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Synthesis of $CuFe_2O_4$-Bentonite Composite for Adsorption of Ni(II) from Electroplating Wastewater

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Abstract. $CuFe_2O_4$-bentonite composite successfully synthesized using chemical co-precipitation method and using to adsorp Ni(II) from electroplating wastewater. The composite was characterized by Fourier Transform Infra Red and Scanning Electron Microscope-Energy Dispersive X Ray Spectroscopy. The FTIR spectra of $CuFe_2O_4$-bentonite composite presented the characteristic of $CuFe_2O_4$ and bentonite. Typical of bentonite obtained by the bands at 1033.8 cm^{-1} correspondent to the intensity of Si-O. The observed two peaks at 432.0 cm^{-1} and 536.2 cm^{-1} attributed to the tetrahedral and octahedral of $CuFe_2O_4$. The result indicated that $CuFe_2O_4$ particles deposited on the surface of bentonite. The main component of $CuFe_2O_4$-bentonite composite contained of $CuFe_2O_4$ and bentonite from EDX spectra. Batch experiments were carried out to investigate optimum condition of adsorption Ni(II) onto $CuFe_2O_4$-bentonite composite. The optimum condition for initial concentration of Ni(II) 50 mg L^{-1} and volume 50 mL obtained at weight of $CuFe_2O_4$-bentonite composite of 100 mg, contact times at 60 minutes and pH of the solution 5. The adsorption efficiency of Ni(II) from electroplating wastewater using $CuFe_2O_4$-bentonite composite at optimum condition was 99.136 %, respectively.

Introduction

The plating process in electroplating industry used about 30-40 % heavy metals [1]. Effluent of electroplating has low pH, high total solids, chlorides, sulphates and heavy metals such as Cr, Cu, Zn and Ni [2]. The presence of heavy metals in the environment is a serious problem because highly toxic, non-biodegradable, carcinogenic and bioaccumulation in organism [1]. For example, Ni(II) causes adverse health cancer, skin allergy, lung fibrosis, kidneys, gastrointestinal distress [2]. Concentration Ni(II) in the wastewater electroplating in the range 2-900 mg L^{-1} [3]. According to EPA standards the maximum Ni(II) content in drinking water is 20 µg L^{-1} [4]. Therefore, the treatment of electroplating wastewater is very essential.

The methods to treatment wastewater expected effective, simple and low cost. Adsorption method is one the most to treatment heavy metals from wastewater. It has been reported the method inexpensive and widely applicable [5]. Various adsorbents can be used to remove heavy metals such as activated carbon [1], chitin and chitosan [6]. Bentonite is one of the adsorbents can be used to absorb heavy metals because has ability to exchange ion at typical layered silicates structure [7]. Bentonite reserves in Indonesia is estimated to reach 380 tons [8]. Potential bentonite has not managed optimally. The effectiveness of adsorption increases if the modification of the adsorbent. Magnetic adsorbent has been widely used in wastewater treatment. Advantages of magnetic adsorbent can be used to adsorb organic and inorganic substances, separation process is simple and fast using permanent magnet. In the research, bentonite-$CuFe_2O_4$ composite adsorbent was employed to developed a new kind of magnetic adsorbent to adsorb Ni(II) from electroplating wastewater. $CuFe_2O_4$ has properties such as magnetic and catalytic [9,10]. In the experiments, batch adsorption are carried out at the temperature 25^0C and effect of some parameters research include weight of composites, contact time and pH solution has been investigated.

Experimental

Bentonite from the South Sumatera, Indonesia. Bentonite dried in the oven at 110^0C for 5 hours. Bentonite is crushed to powder and up to size 200 mesh. All the reagents were of analytical grade and used as received further purification. $CuCl_2$, $FeCl_2$, NaOH and $NiCl_2$ were purchased from Merck. Composite bentonite-$CuFe_2O_4$ synthesize from 2.69 g $CuCl_2$, 5.08 g $FeCl_2$ and 4.79 g bentonite was dissolved in 400 mL double distilled water (Mass ratio of bentonite:$CuFe_2O_4$ = 1:2). NaOH solution 5 M was added slowly to the solution until pH to around 10 under vigorous magnetic stirring at room temperature. The suspension was heated to 95-100^0C for 2 hours [10,11]. After cooling, composite washed with distilled water until neutral pH. Composite separated from water by simple magnetic and dried in oven at 105^0C for 3 hours. The characterization and morphology of the composites are identified using FTIR Shimadzu 5400 and SEM-EDX JEOL-JSM 1400.

