



## Properties of Magnetite-Chitin Composite as Materials for Removal of Ni(II) from Aqueous Solution

Fahma Riyanti<sup>1\*</sup>, Poedji Loekitowati Hariani<sup>1</sup>, and Catur Putri Pertiwi<sup>1</sup>

<sup>1</sup>Department of Chemistry, Faculty Mathematics and Natural Science Sriwijaya University

\*Corresponding author : fatechafj@yahoo.com

### ABSTRACT

In this study, magnetite-chitin composite has been synthesized and their application for removal Ni(II) from aqueous solution. Chitin synthesized from shrimp shell waste. Magnetite-chitin composite were prepared by reaction of Fe<sup>2+</sup> and Fe<sup>3+</sup> ion and NH<sub>4</sub>OH in the presence of chitin. Fourier Transform Infra Red (FTIR), Scanning Electron Microscopy-Energy Dispersive X Ray Spectroscopy (SEM-EDX) and Vibrating Sample Magnetometer (VSM) were used to characterize the adsorbent. The effect of composite dosage, pH and contact time on the adsorption capacity of the adsorbent has also been investigated. The FTIR spectra of magnetite-chitin composite confirmed the successful synthesis which the adsorption peak at 586.3 cm<sup>-1</sup> assigned to Fe-O bond. SEM-EDX characterization of magnetite-chitin composite indicated that the surface of composite more solid than chitin and elements of composite contained of magnetite and chitin elements. The magnetite-chitin composite has magnetic properties which the saturation magnetization was 11.27 emu/g. The optimal adsorption of magnetite-chitin composites an initial concentration of Ni(II) was 50 mg/L attained within 3 g of composite dosage, pH value 5 and contact time of 45 minutes with a maximum adsorption capacity of Ni(II) was 37.81 mg/g.

Keyword: magnetite, chitin, composite, Ni(II)

### 1. INTRODUCTION

Natural materials such as bentonite, zeolite, clay, rice husk, chitosan and chitin has been advantageous to their selectivity, non toxic, biocompatible, biodegradable and an inexpensive. Chitin is one of the most important material and is widely used in industry. Chitin, a biopolymer composed of N-acetyl β-D-glucosamine. It can found in the waste from shrimps, prawns, crabs, lobster, beetles and in certain fungi where it a significant component in shells or exoskeleton about 15-20 % w/w[1,2]. The preparation of chitin involves demineralization, deproteinization, and decolorization.

Chitin has been used in water treatment, especially heavy metals. The group of -NHCO- in the glucose ring has the excellent complexation capacity with metal ions [3]. The mechanisms also proposed that the hydroxyl group (-OH) and metal ions (chunhua. 2010).

To improve chitin's performance as an adsorbent, composite magnetite [Fe<sub>3</sub>O<sub>4</sub>] with chitin have been used. Magnetite or iron oxide has a large area and high affinity toward metal ions. There are, the composite magnetite-chitin have been used as an adsorption for removal of heavy metals.

The application of magnetite particle to solve environmental problems has received considerable attention in recent years. Composite of magnetite-chitin can be used to adsorb contaminant from aqueous and after adsorption process, can be separated from the medium by a simple magnetic process. Several studies of the use of magnetic particle for wastewater treatment such as activated carbon/iron oxide magnetic for organic compounds [4], iron oxide coated zeolite as adsorbent for copper(II) [5] and chitosan/magnetite composite beads for removal of Pb(II) and Ni(II) [6].

The aim of this study was to conduct modification chitin with magnetite and

application to adsorb Ni(II) from aqueous solution. Heavy metals have been reported to be toxic to man and other organisms in the environment. The wastewater from electroplating industries contain considerable amounts of Ni(II).

Batch adsorption experiments were used to investigate the adsorption behavior of magnetite-chitin composite. The effect of various parameters such as composite dosage, pH and contact time on adsorption capacity was studied.

## 2. METHODS

### Extraction of chitin [7, 8]

The shrimp shell waste from shrimp industries in Palembang, Indonesia. All chemicals were of analytical grade. The shrimps shell was crushed into smaller and dried in the sun for 3 days. About of 500 g of shrimp shell was dissolved in 35 % NaOH (v/v) in a magnetic plate by stirring at 65<sup>o</sup>C for 2 h. The residue was added into 1 L of 1 % HCl (v/v) and was stirred for 24 h to remove minerals. The chitin are washed with deionized water, and acetone. The decolorization process is carried out by adding 0.315 % NaOCl (v/v) and stirring for 30 minutes at room temperature. Finally, chitin is washed with deionized water and dried in the oven at 60<sup>o</sup>C for 4 h.

### Preparation of Magnetite-Chitin [6]

About 5 g of chitin was treated with 50 mL of CH<sub>3</sub>COOH and 150 mL of aquabidest (pH at 2-3). The solution was added with FeCl<sub>2</sub> (2.74 g) and FeCl<sub>3</sub> (7.01g) which was stirred for 30 minutes. The resulting solution was dripped into 5 M of NH<sub>4</sub>OH under vigorous stirring at room temperature in an N<sub>2</sub> atmosphere until pH 10. The adsorbent was washed with deionized water and acetone. The product was dried in the oven at 70<sup>o</sup>C for 24 h. Characterization of magnetite chitin were examined by FTIR Shimadzu 5400 in a wide range wavelength between 400 - 4000 cm<sup>-1</sup>, SEM-EDX JEOL JEM 6510 LV and VSM Lakeshore 74004.

