Single and Binary Adsorption of Cu(II) and Ni(II) Ions from Aqueous Solutions by Sunflower Seed Husk

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Abstract—This research presents the possibility of using sunflower seed husk as an adsorbent for the removal of Cu$^{2+}$ and Ni$^{2+}$ ions from simulated aqueous solution. A series of experiments were carried out in a batch reactor to obtain equilibrium data for adsorption of single and binary metal solutions. Experiments parameters such as pH, sorbent dosage, contact time, agitation speed and initial metal ions concentration were studied to optimize the best conditions. The results showed that the best parameters were evaluated to be 5, 7g/l, 120 min, 175rpm and 10mg/l for both ions, respectively. At these parameters, the monolayer adsorption capacity calculated from Langmuir model was obtained 23.4940, 11.3051 mg/g for Cu$^{2+}$ and Ni$^{2+}$ ions, respectively in single component system and it decreased to 18.6962, 9.2366 mg/g for binary component system, respectively and the sequence for metal ions removal in single and binary systems was Cu(II) > Ni(II) with 92.5% and 84.8% maximum removal efficiencies. Kinetic studies showed that a pseudo second order model was more suitable than the pseudo first order model.

Keywords—Heavy metals, Batch sorption, Sunflower seed husk, Isotherm and kinetic models.

1. Introduction

Water pollution by heavy metals is a matter of major concern, because of their high toxicity (carcinogenic properties) and non-biodegradability, which leads to their bio- accumulation, causing not only health troubles in both humans and animals, but also environmental problems [5, 9]. Copper metal ions have become an eco-toxicological hazard of major interest and increasing importance, because of their accumulation in living organisms [7]. Cu$^{2+}$ is considered as a common hazardous pollutant in wastewater and is often released by metallurgical, plating, electric circuits, fertilizer, excessive use of refining industries, and Cu-based agrochemicals. Extended oral administration of excess amount of Cu$^{2+}$ may result in liver injury and acute poisoning to the human body [19]. In addition of copper, nickel ion (Ni$^{2+}$) is a toxic metal ion that is commonly used in silver refineries, electroplating, zinc base casting and storage battery industries [6]. The chronic toxicity of nickel to humans and the environment has been well texted. For example, high concentration of Ni$^{2+}$ causes cancer of lungs, nose and bone. Among the different water-treatment techniques available, adsorption is generally preferred for the removal of heavy metal ions, due to its high efficiency, easy handling, accessibility of different adsorbents and cost effectiveness [20], low-cost adsorbents production from agricultural and by-products which has two advantages. First, these materials are changed into useful value-added adsorbents, and second, these adsorbents are used for water and wastewater purification [5]. In recent years, significant attention has been focused on the removal of heavy metals in single and multicomponent system using low-cost adsorbents such as activated carbon from a new precursor hazelnut husks [5] tea waste [1]. The purpose of this study is to investigate competitive sorption onto sunflower seed husk (SSH) waste from aqueous solution mixtures of Cu$^{2+}$ and Ni$^{2+}$ ions. The two metals are found extensively in effluents from the microelectronics and electroplating industries. Four isotherm models were used to analyze the experimental data. The kinetic experimental data were tested for two kinetics equations, pseudo first-order and pseudo second-order equations.

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2. Mathematical Modeling

2.1 Preparation of Sunflower Seed Husk (SSH)

The SSH waste was collected at local market and extensively washed with tap water and distilled water to remove surface impurities and dried at 105°C for 2 hours in the oven to remove the moisture content. The dried materials were milled and sieved, the particles sizes of 250μm were chosen for this study, as shown in Figure (1). The samples were then stored in a polyethylene bags for further use. No other chemical or physical treatments were used prior to adsorption experiments.

