Removal of Ni(II) and Zn(II) from Aqueous Solutions Using Chitosan

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Background

Heavy metals pollution is an important environmental problem due to its toxic effects and accumulation throughout the food chain and hence in the human body (1,2). The main source of heavy metals (nickel and zinc) pollution in the water derives from industrial production processes such as galvanization, smelting, mining, leather tanning, electroplating, textile industries, batteries manufacturing and metal finishing. Heavy metals are non-degradable, and therefore must be removed from water to eliminate the potential dangerous to human and environment (3). Nickel and zinc were chosen for this study due to their widespread use in industries and potential water pollution impact. Exposure to nickel may cause cancer of lungs, nose and bones. Moreover, it may cause extreme
weakness, dermatitis, headache, dizziness and respiratory distress (4). Exposure to zinc may cause stomach cramps, skin irritations, vomiting, nausea and anemia (5). The World Health Organization recommends that the maximum acceptable concentration of Zn and Ni in drinking water is 5 and 0.025 mg L$^{-1}$, respectively (6). Many conventional methods have been used to remove metal ions from aqueous solutions including oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption (7,8). However, these traditional methods require further research and development due to their high operational cost, low removal efficiency at low concentration, and toxic sludge generation which requires additional treatment. This has focused researchers to find alternative economical methods for wastewater treatment. Adsorption is regarded as dependable and effective techniques for removal of heavy metals from wastewater due to its high efficiency at low concentrations especially, easy handling and cost effectiveness. (9).

From the literature it is clear that CS and its derivatives can be used to remove numerous trace metals (Cu(II), Pb(II), Cr(III), Cr(VI), Cd(II), Zn(II), Co(II), Fe(II), Mn(II), Pd(II), V(V) and V(IV)) from wastewater. Varma et al. (2004) published a review that outlined the various classes of CS derivatives and compared their ion-binding abilities under varying conditions, and described analytical methods, the sorption mechanism, and a structural analysis of the metal complexes using a variety of methods (12). Gamage and Shahidi (2007) discussed about CS for the removal of metal ion contaminants and proteins from water (13). Miretzky and Cirelli (2009) reviewed Hg(II) removal from water, using CS (14).

In these studies, CS has been used in a variety of forms, which include CS beads, flakes and membranes (15,16).

**Aims of the study:**
In the present study, CS was used for removal of Ni(II) and Zn(II) from aqueous solutions. The effect of pH, initial concentration, contact time and CS dose were investigated. Isotherm and kinetics of adsorption were evaluated.

**Materials & Methods**

**Materials**
Chitosan (ash: 0.55%, moisture: 5.4%, deacetylation: 88%) was purchased from Sigma–Aldrich (South, Africa). Ni(NO$_3$)$_2$$\cdot$6H$_2$O, Zn(NO$_3$)$_2$$\cdot$6H$_2$O, hydrochloric acid (HCl) and sodium hydroxide (NaOH) with the highest purity available were purchased from Merck (Darmstadt, Germany). Double-distilled water was used in all experiments.

Stock solution of Ni(II) and Zn(II) were prepared by dissolving Ni(NO$_3$)$_2$$\cdot$6H$_2$O and Zn(NO$_3$)$_2$$\cdot$6H$_2$O in double-distilled water. The solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions.

All Ni(II) and Zn(II) concentrations were measured, using a inductively coupled plasma spectrometry (Verian710-Es Australia). All pH
measurements were made with a 780 pH-meter (Metrohm Switzerland) with a combined glace-calomel electrode. 

**Batch adsorption experiments**

Adsorption studies were performed by adding 5.0 g of CS to 100 mL of 100 mg L\(^{-1}\) of Ni(II) and Zn(II) solutions, and the pH of the solution was adjusted at 6.0 with 0.1 mol L\(^{-1}\) HCl or/and 0.1 mol L\(^{-1}\) NaOH solutions and then the mixture was agitated using a magnetic stirrer with a the stirring speed 160 rpm for 60 min. Subsequently, the CS with adsorbed Ni(II) and Zn(II) were separated from the mixture using Whatman filter paper with a diameter of 42µm. The concentration of the Ni(II) and Zn(II) ions which remained in the solution were determined by inductively coupled plasma (ICP) spectrometry and the concentration of the Ni(II) and Zn(II) ions remained in the adsorbent phase (\(q_e, \text{mg g}^{-1}\)) were calculated using the Eq. (1):

\[
q_e = \frac{(C_0 - C_e)V}{W}
\]

Where \(C_0\) and \(C_e\) are the initial and equilibrium Ni(II) and Zn(II) concentrations in solution, respectively (mg L\(^{-1}\)), \(V\) (L) is the volume of solution and \(W\) (g) is the weight of adsorbent (17-19).

