Removal of heavy metal ions from industrial wastewater using magnetic nanoparticles

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Abstract

In this work Maghemite ($\gamma$-Fe$_2$O$_3$) and Magnetite (Fe$_3$O$_4$) nanoparticles were synthesized using Coprecipitation method and characterization was done using X-Ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS) and Fourier Transform Infra-Red Spectroscopy (FTIR). Size of these particles was found to be in the range of 20 to 100 nm and they were used as nano adsorbents for the removal of heavy metal ions like chromium and copper from the artificial wastewater. Adsorption depends with the optimum conditions of parameters such as pH (2.5 and 6.5), contact time (60 and 80) minutes, dosages with at room temperature for chromium and copper were observed with a removal efficiency of 92 %. These particles showed remarkable efficiency in removal of metals. Further, these particles were regenerated for reuse, desorption was done using HCl and NaOH effluent for copper and chromium metals respectively. The removals of pollutant enhanced with magnetic nanoparticles are evident with obtained results. The separation factor ($r$) lies between 0 and 1 indicating that the favour of Langmuir isotherm for both chromium and copper ions.

Keywords: magnetism; nanoparticle; isotherm; pollutant; wastewater

1. Introduction

Water is one of the basic necessities of man, with the industrial revolution most of the industrial wastes are flowed to the nearby water reservoirs, causing harmful effect on environment. Industrial waste waters mainly contain heavy metals like chromium, copper, arsenic, cadmium, zinc, lead and nickel which are toxic and carcinogenic. So, it’s become a necessity for the removal of heavy metals from the industrial wastewater [1-4].
Chromium and its related metals are used in many industries. The effluents from the industries are having chromium ions and many other harmful unwanted chemicals. The presence of chromium more than optimum is effluents are harmful to causing several issues such as indigestion, ulcer, skin allergy, liver damage and etc. In order to avoid the various harmful metal ions causing diseases for human, the removal of pollutants with proper technique to adsorb harmful metal ions of wastewater of effluents from the industries [5-10]. Cu\(^{2+}\) ions are one of the major pollutants and it cause hemolysis, diarrhea, kidney failure, improper respiration and etc. The pollutants are majorly from industries such as dye, paper, refinery, plating and etc, [11-16]. There is a demand for the method of removal of pollutant is environmental free and cost effective; it may applicable to developing, undeveloped countries worldwide. The sorption, adsorption and kinetics of isotherm phenomena for single-sorbate equilibrium, multi-sorbate equilibrium and etc. I.e., the multicomponent Langmuir models with considering electrostatic binding, the effect of pH and etc., [17]

In recent times many researchers are involving the removal of heavy metal ions. Many technological ideal involved in the removal mechanism by functional groups, surface charge, surface area, absorption, adsorption phenomena etc., [18-22]. In this work maghemite and Magnetite nanoparticles are synthesized and are used for copper and chromium removal from wastewater. In this work the authors adopted the adsorption phenomena and the effluents removal of pollutant of hexavalent Chromium and divalent Copper ions. Analysis used with XRD, FTIR, SEM, EDS and some physicochemical methods.

2. Experimental

Materials: In this study, all the analar grade chemicals of Ferrous chloride, Ferric Chloride, Ethanol, Ammonium Hydroxide, Hydrochloric acid, Sodium Hydroxide, Potassium Dichromate, Cupric Sulphate and Nitric Acid [23].

Preparation: At first, 1:2 ratios of ferrous chloride and ferric chloride were mixed in 50 ml of deionized water using a magnetic stirrer. This mixture was simultaneously heated at a temperature of 80°C. 1.5 M Ammonium Hydroxide was added drop wise to the above mixture till the pH of the solution reached 11, then the solution was allowed to cool and attain room temperature. This, solution was then centrifuged to remove unwanted substances and was dried over night at a temperature of 60°C to obtain black coloured Magnetite nanoparticles. These Magnetite nanoparticles were further heated at a temperature of 250°C for 4 hours to obtain reddish brown Maghemite nanoparticles.
Reaction

\[
\text{FeCl}_2 + 2\text{FeCl}_3 + 8\text{NH}_4\text{OH} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} + 8\text{NH}_4\text{Cl}
\]