![Figure 1: Sunflower wastes before and after grinding](image)

2.1.2 Chemicals and Reagents

All chemicals and reagents used in the experiments were analytical grade. Synthetic wastewater used in this experiment containing the required concentration of metal was prepared by dissolving the calculated amount of CuSO$_4$·5H$_2$O and Ni(NO$_3$)$_2$ in distilled water, the main properties of the metals salts were listed in Table (1). The initial pH of the solutions was adjusted to the best value based on the pH study. The mixture was shaken at a constant speed of 175 rpm for 3 hours until equilibrium was achieved. During the adsorption, a sample was drawn at the preferred time intervals (10, 15, 30, 60, 90, 120, 150 and 180 minute) filtered and analyzed. The biosorption capacity ($q_t$ mg/g) for each time interval was calculated using Eq. (3)

$$q_t = \frac{V(C_o - C_e)}{m}$$

Where: $q_t$ is the experimental equilibrium biosorption capacity (mg/g); $C_o$ and $C_e$ is the initial and equilibrium sorbate concentration in water (mg/L), respectively; $V$ is the volume of used solution (L); and $m$ is the mass of used adsorbent (g).

In this work, the sorption kinetics was modeled using the pseudo-first-order and pseudo-second-order kinetic models. The equations of the kinetic models are presented in Table (2).

The parameters for each kinetic model were determined by fitting the equations with the experimental data by using Microsoft Excel.
Table 2: Kinetic Model.

<table>
<thead>
<tr>
<th>Model</th>
<th>Linear expression</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-First Order Kinetic</td>
<td>( \ln \left( \frac{q_{eq} - q_t}{q_t} \right) = \ln k_1 t )</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>( q_{eq} ) is the amount of metal sorbed at equilibrium, (mg/g); ( k_1 ) is the equilibrium rate constant, (1/min).</td>
<td></td>
</tr>
<tr>
<td>Pseudo Second Order Kinetic</td>
<td>( t = \left( \frac{1}{k_2 q_{eq}^2} + t \right) )</td>
<td>[4]</td>
</tr>
<tr>
<td></td>
<td>( q_{eq} ) is the amount of metal ion sorbed at equilibrium, (mg/g); ( k_2 ) is the rate constant of sorption, (g/mg min).</td>
<td></td>
</tr>
</tbody>
</table>

2.2.3 Isotherm Experiment and Models

The adsorption isotherm of Cu\(^{2+}\) and Ni\(^{2+}\) ions onto SSH was investigated in single and binary systems. The experiments were conducted in conical flasks of 250 ml containing 100 ml of metal solution at initial concentration of 30 mg/l for each metal was used in conjunction with sorbent dosage (1-10g/l) at a constant speed 175 rpm for 2h. The final concentration of the metal ion solution (Ce) at equilibrium was measured to calculate the adsorbed amount of metal ions at final equilibrium (qe) using Eq. (3). The experimental isotherm data were fitted with the two familiar sorption isotherm models, namely, Langmuir and Freundlich models. These two models are represented in Table (3). The similar method of single system experimentation was followed in binary system.

3. Results and Discussion

3.1 Fourier-Transform Infrared (FTIR) Analysis

FTIR spectral analysis is important to identify the characteristic functional groups on the surface of the adsorbent, which are responsible for adsorption of metal ions. The FTIR spectra of the sunflower seed husks before and after sorption of Cu\(^{2+}\) and Ni\(^{2+}\) form aqueous solution was examined using (SHIMADZU FTIR, 8000 series spectrophotometer) at Chemical Dept./Collage of Science/Al-Nahrain University. Normally, the spectra are measured within the range of 400–4000 cm\(^{-1}\) as shown in Figure 2. The results of the FTIR spectrum showed that different functional groups were detected on the surface of the SSH. The broad peak detected in the spectra at 3347.35 cm\(^{-1}\) could be assigned to the hydroxyl and amides groups (–OH and –NH) which shows presence of phenols and alcohols. The functional groups were identified in Table (4).

Table 3: Isotherms models

**Single system Isotherm Models**

<table>
<thead>
<tr>
<th>Model</th>
<th>Linear expression</th>
<th>Plot</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( q_e = \frac{q_m b C_e}{1 + b C_e} )</td>
<td>( \frac{q_e}{q_m} = 1 + \frac{1}{b q_m} \frac{1}{C_e} )</td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>( q_m ) is the maximum sorption capacity for monolayer coverage, (mg/g); ( b ) is the constant related to the affinity of the binding site, (L/mg).</td>
<td>Ln q_e vs ln C_e</td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>( q_e = K C_e^{1/n} )</td>
<td>( \ln q_e = \ln K + \frac{1}{n} \ln C_e )</td>
<td>[16]</td>
</tr>
<tr>
<td>K is constant indicative of the relative adsorption capacity of the adsorbent, (mg/g)(L/mg)(^{1/n}); ( 1/n ) constant indicative of the intensity of the adsorption.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Binary system Isotherm Models**