For studying the effect of solution pH on Ni(II) and Zn(II) ions adsorption, experiments in different pH (2.0 to 9.0) were conducted. To observe the effect of adsorbent dose on Ni(II) and Zn(II) ions adsorption, different amounts of adsorbent (varying from 1.0 to 7.0 g) were used. In order to investigate the effect of contact time used 5, 15, 30, 45, 60, 75, 90, 105 and 120 min contact times.

Finally, the Ni(II) and Zn(II) removal efficiency (R%) was calculated by the Eq. (2):

\[
R(\%) = \frac{C_0 - C_e}{C_0} \times 100
\]

Where: \(C_0\) and \(C_e\) (mg L\(^{-1}\)) were the initial and final Ni(II) and Zn(II) concentrations (20).

**Results**

Effect of initial concentration on the uptake of Ni(II) and Zn(II) was studied at different concentrations (\(C_0= 100-800 \text{ mg L}^{-1}\)) and keeping other parameters constant. As can be seen in Figure 1a, the adsorption capacity decreases with increase of initial Ni(II) and Zn(II) concentrations.

To determine the optimum pH range for the removal of the Ni(II) and Zn(II) ions, the adsorption studies were carried out over a wide pH range of 2.0-9.0. The results are shown in Figure 1b. It was observed that, adsorption quantity increased when the pH of the solution increased and remained nearly constant at higher pHs. The effect of amount of adsorbent on the removal of the Ni(II) and Zn(II) were carried out by varying dose of CS from 1.0 to 7.0 g at constant Ni(II) and Zn(II) concentrations and 25±1 °C temperatures. The results are shown in Figure 1c. It was observed that the removal percentage increased rapidly with the increase in the adsorbent dose till 5.0 g, and after the critical dose, the removal percentage reached almost a constant value.

The effect of contact time on the adsorption of Ni(II) and Zn(II) was studied to determine the time taken by CS to remove 100 mg L\(^{-1}\) Ni(II) and Zn(II) solutions at 25±1 °C temperatures (Figure 1d). The pseudo-first-order and pseudo-second-order kinetic models were applied to determine the rate constants for studying the adsorption process mechanism. The plot of pseudo-first-order model and pseudo-second-order model are shown in Figure 2a, b, and the different kinetic parameters were determined by linear regression and listed in Table 1.

Adsorption isotherms are used for explaining the equilibrium between the solid and liquid phases. The equilibrium data collected in present study were tested by applying Langmuir and Freundlich models. The calculated Langmuir and Freundlich constants are shown in Table 2. The adsorption isotherms of the Ni(II) and Zn(II) ions on CS were shown in Figure 3.
Figure 1) (a) Effect of initial concentration on the removal of Ni(II) and Zn(II) from aqueous solution by CS (pH=5.0 and 6.0, respectively for Ni(II) and Zn(II) ions, contact time 60 min, adsorbent dose 5 g, temperature 25±1 °C). (b) Effect of pH solution on the removal of Ni(II) and Zn(II) by CS (Initial Ni(II) and Zn(II) concentrations 100 mg L\(^{-1}\), contact time 60 min, adsorbent dose 5 g, temperature 25±1 °C). (c) Effect of adsorbent dose on the removal of Ni(II) and Zn(II) by CS (pH=5.0 and 6.0, respectively for Ni(II) and Zn(II) ions, initial Ni(II) and Zn(II) concentrations 100 mg L\(^{-1}\), contact time 60 min, temperature 25±1 °C). (d) Effect of contact time on the removal of Ni(II) and Zn(II) by CS (pH=5.0 and 6.0, respectively for Ni(II) and Zn(II) ions, initial Ni(II) and Zn(II) concentrations 100 mg L\(^{-1}\), adsorbent dose 5 g, temperature 25±1 °C).

Table 1) Pseudo-first order and pseudo-second order kinetic model parameters for the adsorption of Ni(II) and Zn(II) onto CS.

<table>
<thead>
<tr>
<th>C(_0) (mg L(^{-1}))</th>
<th>(q_e) (mg g(^{-1}))</th>
<th>Pseudo-first-order kinetic model</th>
<th>Pseudo-second-order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(q_{e1}) (mg g(^{-1}))</td>
<td>(k_1) (min(^{-1}))</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>100</td>
<td>9.6</td>
<td>1.056</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>100</td>
<td>9.75</td>
<td>0.319</td>
</tr>
</tbody>
</table>
• Removal of Ni(II) and Zn(II) from Aqueous Solutions...


Figure 2) (a) Pseudo-first-order kinetic plot and (b) Pseudo-second-order kinetic plot, for the adsorption of Ni(II) and Zn(II) onto CS at 25±1 °C.

