Rapid removal of metals from aqueous solution by magnetic nanoadsorbent: A kinetic study

ABSTRACT

The effective removal of heavy metals from industrial wastewater is the most important issues for many industrialized countries and it is big challenge for human being. This research focuses on understanding adsorption process and developing a cost effective technology for treatment of heavy metals-contaminated industrial wastewater. In this investigation the Fe$_2$O$_3$ magnetic nano adsorbents are effective and posses’s high adsorption capacity and efficient removal rate. In this research article iron oxide nano adsorbents have been employed for the removal of Cd(II)ions from aqueous solutions by batch adsorption technique. The amount of Cd(II) ions adsorbed increases as temperature increased. The optimal pH values for Cd(II) ions removal was in between 5.5 to 6.5 different other parameters are also studied such as initial concentration of metals, catalyst dose, contact time etc. The kinetic study also have been investigated for this research article and it is observed that Cd(II) ions removed by Fe$_2$O$_3$ magnetic nano adsorbent obey pseudo first order and pseudo second order kinetics model effectively.

Keywords: Cadmium; Magnetic nanoadsorbent; Iron oxide; Adsorption; Ferric oxide.

INTRODUCTION

The presence of heavy metals in the environment is one of the major concerns because of their toxicity and threat to human life. They accumulate in living tissues throughout the food chain which has humans at its top. These toxic metals can cause accumulative poisoning, cancer, and brain damage when found above the tolerance levels. Lead compounds are very toxic to humans. The presence of lead in drinking water above the permissible limit may cause adverse health effects such as anemia, encephalopathy and hepatitis. Hence it is very important that lead should be removed from wastewater before being discharged into an aquatic environment.
The environment and all the life forms on the earth face a very serious threat from the heavy metal pollution due to rapid industrialization and growth in world population [1]. At least 20 metals are classified as toxic and half of these are emitted into the environment in quantities that pose risk to human health [2]. Cadmium is one of the heavy metals, which is highly toxic to human, plants and animals. The metal is of special concern because it is non-degradable and therefore persistent.

The presence of toxic metal ions in wastewater remains a serious environmental concern. Therefore it is necessary to develop various efficient technologies for their removal. A number of techniques have been used to remove the metal ions from wastewater, effluents including chemical precipitations[3], ion exchange processes[4,5], electrolytic methods[6], adsorption onto activated carbon[7], organic based ligand precipitation[8], membrane and reverse osmosis processes[9].

These methods have been found to be limited, because of the high capital and operating costs or the infectiveness in meeting stringent effluent standards. Therefore several approaches have been studied for the development of inexpensive and abundant adsorbents such as sawdust[10], live biomass[11], Clay[12,13] and agricultural byproducts [14-16]. Each method has been found to be limited for the cost, complexity and efficiency, as well as secondary wastes. For example the electrolysis processes often take higher operational costs and chemical precipitation may generate secondary wastes [17].

The main anthropogenic pathway through which cadmium enters environment is via wastes from industrial processes such as electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium-nickel batteries, fertilizers, pesticides, mining, pigments and dyes, textile operations and refining [18-22].

Magnetic nanoparticles show a variety of unusual magnetic behaviour compared to bulk materials, mostly due to surface/interface effects, including symmetry breaking, electronic environment/charge transfer, and magnetic interactions. Furthermore, since nanophase particles can be as much as 50% surface material, new magnetic properties characteristic of surfaces and interfaces become important and may be of practical value. Since the beginning of this century, 2000, science and engineering has seen a rapid increase in interest for materials at the nano-scale. In fact, statistical data from Lux Research, Inc. shows that worldwide spending on research and development of nano-technology is in excess of $8 billion. The United States government alone is spending over $1 billion annually. Nano-materials have attracted such a strong interest because of the physical, electronic, and magnetic properties resulting from their quantum size. The potential for nano-technology is immensely diverse with potential applications in the fields of electronics, biomedical devices, energy applications, military uses, and waste management. Nano-materials could be utilized to design nano-transistors, to develop and deliver medicines for locally treating diseases and ailments within the body, and for the creation of new age weapons and armor for military applications. Ultimately, nano-technology has the potential to offer new, inexpensive, and more efficient materials for a greater range of applications than achievable by bulk materials today. Within the field of nano-materials under worldwide research is the subset of magnetic nano-materials.