<table>
<thead>
<tr>
<th>Models</th>
<th>Non Linear Form</th>
<th>Plots</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extended Langmuir</td>
<td>( q_{e,i} = \frac{b_i q_m i C_{e,i}}{(1 + \sum_{j=1}^{n} b_j C_{e,j})} )</td>
<td>( \frac{1}{q_e} = 1 ) vs ( \frac{1}{C_e} )</td>
<td>[18]</td>
</tr>
<tr>
<td>( q_{m,i} ) and ( b_i ) are the single component Langmuir parameters for component i.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extended Freundlich</td>
<td>( q_{e,i} = \frac{K_i C_{e,i}^{a_{e,i}}}{C_{e,i}^{a_{e,i}} + \sum_{j=1}^{n} K_j C_{e,j}^{a_{e,j}}} )</td>
<td>Ln q_e vs ln C_e</td>
<td>[14]</td>
</tr>
<tr>
<td>( K_i ) and are derived from the corresponding individual Freundlich isotherm equation for the component i.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 4: Summary of functional groups before and after sunflower seed husk biomass loaded with Cu$^{2+}$, and Ni$^{2+}$ ions in single system

<table>
<thead>
<tr>
<th>Assignment Functional Groups</th>
<th>Wave number (cm$^{-1}$) Before adsorption</th>
<th>Wave number (cm$^{-1}$) After adsorption of Cu$^{2+}$</th>
<th>Wave number (cm$^{-1}$) After adsorption of Ni$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl group (-OH), amides (N-H stretch)</td>
<td>3347.35</td>
<td>3332.87</td>
<td>3325.92</td>
</tr>
<tr>
<td>Carboxyl (C=O aldehyde stretch)</td>
<td>2920.68</td>
<td>2897.39</td>
<td>2917.08</td>
</tr>
<tr>
<td>Amides (C=O aldehyde stretch)</td>
<td>1730.82</td>
<td>1730.27</td>
<td>1731.29</td>
</tr>
<tr>
<td>Nitro aliphatic group (-NO$_2$)</td>
<td>1368.96</td>
<td>1369.22</td>
<td>1369.78</td>
</tr>
<tr>
<td>Carboxyl (C-C ketone stretch), alcohol(C-O stretch), Phosphine oxide P=O, Alkyl halides (C-F stretch)</td>
<td>1155.54</td>
<td>1153.48</td>
<td>1153.48</td>
</tr>
<tr>
<td>Alkyl halides (C-F stretch), Alcohol (C-O stretch)</td>
<td>1030.67</td>
<td>1030.80</td>
<td>1029.36</td>
</tr>
<tr>
<td>Aromatic (C-H bend), sulfonate (S-O stretch), Phosphines (P-H bend)</td>
<td>898.15</td>
<td>898.33</td>
<td>898.42</td>
</tr>
<tr>
<td>alkyl halides [(C-Cl) stretch and (C-I) stretch]</td>
<td>555.95</td>
<td>558.38</td>
<td>562.21</td>
</tr>
</tbody>
</table>

### 3.2 Effect of pH

The pH is an important parameter that affects the sorption on the removal of Cu$^{2+}$ and Ni$^{2+}$ by SSH. 100 ml of 30 mg/l metal solutions were carried out in the pH ranges from 4 to 8 and agitated for 3h at 175 rpm speed for single system; the results are plotted in Figure (3). The results indicated that the percentage sorption of Cu$^{2+}$ and Ni$^{2+}$ ions increased with increasing of pH to attain a maximum at 5 and thereafter it decreases with further increase in pH. The minimum sorption was observed at lower pH values which may be due to the solubility of main constituent of SSH sorbent (i.e., CaCO$_3$) which thereby lead to hindering the sorption metal species. The decrease in the removal efficiency at high pH value may be credited to the fact that the negative species of metals, M(OH)$_3^-$ and M(OH)$_4^{2-}$, are not capable of a combination with the negative surface of sorbents [2]. The same behavior was noticed by [12]. In binary system, pH of 5 for Cu$^{2+}$ and Ni$^{2+}$ in single component was selected to achieved the high removal efficiency without metal hydroxide precipitation.