In the adsorption experiment, the flask containing 50 mL of Ni(II) prepared from $NiCl_2$ with concentration 50 mg L^{-1} added composite of onto 100-500 mg with shaking at 25^0C for 15 minutes. After that, the composite were separated from the solution by simple magnet. The effect of contact time at various 15-75 minutes and pH at different pH value 3-9. The pH of the solution was adjusted with NaOH or HCl solutions. Concentration of Ni(II) were determined by Atomic Absorption Spectroscopy Shimadzu AA-6300. The optimum conditions obtained by adsorption capacity (q_t).

$$q_t = (C_0 - C_t)\ V / 1000\ .\ m \qquad (1)$$

Where q_t is the adsorption capacity (mg/g) at time t, C_0 and C_t are initial and equilibrium concentration (mg L^{-1}), m is the adsorbent dosage (mg), and V is the volume of the solution (mL). The optimum condition obtained was applied to adsorp Ni(II) from electroplating wastewater.

Results and Discussion

Characterization of Bentonite-$CuFe_2O_4$ Composite. FTIR spectra showed the functional group in the sample. There were recorded in the range 400-4000 cm^{-1}. Fig.1 showed FTIR spectra of $CuFe_2O_4$ and bentonite-$CuFe_2O_4$ composite.

Two absorption bands at 400-600 cm^{-1} correspondent to the octahedral and tetrahedral sites positive ions of $CuFe_2O_4$ [11]. In this research, the higher absorption band at 594.0 cm^{-1} correspondent tetrahedral form and the lower absorption bands at 443.6 cm^{-1} to the vibrations of octahedral form. Wavenumber on bentonite-$CuFe_2O_4$ composite is a combination of wave numbers $CuFe_2O_4$ and bentonite. This proves the occurrence that $CuFe_2O_4$ has entered into intra layer bentonite. The main component of bentonite is montmorillonite. Montmorillonite has a specific absorption at wave number 3100-3700 cm^{-1} which is the O-H stretching vibration and 1600-1700 cm^{-1} which is the H-O-H bending vibrations of H_2O with hydrogen bonding onto montmorillonite. The peaks at 1033.0 cm^{-1} with high intensity were associated with the Si-O stretching vibration, while supported the peaks at 470.0 and 536.2 cm^{-1} were assigned to the Si-O bending vibration. Wavenumber shift indicates a change in energy levels, increased energy may occur because the bond $CuFe_2O_4$ with bentonite.

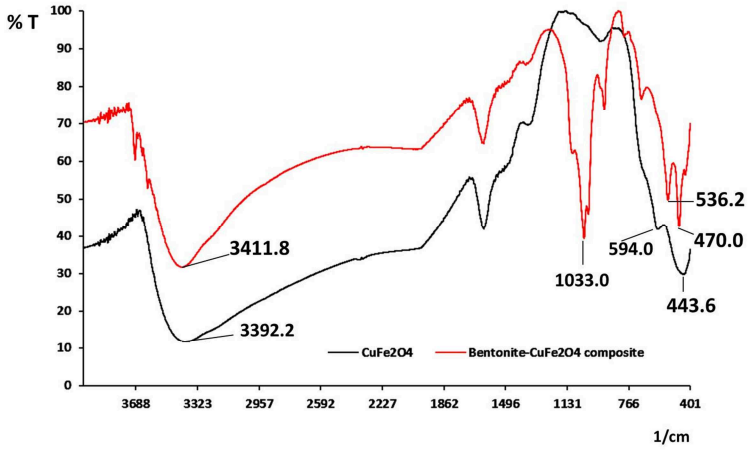

Fig. 1 FTIR spectra of $CuFe_2O_4$ and bentonite-$CuFe_2O_4$.

The morphology of the $CuFe_2O_4$ and bentonite-$CuFe_2O_4$ composite were investigated by SEM observations at Fig.2. The SEM images of $CuFe_2O_4$ was small in size and quite agglomerated while composite was large in size. The main component of $CuFe_2O_4$ from EDX spectra were O(26.7%), Fe(47.64%) and Cu(25.64%) while bentonite-$CuFe_2O_4$ composite contained of $CuFe_2O_4$ and bentonite such as O(30.37%), Na(1.04%), Mg(0.12%), Al(5.73%), Si(8.71%), Ca(0.41%), Fe(35.74%) and Cu(17.88%). It showed synthesize of composite has been successfully.

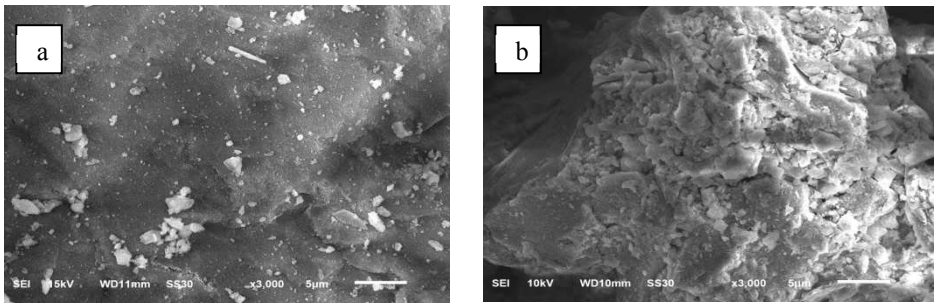

Fig. 2 SEM image of (a) $CuFe_2O_4$ and (b) bentonite-$CuFe_2O_4$ composite.

