Sorptive removal of heavy metals with nano-sized carbon immobilized alginate beads

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A B S T R A C T

A composite adsorbent prepared by immobilizing graphite nano-sized carbon in alginate beads (NCB) was used for the removal of Co(II) and Ni(II) from aqueous solution. Kinetic studies showed that adsorption process reached equilibrium within 8 h at an initial concentration of 10 mg/L and sorption process was well explained by pseudo second order kinetic model. The Freundlich isotherm model correlated well with the adsorption isotherms of Co(II) and Ni(II) onto NCBs. The experimental results showed that the removal of Co(II) and Ni(II) ions from the solution was likely due to ion exchange with calcium(II) ions present in the alginate beads.

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Introduction

Q2 Effective removal of heavy metals from aqueous solution is an important issue in the protection of the environment and also in public health. Because heavy metal ions are not biodegradable, must be removed from contaminated water via physical or chemical processes, such as chemical precipitation, membrane filtration, ion exchange and adsorption [1,2]. Biological adsorbents are currently being considered as cost effective and efficient alternative materials for the removal of toxic metal contaminants [3]. Cobalt is broadly present in various types of industrial wastewater including petrochemical, cobalt-bearing mineral mining and smelting and nuclear wastewater. Acute exposure to cobalt can cause nausea, vomiting and headaches [4–6]. Nickel is another heavy metal frequently found in wastewater streams from a number of industries such as electroplating, battery manufacturing, mineral processing, steam–electric power plants and paint formulation [7]. Excess intake of Ni(II) over permissible levels results in a variety of health problems such as pulmonary fibrosis, renal edema, skin dermatitis and gastrointestinal distress (e.g., nausea, vomiting, diarrhea) [8].

The World Health Organization (WHO) requires that nickel in drinking water should not exceed 0.5 mg/L [9]. Nickel removal is generally more difficult compared with the removal of other heavy metals. According to “hard soft acid base” theory, nickel is an “intermediate” metal that forms less stable complexes, mainly by weaker ionic bonding [10,11]. Alginate, a natural polysaccharide extracted from brown seaweed, is a very promising biosorbent. Alginate consists of linear copolymers composed of β-α-mannurionate (M) and α-α-guluronate (G). Carboxylate groups provide alginate with the ability to form biodegradable gels in the presence of multivalent cations, more specifically with calcium ions via ionic interactions [12]. Alginate is known for its metal binding properties whereby ion exchange between metal ions can occur [13]. It has been widely reported that the sorption of heavy metal ions onto biosorbents takes place via a specific ion exchange mechanism involving the replacement of protons, alkali, alkaline earth, or other cations by heavy metal ions [11]. Even though alginate has mainly been used as an immobilization agent, it plays a prominent role in metal sorption and has been reported to have excellent sorption capacity towards several heavy metal ions. In recent studies, the alginate sorption capacity has been shown to greatly exceed that of the actual sorbents immobilized in its matrix [14]. Due to this property, previous studies of alginate have not only been concerned with the mechanism of metal binding [15] and its metal sorption...
properties [16,17] but also with its role as a composite membrane component [18]. In order to confirm this hypothesis that the sorption process occurs via ion exchange between calcium ions of the sorbent material and Co(II) or Ni(II) ions present in solution, the amount of calcium released by gel beads during kinetic and equilibrium experiments was determined. The effects of contact time and initial metal concentration on the kinetics of metal adsorption were investigated in batch experiments. In a previous study, graphite nano carbon was immobilized in an alginate matrix (referred to as NCBS), and the adsorption characteristics of cobalt [Co(II)] by NCBS were investigated [19]. The aim of this study was to accomplish a follow-up study of heavy metal removal by NCBS with a focus on the mechanism of heavy metal (Co(II) and Ni(II)) removal by NCBS. As part of the effort to understand the removal mechanism, adsorption kinetics and equilibrium experiments were conducted.