Cadmium occurs naturally in the environment by the gradual process of erosion and abrasion of rocks and soils, and from singular events such as forest fires and volcanic eruptions. It is therefore naturally present everywhere in air, water, soils and foodstuffs. The best known cadmium mineral is greenockite, cadmium sulfide (77.6% Cd). Other minerals are otavite (CdCO3), cadmium carbonate (61.5% Cd) and pure cadmium oxide (87.5% Cd). Greenockite (CdS) is nearly always associated with sphalerite (ZnS). As a consequence, cadmium is produced mainly as a byproduct from mining, smelting, and refining of sulfide ores of zinc.

This paper will discuss the Cd(II) metal ions removal by magnetic nano adsorbent Fe2O3 under kinetic study. The investigated result proved that the Cd(II) metal ions removal by Fe2O3 is very effective by performing a batch experimental process. The present investigation was aimed to study the effects of pH, contact time, initial concentration, and equilibrium study for the removal of lead and cadmium ions from wastewater using the magnetic nano adsorbent Fe2O3.
EXPERIMENTAL

Preparation of synthetic wastewater

Synthetic wastewater samples were prepared by using analytical grade cadmium chloride. The batch adsorption study were carried by using different ppm solution ranging from 10mg/L to 100mg/L concentration. For pH adjustment throughout the experiment, 0.1N HCl and 0.1N NaOH solutions were used as necessary.

Images of Synthesized Magnetic Nanoadsorbent

![Magnetic Nanoparticles (Fe_3O_4)](image)

Experimental Methods and Measurement

The batch adsorption studies were carried out by adding 0.50 g magnetic nano adsorbent with 50mL of Cd(II) solution of varying concentration in 250mL conical flask. The dosage of adsorbent was decided by the requirements of the experiments. This experiment was carried by using the dimethyl glyoxime (DMG) method [23].

Absorbance of treated and non treated solutions were taken out by using double beam spectrophotometer (Systronic)-2203 for the adsorption and removal experiments on aqueous solution of Cd(II) metal.

In every experimental stage an accurately weighed amount of Fe_3O_4 added to the 100ml of known concentration solution of Cd(II) metal ions .The mixture was stirred on magnetic stirrer for different interval of time. After stirring of solution stay for centrifugation and settling. Take absorbance of different concentration of Cd(II) metal ions solution. Before and after treatment of adsorbent dosage on the double beam spectrophotometer, at maximum wavelength for Cd (II) metal ion. The experiment was carried out at pH range from 1 to 12. The pH of the experimental solution was maintained by 0.1N HCl and 0.1N NaOH (freshly prepared). Kinetics of adsorption was determined by analyzing adsorptive uptake the metal from aqueous solution at different interval of time. Other parameters are also studied such as initial metal concentration, catalyst dosage, temperature and previously described parameter pH.

The percentage removal of Cd (II) ions was calculated by the following equation.

\[
\text{Percentage removal of Cd (II) ions} = \frac{C_0 - C_e}{C_0} \times 100
\]

Amount adsorbed in Cd (II) ions

\[
q_e = \frac{(C_0 - C_e)}{V m}
\]

Where Co and Ce are the initial and equilibrium concentration of Cd(II) ions (mg/L) respectively, m is the mass of the adsorbent (g) and V is the volume of Cd (II)metals ions solution in liter.

RESULTS AND DISCUSSION

Adsorbent Characterization

For the identification morphological structure and different functional groups the magnetic nanoadsorbent were characterized by SEM, XRD and FTIR.

SEM Analysis

Scanning electron microscopy (SEM) has been primary idea for characterizing the surface morphology and fundamental physical properties of the adsorbent surface. It is useful for determining the particle shape, porosity and appropriate size
distribution of the adsorbent. Scanning electron micrographs of nanosized magnetic adsorbent before treatment and after treatment are presented in Figure 1. It is observed that Fe₂O₃ has considerable for number of pores where there is good possibility for Cd(II) metals ions to be trapped and adsorbed into these pore. The distinguished dark spots which can be taken as sign for effective removal of Cd(II) ions the cavities and pores of catalyst Fe₂O₃.

