Separation of Ni(II) Ions from Aqueous Solutions by Magnetic Nanoparticles

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The separation of Ni(II) from aqueous solutions by magnetic nanoparticles was investigated. Magnetic nanoparticles were prepared by coprecipitation of a Fe^{2+} and Fe^{3+} salt from aqueous solution by ammonia solution. Various instrumentation methods such as X-ray diffraction (XRD), transmission electron microscopy (TEM), vibrating sample magnometry (VSM), and Fourier transform infrared spectroscopy (FTIR) were used to characterize the properties of the magnetic nanoparticles. The sizes of nanoparticles were measured to be between (10 and 15) nm. The saturation magnetization of the prepared nanoiron particles was found to be 55.26 $emu \cdot g^{-1}$. The effect of various parameters such as pH, temperature, and concentration were studied. It was found that the adsorption of Ni(II) is highly dependent on pH. The removal of Ni(II) increases as the pH changes from acidic to basic. Adsorption decreases from (90.47 to 88.25) % by increasing the concentration of Ni(II) in solution from (5 to 15) $mg \cdot L^{-1}$. It was found that the adsorption of Ni(II) increases by increasing temperature from (298 to 318) K. The nature of the reaction is endothermic. The finding of the present studies indicates that nanoiron can be successfully used for separation of nickel from its aqueous solutions.

1. Introduction

Magnetite nanoparticles have attracted much attention because of their unique magnetic properties and widespread application in different fields such as magnetic storage devices, catalysis, magnetic refrigeration systems, mineral separation, heat transfer applications in drug delivery systems, magnetic resonance imaging (MRI), cancer therapy, and magnetic cell separation.[1] The application of magnetite in the field of wastewater treatment is becoming an interesting area of research. Magnetite has a high surface area and can easily be synthesized; several researchers have used it as an adsorbent. Nickel is one of the most commonly used metals by different industries such as electroplating, storage batteries, porcelain enameling, pigments, and steel.[2,3] Though Ni(II) is an essential micronutrient for animals and takes part in the synthesis of vitamin B_{12}, it shows a toxic effect at high concentration. Elevated concentrations of Ni(II) cause dry cough, rapid respiration, cyanosis, nausea, and extreme weakness. Ni(II) is also known to be an embryotoxin and teratogen.[3,4] There are many methods for the removal of metallic pollutants from water and wastewater such as reverse osmosis, ion exchange, precipitation, solvent extraction, flocculation, and sorption.[3,4] However, adsorption is a promising method for the removal of metallic pollutants at a trace level. Adsorption offers high efficiency, cost effectiveness, and easy handling among the majority of physiochemical treatment methods. In the present study nanoparticles of iron were prepared, and the removal of Ni(II) ion was investigated for its efficiency. Batch studies were carried out to investigate the efficiency of nanoiron particles in Ni(II) removal.

2. Materials and Methods

All chemicals used were of analytical grade. The chemicals used in this study were ferrous chloride, ferric chloride, ammonia solution, acetone, nickel sulfate, hydrochloric acid, ethyl alcohol, and dimethyl glyoxime. In this study nanoiron particles were prepared from ferric chloride and ferrous chloride in a 2:1 molar ratio and then characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and vibrating sample magnometry (VSM) for confirmation of its phase, size, and magnetic properties, respectively. Batch experiments were conducted to investigate the removal of Ni(II) from aqueous solution. A stock solution of Ni(II) ions was prepared by dissolving nickel sulfate in 1000 mL of distilled water. Then, this solution was used to prepare Ni(II) solutions of concentrations ranging between (5 and 15) $mg \cdot L^{-1}$. The pH of the solution was adjusted by adding dilute HCl or NaOH. All of the experiments were conducted at room temperature (25 °C) except when studying the effect of temperature. After the equilibration time, which was 60 min in this study, the adsorbent was separated by centrifugation at 10 000 rpm for 10 min. The remaining concentration of Ni(II) in the solution was determined by a UV−visible spectrophotometer at 445 nm using the dimethyl glyoxime (DMG) method.[4] The percentage removal of Ni(II) was calculated by the following equation. The resultant data were analyzed by Langmuir and Freundlich isotherms.[5]

$$\% \text{ removal of Ni(II) ions} = [(C_i \text{ and } C_e)/C_i]100$$

C_i and C_e are the initial concentration and equilibrium concentration, respectively ($mg \cdot L^{-1}$).