Magnetite

\[
\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3 + \text{FeO}
\]

Maghemite

The above procedure was followed for different ratios of ferrous and ferric chloride precursors as ratio of 1:2, 0.1:0.2 and 0.01:0.02 is presented in Table.S1. From the Table.S1, at ratio 1:2 though the weight of the produced particles was high the size of the nanoparticles was large. At ratio 0.01:0.02 the size of the nanoparticles was small but the weight of the produced particles was low, so the ratio 0.1:0.2 was selected for the synthesis of the nanoparticles. At this ratio though the particle was high compared to 0.01:0.02, weight of was higher, this was moderate neither too high nor too low. For adsorption isotherm analysis, the adsorbent and adsorbate play a main role, i.e., the substance whose molecules get adsorbed on the surface of adsorbent is known as adsorbent. In general it takes the following form;

\[ A + B \rightleftharpoons AB, \]

Where, A- adsorbate, B- adsorbent and AB are adsorption respectively. The forward case is adsorption and the reverse case is desorption.

3. Results and Discussions

X-Ray Diffraction analysis: For the interpretation of the X-ray diffraction analysis and compared with the JCPDS reference code 96-900-6317 of Maghemite and standard magnetite nanoparticle of JCPDS code 01-086-1358. The crystalline parameters are shown in Table.1 and their patterns are in Table S2. From this we inferred that the synthesized particles matched with the standard maghemite and gave a score of 71 and the magnetites have a score of 82 [24].

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<tbody>
<tr>
<td>Maghemite</td>
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</tr>
<tr>
<td>11.2746</td>
<td>10.88</td>
<td>2.3616</td>
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<tr>
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<td>36.0250</td>
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<td>5.31</td>
<td>1.1808</td>
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<td>11.22</td>
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<td>12.26</td>
<td>0.5904</td>
<td>1.59244</td>
<td>25.91</td>
</tr>
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Crystal Size Determination: This was done using Sherwood equation, according to which 
Crystal Size = (0.9 \lambda/\beta \cos \theta), where, \lambda- wavelength of the radiation= 0.544nm, \beta-Full Width Half Maximum 
value of the peak in radians( for 100% intensity) =6.8696 \times 10^{-3} \text{ radians} 
\[ \Theta = \frac{20}{2} = 18.0125 \]
And therefore, Crystal size of 21.21 nm for maghemite and 28.21 nm for magnetite was obtained.

**SEM Analysis:** Figures.2. (a) to (c) shown the SEM images of maghemite nanoparticles we can see that the particles were crystalline and size of the particles was found to be in the range of 25-80 nm. And from SEM images (Fig.2 (d-f)) shown the magnetite nanoparticle, we can infer that the particles were in the range of 25 to 100 nm and crystalline in nature [24, 25].

![SEM images of maghemite and magnetite nanoparticles](image)

Fig. 2. SEM images of maghemite at (a) 1μm, (b) 500nm and (c) 500nm and magnetite at (d) 1μm, (e) 500nm and (f) 500nm

**EDS Analysis:** This analysis confirmed the presence of iron and oxygen elements. From Figure.S1.(a) and (b) shows the EDS spectrum of maghemite and magnetite nanoparticles. It shows that the presence of Fe and O ions. In addition it can be observed that the presence of impurities such as chlorine and carbon, from ferrous chloride precursor and ethanol were used during synthesis [25].

**FTIR Analysis:** The characteristic bands from fig. 4 (a) and (b) for maghemite and magnetite particles was checked and they are given in Table. S3.
Figure 3. FTIR spectra of (a) maghemite and (b) magnetite

From the same Fig. 3(a) it can be observed that the sharp peaks at the bands 682.75 cm$^{-1}$, 639.81 cm$^{-1}$, 589.33 cm$^{-1}$ and 460.49 cm$^{-1}$, these values approximately match the characteristic bands of the pure maghemite obtained from the literature, thus indicating the formation of maghemite phase. The band around 639.81 cm$^{-1}$ is a characteristic band of maghemite, which helps us to distinguish from maghrmite phase\cite{27}.