### Experimental

#### Chemicals and reagents

All chemicals and reagents used in the experiments were analytical grade unless otherwise specified. Sodium alginate was purchased from Sigma Aldrich and was used without further purification. Stock solutions of Co(II) and Ni(II) (1000 mg/L) were prepared with reagent grade cobalt chloride (CoCl₂·6H₂O, Sigma Aldrich) and nickel chloride (NiCl₂·4H₂O, Sigma Aldrich) in deionized (DI) water, respectively, which were further diluted to achieve the desired concentration. Calcium chloride (CaCl₂), HCl, and NaCl were purchased from Sigma-Aldrich.

#### Preparation of adsorbent

Graphite nano-sized carbon (GNCC), with an average diameter of 50 nm, was prepared according to the procedure reported by Kim et al. [20]. In brief, electric current with 50–60 V and 150 mA was applied using graphite cathode electrodes in a reactor containing de-ionized (DI) water for GNC preparation. Two anodes and one cathode were submerged in the electrolyte. A two-stage process consisting of anodes activation in the initial stage and GNC generation in the second stage was used. A colloidal solution (pH 3) of GNC at 3000 mg/L was obtained following 15 min of electrolysis. The calcium alginate beads employed as an adsorbent were prepared by the dropwise addition of sodium alginate (5% w/v) into 0.05 M calcium chloride solution under magnetic stirring for 12 h, to obtain a homogeneous colloidal suspension. The suspension was then added dropwise into 1000 mL of 0.05 M CaCl₂ solution using a 5.0 mL syringe with a 1.7 mm diameter needle to form NCBS. Ca alginate beads formed upon contact with the cross-linker solution and were left overnight to stabilize. The excess cross-linker solution was removed, and the beads were washed several times with deionized water. The beads were incubated for 24 h in a CaCl₂ solution at ambient temperature to complete the cross-linking reaction, and the NCBS were rinsed several times with DI water to remove residual GNC particles and non-cross-linked calcium ions from the surface of the beads. To compare the adsorption performance between non-immobilized and GNC-immobilized beads, pure ABs was prepared separately as a control. The diameters of both beads were approximately 3.0 mm.

#### Batch sorption study

The adsorption performance of NCBS with Co(II) and Ni(II) was studied in batch mode and the results were compared with ABs. The experiments were performed in 50 mL capped glass tubes. The sorbate solutions (20 mL) at desired concentrations were equilibrated with 0.2 g of sorbents (ABs and NCBS) in a shaker operated at 100 rpm. The suspensions were filtered after equilibrium has been attained. The sorption capacity at equilibrium (qₑ, mg/g) was determined using the following equation:

\[ qₐ = \frac{(Cₐ - Cₑ)V}{m} \]

where \(Cₐ\) and \(Cₑ\) are the initial and equilibrium concentrations in the supernatant (mg/L), respectively, \(V\) is the volume of solution (L) and \(m\) is the mass of the sorbent (g).

The initial pH of the sorbate solution was adjusted using 0.1 N HCl and 0.1 N NaOH solutions. The effect of contact time on the sorption capacity was studied with 10 mg/L initial sorbate concentration at ambient temperature, while an isotherm study was performed over a wide range of initial sorbate concentrations (0–800 mg/L). At equilibrium, the sorbent was separated from the sorbate system and was washed with DI water to remove unsorbed metal ions from the surface of the adsorbent.

#### Analytical methods

For spectroscopic characterization of ABs and NCBS, samples were thoroughly dried and ground. Energy dispersive X-ray analysis (EDX, Hitachi, SU-70) was employed to confirm Co(II) and Ni(II) sorption on the AB and NCBS surfaces. The concentrations of Co(II) and Ni(II) in aqueous solution were determined by inductively coupled plasma (ICP, Thermo Jarrell Ash). The pH of the solution was measured with a pH meter (Thermo Scientific).