### Batch Adsorption Experiment

Batch adsorption studies were prepared by 50 mL Ni(II) (50 mg/L) from NiCl<sub>2</sub> standard solution with variety of dosages of magnetite-chitin (1, 2, 3, 4 and 5 g), pH values (3, 4, 5, 7, and 8) and contact time (15, 30, 45, 60, 75 and 90 minutes). The adsorption experiments using thermostatic rotary shaker at 120 rpm.

Determination of Ni(II) in the filtrate used Atomic Absorption Spectroscopy Shimadzu AA-6300. The adsorption capacity for composite,  $q_e$  (mg g<sup>-1</sup>), was determined by calculated:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

Where  $C_0$  and  $C_e$  are initial and equilibrium Ni(II) concentration in the solution (mg L<sup>-1</sup>),  $m$  is the adsorbent dosage (mg), and  $V$  is the volume of the solution (mL).

## 3. RESULTS

### Characterization of Magnetite-Chitin Composite

The color of chitin was brown, but the color of magnetite-chitin composite was dark brown colored precipitates, indicating of the presence of iron in the composite. Figure 1 show the FTIR spectra of magnetite-chitin. The adsorption band around 3421.5 cm<sup>-1</sup> is assigned to the -OH and -NH<sub>2</sub> stretching vibrations. The structure of chitin is similar to cellulose. The monomer of cellulose is  $\beta$ -D-glucose and monomer of chitin is N-acetyl  $\beta$ -D-glucosamine while the OH- group of glucose is replaced by -NHCOCH<sub>3</sub> in chitin [2]. The peaks at 1560.3 cm<sup>-1</sup> and 2933.5 cm<sup>-1</sup> are described to the N-H bending vibration and C-H stretching vibration of alkane. The peak at 586.3 cm<sup>-1</sup> is from Fe-O stretching of Fe<sub>3</sub>O<sub>4</sub>, indicating that the magnetite was successfully crosslinked in the chitin.

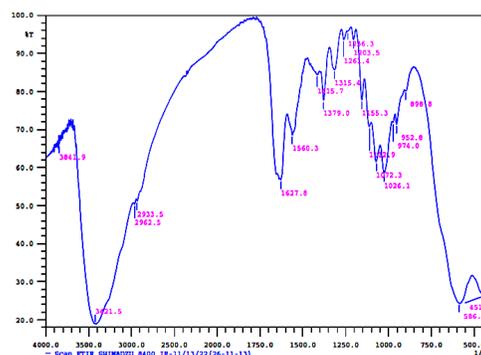
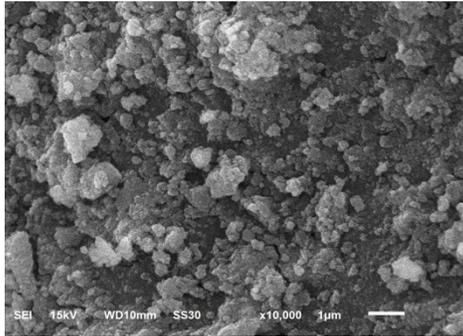


Fig. 1. FTIR Spectra of Magnetite-Chitin Composite

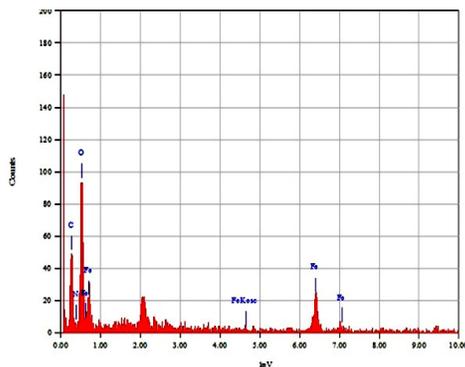
The morphology and microstructure of magnetite-chitin were observed using SEM as show in Figure 2. The surface of magnetite-chitin are solid and non homogenous because of

aggregation. The micro particles of magnetite-chitin causes form aggregates.



**Fig. 2. SEM Micrograph of Magnetite-Chitin Composite**

Figure 3. show EDX spectra of magnetite-chitin. The composition of magnetite-chitin were C (37.11%), N (4.82%), O (18.93%) and Fe (39.14%). The presence of Fe in the composites showed that the composite formation process has been successfully.