Magnetite Nanoparticles: The characteristic bands for magnetite phase were obtained from Fig.4(b), the characteristic bands were seen at 3115.21 cm$^{-1}$, 1620.54 cm$^{-1}$, 1400.76 cm$^{-1}$, 577.24 cm$^{-1}$, 486.18 cm$^{-1}$, 453.88 cm$^{-1}$ and 428.26 cm$^{-1}$, which matched quite well with the characteristic bands of magnetite nanoparticles. The peak at 577.24 is attributed to the vibration of iron oxygen bond of magnetite. Thus indicating the formation of magnetite phase\cite{27,28}.

Application of Nanoparticles for Removal of Copper and Chromium Ions:

Maghemite Nanoparticles: The adsorption experiments were conducted to determine the effect of different parameters such as pH, Temperature, Contact Time and Dosage. A stock solution of 100 ppm was made using Potassium Dichromate and Cupric Sulphate in Deionized water.

Effect of pH: Fig.4.a shows the effect of pH on the maghemite nanoparticles, 50 ml of 8 ppm potassium dichromate and cupric sulphate were mixed with 0.1 grams of maghemite nanoparticles using a shaker at room temperature for a contact time of 1 hour. Then, the concentration of Chromium and Copper in the solutions were checked using Atomic Absorption Spectrophotometer\cite{29}.
Figure. 4. Effect of removal efficiency (Y- Fe$_2$O$_3$) vs (a) pH, (b) contact time, (c) temperature and (d) dosage (◊ - Cr, □ - Cu).

From, the Fig. 4 (a), we can see that for maximum chromium was removed at lower pH and maximum Copper was removed at High basic pH. The removal of metal ions with respect to pH based on surface phenomena by hydroxyl groups. The change of surface charge is neutral at zero point charge (zpc) is 6.3. It is positive below the zpc and favour to anion adsorption through electrostatic attraction. Above zpc, the surface is negatively charged and so cation adsorption taking place. Increasing pH, Cr ion get decreased due to OH$^-$ ions. At the same time the electrostatic repulsion between the Cr ion and negative charged nanoparticles can be released by adsorption of Chromium ions [20, 29].

In this case the charge on surface due to Coulombic repulsion of metals ions. The depence of pzc with pH of copper due to there is an exchange of Cr$^{2+}$ and H$^+$ ions [20, 29]. Thus, a pH of 2.5 and 6.5 were suitable for the removal of Chromium and Copper metal ions.

Effect of Contact Time: From the Fig.4(b) it can be infered that the removal efficiency increased with the increasing contact time, then it slightly decreased indicating the equilibrium time of 60 minutes and 80 minutes for chromium and copper ions respectively [30].

Effect of Temperature: 50 ml of copper and chromium metal solutions were mixed with 0.1 grams of maghemite nanoparticles at their suitable pH at temperatures 25°C, 40°C and 50°C. Fig. 4(c) shows the maximum removal of heavy metals was possible only at room temperature. The adsorption of heavy metals is caused due to the electrostatic attraction between thenanoparticles and metal ions, which is not favoured at higher temperatutre.

Effect of Dosage: 0.05, 0.10, 0.15, 0.20 grams of nanoparticles were mixed with 50 ml of the stock solution using a orbital shaker are shown in fig.5(d), the concentration of heavy metals was checked using AAS [31]. It can be see that the rate of heavy metal removal increased we the increase in the amount of nanoparticles, which means increase in the adsorption surface.
Magnetite Nanoparticles: In order to determine the effect of parameters same procedure and conditions were followed which we were maintained for maghemite nanoparticles.

Effect of pH: 50 ml of 8 ppm, potassium dichromate and cupric sulphate solutions were mixed with 0.1 grams of nanoparticles, at a pH range of 2 to 6 using an orbital shaker. From the fig. 5(a), it can be shown that the removal of chromium is maximum at lower pH, may due to the formation of OH\(^{-}\) ions which compete with the chromium species for the adsorption sites on the magnetite nanoparticles [32].

\[
\text{sH}_2\text{O} + q \equiv \text{FeOH} + r\text{Cu}^{2+} \leftrightarrow (\equiv \text{FeO}) q\text{Cu}_r ((\text{OH})^{(2-q-s)})_s + (s + q)\text{H}^+
\]

where, s, q and r indicates the stoichiometric coefficients. The increase in pH helps to increase more number of sites influencing higher Cu\(^{2+}\) gets absorbed as magnetite.

