SYNTHESIS AND CHARACTERIZATION OF HEMATITE NANOPARTICLES FOR REMOVAL OF Pb²⁺ AND Cu²⁺ FROM WATER SAMPLES

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ABSTRACT

Heavy metal ions in water samples have potential hazard to human health. So, treatment of waste water is a necessity to decrease the levels of such hazard metals. The present study described a method for wastewater samples treatment using magnetic nanoparticles. Hematite nanoparticles (αFe₂O₃NPs) were synthesized and characterized using transmission electron microscope (TEM) and X-ray diffraction (XRD). The prepared αFe₂O₃NPs were used for solid phase adsorption of Pb²⁺ and Cu²⁺ from aqueous solutions. The effects of various parameters, including solution pH, shaking time, and adsorbent dose on adsorption efficiency were investigated. Langmuir adsorption isotherm was effectively described the adsorption process onto αFe₂O₃NPs. The study found that Pb²⁺ and Cu²⁺ adsorption was quantitative at pH 5.5, with maximum adsorption capacities of 200 mg g⁻¹ and 15.3 mg g⁻¹ for Pb²⁺ and Cu²⁺, respectively, under optimum conditions. This method was found to be applicable for the removal of Pb²⁺ and Cu²⁺ from water samples.

Keywords: αFe₂O₃; nanoparticles; adsorption, metal ions; solid phase extraction

INTRODUCTION

Heavy metal ions are widespread environmental pollutants, and the presence of these elements including Pb²⁺ and Cu²⁺ in river water is a major concern due to their potential harm to public health, living organisms, and freshwater supply [1,2]. These non-biodegradable metal ions can cause kidney damage, nervous system damage, and renal dysfunction when exposure exceeds safe levels [3,4]. As a result, regulations to reduce heavy metal ions concentration in water are becoming increasingly stringent to mitigate these harmful effects [5]. While the simultaneous removal of multiple hazardous heavy metal ions offers a cost-effective solution, it has been challenging to achieve due to the
competing adsorption of these heavy metal ions. Nevertheless, it is crucial to develop an effective and low-cost strategy to avoid the repeated one-by-one removal of pollutants. Solid phase extraction (SPE) is a highly effective and affordable method for recovery or removal of substances, and its versatility has made it widely used [4]. The success of SPE relies heavily on the sorbent used, and the search for new sorbents with high surface area, fast sorption kinetics, and stability over a wide pH range has become increasingly important. However, traditional sorbents such as clay minerals and oxides have limited sorption capacity and efficiency. Recent studies have shown that nanomaterials, such as nano-oxides, nanocarbon, and carbon-based nanocomposites [5–9], exhibit exceptional sorption capacity. Despite their potential, the high dispersibility of nanomaterials in aqueous solutions has made it difficult to separate the sorbents from the aqueous phase once saturation is reached, limiting their application in large volumes of water.

In recent times, there has been an increasing interest in magnetic nanoparticles (MNPs), particularly iron oxide due to their remarkable characteristics such as low toxicity and ease of separation [10-13]. By placing a magnet outside the extraction container, MNPs can be readily separated from the sample solution. Consequently, magnetic solid phase extraction (MSPE) is advantageous because of its speed, affordability, simplicity, and reusability.

In this work, \( \alpha \text{Fe}_2\text{O}_3 \) NPs as low-cost abundant material was synthesized in nano form and characterized using XRD and TEM. The prepared nano magnetite was used for \( \text{Pb}^{2+} \) and \( \text{Cu}^{2+} \) removal from aqueous solution. The effect of different factors on the adsorption was investigated and optimized. The nano magnetic material was used to adsorb metal ions from real sample solution.

**EXPERIMENTAL**

**Reagents**

All chemicals and reagents were of analytical grade. Every day, a working standard solution of \( \text{Pb}^{2+} \) and \( \text{Cu}^{2+} \) was prepared by progressively diluting a standard stock solution of 1000 mg L\(^{-1} \), obtained from Merck (Darmstadt, Germany), in ultra-pure water.

**Synthesis of \( \text{Fe}_3\text{O}_4 \) nanoparticles**

The conventional co-precipitation method was used with slight modifications [14, 15] to synthesize \( \alpha \text{Fe}_2\text{O}_3 \) nanoparticles. A mixture of 11.68 g of ferric chloride and 4.30 g of ferrous chloride was dissolved in 200 mL of high-purity water under nitrogen gas with vigorous stirring at 85°C. Then, 40 mL of 30% (v/v) \( \text{NH}_3 \) was added with increased nitrogen passing rate and stirring speeds, resulting in an immediate color change from orange-red to black. After half an hour, the reaction was stopped, and the obtained suspension was left to cool naturally to room temperature. The nanoparticles were then washed repeatedly with high-purity water, 0.02 mol/L sodium chloride, and ethanol. Finally, the cleaned nanoparticles were stored in an ethanoate solution with a concentration of 40 g/L.

