Production of Nanocrystalline Magnetite for Adsorption of Cr(VI) Ions

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Higher environmental standards have made the removal of toxic metals such as hexavalent chromium from wastewater; an important problem for environmental protection. Iron oxide is a particularly interesting adsorbent to be considered for this application.

In this study, a new method combining adsorption and magnetic separation was developed to remove Cr(VI) from wastewater. The nanocrystalline magnetite as adsorbent was produced via thermo-mechanical reduction of hematite. Various parameters which affect the adsorption of Cr(VI) such as time, pH, temperature and initial concentration were investigated using thermo-gravimeters (TG), X-Ray diffraction (XRD), scanning electron microscopy (SEM) and atomic adsorption spectroscopy (AAS) techniques. The maximum adsorption was occurred at pH 2. The adsorption data were fitted well to Langmuir isotherm model. The adsorption of Cr(VI) increased significantly with increasing of temperature and time.

Keywords: Nanocrystalline magnetite; Adsorption; Cr(VI); Mechanical Activation.

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1. Introduction

Trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI), are the two common existing oxidation states of chromium found in the environment. Public concerns over Cr are mostly related to Cr(VI) due to its high toxic nature for biological systems. Major sources of chromium to aquatic systems are effluents from electroplating, metal finishing, magnetic tapes, leather tanning, chromium mining and milling, electrical and electronics' equipments manufactures and catalysis.¹ U.S.EPA² has fixed an enforceable maximum contamination level for Cr in drinking water 0.1 mg/l for public water system.

To compliance this limit, it is imperative for industries to reduce the chromium in their effluents to an acceptable level before discharging into municipal sewers. A variety of methods have been developed for removal of chromium compounds from industrial wastewater. Hexavalent chromium usually exists in wastewater as oxyanions such as chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) and dose not precipitate easily using conventional precipitation methods. Chemical redox followed by precipitation is the most widely used technique for Cr(VI) removal.³ As one of the most promising technique for removal of chromium from industrial wastewaters, adsorption technology has been employed for many years and the effectiveness of various adsorbents has been demonstrated.⁴ Activated carbon as the most common adsorbent used in the adsorption process shows higher efficiency for the adsorption of the organic than inorganic matters.⁵ In this study, a new method combining nanoparticle adsorption with magnetic separation has been developed for the removal and recovery of Cr(VI). The main techniques that have been used on metal content reduction from industrial waste are chemical precipitation, ion exchange, membrane filtration, electrolytic methods, reverse osmosis, solvent extraction and adsorption.⁶

The application of magnetic adsorbent technology to solve environmental problems has received considerable attention in recent years. Magnetic adsorbent can be used to adsorb contaminants from aqueous or gaseous effluents. After ion adsorption, the adsorbent can be separated from the medium by a simple magnetic process.⁷

In recent years, many researches were performed in order to investigate the effect of mechanical activation or ball milling on the reduction process of hematite. Transformation of hematite to magnetite in argon and vacuum atmosphere has been reported.⁸

In this study, magnetite was prepared by thermo-mechanical reduction of hematite and then used as an adsorbent for removal of Cr(VI) from aqueous solution.

2. Experimental

2.1. Materials and Instruments

In this study all chemicals (Fe_2O_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, NaOH, HNO_3 and Graphite) were high purity reagent grade. Ultra pure water was used in all adsorption tests. For this research

planetary mill (Fritsch pulveristte6) and hardened steel balls were used for mechanical activation.

2.2. Synthesis of nanocrystalline magnetite and characterization

2.2.1. Reduction of hematite to magnetite

Mixture of hematite and graphite powder was milled with ball to powder mass ratio of 25/1 and 45/1. The rotating speed of vial was 300rpm. After milling of hematite and graphite powder mixture, some powder samples were analyzed with TG (Thermogravimeter) (Netzsch STA 409 PC/PG) with heating rate of 20°C/min up to 1100°C for identification of reduction temperature of hematite to magnetite. The powders were also heated isothermally in argon atmosphere for 30 minutes in obtained temperatures from the results of TG experiment.

The elemental information of samples powder was determined by X-ray diffractometer (XRD) (Philips Xpert Pro) at ambient temperature. The instrument was equipped with a cobalt anode generating Co k_{α} radiation ($\lambda=1.79$ nm). The morphological characteristics of magnetite were evaluated using a scanning electron microscope (SEM) (CAM SCAN MV2300).