Adsorption of Ni(II). Weight of adsorbent is an important parameter for the determination of adsorption capacity of Ni(II). Fig. 3. showed the effect of weight of bentonite-$CuFe_2O_4$ composite on the adsorption capacity to Ni(II). The adsorption capacity decreased with the increase the weight of composite. Increasing weight of composite reduces unsaturation of the adsorption sites, so the number of such sites per unit mass down resulting in comparatively less adsorption.

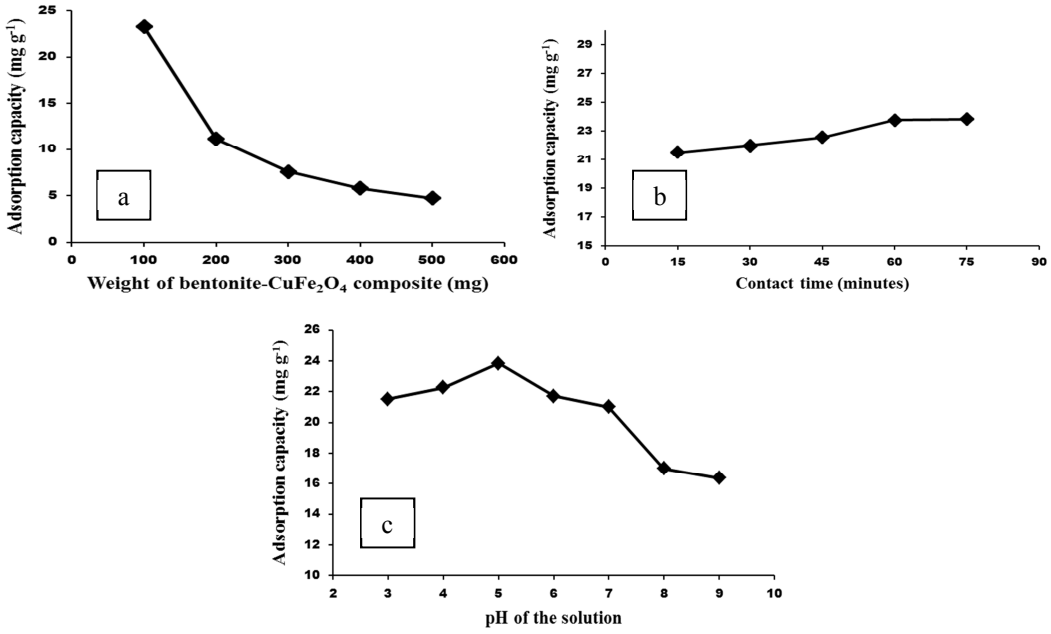

Fig. 3 Effect of (a) weight of bentonite-$CuFe_2O_4$ composite (b) contact time and (c) pH.

The effect of contact time on the adsorption capacity of Ni(II) by bentonite-$CuFe_2O_4$ composite that the adsorption process divided into two steps. The adsorption capacity increases regularly from 15 to 60 minutes and the adsorption capacity has a constant value at 60 minutes. Optimum of contact time adsorption Ni(II) onto modified (*Eriobotrya japonica*) loquat bark at 30 minutes [2], by pyrophosphate modified bentonite at 120 minutes [12] and using ceralite IR 120 was attained within 35 minutes [13]. It is clear that adsorption capacity dependent contact time.

The pH value affects the surface charge of adsorbent. To determine the optimum pH condition for the adsorption Ni(II) onto composite investigated by initial concentration of Ni(II) 50 mg L^{-1}, weight of composite 100 mg and contact time 60 minutes. The optimum pH for adsorption of Ni(II) was found to be 5. From Fig. 3 (c) showed that adsorption capacity increased with increase pH from

3 to 5. At the low pH there is competition between H^+ and Ni(II) for the ion exchange with Ca or Na ions in the bentonite. Adsorption capacity decreased after pH 5 because at higher pH of the solution the metal cation begin to hydrolyze and precipitate so became not available to adsorption.

The optimum conditions were obtained which weight of composite 100 mg, contact time of 60 minutes and the pH of the solution 5 was applied to adsorp Ni (II) from electroplating wastewater. Initial concentration of Ni(II) from electroplating wastewater was 5.289 mg L^{-1} and after treatment using bentonite-$CuFe_2O_4$ into 0.061 mg L^{-1} with adsorption efficiency 99.136 %. The result is greater compared adsorption Ni(II) from electroplating wastewater using pyrophosphate modified bentonite was 88.74 % [12].

Summary

Bentonite-$CuFe_2O_4$ composite have been proven to be an effective adsorbent for removal Ni(II). The optimum condition for adsorption was attained at weight of bentonite-$CuFe_2O_4$ composite 100 mg, contact time 60 minutes and pH of solution 5. The result showed the use of bentonite-$CuFe_2O_4$ composite an alternative adsorbent for treatment electroplating wastewater.

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