Fig. 1. Scanning Electron Microscopic Images of Fe₂O₃. a) & c) Before treatment b) & d) After treatment
Fig. 2. FTIR of Fe$_2$O$_3$
Adsorption Kinetics

In order to investigate the mechanism of sorption of metals on adsorbent several kinetics model were studied including pseudo first order model and pseudo second order model.

Pseudo first order model

Lagergrens rate equation is most widely used [24, 25] for the adsorption of adsorbate from solution. The first order Lagergrens rate equation is as follow:

\[
\ln(q_e - q_t) = \ln(q_e) - k_1 t
\]  

(3)

Where \( q_e \) (mg/g) and \( q_t \) (mg/g) are the amount of Cd(II) metal ions adsorbed at equilibrium and at time \( t \), respectively, and \( k_1 \) is the first order rate constant (min\(^{-1}\)). The values of \( k_1 \) were calculated from plots of \( \ln(q_e - q_t) \) Vs. \( t \) as shown in (Figure 3) for different concentration of Cd(II) metal ions. The experimental \( q_e \) values do not agree with the calculated ones obtained from linear plots (Figure 4). This shows that adsorption of Cd(II) metal ions onto Fe\(_2\)O\(_3\) is not a pseudo second order kinetics.

Pseudo second order model

Pseudo second order equation [26] based on equilibrium adsorption is expressed as:

\[
t/q_t = 1/k_2 q_e^2 + t/q_e
\]  

(4)

Where \( k_2 \) (g/mg min) is the rate constant of second order adsorption. If second order is applicable, the plot of \( t/q_t \) Vs. \( t \) should show a linear relationship. \( q_e \) and \( k_2 \) can be determined from the slope and intercept of the plot respectively. The linear plot of \( t/q_t \) Vs. \( t \) is represented in Figure 4 show a good agreement between experimental \( q_e \) and calculated \( q_e \) values. The correlation coefficient for the second order kinetics model are greater than 0.98 and experimental \( q_e \) values agree with the calculated ones indicating the applicability of this kinetics equation, this can be determined from the Table 1. This shows that the adsorption process of Cd(II)metals ions onto Fe\(_2\)O\(_3\) follows second order nature.

Fig. 3. Pseudo First Order kinetics of Cd(II) metal ions Adsorption on Fe2O3 magnetic nanoadsorbent.

Fig. 4. Pseudo second order kinetics for Adsorption of Cd(II) ions on Fe2O3.
**Table 1.** Comparison of the pseudo first order and pseudo second order adsorption rate constants and calculated and experiments $q_e$ values for different initial concentration.

<table>
<thead>
<tr>
<th>Adsorbent dose (g/L)</th>
<th>Initial Metal concentration in mg/L</th>
<th>Adsorbent</th>
<th>$q_e$ (exp)</th>
<th>first order kinetics</th>
<th>$q_e$ (cal)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$Fe_2O_3$</td>
<td></td>
<td>$K_1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>30</td>
<td></td>
<td>3.87</td>
<td>0.079</td>
<td>3.84</td>
<td>0.964</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td></td>
<td>3.79</td>
<td>0.056</td>
<td>3.72</td>
<td>0.961</td>
</tr>
<tr>
<td>5</td>
<td>90</td>
<td></td>
<td>2.98</td>
<td>0.052</td>
<td>3.65</td>
<td>0.959</td>
</tr>
<tr>
<td>Adsorbent dose (g/L)</td>
<td>Initial Metal concentration in mg/L</td>
<td>$Fe_2O_3$</td>
<td>$q_e$ (exp)</td>
<td>Pseudo second order $K_2$</td>
<td>$q_e$ (cal)</td>
<td>$r^2$</td>
</tr>
<tr>
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<td></td>
<td>3.95</td>
<td>0.033</td>
<td>3.93</td>
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<tr>
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<td>3.85</td>
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</tr>
<tr>
<td>5</td>
<td>90</td>
<td></td>
<td>3.8</td>
<td>0.02</td>
<td>3.78</td>
<td>0.999</td>
</tr>
</tbody>
</table>