**Apparatus**

The JEOL 1011 microscope was utilized to perform transmission electron microscopy (TEM) characterization at 100 kV. A \( \text{Fe}_3\text{O}_4 \) NPs suspension in ethanol was placed on a carbon-coated copper grid and dried under vacuum. X-ray diffraction was conducted using a PANalytical Empyrean diffractometer equipped with a cobalt source, a Bragg-Brentano HD optics, and a PIXcel1D-Medpix3 detector with specified parameters. Measurement of the pH of the
test solutions was performed using pH meter electrodes (Horiba F-22). To determine the concentration of heavy metal ions, a Thermo Electron Corporation-S series Atomic Absorption Spectrometer was utilized. The spectrometer was equipped with a deuterium lamp for background correction, the manufacturer's recommended operating conditions were followed, unless otherwise specified.

**Experimental uptake of heavy metal ions**

The adsorption experiments for heavy metal ions uptake were conducted using the batch technique in a series of flasks. In each flask, 10mg of αFe₂O₃NPs was added to 20 mL of Cu²⁺ and Pb²⁺ solution. The flasks were agitated on a Vibromatic-384 shaker at 120 rpm for 15 minutes at room temperature. The pH of the solution was measured using a Corning 125 pH-meter. The residual concentration of heavy metal ions at equilibrium was analyzed using Flame Atomic Absorption spectrometry.

The removal Percentage (R) and the adsorption capacity for Pb²⁺ and Cu²⁺ were calculated according to Eq. 1 and Eq. 2, respectively.

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

(1)

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

(2)

where \( Q_e \) is the adsorption capacity (mgg⁻¹), \( C_o \), \( C_e \) is the initial and equilibrium Pb²⁺ and Cu²⁺ concentrations in the aqueous phase (mgL⁻¹), respectively, \( V \) is the volume of heavy metal ions solution, (L) and \( W \) is the weight of dry \( \alpha \)Fe₂O₃ NPs(g).

**RESULTS AND DISCUSSION**

**Characterization of \( \alpha \)Fe₂O₃ nanoparticles**

Fig. 1 displays the X-ray diffractogram of the produced \( \alpha \)Fe₂O₃ nanoparticles. The diffractogram reveals that only six characteristic peaks of hematite \( \alpha \)Fe₂O₃, specifically \((2\theta = 21.1°, 35.1°, 41.4°, 50.5°, 63° and 67.4°)\) with Miller indices \((012), (110), (113), (024), (214) and (441), \) respectively, were identified in both samples (a and b).

TEM was used to determine the morphology and size of the prepared NPs. TEM micrographs of \( \alpha \)Fe₂O₃ at different magnification were presented in Fig. 2a, b, c. The nanoparticles are spherical and polydisperse with an average size of 11 nm as observed by TEM and the corresponding size distribution histograms of these NPs (Fig. 2d).

![Fig. 1. XRD patterns of the synthesized \( \alpha \)Fe₂O₃ nanoparticles.](image-url)
Optimization of adsorption of metal ions onto αFe₂O₃ nanoparticles

Effect of pH

The pH value of the aqueous solution plays a crucial role in controlling the adsorption process of metal ions at the solid-liquid interface. To investigate the effect of pH on Pb^{2+} and Cu^{2+} adsorption onto αFe₂O₃ nanoparticles, experiments were carried out at different pH levels ranging from 1 to 8 while maintaining other experimental parameters constant. The results, presented in Fig. 3, demonstrate that the adsorption efficiency increases with an increase in pH reaching maximum at pH 5.5 for both Pb^{2+} and Cu^{2+}. It is possible that the reason for the lower adsorption efficiency of metal ions at lower pH is due to the higher proton (H⁺) density in the medium. This can lead to competition between H⁺ and metal ions for active sites on the αFe₂O₃ nanoadsorbents, resulting in fewer active adsorption sites being available for metal ions [16]. Another reason was attributed to the surface charge of the αFe₂O₃ nanoadsorbents, as magnetite nanoparticles have amphoteric surface activity [17]. In water-based environments, the surface of magnetite nanoparticles is covered with FeOH. This layer can either gain or lose protons depending on the pH of the medium, resulting in the formation of FeO⁻ or Fe(OH)⁻²⁺ species.