#### Results and discussion

##### Effect of contact time

In order to understand the sorption mechanism and to identify the equilibration time for maximum uptake, the sorption of Co(II) and Ni(II) on ABs and NCBS was studied as a function of contact time. Fig. 1 shows the adsorption kinetics of Co(II) and Ni(II) on ABs and NCBS with 10 mg/L initial Co(II) and Ni(II) concentrations. The adsorbents exhibited an initial rapid uptake removing 82.0% and 93.1% of the Co(II) within 2 h followed by slow kinetics that reached a plateau. The Co(II) removal efficiency increased almost 100% within 8 h. There was no significant change in the amount of metal ion adsorption after equilibration for 8 h and/or 24 h. The adsorption capacities of ABs and NCBS for Ni(II) were 0.89 and 0.90 mg/g, respectively, which correspond to 85.7% and 91.9% removal efficiency, respectively, during the initial 2 h contact, equilibrium was reached after 16 h. In the initial stage, the higher driving force allowed external mass transfer resistances to be overcome, and active sites with a higher affinity were occupied [21]. Once the high affinity binding sites are occupied, residual binding sites with a lower affinity become occupied, leading to the slow attainment of equilibrium. Similar equilibration times of 8 h were observed for both ABs and NCBS, which suggests that GNC impregnation had little influence on the sorption rate, which is in good agreement with the results of previous studies on the adsorption of heavy metals with alginate and reactive materials composites [22,23]. The observed equilibration time for Co(II) sorption during the present study was comparatively faster than the sorption kinetic in our previous study [24] (Fig. 2).

##### Kinetic model

Pseudo-first-order [25] and pseudo-second-order kinetic models [26] were employed to model the sorption data over the reaction time range. The pseudo-first order equation of Lagergren
Fig. 1. Adsorption kinetics of (a) Co(II) and (b) Ni(II) by alginate beads (ABs) and nano-sized graphite carbon immobilized alginate beads (NCBs), respectively (Contact time: 24 h, adsorbent amount: 10 g/L, pH: 5.0).

Fig. 2. Adsorption isotherm of (a) Co(II) and (b) Ni(II) by alginate beads (ABs) and nano-sized graphite carbon immobilized alginate beads (NCBs), respectively (Contact time: 24 h, adsorbent amount: 10 g/L, pH: 5.0).

Table 1

<table>
<thead>
<tr>
<th>Metal</th>
<th>AB</th>
<th>NCB</th>
<th>K1 (L/h)</th>
<th>qe (cal) (mg/g)</th>
<th>R²</th>
<th>K2 (g/mg/h)</th>
<th>qe (exp) (mg/g)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(II)</td>
<td>0.80</td>
<td>0.84</td>
<td>0.235</td>
<td>0.24</td>
<td>0.7979</td>
<td>2.079</td>
<td>1.2</td>
<td>0.9999</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>0.87</td>
<td>0.87</td>
<td>0.258</td>
<td>0.28</td>
<td>0.7775</td>
<td>3.128</td>
<td>1.2</td>
<td>0.9997</td>
</tr>
</tbody>
</table>

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The Freundlich isotherm assumes that adsorbent surface sites have a spectrum of different binding energies. The Freundlich model has also been widely applied and can be written as follows: 

\[ q_e = k_f C_e^{1/n} \]  

where \( k_f (\text{mg/g})(\text{L/mg})^{1/n} \) and \( n \) are the Freundlich constant and a heterogenic factor, respectively.