### 3.3 Effect of Agitation Speed

The effect of the agitation speed on the removal efficiency of metal ions in single system was investigated at three different agitation speed 125, 175 and 250 rpm by using 5 g/l SSH, 30 mg/l initial metal concentration, pH 5 and contact time 180 min. Figure (4) below, shows that the removal efficiency of metal ions increased with
increasing agitation speed from 125 to 175 rpm and further increases has no considerable effect (i.e., above 175 rpm). The increase in efficiency is due to the increase in turbulence and as a consequence, decreases the film resistance to mass transfer surrounding the adsorbent particles [11], in addition, these results indicate that agitation speed of 175 rpm is sufficient to obtain maximum removal by reducing the boundary layer thickness to a minimum value.

![Figure 4: Effect of agitation speed on removal of Cu\(^{+2}\), and Ni\(^{+2}\) by SSH for single system](image)

3.4 Effect of Contact Time

The removal of Cu\(^{+2}\) and Ni\(^{+2}\) from aqueous solution was studied as a function of contact time in the time interval 0-180 minute at 30 mg/l initial metal concentrations, pH 5, 5g/l SSH dosage and 175 rpm agitation speed for single system. Figure (5) shows that the percentage of metals ion sorbed increased with increasing time and it reached equilibrium at about 120 min. Further increases in contact time had no significant effect on metal removal and the sorption rate become practically very slow. It can be concluded that 120min. contact time is sufficient to reach equilibrium conditions for both metals.

![Figure 5: Effect of contact time on the removal of Cu\(^{+2}\) and Ni\(^{+2}\) by using SSH in single system](image)

3.5 Effect of Sunflower Seed Husk Dosage

The effect of SSH dosage on the removal efficiency of metal ions was studied using 1-10 g/l SSH dosage by shaking at 175 rpm with 30 mg/l of Cu\(^{+2}\) and Ni\(^{+2}\) concentrations for 2 h, at pH 5 for single and binary systems. The results are plotted in Figure (6). For single system, the results showed that the retention of metals increased with increasing amount of sorbent up to 7 g/l. A further increase in sorbent dosage has a small or limited increase in the removal efficiency. The increased in the sorption with sorbent dose may be attributed to increased sorbent surface area and hence the number of binding sites available to the metal ions [17]. Figure (6) shows that the removal efficiency of Cu\(^{+2}\) and Ni\(^{+2}\) by 7g/l SSH dosage were about 92.5% and 84.8% for single system and decreases to 86.5% and 75.6 % for binary system. These results indicated that the metal removal efficiency was greater in the single systems as comprised with the multi component one; this may be due to the absence of competitive processes between metals and sorbent mass in single component system [10]. The removal efficiency of Cu\(^{+2}\) was higher than that of Ni\(^{+2}\). This may be due to the physical and chemical properties of Cu\(^{+2}\) to be more favorable to be adsorbed than Ni\(^{+2}\). This might be explained on the basis of the hydrated ionic radius. Ionic radii of Cu\(^{+2}\) and Ni\(^{+2}\) are 255.6 and 249.2 respectively. Cu\(^{+2}\) having higher ionic radii, the therefore, it will be removed more efficient [3].

![Figure 6: Effect of sorbent dose on the removal of Cu\(^{+2}\) and Ni\(^{+2}\) by SSH for (a) single system; (b) binary system](image)

3.6 Effect of Initial Metal Concentration

Different concentrations (10, 30, 60, 120 and 180 mg/l) for Cu\(^{+2}\) and Ni\(^{+2}\) ions were selected to study the variation of removal efficiency at the best previous conditions for single and binary systems as shown in Figure (7), the results for single system indicated that the percentage removal of metals was slightly decreased with an increase in the initial metals concentration from 10 to 30 mg/l whereas a rapid decrease in the removal percentage was
observed at the initial concentration between 30 and 180 mg/l. This behavior can be attributed to the decrease in the available sorption sites on the surface area of the sorbent at a metal ion concentration from 60 to 120 mg/l. At higher metal ions concentration, the ratio of initial number of moles in metal ions to the sorption sites available was high resulted a lower sorption percentage [2, 13].