2.3. Adsorption studies

The adsorption experiments were performed by mixing 0.1 g nanocrystalline magnetite with 20 ml $K_2Cr_2O_7$. Standard acid of 0.1 M HNO_3 and base of 0.1 M NaOH solutions were used for pH adjustment. All the adsorption experiments were carried out in constant condition.

Adsorption isotherm studies were conducted by varying the initial Cr(VI) concentration from 20 to 180 mg/l. After equilibrium, the adsorbent was separated via an external magnetic field. The concentration of chromium was measured by an atomic adsorption instrument (Varian AA240).

The uptake percentage (Up) can be defined as equation 1:

$$Up(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

The amount of adsorbed metal was calculated according to the mass balance equation:

$$q_e = \frac{(C_i - C_e) \times V}{M} \quad (2)$$

Where C_i is the initial metal concentration (mg/l), C_e is the metal concentration in the aqueous solution (mg/l), V is the volume of the aqueous solution (l) and M is the weight of adsorbent (g).

3. Results and Discussion

3.1. Characteristic of nanocrystalline magnetite

Figures 1 and 2 show the XRD patterns of ball milled hematite and graphite powder mixture with ball to powder mass ratio of 25/1 for 2, 5, 10, 15, 20 hours and with ball to powder mass ratio of 45/1 for 5, 10, 15 hours, respectively.

XRD patterns show that the initial appearances of magnetite are observed after 15 and 10 hours milling with ball to powder mass ratio of 25/1 and 45/1, respectively.

Fig 1- XRD patterns of ball milled powder mixture of hematite and graphite with ball to powder mass ratio of 25/1.

Fig 2- XRD patterns of ball milled powder mixture of hematite and graphite with ball to powder mass ratio of 45/1.

TG diagrams of 15 and 10 hours ball milled mixture of hematite and graphite powder with ball to powder mass ratio of 25/1 and 45/1 are shown in Fig 3.

Fig 3- TG diagrams of a)15 hours ball milled powder (25/1) and b) 10 hours ball milled powder (45/1).

The temperature of reduction of hematite to magnetite was obtained from RTG curve (i.e. hematite to magnetite (H_p), Magnetite to wustite (M_p)). RTG curve is shown in Fig 4 for 10 hours ball milled powder with ball to powder mass ratio of 45/1.

Fig 4- RTG curve for 10 hours milled powder with ball to powder mass ratio of 45/1.

The curve shows that the reduction temperature of hematite to magnetite (H_V) of 10 hours ball milled powder with ball to powder mass ratio of 45/1 is obtained at 600°C. This temperature (H_V) is 570°C for 15 hours ball milled powder with ball to powder mass ratio of 25/1.

Figure 5 shows the XRD patterns after reduction of 15 hours ball milled powder with ball to powder mass ratio of 25/1 at 570°C (sample 1) and 10 hours ball milled powder with ball to powder mass ratio of 45/1 at 600°C (sample 2) in argon atmosphere for 30 minutes.

Fig 5- XRD patterns of ball milled powder after reduction.

The XRD patterns show that the products are magnetite. The crystalline size of sample 1 and 2 were calculated at approximately 32 and 30 nm with scherer equation, respectively.⁹

Figure 6 show the SEM images of sample 1 and 2. The images show the agglomeration of small particles.

Fig 6- SEM images of (a) sample 1 and (b) sample 2.

3.2. Sorption studies

The uptake percentage and amount of adsorbed Cr(VI) from solution were studied as a function of temperature, contact time, initial Cr(VI) concentration and pH for samples 1 and 2.

3.2.1. Effect of temperature

In order to determine the optimum temperature, adsorption experiments were performed for 20 mL (100 mg/l) of the metal ion solution with 0.1 g of magnetite at pH 2 for 20 minutes of contact time at 15, 25, 35, 45 and 55 °C.

The effect of temperature is shown in figure 7. The results show that the uptake percentages and amount of adsorbed Cr(VI) are increased with increasing of temperature which indicates the endothermic nature of adsorption. According to the results of this test, the experiments were continued at 45 °C because of the surface evaporation at higher temperatures.

(a)

(b)

Fig 7-a) The uptake percentages of Cr(VI) ions and b) the amount of Cr(VI) adsorbed from aqueous solutions using magnetite as a function of temperature.

3.2.2. Effect of contact time

The effect of contact time between Cr(VI) ions and magnetite particles in aqueous solution is shown in Fig 8. The experiments were performed by mixing of 20 mL (100 mg/l) solution of metal ions and 0.1 g magnetite at 45 °C and pH 2 for 2, 5, 10, 15, 20 and 30 minutes.