Table 2) Isotherm parameters of adsorption of Ni(II) and Zn(II) onto CS.

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>b (L mg⁻¹)</td>
<td>qₘₑ (mg g⁻¹)</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>0.031</td>
<td>52.6</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>0.052</td>
<td>45.4</td>
</tr>
</tbody>
</table>

Figure 3) (a) Langmuir and (b) Freundlich isotherms for Ni(II) and Zn(II) adsorption onto CS at 25±1 °C.

Discussion

Initial concentration of metals is an important factor for practical application. As seen from Figure 1a, at a constant CS dose, the decrease in the adsorption efficiency is probably due to the saturation of the active binding sites on the CS surface at higher Ni(II) and Zn(II) concentrations. On the other hand, by increasing the initial Ni(II) and Zn(II) concentrations the actual amount of metals adsorbed per unit mass of the CS increased.
The higher initial Ni(II) and Zn(II) concentrations provides an important driving force to overcome the mass transfer resistance for Ni(II) and Zn(II) transfer between the solution and the surface of the CS. A similar trend was reported in the adsorption of Ni(II) and Zn(II) onto magnetite nanorods (21).

The initial pH of solution plays an important role in the adsorption process and particularly on the adsorption capacity by controlling the surface charge of the adsorbent and the degree of ionization of the materials in the solution. As was seen in the Figure 1b, the removal efficiency of Ni(II) increases from about 30–85% at pH 2.0–5.0 and then remained nearly constant at higher pHs. Also removal of Zn(II) increased from 34% to 88% when the pH increased from 2.0 to 6.0. The increase of Ni(II) and Zn(II) adsorption on CS with increasing pH is probably attributed to the hydrolysis of Ni(II) and Zn(II) ions and the surface properties of CS.

The Ni and Zn presents in the species of Ni$^{2+}$, Ni(OH)$^{+}$, Ni(OH)$_2$$^-$, Ni(OH)$_3$$^-$$^-$, Ni(OH)$_4$$^{2-}$ and Zn$^{2+}$, Zn(OH)$^+$, Zn(OH)$_2$$^+$, Zn(OH)$_3$$^-$$^-$, Zn(OH)$_4$$^{2-}$ at different pH values. At low pH, the predominant species is Ni$^{2+}$ and Zn$^{2+}$. Therefore, the low Ni$^{2+}$ and Zn$^{2+}$ adsorption at low pH is attributed partly to the competition between H$^+$ and Ni$^{2+}$, so H$^+$ and Zn$^{2+}$ on the surface sites. Furthermore, at lower pH, the CS surface will be positively charged, creating electrostatic repulsion between the positively charged surface of the CS and the Ni(II) and Zn(II) ions. At higher pH the number of positively charged sites are reduced and raised the number of negatively charged sites, which increases the electrostatic attractions between Ni(II) and Zn(II) ions and CS surface. The similar phenomenon has been reported by Sheela et al. (2012) (22).

Figure 1c, shows that the removal efficiency increased with the increase in dose of the CS and the maximum adsorption was observed at 5.0 g for Ni(II) and Zn(II). This phenomenon was also observed by Madrakian et al. (2012), who studied the adsorption efficiency of U(VI) on modified maghemite nanoparticles and indicated that adsorption percentage increases with increasing adsorbent dose (23).

The contact time between the adsorbate and the adsorbent is important in the metals removal from the solution by the adsorption process. As was seen in the Figure 1d, the removal efficiency of Ni(II) and Zn(II) by CS increased with increasing contact time and then became constant. Equilibrium was reached within 75 and 60 min for Ni(II) and Zn(II), respectively. The initial adsorption stage, the rapid adsorption occurred due to the availability of more active sites over the adsorbent surface and the second adsorption stage, the later slow rate of Ni(II) and Zn(II) adsorption probably occurred due to the less availability of active site onto the surface of adsorbent as well as the slow pore diffusion of the solute into the adsorbent. Similar results have been found by Zhang et al. (2011) (24).

In order to explore the adsorption mechanism of Ni(II) and Zn(II) onto CS, two kinetic models including the pseudo-first-order (Eq. (3)) and the pseudo-second-order (Eq. (4)) models were used. The linear forms of pseudo-first-order and pseudo-second-order models are expressed as follows (25,26):

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \frac{k_1 t}{2.303}$$

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

where $q_e$ and $q_t$ are the amount of Ni(II) and Zn(II) ions adsorbed (mg g$^{-1}$) at equilibrium and time t (min); $k_1$ is the rate constant of pseudo-first-order (min$^{-1}$); $k_2$ is the rate constant of pseudo-second-order (g mg$^{-1}$ min$^{-1}$) for adsorption.