Effect of contact time

The impact of shaking time on the adsorption of Pb^{2+} and Cu^{2+} at an initial concentration of 20 mg L⁻¹ using 20 mg of αFe₂O₃ NPs was
examined by varying the shaking time between 3 and 30 minutes, as shown in Figure 4. The findings revealed that the highest adsorption efficiency of Pb$^{2+}$ and Cu$^{2+}$ was achieved after 15 minutes of shaking.

![Fig. 3. Effect of pH on adsorption efficiency of Pb$^{2+}$ and Cu$^{2+}$ on αFe$_2$O$_3$ nanoparticles. Conditions: αFe$_2$O$_3$ nanoparticles (20 mg), Pb$^{2+}$ (20 mg L$^{-1}$), Cu$^{2+}$ (20 mg L$^{-1}$), V (20 mL) at room temperature.](image)

**Effect of adsorbent amount**

The experiments were conducted using different amounts of adsorbent ranging from 5 to 20 mg, with an initial concentration of 10 mg L$^{-1}$ for both Pb$^{2+}$ and Cu$^{2+}$, in 20 mL of solution at a temperature of 25℃ and pH of 5.5. The results, shown in Figure 5, indicate that the adsorption efficiency of Pb$^{2+}$ and Cu$^{2+}$ increased with the dosage of αFe$_2$O$_3$ up to 15 mg, reaching maximum of 87% and 60% for Pb$^{2+}$ and Cu$^{2+}$, respectively. Further increase in the adsorbent dosage did not result in significant improvement in adsorption efficiency, followed by a plateau.

![Fig. 5. Effect of αFe$_2$O$_3$ NPs amount on the adsorption efficiency of Pb$^{2+}$ and Cu$^{2+}$. Conditions: Pb$^{2+}$ (10 mg L$^{-1}$), Cu$^{2+}$ (10 mg L$^{-1}$), pH (5.5), shaking time (15 min), (20 mL) at room temperature.](image)

**Adsorption isotherms**

Freundlich and Langmuir models were used to discuss the adsorption isotherm of Pb$^{2+}$ and Cu$^{2+}$ on αFe$_2$O$_3$ NPs.

**Freundlich isotherm** model was employed to describe an empirical relation between the concentration of Pb$^{2+}$ and Cu$^{2+}$ adsorbed on
the surface of αFe₂O₃ NPs and the concentration of the metal ions in the solution, which characterizes a heterogeneous adsorption system. The linear form of the Freundlich model is shown in Equation (3) [19],

\[
\ln Q_e = \ln K_f + \frac{\ln C_e}{n}
\]  

(3)

where \(Q_e\) is the equilibrium adsorption capacity (mgg⁻¹), \(C_e\) is the equilibrium concentration of Pb²⁺ and Cu²⁺ in solution (mgL⁻¹), \(K_f\) and \(1/n\) are Freundlich constants.

A Freundlich plot of \(\ln Q_e\) versus \(\ln C_e\) would result in a straight line with a slope of \(1/n\) and an intercept of \(\ln K_f\), as shown in Fig. 6b and Fig. 6d for Pb²⁺ and Cu²⁺, respectively. The values of \(1/n\) indicate whether the nature of the isotherm is unfavorable (\(1/n > 1\)), favorable (\(0 < 1/n < 1\)), or irreversible (\(1/n = 0\)). In this study, the values of \(1/n\) were found between 0 and 1 (Table 1), which means that the adsorption of Pb²⁺ and Cu²⁺ onto αFe₂O₃ NPs is favorable.

**Langmuir isotherm:** The linear form of the Langmuir model is expressed in Equation (4) [20],

\[
\frac{C_e}{Q_e} = \frac{1}{bQ_{\text{max}}} + \frac{C_e}{Q_{\text{max}}}
\]  

(4)

where \(C_e\) is the equilibrium concentration of the metal ions in the solution, \(Q_e\) is the adsorption capacity at equilibrium, \(Q_{\text{max}}\) is the maximum adsorption capacity, and \(b\) is the binding constant. A straight line is obtained by plotting \(C_e/Q_e\) versus \(C_e\), as shown in Fig. 6a and Fig. 6c for Pb²⁺ and Cu²⁺, respectively. The Langmuir parameters can be used to predict the affinity between the sorbate and sorbent. According to the Langmuir isotherm model, the adsorption process is uniform on the surface of adsorbent and once the active sites occupied by the sorbate, no more sorption occurs at these sites.

