

Magnetic CuFe_2O_4 Nanoparticles for Adsorption of Cr(VI) from Aqueous Solution

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Abstract. CuFe_2O_4 nanoparticles were synthesized by co-precipitation method from the solution of CuCl_2 and FeCl_3 in alkaline condition. The prepared magnetic CuFe_2O_4 can be used to adsorb Cr(VI) ions from aqueous solution and separated from medium by magnetic technique. The characterization of CuFe_2O_4 with X-Ray diffraction (XRD) showed cubic units shells with diameter in the range 15-20 nm which obtained by Transmission Electron Microscope (TEM). The saturation of magnetization was around 13 emu g^{-1} measured with Vibrating Sample Magnetometer (VSM). Batch adsorption studies were carried out to optimize adsorption condition. Effective conditions for adsorption of Cr(VI) were found at the weight of CuFe_2O_4 was 1.0 g with contact time of 60 minutes and pH 3 with adsorption capacity 9.20 mg g^{-1} .

Introduction

Heavy metals in the environment are problem that cannot be resolved until now. Various treatments such as coagulation, precipitation, sedimentation, ultrafiltration, ozonation, electrochemical, and reverse osmosis had been applied to remove heavy metal in solution. One of heavy metal pollutants in the environment is chromium. Chromium has wide applicability in the steel and alloy industries. Chromium species exist mainly in two different oxidation states in water environment, Cr(VI) and Cr(III) ions [1]. Cr(VI) and Cr(III) have contrast different in physiological effects. Cr(III) is essential for human beings [2], and necessary for maintenance of glucose, lipid and protein metabolism in mammals [1], but Cr(VI) can be toxic for biological system, carcinogenic in humans and mutagens and teratogens in biological system [3,4]. Exposure to Cr(VI) and its compounds cause irritation to skin, resulting dermatitis and ulcer formation [2,5]. It has been reported that Cr(VI) is about 500 times more toxic than Cr(III) and the common concentration of Cr(VI) found in wastewater are around 50-100 mg/L [6]. According to EU and WHO standards the maximum total chromium content in drinking water is 0.05 mg L^{-1} [5]. Therefore, developing techniques to removal Cr(VI) from wastewater is an important.

There are several methods used to treat wastewater which contain Cr(VI), such as reduction [7], adsorption [6, 8, 9], and extraction [10]. Adsorption has obtained favor in recent years due to proven efficiency in the removal pollutants from wastewater because availability, profitability, ease of operation and economic. Ferrites of type MFe_2O_4 (M is a different metal cation) have been exploited for wastewater treatment and resulting excellent adsorptive properties with capability of effective recovery by a magnetic separation technique [11]. Ferrites is also known to its excellent chemical stability [12]. Magnetic nanoparticles have large surface area also easy and inexpensive to synthesize [13]. In this study, copper ferrite (CuFe_2O_4) was prepared and the adsorption of Cr(VI) ions were demonstrated. Interaction of magnetic nanoparticles with Cr(VI) caused by attractive electrostatic is influenced by pH solution [8].

Experimental Procedures

Analytical grade CuCl_2 , FeCl_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ were obtained from Merck. CuFe_2O_4 was prepared by co-precipitation method. Prepare 400 mL solution consisting of 0.02 mole of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and

0.04 mole FeCl_3 at room temperature under vigorous magnetic stirring, slowly raised the pH by adding NaOH (5 mole L^{-1}) up to about 10. Stirring was continued for 30 minutes and the suspension was heated to $95\text{--}100^\circ\text{C}$ for 2 h [6,14]. Synthesis of CuFe_2O_4 reaction[14]:



After cooling, the prepared CuFe_2O_4 was repeatedly washed with distilled water until the pH is neutral. By simple magnetic procedure, the obtained materials were separated from water and dried in oven at 105°C . The crystalline structure of CuFe_2O_4 was determined using X-Ray diffraction Shimadzu XD-610 with $\text{Cu K}\alpha$ radiation in the 2θ range $10\text{--}80^\circ$, Transmission Electron Microscope JEOL JEM 1400 and Vibrating Sample Magnetometer Lakeshore 74004.

Batch adsorption studies were performed by mixing CuFe_2O_4 particles with 100 mL of the 100 mg L^{-1} Cr(VI) ions solution in a flask. This process was carried out using shaker at a constant speed of 120 rpm. All adsorption experiment was carried out at a fixed temperature of $25^\circ\text{C} \pm 1$. The effect of weight of CuFe_2O_4 on the adsorption capacity was studied using weight variation from 0.8 to 1.2 g at pH 5 and contact time of 75 minutes. The effect of pH on the adsorption capacity was studied with pH adjustment from 3 to 8 using 0.1 M HCl and 0.1 M NaOH solutions. The contact time for adsorption process varied at 15, 30, 45, 60 and 75 minutes. Determination of Cr(VI) ions in solution used Atomic Absorption Spectroscopy (AAS) Shimadzu AA-6300 at 540 nm.

