USING NANOCOMPOSITES OF CHITOSAN AND MONTMORILLONITE FOR ADSORPTION OF HEAVY METAL IONS FROM WASTEWATER

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Summary

In this study, chitosan/montmorillonite nanocomposites were synthesised from chitosan and montmorillonite by dispersion of montmorillonite into chitosan solution which was prepared by dissolving the chitosan in an aqueous acetic acid solution. The resulting nanocomposites were characterised by XRD (X-ray diffraction), FTIR (Fourier transform infrared) and SEM (scanning electron microscopy) measurements. Batch equilibrium experiments of Cu (II) (Cu^{2+}) and Cd (II) (Cd^{2+}) ions adsorption were carried out on chitosan/montmorillonite nanocomposites. Models of adsorption isotherms were applied to describe the adsorption isotherms of heavy metal ions by nanocomposite. The relationship between adsorbing capacity \( q_e \) and equilibrium mass concentration \( C_e \) is in accordance with the isothermal adsorption equation of Langmuir. Two kinetic models, including pseudo-first-order and pseudo-second-order, were used to analyse the heavy metal ions adsorption process. The pseudo-second-order chemical reaction kinetics provide the best correlation of the experimental data, therefore the adsorption dynamic follows the laws of pseudo-second-order kinetics.

Key words: Chitosan/montmorillonite nanocomposites, copper, cadmium, kinetic, adsorption isotherm.

1. Introduction

Common technologies for heavy metal removal are membrane separation, ion exchange, electro-deposition, and chemical precipitation. These methods prove to be costly and inept, especially in removing trace amounts of heavy metals [2]. Another disadvantage is the production of sludge or mud, which requires proper disposal and confinement [3]. On the other hand, adsorption effectively removes contaminants in wastewater with high solute loadings and even at dilute concentrations (< 100mg/L). Use of natural adsorbents like peat, banana pith, rice hull and chitosan proves to be economical and effective in removing a variety of contaminants [2, 4].

Chitosan contains reactive hydroxyl (-OH) groups and amino (-NH\textsubscript{2}) groups that have the potential to bind heavy metals. Pure chitosan tends to agglomerate and form a gel in aqueous media, rendering most of the hydroxyl and amino groups inaccessible for metal binding. Coating chitosan as a thin layer onto an immobilisation support increases the accessibility of its binding sites, and improves the mechanical stability [5, 6]. Montmorillonite has a net negative surface charge and has little or no affinity to anionic, in there, chitosan, a natural biopolymeric cation, is an excellent candidate to modify montmorillonite for the adsorption. Recent research works have shown that chitosan/montmorillonite composites represent an innovative and promising class of sorbent materials. Gecol et al. investigated the removal of tungsten species from water using chitosan coated montmorillonite biosorbent [7, 8]. Chang and Juang studied the adsorption of tannic acid, humic acid, and dyes from water using the composite of chitosan and activated clay [9]. However, studies about the removal of heavy metal ions by chitosan/montmorillonite nanocomposites as an adsorbent are very scarce. Therefore, in this study chitosan/montmorillonite (CTS/MMT) nanocomposite was synthesised, characterised, and the adsorption kinetics and isotherms for Cu\textsuperscript{2+}, Cd\textsuperscript{2+} from water solution onto nanocomposite with chitosan and montmorillonite.

2. Materials and method

2.1. Materials

Chitosan of medium molecular weight (average molecular weight M\textsubscript{v}Z 92,700g mol\textsuperscript{-1}), used in this work was bought from Aldrich Chemicals. This chitosan was obtained by deacetylation of chitin from crab shells and it had a degree of deacetylation of 80%. Glacial acetic acid (HAC) obtained from Sigma-Aldrich® Co. LLC. was used as the solvent for chitosan. The montmorillonite, with a cationic exchange capacity (CEC) of 92.7mequiv/100g,
was supplied by Sigma-Aldrich®Co. LLC. Analytical grade of Cu(NO₃)₂.2.5H₂O, Cd(NO₃)₂ were procured from China.