The phase of the synthesized sample was determined by XRD (CISERT & Co., Model ID 3000), and TEM (FEI, Tecani, G^2 20 S-Twin) was used to ascertain the size of the particles. The Brunauer−Emmett−Teller (BET) surface area of the nano iron powder was determined by a surface area analyzer (Micromeritics ASAP 2020,V302G single port). The value of saturation magnetization (M_s) was determined by a vibrating sample magnetometer (Lakeshore 73504).

3. Results and Discussion

The XRD pattern of the prepared particles shows the formation of Fe_3O_4. The peaks were confirmed by the Joint

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Table 1. Characterization of Magnetic Nanoiron Particles

phase	Fe_3O_4
size (nm)	10 to 15
pH_{zpc}	6.3
BET surface area ($m^2 \cdot g^{-1}$)	86.55
saturation magnetization (M_s) $emu \cdot g^{-1}$	55.26

Table 2. Optimum Values of Different Parameters for Maximum Removal of Ni(II) from Aqueous Solutions

parameters	optimum value
concentration ($mg \cdot L^{-1}$)	5.0
pH	2.0
temperature (K)	298
dose	0.20
agitation speed (rpm)	100

Table 3. Values of Different Constants for Langmuir and Freundlich Isotherms

Langmuir constants		Freundlich constants	
Q^o ($mg \cdot g^{-1}$)	11.53	K_f ($mg \cdot g^{-1}$)	2.1040
b ($L \cdot mg^{-1}$)	0.228	$1/n$ ($mg \cdot L^{-1}$)	0.8244
R^2	0.9993	R^2	0.9986

Table 4. Comparison of Adsorption Capacity of Various Adsorbents for Ni(II)

adsorbents	adsorption capacity ($mg \cdot g^{-1}$)	ref
bagasse	0.001	6
bituminas coal	6.47	7
calcium alginate	10.5	8
coir pith	9.5	9
fly ash	0.03	6
granular activated carbon	1.49	10
sheep manure waste	7.20	11
sphagnum moss peat	9.2	12
nanoiron	11.53	present study

Committee on Powder Diffraction Standards (JCPDS, 19-0629). The crystallite size was calculated to be in the range of (10 to 15) nm by using the Scherrer formula.[5] In addition to peaks of Fe_3O_4, some peaks of γ-Fe_2O_3 were also found in the prepared powder. The TEM of the nanoiron also confirms that the prepared powder was in the nano range. Characterization data of the magnetic nanoiron powder are given in Table 1. The value of M_s was found to be 55.26 $emu \cdot g^{-1}$ (Table 1) at room temperature, which is comparatively lower than that of bulk magnetite, which is 93 $emu \cdot g^{-1}$. The smaller the particle size, the larger is the part of the atoms present in the surface layer where the crystal structure is disordered, preventing magnetism. Therefore, the smaller particles apparently have lower values of magnetization saturation which is important in the present findings.

Adsorption Studies. The adsorption studies revealed that the separation of Ni(II) from aqueous solutions is highly affected by pH variation. By increasing the Ni(II) concentration, the removal percentage decreases. It can be explained on the basis that, by increasing the Ni concentration, removal decreases because of a decrease in the availability of active sites for a fixed amount of adsorbent dose. The percentage removal increases by increasing temperature, which indicates the endothermic nature of the present system. After the batch experiments, the optimum conditions for maximum removal of Ni(II) were decided as shown in Table 2.

On the basis of the isotherm studies, it was found that this system follows both Langmuir as well as Freundlich isotherms. The values of the different constants for both isotherms are given in Table 3. The adsorption capacity for Ni(II) adsorption on magnetic nanoparticles was found to be 11.53 $mg \cdot g^{-1}$. For a comparison of the adsorption capacity of the prepared nanoiron particles with some conventional adsorbents, the value of the adsorption capacity of adsorbents is tabulated in Table 4. It is clear from Table 4 that nanoiron has a good adsorption capacity.

4. Conclusions

From the present studies the following conclusions may be drawn:

1. Nanoiron particles are an effective adsorbent for the removal of Ni(II) from aqueous solutions.
2. The adsorption was found to be highly dependent on pH.
3. The percentage removal of Ni(II) was higher at lower Ni concentration.
4. The adsorption data were well-fitted by both the Langmuir and the Freundlich isotherms. The adsorption capacity was found to be 11.53 $mg \cdot g^{-1}$.
5. The adsorption of Ni(II) increases by increasing temperature. It indicates the endothermic nature of the reaction.

The resultant data can be useful for designing treatment plants enriched with nickel even by small-scale industries.

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