Result and Discussion

Characterization of CuFe_2O_4 .

Fig.1 show XRD patterns of CuFe_2O_4 , indicated that the metal oxides can be indexed on a cubic structure. Nine characteristic peaks at 18.7° , 30.2° , 35.6° , 37.2° , 43.6° , 57.1° , 62.8° , 74.5° , and 79.5° were corresponding to the (111), (220), (311), (222), (400), (511), (440), (533) and (440) crystal planes of CuFe_2O_4 [15].

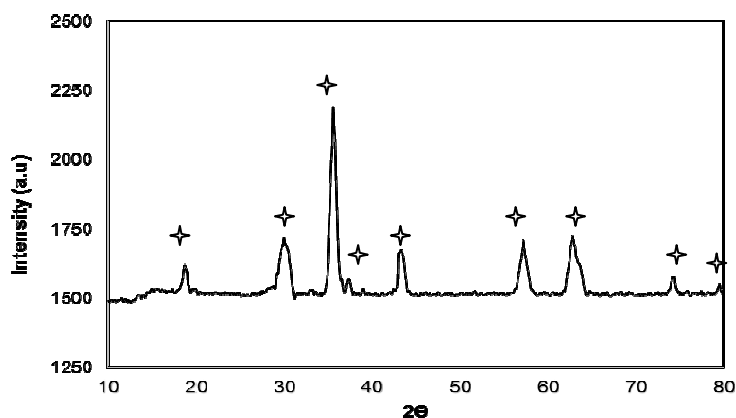


Figure 1. XRD pattern of CuFe_2O_4

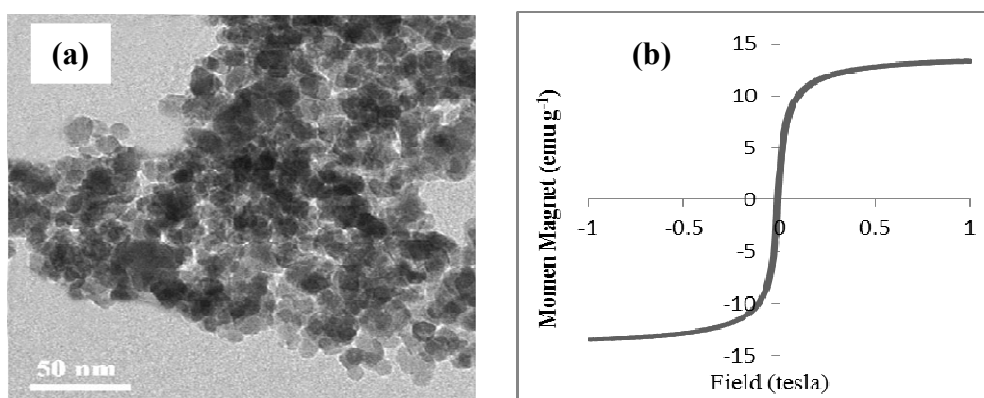


Figure 2. Characteristics of the CuFe_2O_4 by (a) TEM and (b) VSM

Fig. 2 (a) shows TEM image of CuFe_2O_4 , the particle size of the CuFe_2O_4 was found about 15 to 20 nm. Hence, the prepared CuFe_2O_4 by co-precipitation method is found to be nanophase. Fig. 2 (b) show the saturation of magnetization of CuFe_2O_4 was 13 emu g^{-1} . Saturation of magnetization obtained is smaller than the standard saturation magnetization of CuFe_2O_4 as 22.5 emu g^{-1} at room temperature [16].

Optimum adsorption condition. Fig. 3 (a) shows the weight adsorbed of Cr(VI) (mg g^{-1}) with change in the weight of CuFe_2O_4 . It can be observed that the adsorption capacity of Cr(VI) increased with an increased in the weight of CuFe_2O_4 nanoparticles. After equilibrium, the adsorption capacity of Cr(VI) decreased because the weight of CuFe_2O_4 increased but amount of Cr(VI) is limited. Effective weight was found at 1 g CuFe_2O_4 with the adsorption capacity 8.20 mg g^{-1} .