2.2. Film preparation

Formation of chitosan/montmorillonite nanocomposites: chitosan solution was prepared by dissolving chitosan in a 2% (v/v) aqueous acetic acid solution at a concentration of 2wt% followed by centrifuging to remove the insoluble material. Montmorillonite was first swelled by 50ml distilled water and then added to 50ml chitosan solution with montmorillonite contents of 1 wt% followed by stirring at 60°C for 6 hours. After that, chitosan/montmorillonite solutions were cast on a plastic dish at 60°C for 24 hours. They were termed chitosan/montmorillonite - 1% (1 is concentration of montmorillonite).

2.3. Characterisation of the composite film

IR spectra of the samples were characterised using a FTIR Spectrophotometer (IMPAC-410) in KBr pellets in the range of 4,000 - 400cm⁻¹. XRD analyses of the powered samples were performed using an X-ray diffractometer with Cu anode (D8-Advance, Bruker), running at 40kV and 40mA, scanning from 0.5° to 5° at 3°/min. The scanning electron microscope (SEM) were measured using a Hitachi S-4800.

2.4. Adsorption kinetic studies

Single metal solutions of Cu²⁺, Cd²⁺ were prepared with concentrations of 10 - 120mg/L, with pH 5 - 6. The three-necked flask is filled with 0.3g nanocomposite of chitosan/montmorillonite and 30mL of metal solution. The metal solution was agitated using thermostated shaker with a shaking of 200rpm and the pre-determined contact times ranged from 1 min. up to 90 min. The filtrate was analysed using atomic absorption spectroscopy (AAS) method to determine Cu²⁺, Cd²⁺. The adsorption capacity was calculated:

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

Where:

- \( C_o \) is the initial metal concentration (mg/L);
- \( C_e \) is the final or equilibrium concentration (mg/L);
- \( V \) is the volume of the metal solution (mL);
- \( W \) is the weight of chitosan/montmorillonite (g).

2.5. Adsorption isotherm studies

Single metal solutions of Cu²⁺, Cd²⁺ with concentrations of 10 - 120mg/L, were utilised for isotherm studies. The experiments were performed using 0.3g of chitosan/montmorillonite in 30mL of the metal solution in the three-necked flask. Solutions with an initial pH 6 were agitated using a shaking of 200rpm for 90 min. at room temperature.

3. Results and discussion

3.1. IR analysis of nanocomposites

Fig.2 shows the IR spectra that were obtained for montmorillonite, chitosan, and the biopolymer clay nanocomposite prepared from 1% montmorillonite and chitosan, in the 4,000 - 450cm⁻¹ wavenumber range. The band at 3,446cm⁻¹, 1,638cm⁻¹, 1,042cm⁻¹, 791cm⁻¹, 466cm⁻¹ corresponding to the vibration bands of the silicate and the vibration band (Al-O) at 921cm⁻¹ remain unaffected in the nanocomposite. The other bands of the nanocomposite at 2,923cm⁻¹, 1,324cm⁻¹ are consistent with those observed in the film of pure chitosan, while the vibration bands at 3,443cm⁻¹, 1,575cm⁻¹, 1,042cm⁻¹ in the starting chitosan is overlapped with the bands of the silicate. The vibration band at 1,560cm⁻¹ corresponding to

![Fig.1. Procedure of synthesis material from chitosan and montmorillonite](image-url)
3.2. X-ray diffraction analysis of nanocomposites

