Magnetic nanoparticles with a proper surface coating acts as a glue to keep the magnetic core together. These magnetic nanoparticles can be dispersed into suitable solvents, forming homogeneous suspensions called ferrofluids. Although a variety of examples exist for the use of bare magnetic particles for species extraction in effluent processing and metal ion removal, other recent studies have demonstrated that nanomaterials usually enhance removal of toxic metals from wastewater.

In present work, monocrystalline iron oxide nanoparticles based ferrofluid (maghemite, synthesized by the method described elsewhere) was used as possible adsorbent for the removal of zinc metal. In order to study the influence of magnetic field environment, the work has been done in absence and presence of magnetic field. Contact time and adsorption isotherms in presence of magnetic field have also been discussed.

Experimental

Following reagents were used in appropriate proportions: FeCl$_3$ (Anhydrous, Loba), FeSO$_4$.7H$_2$O (Extrapure AR, Merck ), KCl, KOH (both Merck) etc.

Synthesis of maghemite nanoparticles was done by mixing powders of 0.81 g FeCl$_3$ (0.005 M), 0.70 g of FeSO$_4$.7H$_2$O (0.0025 M) and 3.9 g of KCl in a mortar at room temperature for 30 minutes followed by addition of 1.12 g (0.02 M) KOH powder and further grinding for another 30 minutes at room temperature. Finally, a dark brown transparent colloid was obtained with a loading of $\gamma - $Fe$_2$O$_3$ nanoparticles. The pH value of the colloid was between 4 and 5. To obtain a powder sample the colloid was centrifuged, dried at 50 °C for 6 h, and then cooled down to room temperature.

Wastewater containing zinc ions was collected from IFFCO, Phulpur, Allahabad. Batch adsorption studies were carried out taking a certain amount of maghemite and 50 mL solution of zinc ion and observations were recorded in the presence (vertical field of ~1.0 tesla applied with the help of 1"×1"×3" bar magnets) and absence of magnetic field. A mechanical shaker operating at 120 rpm was used for agitation. Metal concentration was determined by Atomic Absorption Spectrophotometer (AAS, ECIL - 4141) using the standard method.

The removal efficiency $\phi$ was calculated by the following equation:

$$\phi = \frac{A - B}{A} \times 100$$

where, $A$ and $B$ are the initial and final metal ion concentrations (mg L$^{-1}$) respectively.

Results and discussion

Adsorption of heavy metals from aqueous solutions depends on the properties of adsorbent and transfer of molecules, ions of adsorbate from the solution to the solid phase. Adsorption efficiency of heavy metals is strongly sensitive to pH of the solution. It has also been reported that as the solution pH increases, sorption also increases. The adsorption efficiency of maghemite nanoparticles for zinc ions at different pH (pH=2-7) in the presence of magnetic field and without magnetic field is shown in Figure 1, which suggests that the maghemite possessed maximum sorption efficiency for the zinc ions at pH value 3 in both the cases. In contrast to this, it has been found that the adsorption efficiency of maghemite for zinc ions was 97.10 % in the presence of magnetic field but it was 85.34 %, without applying magnetic field.

Kinetic study revealed that maximum adsorption efficiency/metal removal efficiency for zinc was achieved generally in the first 60 minutes of contact. Metal removal was rapid during this period, after that, it reaches equilibrium.
Magnetic field induced enhanced adsorption efficiency of iron oxide nanoparticles

Section B-Short Communication


Figure 1. Effect of pH on Zn(II) removal using maghemite ferrofluid in presence and absence of magnetic field.

Figure 2. The linearized Langmuir adsorption plot for Zn(II) on maghemite nanoparticles in presence of magnetic field at 25°C

Data in presence of magnetic field was also fitted to the classical Freundlich and Langmuir isotherm equations. The linearized forms of isotherm equations used are (see supporting information for more detail):

\[ \log Q_e = \log K + \frac{1}{n} \log C_e \]  

(Freundlich equation)

Plot of log \( Q_e \) versus log \( C_e \) gives a straight line of slope \( 1/n \) and intercept \( \log K \). The correlation coefficient \( (R^2) \) was found to be 0.9872.

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

(Langmuir Equation)

Plot of the specific sorption \( C_e/Q_e \) against equilibrium concentration \( C_e \), as shown in Figure 2, gave the linear isotherm parameters \( Q_{\text{max}} \) and \( b \). The correlation coefficient \( (R^2) \) in this case was found to be 0.9799.

An essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, \( R_L \). The \( R_L \) values between 0 and 1 indicate favourable adsorption.\(^6\) In the present study the \( R_L \) were 0.1159, 0.0615, 0.0419, 0.0317 and 0.0255, for the initial concentrations of zinc ions from 5-25 mg L\(^{-1}\), indicating that the adsorption of zinc ions on maghemite nanoparticles was favourable.

Figure 3. SEM image of maghemite nanoparticles

Scanning electron microscopy (SEM) was used for analysis of the samples morphology. SEM image of maghemite nanoparticles (Fig. 3) indicates the presence of granular structure of various sizes for these nanoparticles.

Conclusion

In present work, the adsorption of zinc from industrial wastewater by magnetic nanoparticles, i.e., maghemite loaded ferrofluid, was carried out in the presence of magnetic field. Equilibrium was attained within 60 minutes of contact time between maghemite and zinc sample. It was observed that maximum removal of zinc from wastewater occurred at pH 3. The experimental results were examined using Freundlich and Langmuir isotherms over the studied concentration range.

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