To determine the adsorption capacity of ABs and NCBs, the equilibrium adsorptions of Co(II) and Ni(II) were studied as a function of the initial concentration and the results are shown in Fig. 3. Increases in the initial Co(II) concentration from 59.50 to 662.32 mg/L enhanced the sorption capacity of ABs and NCBs from 0.26 to 8.12 mg/g and from 0.29 to 8.87 mg/g, respectively. The sorption of Ni(II) on ABs and NCBs increased from 0.01 to 9.01 mg/g and 0.26 to 10.74 mg/g, respectively, with an increase in its initial concentration from 56.32 to 631.32 mg/L. The higher sorption rate during the initial phase was due to the large number of strong affinity binding sites, producing an increased concentration gradient between divalent metal ions in solution and the sorbent surface. It is clear that the isotherm rises sharply in the low concentrations ranges, indicating that a great number of readily accessible sites are available for adsorption. However, as the concentration was increased, site saturation of ABs and NCBs occurred, and the isotherm reached a plateau, indicating that no more sites were available for adsorption [30]. The adsorption equilibrium data were analyzed using two the Freundlich and Langmuir isotherm models to determine the adsorption process of the adsorbents for Co(II) and Ni(II). The Langmuir and Freundlich constants for the adsorption of Co(II) and Ni(II) on ABs and NCBs are given in Table 2. The correlation coefficient \((R^2)\) of the Langmuir model for Co(II) adsorption by ABs (0.9587) was higher than that of the Freundlich model (0.9198), while the Freundlich model fit well the experimental data of Co(II) adsorption on NCBs. The adsorption isotherm of Ni(II) by both adsorbents was suitably described by the Freundlich model, with similar correlation coefficients. The observed \( n \) values ranging from 2.52 to 2.75 indicate that sorption feasibility was favorable over the entire range of concentrations studied [31] (Table 3).

**Adsorption mechanism of heavy metal ions**

To study the mechanism of Co(II) and Ni(II) sorption onto ABs and NCBs, kinetic and equilibrium studies were undertaken. The experiments were conducted under the same set of conditions as the kinetic experiments performed in Section 3.1. Fig. 3 shows the release of Ca(II) from alginate beads along with the adsorption of Co(II) and Ni(II) as a function of contact time. The Co(II) ion concentration decreased from 0.182 to 0.053 mmol/L (ABs) and 0.034 mmol/L (NCB) during 4 h and reached 0.045 mmol/L and 0.034 mmol/L at 24 h equilibrium time, respectively (Fig. 3(a)). The Ca(II) ion concentration in suspensions of ABs and NCBs increased from 0.135 and 0.138 mmol/L, respectively, during the same period of contact. The Ni(II) ion concentration decreased from 0.181 to 0.042 mmol/L (ABs) and 0.034 mmol/L (NCB) after 24 h, respectively. A similar decreasing trend was observed for the release of Ca(II) ions (Fig. 3(b)). The release of Ca(II) ions observed in the adsorption kinetics with ABs and NCBs probably resulted from the ion exchange reaction between Ca(II) and the metal ions (Me(II)) on exchangeable sites of the alginate beads. The stoichiometric ratio of released calcium ions to adsorbed metals was close to 1:1, suggesting that ion exchange was the main removal mechanism for heavy metal ions. The ion exchange reaction occurring on the alginate matrix can be presented as follows [32]:

\[ \text{Ca(Alginate-COO)}_2 + \text{Me}^{2+} \rightarrow \text{Me(Alginate-COO)}_2 + \text{Ca}^{2+} \]  

\[ \text{Ca(Alginate-COO)}_2 + 2\text{H}^+ \rightarrow 2\text{Alginic-COOH} + \text{Ca}^{2+} \]  

**Table 2**

<table>
<thead>
<tr>
<th>Co(II)</th>
<th>AB</th>
<th>9.04</th>
<th>0.0044</th>
<th>0.9587</th>
<th>0.4046</th>
<th>2.0717</th>
<th>0.9198</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCB</td>
<td>11.63</td>
<td>0.0097</td>
<td>0.8537</td>
<td>0.7936</td>
<td>2.6961</td>
<td>0.8720</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ni(II)</th>
<th>AB</th>
<th>10.93</th>
<th>0.0087</th>
<th>0.9324</th>
<th>0.8009</th>
<th>2.5157</th>
<th>0.9540</th>
</tr>
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<tbody>
<tr>
<td>NCB</td>
<td>11.48</td>
<td>0.0111</td>
<td>0.9446</td>
<td>1.0970</td>
<td>2.7533</td>
<td>0.9860</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3**