The nanocomposite was analysed by XRD and the power patterns of montmorillonite are presented in Fig. 3. A typical diffraction peak of montmorillonite is 6.94°, responding to a basal spacing of 14.87 Å. After intercalation with chitosan, this peak disappears. The movement of the typical diffraction peak of montmorillonite to lower angle (3°) indicates the formation of the flocculated-intercalated nanostructure. It is reported that the formation of flocculated structure in chitosan/montmorillonite nanocomposites is due to the hydroxylated edge-edge interaction of the silicate layers [11]. The intensity of the peak decreases and even disappears, indicating the formation of an intercalated-exfoliated structure in chitosan/montmorillonite nanocomposites. According to the results of XRD and FTIR, it can be concluded that almost all chitosan were intercalated into the montmorillonite interlayer and destroyed the crystalline structure of montmorillonite.
nanocomposite is due to the hydroxylated edge-edge interaction of the silicate layers because of the hydrogen-bonding interaction between the silicate hydroxylated edge groups and the amino or hydroxyl functional groups in chitosan chains.

### 3.4. Adsorption isotherms

Tables 1 and 2 show the adsorption capacity of the nanocomposite at different heavy metal ions concentrations and 25°C for samples. The adsorption capacity of the nanocomposite increases corresponding to level the metal ions concentration.

It can be seen from tables 1 and 2 that the sharp increase in adsorption capacity from 75 to 120mg/L and 50 to 100mg/L for Cu²⁺ and Cd²⁺, respectively. However, only a slight increase in the adsorption capacity of the nanocomposite can be observed with further increase of the initial concentration of metal ions.

The adsorption process can be generally expressed by two isotherm equations, namely, the Langmuir and the Freundlich equations [12], which are represented by the following equations, respectively:

\[
\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}
\]

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

Where \( q_m \) (mg/g) and \( b \) (L/mg) are Langmuir isotherm coefficients. The value of \( q_m \) represents the maximum adsorption capacity. \( K_f \) (mg/g) and \( n \) are Freundlich constants. The linear plot of \( C_e/q_e \) versus \( C_e \) is drawn for the Langmuir model of the adsorption of Cu²⁺ (Fig.5), and Cd²⁺ (Fig.6).

**Table 1. Adsorption of Cu²⁺ ion at different concentration.**

<table>
<thead>
<tr>
<th>( C_e ) (mg/l)</th>
<th>10</th>
<th>50</th>
<th>75</th>
<th>100</th>
<th>120</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_e ) (mg/l)</td>
<td>0.54</td>
<td>5.68</td>
<td>16.36</td>
<td>36.31</td>
<td>53.45</td>
<td>53.55</td>
</tr>
<tr>
<td>( q_e ) (mg/g)</td>
<td>3.15</td>
<td>14.77</td>
<td>19.55</td>
<td>21.23</td>
<td>22.18</td>
<td>22.05</td>
</tr>
</tbody>
</table>

**Table 2. Adsorption of Cd²⁺ ion at different concentration.**

<table>
<thead>
<tr>
<th>( C_e ) (mg/l)</th>
<th>10</th>
<th>50</th>
<th>75</th>
<th>100</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_e ) (mg/l)</td>
<td>0.10</td>
<td>0.84</td>
<td>2.44</td>
<td>6.66</td>
<td>16.44</td>
</tr>
<tr>
<td>( q_e ) (mg/g)</td>
<td>3.30</td>
<td>16.38</td>
<td>24.19</td>
<td>31.11</td>
<td>34.52</td>
</tr>
<tr>
<td>( C_e/q_m )</td>
<td>0.03</td>
<td>0.051</td>
<td>0.10</td>
<td>0.214</td>
<td>0.476</td>
</tr>
</tbody>
</table>

