Adsorption of copper ions from waste water using PPy/Al₂O₃-Fe₂O₃ nanocomposite

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Abstract. The performance of Alumina- Iron Oxide nanocomposite as an adsorbent in the removal of Copper has been investigated. The experimental studies reveal that the removal of heavy metal from waste water can be increased within shorter duration when the nanocomposite is coated with a suitable polymer. The adsorptive properties of prepared nanocomposite with and without polymer were evaluated for the removal of copper ions using batch mode adsorption system. Characterization of the prepared nanocomposite using SEM, TEM and XRD analysis was done to check the removal efficiency before and after adsorption. This paper deals with the removal of copper from synthetic waste water using alumina/iron oxide nano composite and the increase in removal efficiency within a short period of time when it is treated with polymer coated alumina Iron/Oxide nanocomposite. The effects of pH, adsorbent dosage and time were investigated for optimum adsorption on the uptake of copper ions and observed 98 % removal. An ideal experimental response design has been carried out using Box Behnken design to evaluate the effect of different parameters in the batch mode study.

1. Introduction
Copper is available in rock, soil, water and sediment. Its concentration above 20µg/g can be toxic. It is soluble in water and its bioconcentration is higher in plants and animals [1]. Removal of toxic Cu²⁺ from wastewater is essential for health and environmental protection [2]. The presence of toxic heavy metals like chromium, copper, Zinc, lead and cadmium toxic metals adversely affect the normal growth and metabolism [3]. Higher doses of heavy metal ions can cause anaemia, liver and kidney damage even including damage to circulatory and nervous systems [4].

Various physiochemical processes like membrane technology, flocculation, coagulation, electrodialysis, reverse osmosis etc. is being used. But the requirement of high reagent, less economic feasibility, less percentage removal, and the difficulty to dispose is the limitations of these techniques [5]. Many research studies have been conducted for the removal of heavy metal ions using activated carbon, silicates, natural zeolite, chitosan polymer and biomass [6]. Among the present conventional techniques, the adsorption process is the most suitable method because of its high efficiency and...
economic consideration [7]. Conducting polymers such as polyacetylene, polyaniline, polypyrrole, and polythiophene have drawn much attention to the researchers for the removal of heavy metal ions [8]. Polypyrrole coated nanocomposite is found as one of the most promising conducting polymers due to its excellent characteristics including easy preparation, environmental stability, high conductivity and so on [9]. Polypyrrole is a conjugated polymer with alternating single and double bonds and is found effective in the removal of copper ions [10]. This paper mainly focuses on the removal of copper ions from synthetic waste water using the prepared polypyrrole alumina iron oxide nanocomposite. Effect of various parameters like pH, contact time, adsorbent dosage and initial concentration were also investigated.

2. Materials and Methods

2.1 Preparation of Alumina Iron/Oxide Nanocomposite

The alumina/iron oxide nano composite was prepared by mixing required amount of FeSO₄ and FeCl₃ in 200ml of distilled water. Activated alumina was added to the above solution with constant heating. The activated alumina/iron oxide was taken with a weight ratio of 3:1. A solution of NaOH was prepared and added drop wise to precipitate the iron oxides. The obtained precipitate was cooled in chilled water bath and then filtered and dried [11].

2.2 Characterization of Nanocomposite

The alumina/iron oxide nanocomposite was characterized by using X-ray diffraction analysis (XRD), Scanning electron microscopy (SEM), Transmission electron microscope (TEM) [12]. SEM micrographs show the surface morphology of particles. It could be observed that the particles had definite rectangular shapes. From the SEM image presence of nano particles could not be predicted. The SEM analysis of Nanocomposite before and after adsorption of copper ions is shown in figure 1 and figure 2.

![Figure 1. SEM image before adsorption](image1)

![Figure 2. SEM image after adsorption](image2)

![Figure 3. TEM Analysis](image3)

TEM analysis confirms that the produced composite are in the form of nanoclusters with uniform spherical nanoparticles as shown in figure 3. The peaks in XRD analysis were analysed and they showed the possibility of presence of nano particles. In figure 4, EDX analysis shows the presence of elements Al, Fe, C, and O present in the prepared nanocomposite.