<table>
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<tr>
<th>Element, line</th>
<th>Atomic %</th>
<th>ABs</th>
<th>ABs + Co(II)</th>
<th>ABs + Ni(II)</th>
<th>NCBs</th>
<th>NCBs + Co(II)</th>
<th>NCBs + Ni(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, K</td>
<td>48.27</td>
<td>53.56</td>
<td>48.18</td>
<td>52.89</td>
<td>51.67</td>
<td>41.38</td>
<td></td>
</tr>
<tr>
<td>O, K</td>
<td>41.71</td>
<td>40.80</td>
<td>43.33</td>
<td>39.85</td>
<td>43.12</td>
<td>46.65</td>
<td></td>
</tr>
<tr>
<td>Ca, K</td>
<td>8.54</td>
<td>1.69</td>
<td>0.00</td>
<td>6.48</td>
<td>0.00</td>
<td>0.51</td>
<td></td>
</tr>
<tr>
<td>Co, K</td>
<td>--</td>
<td>3.95</td>
<td>--</td>
<td>5.21</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Ni, K</td>
<td>--</td>
<td>8.49</td>
<td>--</td>
<td>--</td>
<td>11.51</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 4. EDX spectra for NCBs after adsorption of Co(II) and Ni(II) and elements detected on NCBs.

Fig. 5. Equilibrium studies for the ion exchange of (a) Co(II) and (b) Ni(II) with calcium by ABs and NCBs, respectively (Contact time: 24 h, adsorbent amount: 10 g/L, pH: 5.0).
2Alginate-COOH + Me^{2+} \rightarrow (Alginate-COO)_{2} Me + 2H^{+} \quad (8)

EDX (Energy dispersive X-ray) analysis data confirmed the replacement of Ca(II) with Me(II) via the decrease in Ca atomic weight (%) after adsorption of the metal ions (Fig. 4). Similar observations have been reported in previous studies that investigated heavy metals sorption by algal-based adsorbents [33–35]. In contrast, the released concentrations of Ca(II) in NCB suspensions were slightly lower than those in AB suspensions, although the amount of adsorbed heavy metals by NCBs was higher than that by ABs. These data provide evidence that immobilized GNC in the NCB contributed to the removal of heavy metals. Considering the surface characteristics of carbon-based adsorbents used in previous studies [36,37], functional groups, such as –COOH, –OH, or –C=O on surface sites of GNC presumably removed heavy metals from the aqueous solution. Despite the low mass ratio of GNC to alginate (GNC:alginate = 3:50) in the beads, the high surface area of GNC possibly facilitated the improved performance of the adsorbent toward heavy metals.

To further confirm this phenomenon, equilibrium experiments were conducted using the same conditions presented in Section 3.2. The concentrations of released Ca(II) ions increased with decreases in the initial concentrations of Co(II) and Ni(II) (Fig. 5). For Co(II), the amount of adsorbed Co(II) ions appeared similar to the amount of released Ca(II) over the entire range of initial concentrations (Fig. 5(a) and (b)). However, the difference between the amount of adsorbed Ni(II) and the amount of released Ca(II) apparently increased in the range of high concentration of Ni(II) (Fig. 5(c) and (d)), which suggests that the portion of electrostatic attraction by functional groups (–COO–) was relatively large at high Ni(II) concentrations.

Conclusion

The materials prepared by immobilization of graphite nano carbon on alginate polymer material has shown high affinity for heavy metal ions such as Co(II) and Ni(II). The kinetic results indicated that the sorption process is well explained by the pseudo-second-order kinetic model. The Freundlich isotherm model correlated well with the adsorption isotherm of Co(II) onto NCBs, while the Langmuir isotherm model showed good prediction for ABs. Ni(II) adsorption by both adsorbents was satisfactorily described by the Freundlich isotherm model. The results obtained from the kinetic investigation clearly showed that removal of Co(II) and Ni(II) ions from solution was likely due to ion exchange with the calcium(II) ions present in the gel beads. In addition, good correlations between the amount of adsorbed Co^{2+} or Ni^{2+} and the released Ca^{2+} confirmed that ion exchange is the main removal mechanism. Graphite nano carbon-impregnated alginate beads were found to be an efficient sorbent system for the removal of Co(II) and Ni(II) from aqueous solutions.

Acknowledgement

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References