**Effect of contact time**

After optimization of $Fe_2O_3$ dose at 2.5 g per 100 ml test solution 5.8 for cadmium ion solution, the effect of contact time for the efficient removal of metal ions was studied. The Cd(II) metal ions showed a steady rate increase of sorption during the sorbate-sorbent contact process and the rate of removal became almost insignificant due to a quick blocking of the adsorption sites. The Figure 5 clearly indicates the rate of metal removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the metals (27). In these studies, 85% removal of cadmium was achieved at 180 min. Further, no significant changes were observed in the removal of Cd(II) metal ions from the solution after 48 hrs of equilibration.

**Effect of Initial Concentration of metal**

The effect of initial concentration of metal (in terms of percentage removal). The percentage removal of Cd(II) was found to be decrease with the increase in initial metal concentration. This indicates that there exist reduction in immediate solute adsorption, owing to the lack of available active sites required for the high initial concentration of Cd(II). The result obtained from experimental data shown that percentage removal of metal decreases from 100 to 72.98 to 70,90 to58 as the initial metal concentration increase from 10mg/L to 90mg/L for 4g/L of . This shown in Figure 6:

![Fig. 5. Effect of contact time on the removal of Cd(II) metal ions, $C_0 = 100$ mg/L $Fe_2O_3$ dose = 2.0 g.](image1)

![Fig. 6. Effect of initial metal concentration.](image2)
Effect of pH

The removal of Cd(II) metals ions from synthetic wastewater by using magnetic nano adsorbent Fe$_2$O$_3$ as a photocatalysts is highly dependent on the pH of the solution which affects on structure, it changes the surface and the degree of ionization and speculation [26]. Removal of typical inorganic metal pollutants from wastewater is increased with decreasing pH. The effect of pH on the removal of Cd(II) metals ions is shown in Figure 7. The graph indicates that form the starting as the pH increases the % removal of Cd (II) metals ions also increases during this experiment got the optimal pH 5.5 at which maximum removal of Cd(II) observed and finally % removal of Cd(II) metals ions decreases with increase in pH.

Effect of Catalyst dose

The effect of Catalyst dose on the percentage removal of Cd(II) is shown in Figure 8. The percentage removal Cd(II) metals ions increases with increase in dose of catalyst. This due to the increase availability of surface active sites resulting from the increase in dose of catalyst.

![Graph showing the effect of pH on the removal of Cd(II) metals ions.]

**Fig. 7.** Effect of different pH on the removal of Cd(II) metals ions from Synthetic wastewater.

![Graph showing the effect of Catalyst dose on the removal of Cd(II) metals ions.]

**Fig. 8.** Effect of amount of Fe$_2$O$_3$ on the removal of Cd(II) metals ions.
CONCLUSIONS

Cadmium(II) is amongst the most toxic ions hazardous to living organism and its permissible limit in drinking water is 0.005 mg/L. Removal of cadmium from aqueous solutions can be accomplished by several techniques which include cementation, chemical precipitation, ion exchange, solvent extraction, membrane separation and adsorption. Adsorption is one of the most studied techniques. The main experimental parameters which are studied to evaluate the adsorption behavior are time, pH, temperature, concentration of adsorbate and adsorbent, competing ions etc. The Characterization data like SEM and FTIR of Synthesized Fe$_2$O$_3$ gives good results. The time data is generally fitted to pseudo-first order and pseudo-second order kinetics. This study is applicative for the treatment of electroplating and metal industries wastewater.

ACKNOWLEDGMENTS

Authors are gratefully acknowledged to Shri.G.H.Raisoni Doctoral Fellowship at North Maharashtra University, Jalgaon for Financial Support and the Director, SICART, Vallabh Vidyanagar for SEM studies. Thanks are also due to Dr. Z. Benzo, IVIC, Caracas, and Venezuela for useful discussions. Authors are also thankful to the Principal G.T.P. College, Nandurbar for providing necessary laboratory facilities.

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