Effect of Contact Time: 100 ml of potassium dichromate and cupric sulphate from stock solution was mixed with 0.1 grams of magnetite nanoparticles using an orbital shaker. Samples were collected at specific intervals of time and the metal concentration was measured using atomic absorption spectroscopy. The Fig. 5(b) shows the removal rate for both the metals increased with the increase in contact time [33].

Effect of Temperature: 50 ml of stock solution was mixed with 0.1 grams of magnetite nanoparticles at 25\(^{\circ}\)C, 50\(^{\circ}\)C and 60\(^{\circ}\)C in an incubator shaker at their suitable pH. From the graph (Fig. 5(c)), it can be seen that the maximum removal of both the metals was possible at room temperature. Indicating that maximum physical adsorption happened at room temperature [34]. The removal rate increased with the increase in dosage, as the adsorption sites increased were depicted in Fig. 5(d) [35].
Analysis of Adsorbed Nanoparticles

FTIR Analysis: The characteristic bands for chromium is seen at wavenumbers 3500 cm\(^{-1}\), 1100 cm\(^{-1}\), 609 cm\(^{-1}\), 556 cm\(^{-1}\) and 443 cm\(^{-1}\). Below we can see the FTIR graphs of maghemite and magnetite nanoparticles. We can see the peaks at 928 cm\(^{-1}\), 598.67 cm\(^{-1}\), 476.71 cm\(^{-1}\) and indicates the adsorption of chromium ions on the surface of maghemite nanoparticles. The peaks at 1622.64 cm\(^{-1}\), 571.72 cm\(^{-1}\), 478.17 cm\(^{-1}\), 426.67 cm\(^{-1}\) indicate the chromium adsorption on magnetite nanoparticles (Fig.6 a & b) [28, 34].

The characteristic bands for copper ions is at 1093 cm\(^{-1}\) and 465 cm\(^{-1}\). The Fig. 8(a) shows the graph of FTIR spectra for maghemite nanoparticles we see the peaks at 571.72 cm\(^{-1}\), 478.17 cm\(^{-1}\) and 426.67 cm\(^{-1}\), which can be considered for copper metal ion adsorption. For magnetite we have peaks at 587.23 cm\(^{-1}\), 476.97 cm\(^{-1}\) and 425.42 cm\(^{-1}\), which also indicate copper adsorption on magnetite nanoparticles observed in Fig.6 c & d [35].
Figure 6. FTIR spectra of Chromium adsorbed (a) Maghemite and (b) Magnetite Nanoparticles, and Copper adsorbed (c) Maghemite and (d) magnetite nanoparticles

Energy Disspersive Spectrum of Chromium adsorbed Nanoparticles: These results prove the adsorption of chromium ions on maghemite and magnetite nanoparticles (Figure S2).

Desorption Studies: Maghemite and Magnetite nanoparticles were regenerated using 0.2 M HCl and 0.01M NaOH effluent for desorption of Copper and Chromium metal ions. 0.1 grams of chromium adsorbed nanoparticles were mixed with 20 ml 0.01M NaOH, which is a base, this caused the desorption of chromium species due to electrostatic repulsion as the surface charge of nanoparticles was negative because the pH was above zero point of charge. Similarly, Copper adsorbed nanoparticles were regenerated using 0.2M HCl; due to decrease in pH the nanoparticle surface charge was below zero point of charge, thus causing electrostatic repulsion between copper ions and nanoparticles [36, 37]. These regenerated particles were then used for removal of Chromium and Copper metal ions from waste water are shown in Table. S4.

Adsorption Isotherm: Langmuir isotherm was found to be best fit for both maghemite and magnetite nanoparticles. The metal removal levels for isotherm plots curve determined using Langmuir model. The isotherm equation relate with adsorbent surface with number of binding sites. They are modeled according to following equation.
Where, \( b \) and \( Q_m \) are the Langmuir constant and Maximum capacity of adsorption and the values are obtained through \( \frac{C_e}{Q_e} \) vs \( C_e \) values.