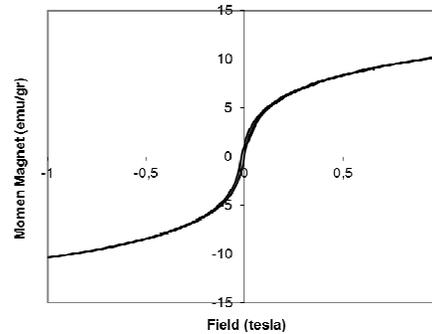


**Fig. 3. EDX Spectra of Magnetite-Chitin Composite**

The magnetic properties of magnetite-chitin were measured using VSM. Figure 4 shows the magnetization hysteresis of magnetite-chitin composite. The saturation magnetization of magnetite-chitin composite was 11.27 emu/g. The advantage of the magnetic properties of the magnetite-chitin composite that the composite can be separated from a solution using a simple magnet.

The magnetic properties of magnetite-chitin composite is smaller than the magnetic properties of  $Fe_3O_4$  (92 emu/g) [9]. The formation magnetite and chitin to be composite reduced of magnetite properties of  $Fe_3O_4$ . The same result when the zeolite doped magnetite,

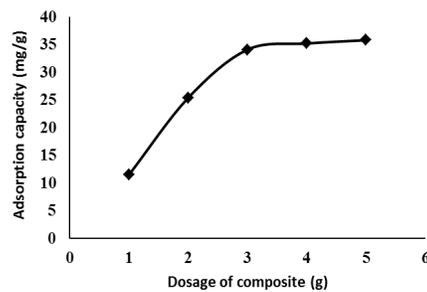
the saturation magnetization of 2 % magnetite in the zeolite is lower than 1 % magnetite in the zeolite [10].



**Fig. 4. VSM Spectra of Magnetite-Chitin Composite**

#### Application of Magnetite-Chitin Composite for Adsorption of Ni(II)

The magnetite-chitin composite was applied to Ni(II) solution. In order to optimize the optimal dosage for bringing down Ni(II) concentration from aqueous solution, varying the amount of magnetite-chitin composite of 1-5 g while keeping other parameters (pH solution and contact time). From figure 5. It can be observed that the adsorption capacity of the composite generally improved by increasing its dosage. This is clear that the higher dosage of the composite, the greater availability of exchangeable sites for the ions. The optimum dosage obtained at 3 g and after that the adsorption capacity was constant.



**Fig. 5. Effect of composite dosage**

The effect of pH solution is one of the most important factors influencing not only site dissociation, but also the solution chemistry of the heavy metals [11]. In this research, effect of the pH solution was presented in figure 6. The result indicated that the adsorption capacity of composite for Ni (II) removal was increased to



maximum and then decreased with pH variation from 3 to 8, respectively. The optimum adsorption capacity in this study at pH solution 5. This result is not much different than adsorption of Ni(II) solution using chitosan where optimum pH solution at 5.5 [12].

The increased of adsorption capacity with the increased pH solution can be explained that the electrostatic bonding between Ni [II] and functional groups of chitin and magnetite. Decrease in the adsorption capacity of composite at a higher pH solution >5 is due to the formation of soluble hydroxy complexes [13].

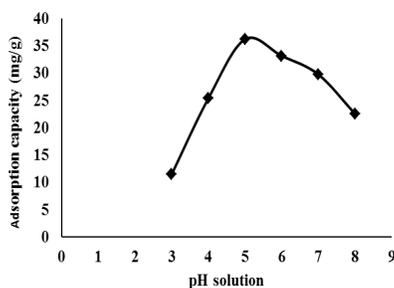


Fig. 6. Effect of pH solution

Figure 7 show the effect of contact time on the adsorption capacity of Ni(II) solution by magnetite-chitin composite. In the first, the adsorption rate was fast and a gradual adsorption stage from 45 to 90 minutes of the adsorption process. In the 45 minutes indicated the high diffusion of the Ni(II) into the surface of the composite.

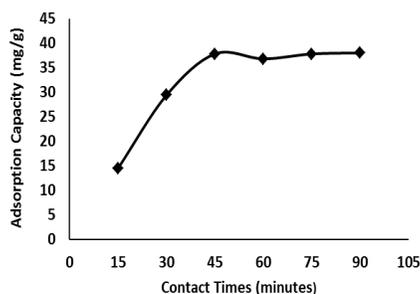


Fig. 7. Effect of Contact Times

The maximum adsorption capacity of Ni(II) solution onto magnetite-chitin at optimum condition (3 g of composite, pH solution 5 and contact time 45 minutes) was 37.81 mg/g. The removal of Ni(II) solution using chitosan coated bentonite with fixed bed methods was 17 mg/g [14].

#### 4. CONCLUSION

The present study investigated the performance of magnetite-chitin composite of batch method for removal of Ni(II) from aqueous solution. The magnetite-chitin composites were successfully prepared by co-precipitation method and due to their magnetic properties, can be separated from a solution by a simple magnetic. The adsorption Ni(II) is dependent on weight of composite, pH solution and contact time. At an initial concentration of Ni(II) was 50 mg/L, 3 g of composite, pH solution of 5 and 45 minutes of contact time, the maximum adsorption capacity obtained was 37.81 mg/g.

#### ACKNOWLEDGMENTS

The author would like to acknowledge the Sriwijaya University for their financial support. (Unggulan Kompetitif, Sriwijaya University No.215/UN9.3.1/LT/2014).

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