XRD analysis is an analytical technique used for phase identification of a crystalline structure as shown in figure 5. The peaks at 2θ values of 39.758 corresponds to the presence of -Fe₂O₃ phase (JCPDS FILE NO-(79-1741)) whereas the peaks at 45.897 and 67.475 corresponding to the presence of AlO(OH) phase. The additional peaks are due to the presence of maghemite (γ-Fe₂O₃) and α-Al₂O₃ which interferes with the results obtained [13].

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2.3 Preparation of PPY/Al₂O₃-Fe₂O₃ nanocomposite
Experimental studies were conducted using polymer coated alumina Iron Oxide nanocomposite in order to increase the removal efficiency. Polypyrrole monomer was selected as polymer. Chemical polymerization of pyrrole was done using ferric chloride as the chemical oxidant and water as the best solvent. Ferric chloride of 5g was added to 100 ml of water and a uniform sample is made with magnetic mixer. Alumina Iron oxide nanocomposite of 1g was put into the solution along with 1ml pyrrole monomer. The reaction was observed for 4 hrs at room temperature. Thereafter it was filtered and kept in an oven at a temperature of 60°C for 24 hrs [14].

2.4 Characterization of PPY/Al₂O₃-Fe₂O₃ nanocomposite
XRD analysis is an analytical technique used for phase identification of a crystalline structure as shown in figure 6. The pattern indicates the crystal structure of PPY/Al₂O₃-Fe₂O₃ Nanocomposite. The crystallite size of prepared material is identified from 2θ= 54.135°, 35.801°, 33.287°, 24.285°, 11.564°, 49.581°, 40.980°, 64.097° using Scherrer equation (1)

\[ L = \frac{0.9 \lambda}{\beta \cos \theta} \] (1)

\( \beta \) represents FWHM of different peak, \( \lambda \) for X-ray wavelength (0.154 nm), size of crystallite denoted by \( L \) and diffraction peaks indicated with \( \theta \).

The microscopic crystal sizes were 23.66nm, 24.89nm, 23.75nm, 24.61nm, 13.26nm, 22.35nm, 21.66 nm for the respective peaks. The broad peak at 2θ value of 24.285 shows the presence of PPy indicating the amorphous behaviour of the polymer [15]. The broad peak results from the scattering of X-rays from PPy chain. The peaks at 2θ values of 33.287, 35.801 and 54.135 corresponds to the presence of -Fe₂O₃ phase with rhombohedral structure (JCPDS 79-1741) whereas the peaks at 40.98 and 64.097 corresponding to the presence of AlO(OH) phase having orthorhombic structure (Bibhu,2010). The composite oxide synthesized by hydrothermal process contains a mixture of -Fe₂O₃ and AlO(OH) phases (JCPDS 81-0464). All other diffraction peaks corresponds to the presence of \( \alpha \)-Al₂O₃ (JCPDS FILE NO-(42-1468) and \( \alpha \)-Fe₂O₃ (JCPDS FILE NO (79-1741).

2.5 Adsorbate
A solution of copper concentration of 1000 mg/l was prepared by dissolving required amount of CuSO₄⋅5H₂O in distilled water. The solution was diluted with distilled water to obtain desired concentration. pH was adjusted by adding HCl and NaOH solutions. The concentration of copper before and after adsorption was determined by using UV visible spectrophotometer.
2.6. Adsorption studies

Effects of experimental parameters like pH (2-10), adsorbent dosage (0.05-0.5g/50ml), Initial copper concentrations (200-1000 mg/l) and time of contact (5-30 minutes) were studied in batch mode adsorption system. Varying copper concentration of 100ml was taken in 250 ml erlenmeyer flask to which adsorbent dosages were added and constant mixing was done at 125rpm in an orbital shaker. Settling time of 20 minutes was provided for the nano particles to settle. The sample was filtered and was tested using UV-VIS Spectrophotometry. Using spectrophotometer, the optimum wavelength corresponding to maximum absorbance was measured as 645nm. Setting the optimum wavelength so obtained, the initial and final concentrations were determined from the calibration curve. Percent metal ion removal was calculated using the equation (2).

\[
\text{% Removal} = \left(\frac{C_0 - C_e}{C_e}\right) \times 100
\]  

(2)