![Figure 7: Effect of metal ions concentration on the removal of Cu\(^{2+}\) and Ni\(^{2+}\) by SSH for (a) single system; (b) binary system.](image)

3.7 Kinetic Study

The kinetics of copper and nickel ions sorption onto SSH for single system were examined by using pseudo-first-order and pseudo-second-order as shown in Table (5) and Figures 8 and 9. It is clear that the values of correlation coefficient (R\(^2\)) indicate a better fit of pseudo-second-order model with the experimental data compared to first-order model. The values of q\(_e\) calculated from the second-order kinetic model accepted very well with the experimental value, and the regression coefficients are over 0.99. Thus, the second-order model can be applied for Cu\(^{2+}\) and Ni\(^{2+}\) sorption process.

![Figure 8: Pseudo-first-order kinetic model for sorption of Cu\(^{2+}\) and Ni\(^{2+}\) on SSH in single system](image)

![Figure 9: Pseudo-second-order kinetic model for sorption of Cu\(^{2+}\) and Ni\(^{2+}\) on SSH in single system](image)

3.8 Sorption Isotherms

The sorption data parameters for Cu\(^{2+}\) and Ni\(^{2+}\) ions onto SSH for each model in single and binary systems were obtained by fitting the equations to the experimental data using Microsoft Excel as shown in Figures 10 and 11 for Langmuir and Freundlich models respectively. Tables 6 and 7 represent all parameters with correlation coefficient. From these tables the Langmuir model described the sorption data slightly better than the other model depending on the value of coefficient of determination (R\(^2\)).

![Table 5: Comparison of sorption rate constants, experimental and calculated q\(_e\) values for the pseudo first and second order reaction kinetics](image)
4. Conclusions

The present study evaluated the feasibility of sunflower seed husk (SSH) waste as a low economic value adsorbent for the competitive removal for Cu$^{2+}$ and Ni$^{2+}$ ions from aqueous systems at best condition for environmental cleaning purposes. Langmuir and Freundlich isotherms were utilized to represent the experimental data. Both Langmuir and Freundlich results fitted to the experimental data for the two metals. The modeling of kinetics data showed the sorption Cu$^{2+}$ and Ni$^{2+}$ ions on sunflower wastes followed Pseudo-second order kinetics with regression coefficients more than 0.99. The monolayer adsorption capacity of Cu$^{2+}$ and Ni$^{2+}$ ions calculated from Langmuir model in single system was found 23.4941, 11.3051 mg/g respectively, while it was 18.696, 9.2366 mg/g for binary system. The sequence for metal ions removal in single and binary system was Cu$^{2+}$ > Ni$^{2+}$ as compared with the metals removal rate in single component system, the removal
efficiencies of both metals decreased in the binary system.

**Nomenclature**

AAS Flame Atomic Absorption spectrophotometer.

SSH Sunflower seed husk

FTIR Fourier-Transform Infrared Analysis

R² correlation coefficient

Pm Picometre (unit of length in the metric system)

**References**


الخلاصة - يهدف هذا البحث إلى دراسة إمكانية استخدام قشور بذور عباد الشمس كمادة متقدرة لإزالة أيونات النحاس والنيكل من المياه الصناعية المحضررة. استُخدمت طريقة الامتزاز بالدفع وقد أجريت سلسلة من التجارب في مفاصل الدفع من أجل الحصول على أفضل ظروف لازالة أيونات في النظام المنفرد والثاني حيث تم دراسة تأثير التغير في النتائج المقصودة. وكما تم دراسة وقوع النمط الموردي والتركيز الأبدائي لأيونات المعادن. وقد وصلت النتائج إلى أن أفضل الظروف كانت 5 و 7 غ/لتر و 120 دقيقة. في نظام المعادن حيث تم الحصول على درجة مقدار 23.4940 و 11.3051 غ/لتر للنظام المنفرد. وأما في النظام الثاني حيث تم الحصول على درجة مقدار 18.6962 و 9.2366 غ/لتر للنظام المنفرد والثاني، وكانت درجة مقدار 92.5 و 84.8% على التوالي وانخفاض في النظام الثاني كما كان موديل التفاعل الحركي من الدرجة الثانية.

الكلمات الرئيسية - المعادن الثقيلة، الامتزاز الدفعي، قشور بذور عباد الشمس، الموديلات الحركية، التوازن.