(a)

(b)

Fig 8-a) The uptake percentages of Cr(VI) ions and b) the amount of Cr(VI) adsorbed from aqueous solutions using magnetite as a function of contact time.

The uptake percentages of Cr(VI) from solution and the amount of adsorbed Cr(VI) ions are increased with increasing of contact time.

It can be seen that the rate of Cr(VI) uptake is initially high and gradually reaches an equilibrium condition. The adsorption of Cr(VI) by nanocrystalline magnetite is attributed to the external surface adsorption, which is different from the micro-porous adsorption process. Compared to the porous adsorbent, nearly all the adsorption sites of magnetite exist in the exterior of the adsorbent. Thus, it is easy for the adsorbate to access these active sites and the adsorption process reaches equilibrium in a short time.

3.2.3. Effect of initial concentration of Cr(VI) ions

Figure 9 shows the effect of initial concentration of Cr(VI) ions on the adsorption. These experiments were carried out by mixing of 20 ml of solution with 0.1 g magnetite for 20 minutes at 45 °C and pH 2.

Fig 9-a) The uptake percentages of Cr(VI) ions and b) the amount of Cr(VI) adsorbed from aqueous solutions using magnetite as a function of initial concentration of Cr(VI).

The uptake percentages of Cr(VI) from solution is decreased and the amount of adsorbed Cr(VI) ions is increased with increasing of initial concentration of Cr(VI). This is due to the fact that for a fixed adsorbent dosage, the total available adsorption sites are limited leading to a decreased amount of removal of adsorbate. The amount of metal ions adsorbed is increased according to equation 2.

3.2.4. Effect of pH

In order to indicate the effect of pH, the experiments were performed by mixing of 20 ml (20 mg/l) solution with 0.1 g magnetite at 45 °C, time of 20 minutes and pH 2, 6 and 9.2. The effect of pH is shown in Fig 10. The results show that the best uptake of Cr(VI) adsorption is occurred at pH 2.

Fig 10-a) The uptake percentages of Cr(VI) ions and b) the amount of Cr(VI) adsorbed from aqueous solutions using magnetite as a function of pH.

3.3. Adsorption isotherm

The analysis of equilibrium data is essential to develop an equation that can be used to compare different adsorbents under different operational conditions and to design and optimize an operating procedure. To examine the relationship between sorption and aqueous concentration at equilibrium, various sorption isotherm methods are employed for fitting the data. In this study, the Langmuir model used to estimate the maximum metal uptake values. This model uses two parameters in the sorption system, i.e. q_m and b^{10} :

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{b \cdot q_m} \quad (3)$$

where q_e is the amount of chromium species adsorbed at equilibrium in mg/g, C_e is the solute equilibrium concentration in mg/l, q_m is the maximum adsorption capacity in mg/g and b is a constant which relates to temperature.

The Langmuir isotherm model exhibited well fit to the experimental sorption at temperature 20°C for sample 1 and 2 (Fig 11). The q_m for Cr(VI) on magnetite for samples are 10.5 and 9.4 mg/g, respectively.

sample	Langmuir constant		R^2
	$q_m(\text{mg/g})$	$b(\text{L/mg})$	
1	10.5	0.018	0.970
2	9.4	0.017	0.950

Fig 11- Langmuir isotherm.

Separation Factor (R), indicates the basic properties of Langmuir isotherm with equation 4:¹¹

$$R = \frac{1}{1 + bC_0} \quad (4)$$

where b is Langmuir constant and C_0 is the initial concentration of Cr(VI). If $0 < R < 1$, isotherm is favorable[11]. Amounts of R in this study are shown in Fig 12. The results show that the adsorption of Cr(VI) with nanocrystalline magnetite is favorable.

Fig 12- Calculated R according to Langmuir isotherm versus C_0 .

4. Conclusions

In this study, nanocrystalline magnetite which was produced via thermo-mechanical reduction of hematite was used as an adsorbent for Cr(VI). It was demonstrated that Cr(VI) ions in an aqueous solution could be removed by using relatively small amount of magnetite. A major advantage of using magnetite was the possibility of recovering the particles through the application of a magnetic field. The Cr(VI) adsorption was optimal at pH 2. The equilibrium time was found to less than 30 minutes. Magnetite had a maximum loading of 10.5 and 9.4 mg/g for sample 1 and 2, respectively. The magnetite particles showed high affinity for Cr(VI) ions.

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