3. Results and Discussions

3.1 Batch mode studies with Alumina/Iron Oxide Nanocomposite

The effect of pH is a very important parameter which controls the rate of adsorption of heavy metal onto nano composite. Therefore, change in amount of copper adsorbed with variation of pH was studied. It can be observed that, as pH of the solution was increased from 2 to 10, the percentage removal of copper increased. The maximum percentage removal was noted at a pH of 8 within a contact period of 1 hour as shown in figure 7. With further increase of pH, the copper got precipitated as Cu(OH)$_2$. So, the optimum pH was selected as 8.
The effect of contact time on the adsorption of copper was studied while all other variables such as adsorbent dosage, pH and concentration of copper are kept constant. The effect of adsorbent dosage determines the minimum amount of adsorbent needed for an adsorption process. The amount of adsorbent was increased from 0.05g upto 1g and % removal was checked with time at a regular interval of 30 minutes.

The studies show that the removal of copper on alumina/iron oxide nano composite is pH dependent and the highest removal was found at pH 8. It was found that copper was removed only about 25 % within 30 minutes with an adsorbent dosage of 0.4g as shown in figure 8. Further addition of adsorbent dosage was not effective in the percentage removal of copper. By considering these factors, it can be concluded that alumina/iron oxide nano composite is less effective in the removal of copper ions from wastewater due to loss of activity due agglomeration, difficulty to separate in aqueous solution and hence they need modification as to improve adsorption capacity of nanocomposite. As per the literature review it was found that the efficiency can be increased if a polymer is coated onto the nanocomposite. Hence further studies were conducted with Polypyrrole coated Alumina/ Iron-oxide nanocomposite.

3.2. Adsorption studies using PPy/Al₂O₃-Fe₂O₃ nanocomposite

Batch mode adsorption studies were conducted to check the efficiency of adsorption process using PPy/Al₂O₃-Fe₂O₃ nanocomposite. The effects of experimental parameters such as pH (2-10) using pH meter, adsorbent dosage (0.05-0.5g/100ml), temperature (22-52⁰C), Initial Copper concentrations (200-1000mg/l) and contact time (5-30 minutes) on the adsorptive removal were studied in a batch mode operation. 100 ml of Copper concentration was taken in a 250 ml erlenmeyer flask into which varying adsorbent dosages were added. Mixing in an orbital shaker at a speed of 125 rpm enabled the thorough mixing of nano composite particles thereby increasing the adsorption rate. The solutions were taken in different conical flasks and were placed in the shaker. After every period of shaking, 20 minutes settling time was provided for the nano particles to settle. The sample was filtered using a 0.2µm filter paper and was tested using UV-VIS Spectrophotometry [16].

3.2.1. Effect of adsorbent dosage. The effect of adsorbent dosage determines the minimum amount of adsorbent needed for an adsorption process. The amount of adsorbent was increased from 0.05g upto 0.5 g and % removal was checked at a time of 5 minutes. Figure 9 shows that 100 % removal has been obtained with 0.1 g adsorbent dosage. With further increase in the adsorbent dosage it was found that the removal efficiency is getting decreased. When more nano particles are added, they tend to form clusters and the effective area of adsorptive sites decreases and hence efficiency decreases.
3.2.2 Effect of Initial Concentration. Figure 10 shows that, by increasing the initial copper concentration, the percentage of copper removal decreased due to the decrease in the effective area of adsorptive sites. At higher initial concentration, the total available adsorption sites are limited thus resulting in a decrease in percentage removal of copper ions.

3.3. Response surface analysis using Box-Behnken Design

The effects of the three significant variables copper concentration, reaction time and pH were analyzed with a Box-Behnken design to build a quadratic response surface model that explains the effects on the product properties and can predict the reaction condition. The studies show that 99.9% removal has taken place within 5 minutes at pH value of 8. The amount of adsorbent was increased from 0.05g upto 0.5 g and % removal was checked at a time of 5 minutes. At higher initial concentration, the total available adsorption sites are limited thus resulting in a decrease in percentage removal of copper ions.