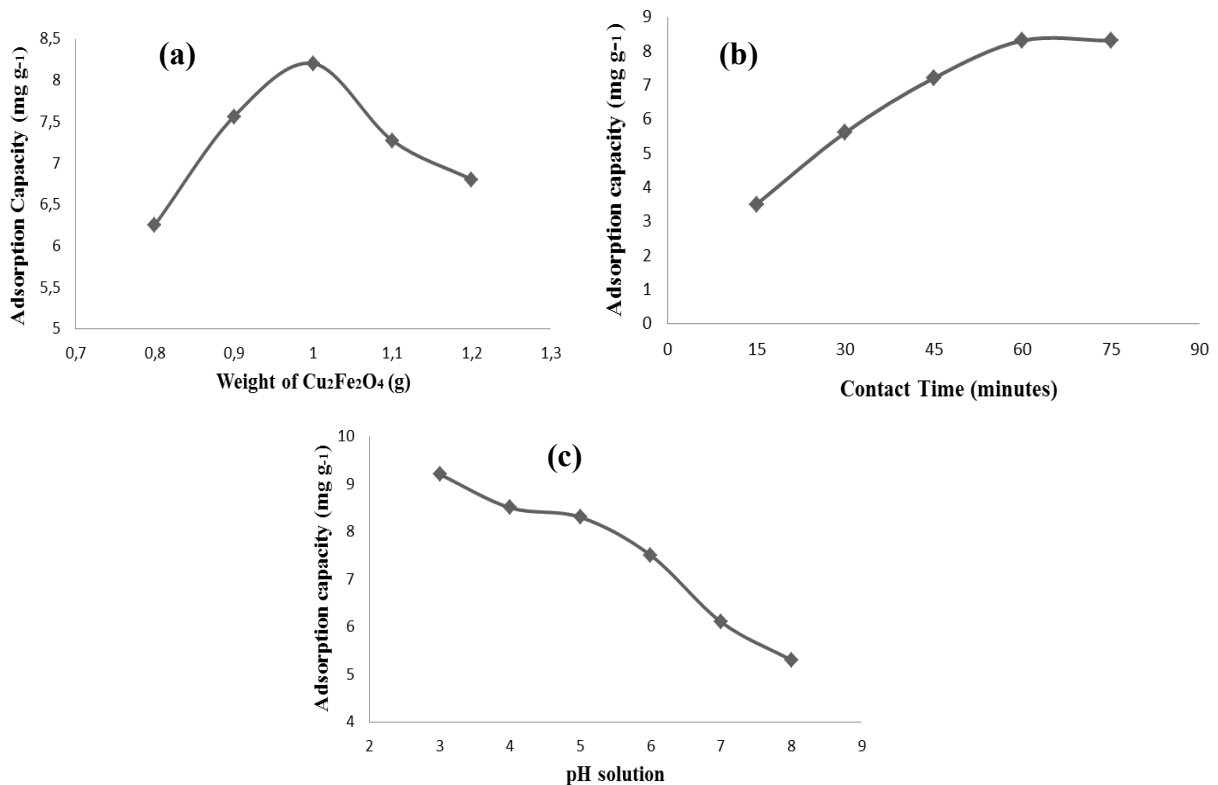


Figure 3. Adsorption capacity by varying of (a) weight CuFe_2O_4 (b) contact time and (c) pH solution

Fig. 3 (b) shows the effect of contact time on the adsorption capacity of Cr(VI). It can be seen that the adsorption process consist of two steps. In the first step, the adsorption capacity rate was at 0 to 60 minutes. The second step, the adsorption capacity was constant at 60 to 75 minutes. The effective contact time was found at 60 minutes with adsorption capacity 8.3 mg g^{-1} . The pH of solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. The effect of pH on adsorption capacity of Cr(VI) arose apparently from the charge properties of both Cr(VI) ions and CuFe_2O_4 . Fig. 3 (c) shows the effect of pH solution on the adsorption capacity of Cr(VI). The maximum of adsorption capacity was observed at pH 3 with adsorption capacity as 9.20 mg g^{-1} . At pH solution $< \text{pH}_{\text{pzc}}$ CuFe_2O_4 (6.3-6.8) adsorbent surface could be positively charged due to the adsorption of H^+ . Therefore, Cr(VI) at the pH from 2 to 6.5 exists mainly in the soluble forms of HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ [6] so the anions are adsorbed by electrostatic attraction.

The adsorption capacity of CuFe_2O_4 to Cr(VI) was smaller when compared to the reduction method using H_2SO_4 and modified chitosan [7,9] but CuFe_2O_4 has the advantage such as it does not

require filtration and adsorption time was faster. The adsorption capacity of CuFe_2O_4 was calculated 9.20 mg g^{-1} . This value is not different with using Fe_3O_4 nanoparticles as 9.7087 mg g^{-1} [8].

Conclusions

Magnetic CuFe_2O_4 nanoparticles were successfully prepared by a chemical co-precipitation method, have cubic phase formed with 15-20 nm diameters size and magnetic saturation as 13 emu g^{-1} . The result of batch experiment for adsorption 100 mL of Cr(VI) with a initial concentration 100 mg g^{-1} showed that the optimum adsorption condition at weight of CuFe_2O_4 1 g, solution pH 3 and contact time of 60 minutes with adsorption capacity as 9.20 mg g^{-1} .

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