The important factor which determine the adsorption phenomena, if \( r > 1 \) is unfavor, \( r = 1 \) is linear, \( r < 1 \) is favour and \( r = 0 \) is completely irreversible (27) and this \( r \)- value is calculated through the following expression.

\[
r = \frac{1}{(1 + bC_0)}
\]

here, \( C_0 \)-initial concentration (8 ppm), \( r \)- lies in the range 0 – 1 is favour to adsorption of Chromium and Copper as maghemite and magnetite nanoparticles [25]. The Langmuir model is the one of the accepted (isothermal model for single solutions). The steep initial slope of sorption isotherm is indicating desirable high affinity for absorbance phenomena. Thus for a good sorbents having high and steep initial sorption isotherm slope [38].

Adsorption Isotherm for Chromium Ions: From Fig 7(a) the value of \( Q_m \) and \( b \) was 6.77 mg g\(^{-1}\) and 677 Lmg\(^{-1}\). Separation factor ‘r’ value was between 0 and 1, indicating favorability of Langmuir isotherm. And from fig. 7(b) the value of \( Q_m \) and \( b \) was 7.46 mgg\(^{-1}\) and 466.41 Lmg\(^{-1}\). Separation factor ‘r’ value was between 0 and 1, indicating favorability of Langmuir isotherm [39].

Adsorption Isotherm for Copper Ions: The value of \( Q_m \) and \( b \) was 4.675 mg\(^{-1}\)and 677 Lmg\(^{-1}\). Separation factor ‘r’ value was between 0 and 1, indicating favorability of Langmuir isotherm is

\[
y = 0.1475x + 0.0111 \\
R^2 = 0.9579
\]

\[
y = 0.1343x + 0.0163 \\
R^2 = 0.9139
\]

\[
y = 0.2139x + 0.0208 \\
R^2 = 0.8777
\]

\[
y = 0.2852x + 0.0119 \\
R^2 = 0.8961
\]
shown in Fig. 7(c). And from Fig. 7(d) the value of $Q_m$ and $b$ was $3.5 \text{mg}^{-1}$ and $318.75 \text{Lmg}^{-1}$. Separation factor ‘r’ value was between 0 and 1, indicating favorability of Langmuir isotherm [40]. The similar and a best results reported through Langmuir isotherm model with ($R^2 = 0.999$) is better than Freundlich model ($R^2 = 0.918$) for the removal of Zinc (II) [41], for cadmium (Cd$^{2+}$) and lead (Pb$^{2+}$) [42] and were found to be highest for Freundlich model, (0.9946) and (0.997) for Langmuir model for Cd (II) and Zn (II) biosorption, respectively [43]. This indicates the chosen Langmuir isotherm is good for fit and analysis.

4. Conclusions

The Maghemite (25nm-80nm) and Magnetite (25nm-100nm) nanoparticles were synthesized which showed more percentage metal ions removal. Crystallite size of 21.21 nm for maghemite and 28.21 nm for magnetite were confirmed through XRD spectra’s. The presence of Fe and O are confirmed from the EDS analysis. Chromium adsorption on magnetite is evident from the peaks at 1622.6 cm$^{-1}$, 571.72 cm$^{-1}$, 478.17 cm$^{-1}$ and 426.67 cm$^{-1}$, and copper adsorption at peaks at 587.23 cm$^{-1}$, 476 cm$^{-1}$ and 425.42 cm$^{-1}$ are confirmed from the FTIR analysis. The band around 639.81 cm$^{-1}$ is a characteristic band of maghemite. Adsorption depends with the optimum conditions of parameters such as pH (2.5 and 6.5), contact time (60 and 80) minutes, dosages with at room temperature for chromium and copper were concluded with removal efficiency (92%). It was observed that the removal of chromium ions was high (41.66% and 33.33%) at acidic pH and removal of copper ions was high (30.56 and 25.90) at basic pH from desorption analysis. Thus, proving that these nanoparticles can be used for removal of both cation and anion heavy metal ions. The data’s fit in well for Langmuir Adsorption Isotherm and Desorption studies showed that these particles can be reused for water treatment.

Conflict of interest statement

The authors have no conflict of interest.

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