The Langmuir adsorption isotherm can be represented using a dimensionless constant called the equilibrium parameter \(R_L\), which is defined Equation (5):

\[
R_L = \frac{1}{1+bC_o}
\]  

(5)

The \(R_L\) value is an indicator of the nature of the isotherm, which can be unfavorable (\(R_L > 1\)), linear (\(R_L = 1\)), favorable (\(0 < R_L < 1\)), or irreversible (\(R_L = 0\)) [21,22]. Fig. 7 shows the plot of \(R_L\) vs. \(C_o\) for both Pb²⁺ and Cu²⁺. The calculated \(R_L\) values ranged between 0 and 1 for Pb²⁺ (Fig. 7a). This suggests that the adsorption of Pb²⁺ onto αFe₂O₃ NPs is favorable under the conditions used in this study. As the initial concentration of Pb²⁺ increased, the \(R_L\) values decreased, indicating that the adsorption of metal ions is more effective at higher initial concentrations.

On the otherside, the \(R_L\) of Cu²⁺ is more than 1 for Cu²⁺ (Fig. 7b). The \(R_L\) values increased as Cu²⁺ initial concentration increased. It suggests that the adsorption of Cu ions onto αFe₂O₃ NPs is unfavorable. This finding explains the lower adsorption capacity of Cu²⁺ onto αFe₂O₃ NPs.

The results of Adsorption isotherms models indicated that the adsorption of both Pb²⁺ and Cu²⁺ onto αFe₂O₃ NPs was well-fitted with the Langmuir model (\(R^2 = 0.99\)), which is closer to unity than the Freundlich model.

The Langmuir and Freundlich constants for Pb²⁺ and Cu²⁺ are summarized in Table 1.
Fig. 6. Adsorption isotherms of Pb\textsuperscript{+2} and Cu\textsuperscript{+2} onto hematite NPs. (a) Langmuir isotherm of Pb\textsuperscript{+2}. (b) Freundlich isotherm of Pb\textsuperscript{+2}. (c) Langmuir isotherm of Cu\textsuperscript{+2}. (d) Freundlich isotherm of Cu\textsuperscript{+2}.

Fig. 7. Variation of adsorption intensity (RL) with initial concentration (C\textsubscript{0}). (a) Pb\textsuperscript{2+} and (b) Cu\textsuperscript{2+}.
Table 1. Langmuir and Freundlich parameters for Pb\(^{2+}\) and Cu\(^{2+}\) adsorption onto αFe\(_2\)O\(_3\) NPs.

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Linear Langmuir model parameters</th>
<th>Freundlich model parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Q_{\text{max}}) (mg g(^{-1}))</td>
<td>(b) (L mg(^{-1}))</td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>15.3</td>
<td>0.036</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>200</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Application

The αFe\(_2\)O\(_3\) NPs were utilized for the removal of Pb\(^{2+}\) and Cu\(^{2+}\) ions from spiked real water samples including tap water and wastewater. The wastewater sample solution was collected from sewage. Table 2 summarize the chemical analysis of the major elements present in tap water and wastewater.

Table 2. Chemical analysis of major elements in water samples.

<table>
<thead>
<tr>
<th>Na (ppm)</th>
<th>K (ppm)</th>
<th>Ca (ppm)</th>
<th>Mg (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>33.3</td>
<td>5.55</td>
<td>400.8</td>
</tr>
<tr>
<td>Wastewater</td>
<td>4000</td>
<td>60</td>
<td>481</td>
</tr>
</tbody>
</table>

Table 3. Application of αFe\(_2\)O\(_3\)NPs for removal of different amounts of Pb\(^{2+}\) and Cu\(^{2+}\) in spiked water samples.

<table>
<thead>
<tr>
<th></th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Added (ppm)</td>
<td>After (ppm)</td>
</tr>
<tr>
<td>Tap water</td>
<td>2.05</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>4.28</td>
<td>0.33</td>
</tr>
<tr>
<td>Wastewater</td>
<td>2.48</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>4.34</td>
<td>0.13</td>
</tr>
</tbody>
</table>
CONCLUSION

αFe₂O₃NPs as adsorbent material was successfully synthesized and characterized. Its effectiveness for adsorbing heavy metal ions such as Pb²⁺ and Cu²⁺ was investigated using traditional Langmuir and Freundlich adsorption isotherms, showing a good fitting with Langmuir model. αFe₂O₃ NPs demonstrated high adsorption capacity for Pb²⁺ and lower affinity toward Cu²⁺. The adsorbent was successfully used for removing heavy metal ions from waste sample solutions, highlighting its potential as a promising material in the field of separation science.

REFERENCES


