 was contacted by varying zeolite NaX dosage from 1 to 10 g/L. All the mixtures were shaken for 30 min. The obtained results are illustrated in Figure 5. As can be seen, the loading behavior of Co(II) with zeolite NaX increased steadily from 41% to 99% with the increase of zeolite NaX dosage from 1 to 7.5 g/L and then was constant with the further increase of zeolite NaX concentration. It can be concluded that most Co(II) in the solution was adsorbed when the zeolite NaX concentration was higher than 7.5 g/L.

![Figure 5. Effect of NaX dosage on the adsorption percentage of Co(II) using zeolite NaX. Co(II) concentration: 100 mg/L, pH 3.0; Zeolite NaX: 1-10 g/L; Time: 30 min](image)
3.3. Effect of reaction time

To determine the effect of time on the loading of Co(II) with zeolite NaX, 5 g/L of zeolite NaX was contacted with the 100 mg/L Co(II) solution by varying shaking time from 30 to 120 min. The results are highlighted in Figure 6. It can be seen that the adsorption percentage of the Co(II) increased from 65.0% to 99.5% when the reaction time rose from 30 to 75 min. After 75 min shaking, the adsorption efficiency of Co(II) by zeolite NaX remained unchanged. The obtained results indicate that a shaking time of 75 min is sufficient to attain the equilibrium state in the adsorption system.

3.4. Adsorption isotherm

The adsorption behavior of metals on the adsorbent are more precisely studied through adsorption isotherms. Freundlich and the Langmuir isotherms are the simplest models describing the adsorption equation (Igwe & Abia, 2007; Nguyen et al., 2013). The Langmuir isotherm assumes that metal ions are chemically adsorbed at a fixed number of well-defined sites; each site can hold only one ion, while the Freundlich isotherm describes the adsorption of metal ions on a highly heterogeneous surface with a multi-layer mechanism (Igwe & Abia, 2007; Nguyen et al., 2013). Langmuir and Freundlich isotherm models are represented in equations (2) and (3), respectively.

\[
\frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{q_{\text{max}} K_L} \quad (2)
\]

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)
\]

where \(q_e\) is the amount of metal per one-gram adsorbent at equilibrium (mg/g); \(C_e\) is the Co(II) concentration at equilibrium (mg/L); \(K_F\) and \(n\) are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity respectively; \(q_{\text{max}}\) is described the maximum mass of adsorbed ions (mg/g); \(K_L\) is the Langmuir constant.

The adsorption isotherm of Co(II) by zeolite NaX was also investigated in the present work by varying the concentration of Co(II). In these experiments, the dosage of zeolite NaX was fixed at 2.5 g/L. The Co(II) adsorption equilibrium data obtained by using the zeolite NaX were fitted to the Langmuir and Freundlich isotherm. Adsorption isotherms of Co(II) ions on the surface of the zeolite NaX are presented in Figure 7 and Figure 8. The correlation coefficient value of the Freundlich isotherms model was 0.995 (Figure 8) while that of the Langmuir isotherms model was 0.557 (Figure 7). Therefore, the Freundlich isotherms model describes well the
experimental data in comparison to the Langmuir isotherms model. From the slope of Figure 8, the value of n was calculated to be around 3, which represented beneficial adsorption of Co(II) onto the zeolite NaX surface (Igwe & Abia, 2007; Nguyen et al., 2013). Since the $R^2$ of Figure 8 was close to unity, this suggests that the loading of Co(II) onto zeolite NaX follows the Freundlich isotherm and multi-layer adsorption was the best model to describe the adsorption of Co(II) ions by zeolite NaX.

3.5. Loading capacity of zeolite NaX

Loading capacity experiments for Co(II) from the solution at pH 3.0 were undertaken to determine the applicability of zeolite NaX. The results are shown in Figure 9. The cumulative loading of Co(II) increased with the increase of contacting stage and became constant after seven stages. The loading capacity of zeolite NaX for Co(II) from the simulated solution at pH 3.0 was found to be 37.9 mg/g of zeolite NaX. A comparison of the loading capacity of zeolite NaX for Co(II) with other adsorbents reported in the literature is shown in Table 2. Zeolite NaX derived from rice husk ash in the present study offered a higher loading capacity for Co(II) than some other synthesized activated carbons such as granular activated carbon, carbon gels, phthalate-functionalized sugarcane bagasse, and activated disordered mesoporous carbons, and Lewatit MonoPlus SP 112 resin. In particular, the adsorption capacity of zeolite NaX derived from rice husk ash in this study was more than four times higher than that of activated carbon prepared from white lupine husk. Therefore, it can conclude that synthesized zeolite NaX is promising adsorbent for the absorption and removal of Co(II) from waste solutions.

![Figure 9. Co(II) loading capacity of zeolite NaX. Co(II) concentration 100 mg/L, pH 3.0; Zeolite NaX: 10 g/L; Time: 75 min.](image)

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>Loading capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lewatit MonoPlus SP 112 resin</td>
<td>21.9</td>
<td>(Aşçı &amp; Kaya, 2013)</td>
</tr>
<tr>
<td>Granular activated carbon</td>
<td>1.2</td>
<td>(Sulaymon et al., 2009)</td>
</tr>
<tr>
<td>Carbon gels</td>
<td>8.0</td>
<td>(Osińska, 2016)</td>
</tr>
<tr>
<td>Phthalate-functionalized sugarcane bagasse</td>
<td>33.7</td>
<td>(Ramos et al., 2016)</td>
</tr>
<tr>
<td>Activated disordered mesoporous carbons</td>
<td>&lt; 5.0</td>
<td>(Bernabé et al., 2019)</td>
</tr>
<tr>
<td>Activated carbon prepared from white lupine husk</td>
<td>8.5</td>
<td>(Getasew et al., 2020)</td>
</tr>
<tr>
<td>Zeolite NaX derived from rice husk ash</td>
<td>37.9</td>
<td>Present study</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

The loading efficiency of Co(II) from the simulated solution by zeolite NaX derived from rice husk ash was investigated. Most of Co(II) was adsorbed by zeolite NaX when the concentration of Co(II) in the simulated solution was lower than 100 mg/L and the pH of the solutions was 3.0. The adsorption behavior of Co(II) by zeolite NaX showed good agreement with the Freundlich adsorption isotherm model, which described the adsorption of Co(II) by zeolite NaX based on a multi-layer mechanism. The maximum loading capacity for Co(II) by zeolite NaX was around 38 mg/g which was higher than other synthesized absorbents in the reported literature. The obtained results indicate that zeolite NaX has the potential for the treatment of waste solutions containing cobalt. Particularly, zeolite NaX can be used to remove Co(II) from the leach liquors of spent lithium-ion batteries.

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