As shown in Table 1, higher values of $R^2$ were obtained for pseudo-second-order than for pseudo-first-order adsorption rate models, indicating that the adsorption rates of Ni(II) and Zn(II) onto the CS can be more appropriately described using the pseudo-second order rate model.
• Removal of Ni(II) and Zn(II) from Aqueous Solutions...


rather than pseudo-first-order rate (Figure 2a, b).

Adsorption isotherm can provide the most important parameter for designing a desired adsorption system. In this study, the Langmuir (Eq. (5)) and Freundlich (Eq. (6)) isotherms are applied to describe the adsorption behaviors of Ni(II) and Zn(II) onto CS. The linear equations are as follows (27,28);

\[ \frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m b_1} \]  \hspace{1cm} (5)

\[ \ln q_e = \frac{1}{n} \ln c_e + \ln k_f \]  \hspace{1cm} (6)

where \( c_e \) (mg.L\(^{-1}\)) is the equilibrium concentration of Ni(II) and Zn(II) ions in solution, \( q_e \) (mg.g\(^{-1}\)) is the equilibrium adsorption capacity of CS, \( q_m \) (mg.g\(^{-1}\)) is the maximum adsorption capacity of CS for monolayer coverage, \( b \) (L.mg\(^{-1}\)) is a constant related to the adsorption free energy, \( K_f \) (mg\(^{-1}(1/n)\) L\(^{1/n}\) g\(^{-1}\)) is a constant related to adsorption capacity, and \( n \) is an empirical parameter related to adsorption.

The experimental data were fitted well with Langmuir isotherm model (Figure 3a, b), thereby indicating the monolayer adsorption of Ni(II) and Zn(II) ions onto adsorbent surface. The results showed that the maximum adsorption capacity of CS for Ni(II) and Zn(II) ions were 52.6 and 45.4 mg g\(^{-1}\), respectively. In Table 3 we compared ability of the proposed adsorbent in removal of Zn(II) and Ni(II) ions from water with some other works. Comparison of the presented data indicates that the chitosan is one of the best adsorbents for removal of metal ions from the aqueous solution.

Also, in previous studies, the adsorption of Ni(II) ions on adsorbents, Novel chelating sponge (29), carbon nanomaterials (5), and oxidized multi-walled carbon nanotubes (3) was also found to follow the Langmuir isotherm better than the Freundlich isotherms.

### Table 3) Comparison of maximum adsorption capacity (q_m) of different adsorbents for Zn(II) and Ni(II).

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Maximum adsorption capacity (mg g(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xanthate-modified magnetic chitosan</td>
<td>20.8 - 30</td>
<td></td>
</tr>
<tr>
<td>Multi-carboxyl-functionalized silica gel</td>
<td>39.9 - 31.92</td>
<td>31</td>
</tr>
<tr>
<td>Sulphurised activated carbon</td>
<td>23.7 - 32</td>
<td>32</td>
</tr>
<tr>
<td>Bagasse fly ash</td>
<td>9.43 - 6.48</td>
<td>33</td>
</tr>
<tr>
<td>Coconut shell-based activated carbon fiber</td>
<td>19.53 - 22.07</td>
<td>34</td>
</tr>
<tr>
<td>Amino functionalized graphenes composite material</td>
<td>45.6 - 52.6</td>
<td>35</td>
</tr>
<tr>
<td>Activated carbon from scrap tyre</td>
<td>- 20.408</td>
<td>36</td>
</tr>
<tr>
<td>Coal dust</td>
<td>- 20.408</td>
<td>37</td>
</tr>
<tr>
<td>Chitosan</td>
<td>- 45.6</td>
<td>This work</td>
</tr>
</tbody>
</table>

### Conclusion

The present study shows that the CS can be used as an effective adsorbent for removing Ni(II) and Zn(II) from contaminated water sources. The adsorption of Ni(II) and Zn(II) on CS were strongly dependent on the pH, and the maximum removal was attained at pH 5.0 and 6.0 for Ni(II) and Zn(II), respectively. The adsorption of Ni(II) and Zn(II) on CS increases with increasing adsorbent dose and contact time. The adsorption efficiency of Ni(II) and Zn(II) on CS decreased with the increase initial Ni(II) and Zn(II) concentrations. Kinetic studies demonstrated that the adsorption mechanism of Ni(II) and Zn(II) ions followed the pseudo-second-order model and equilibrium data was described well with Langmuir isotherm.

### Footnotes

**Conflict of Interest:**

The authors declared no conflict of interest.
References


• Removal of Ni(II) and Zn(II) from Aqueous Solutions...