The mathematical statistical significance of the quadratic model was evaluated by the analysis of variance (ANOVA). The influence of prominent factors such as time ($X_1$), adsorbent dosage ($X_2$) and initial concentration ($X_3$) on copper removal was evaluated by response surface methodology (RSM). This work employed three test variables following the second order polynomial equation as:

$$Y=45.61+2.318X_1+747.9X_2+0.0648X_3+0.3105X_1X_1-4123X_2X_2-0.0001X_3X_3+16.27X_1X_2+0.002573X_1X_3-0.2042X_2X_3$$

Polynomial regression analysis has been conducted for second order response surface model and the results are given in Table 1. The effects of copper concentration, reaction time and adsorbent dosage with PP$_Y$/Al$_2$O$_3$-Fe$_2$O$_3$ nanocomposite are illustrated with the three-dimensional response surface and contour plots in figure 11 (a, b, c) and (d,e,f).

The combined effect of time and initial concentration, adsorbent dosage and initial concentration, adsorbent dosage and time was influencing the highest percentage removal of copper ions as shown in surface plots and contour plots. The fit of the model is verified by the determination of multiple correlation coefficients. The adsorption capacity response ($R^2= 98.81 \%$) indicates that 1.19 % of the variation is not explained by the model.
### Table 1. Analysis of Variance

| Source                           | DF | Adj SS   | Adj MS   | F-Value  | P-Value |
|----------------------------------|----|----------|----------|----------|---------|
| Model                            | 9  | 1281.35  | 142.37   | 297.65   | 0.000   |
| Linear                           | 3  | 225.06   | 75.02    | 156.84   | 0.000   |
| pH                               | 1  | 221.13   | 221.13   | 462.30   | 0.000   |
| Time                             | 1  | 2.92     | 2.92     | 6.10     | 0.057   |
| Adsorbent Dosage                 | 1  | 1.02     | 1.02     | 2.12     | 0.205   |
| Square                           | 3  | 1048.21  | 349.40   | 730.48   | 0.000   |
| pH*pH                            | 1  | 1048.02  | 1048.02  | 2191.02  | 0.000   |
| Time*Time                        | 1  | 8.36     | 8.36     | 17.48    | 0.009   |
| Adsorbent Dosage*Adsorbent Dosage| 1  | 7.29     | 7.29     | 15.24    | 0.011   |
| 2-Way Interaction                | 3  | 8.07     | 2.69     | 5.63     | 0.047   |
| pH*Time                          | 1  | 0.03     | 0.03     | 0.07     | 0.800   |
| pH*Adsorbent Dosage              | 1  | 2.84     | 2.84     | 5.94     | 0.059   |
| Time*Adsorbent Dosage            | 1  | 5.20     | 5.20     | 10.87    | 0.022   |
| Error                            | 5  | 2.39     | 0.48     |          |         |
| Lack-of-Fit                      | 3  | 2.39     | 0.80     |          |         |
| Pure Error                       | 2  | 0.00     | 0.00     |          |         |
| Total                            | 14 | 1283.74  |          |          |         |
Figure 11. Response surface plots (a, b, c) and contour plots (d, e, f) showing the effect of independent variables on copper adsorption onto PP$_Y$/Al$_2$O$_3$-Fe$_2$O$_3$ nanocomposite.

4. Conclusions

Effects of pH, adsorbent dosage, time of contact were studied through batch mode adsorption system using Al$_2$O$_3$-Fe$_2$O$_3$ and PP$_Y$/Al$_2$O$_3$-Fe$_2$O$_3$ nanocomposite for copper remediation. It is clearly evident that the removal of copper on PP$_Y$/Al$_2$O$_3$-Fe$_2$O$_3$ nanocomposite depends on pH and the highest removal was found at pH 8. About 99.9% of copper ions was removed within 5 minutes with an adsorbent dosage of 0.1g. When adsorbent dosage was increased beyond a certain value, the removal efficiency of copper ions was decreased due to the formation of nanoclusters which caused decrease in the effective area of adsorptive sites. Maximum Copper removal of 90.97% predictably and 98.81% experimentally were achieved under the optimal conditions ($X_1 = 5.8$ min, $X_2 = 0.1$ g and $X_3 = 345.45$ mg/l). Hence it can be concluded that PP$_Y$/Al$_2$O$_3$-Fe$_2$O$_3$ nanocomposite is having high adsorption capacity in the removal of copper ions within a short period of time.
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