### 3.3. Scanning electron microscope (SEM) of materials

In the SEM image (Fig.4c) stacked flakes (stacks of multilayers of montmorillonite) and flocculated fraction of montmorillonite were observed. The nanocomposite clearly shows intercalated morphology with strong flocculation. Some stacks of montmorillonite multilayers appears. This result is consistent with the conclusion of XRD. The formation of a flocculated structure in the
The applicability of Langmuir isotherm suggests the monolayer coverage of the ions on the surface of nanocomposite. The linearisation of the equation and the values of $R^2$ for Cu$^{2+}$ and Cd$^{2+}$ are 0.9999; 0.999, respectively. The $q_m$ values for the adsorption of Cu$^{2+}$ and Cd$^{2+}$ are 23.81 and 35.71 mg/g, respectively. The $q_m$ value for the adsorption of Cu$^{2+}$ by waste banana pith is 20.29 mg/g [13]. So, the chitosan/montmorillonite nanocomposite can be used as an alternative-adsorbing agent in heavy metal ions wastewaters. Figs 7 and 8 show that the values $R^2$ of Freundlich model for Cu$^{2+}$ and Cd$^{2+}$ are 0.9148 and 0.907.

Therefore, the adsorption of Cu$^{2+}$ and Cd$^{2+}$ on the chitosan/montmorillonite nanocomposite do not follow the Freundlich isotherm.

3.5 Adsorption kinetics

Two simplified kinetic models including pseudo-first-order and pseudo-second-order equations are analysed. A simple kinetic model that describes the process of adsorption is the pseudo-first-order equation. It was suggested by Lagergren [14] for the adsorption of solid/liquid systems and its formula is given as

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

(1)

Where $k_1$ is the pseudo-first-order rate constant (mim$^{-1}$), $q_e$ and $q_t$ are the amounts of metal ions adsorbed (mg/g) at equilibrium and at time $t$ (min.). After integration with the initial condition $q_t = 0$ at $t = 0$, Eq. (1) can be obtained:

$$\log (q_e - q_t) = \log q_e - \frac{k_1t}{2.303}$$

(2)
Pseudo-second-order model is based on adsorption equilibrium capacity and it can be expressed as [15]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

When the initial condition is $q_t = 0$ at $t = 0$, integration leads to Eq. (3)

$$\frac{1}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}$$

\[ (3) \]

where $k_2$ (g/mg.min) is the rate constant of the pseudo-second-order adsorption. The linear plots of $\log (q_e - q_t)$ versus $t$ and $(t/q_t)$ versus $t$ are drawn for the pseudo-first-order and the pseudo-second-order models, respectively. The rate constants $k_1$ and $k_2$ can be obtained from the plot of experimental data. Figs. 9 and 10 show the pseudo-first-order and pseudo-second-order models for the adsorption of Cu$^{2+}$ by chitosan/montmorillonite nanocomposite.

Figs. 11 and 12 show the pseudo-first-order and pseudo-second-order models for the adsorption of Cd$^{2+}$ by chitosan/montmorillonite nanocomposite.

As seen from the Figs above, the correlation coefficients ($R$) of the pseudo-first-order model are 0.9714 and 0.9869 for Cu$^{2+}$ and Cd$^{2+}$, respectively. For the pseudo-second-order, the correlation coefficients ($R$) are 0.998 and 0.993 for Cu$^{2+}$ and Cd$^{2+}$, respectively.

Therefore, the adsorption of Cu$^{2+}$ and Cd$^{2+}$ on chitosan/montmorillonite nanocomposite are better described by the pseudo-second-order than by the pseudo-first-order. This result also indicates that the adsorption rate of metal ions depends on the concentration of metal ions at the absorbent surface at equilibrium.

4. Conclusions

The chitosan/montmorillonite nanocomposites were prepared from chitosan and montmorillonite. The results show that the relationship between adsorbing capacity ($q_e$) and equilibrium mass concentration ($C_e$) is in accordance with the isothermal adsorption equation of Langmuir. Two kinetic models, including the pseudo-first-order and pseudo-second-order, were used to analyse the heavy metal ions adsorption process. The pseudo-second-order chemical reaction kinetics provide the best correlation of the experimental data, therefore the
adsorption dynamics follow the laws of pseudo-second-order kinetics. The nanocomposite can thus be effectively used as an adsorbent for the removal of heavy metal ions from wastewaters.

References


