

Adsorption Potential of Magnetite Nanoparticles for Copper Removal From Aqueous Solution

Syazana Sulaiman, Raba'ah Syahidah Azis, Ismayadi Ismail, Hasfalina Che Man, Nur Asyikin Ahmad Nazri

Abstract : *In this study, the magnetite nanoparticles (MNP) was successfully synthesized from mill scale waste to analyze the removal of Cu (II) ions from the aqueous solution. The micron-sized magnetite was milled using the high energy ball mills (HEBM with the variation of milling hours 3,5 and 7 to produce nano-sized particles. The MNP were measured by X-Rays Diffraction (XRD), Transmission Electron Microscopy (TEM), Brunauer-Emmett-Teller (BET) and Atomic Absorption Spectroscopy (AAS). Studied parameters are contact time, the initial concentration and particle size. The adsorption kinetics was relatively quick and equilibrium is reached at about 30 minutes. In kinetic studies, the pseudo-second-order model was employed. Langmuir model ($R^2 > 0.9987$) corresponded with the adsorption isotherm data of Cu (II) ions. The adsorption capacity of Cu (II) ions onto magnetite nanoparticles (MNP) is 11.36 mgg^{-1} at 7 hours milling hours. Pseudo-second-order model and Langmuir isotherm were obeyed with experimental results.*

Keywords : *Magnetite nanoparticles, milling hour, particle size, copper ions, Adsorption kinetics, Isotherm*

I. INTRODUCTION

Recently, heavy metal pollution has become one of the major global concern to the environment due to rapid industrialization and urbanization [1]. The environmental problem causes severe health issue because they are persistent, non-biodegradable, carcinogenic and toxic in nature [2],[3].

Copper ions are one of the trace elements which is vital for the human body and flora and fauna. Cu (II) ions generally pass through waste and effluents into water bodies from industrial processes such as manufacturing of plastic, copper polishing, electroplating, and mining activities [4],[5]. Cu (II) ions are one of the necessary but trace elements. Continuous inhalation will increase the risk of lung cancer [6]. Long-term exposure to drinking water containing copper, at even trace level should be strictly prohibited. Besides, high doses of copper can cause anaemia, intestinal irritation, liver, and kidney damage [7]. Due to their toxicity, non-degradability,

Revised Manuscript Received on July 22, 2019.

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easy accumulation of element, the removal of copper from wastewater has attracted much interest worldwide [8].

Nowadays, a few technologies were used for removal of copper from wastewater including ion exchange, precipitation and advanced oxidations. Nevertheless, these techniques are costly. Over the past decades, adsorption separation technology has rapidly evolved and utilized in various industries globally [9]. Adsorption is considered as a simple, attractive, universal, and efficient treatment to remove contaminant within the aqueous phase method for water purification [10]-[12].

There are numerous approaches have been studied for a minimal cost adsorbent for removing heavy metals from wastewater. Due to their unique characteristics of magnetic nanoparticles (MNP) such as superparamagnetic, high adsorption capacities and surface area to volume, it has received significant attention nationwide [13]. Besides, magnetic separation has widely used because of the fast, efficient, cost-effective method in water treatment technology [14]. In conjunction with biotechnology, MNP with low chemical inertness, toxicity and biocompatibility indicate enormous potential [15]-[17].

In this work, MNP from the mill scale waste was synthesized. The efficiency of MNP and adsorption kinetics were studied.

II. EXPERIMENTAL

A. Preparation of Adsorbents

The iron oxides were extracted from the mill scale waste product. The mill scale waste was weighed and crushed using conventional milling for 48 hours. The milled powder then was purified by using Magnetic Separation Technique (MST) and Curie Temperature Separation Technique (CTST) as reported by previous literature [18]-[21]. The magnetic materials powder was dried in the oven for 48 hours at 80°C . The magnetite powder was milled using high energy ball milling (HEBM) using SPEX D8000 dual-drive high energy mills for 3,5 and 7 h respectively to get the nano-sized particles.



B. Adsorption Preparation

The reagents used for synthesis 20 mgL^{-1} of copper stock solutions were prepared by dissolving 1 L deionized water and copper nitrate in Erlenmeyer flask. The 0.3 g of MNP was added to 200 mL of copper solution in the conical flask. The solution was stirred for several minutes before being separated by applying an external magnet. The effect of contact time was analyzed to find the suitable contact time at adsorption is equilibrium. 200 mL of copper stock solution was treated with 0.3 g of MNP after a different period. The time of treatments was 0, 5, 10, 15, 20, 25, and 30 minutes respectively. Subsequently, 3 different copper ions concentrations; 1, 7, 11 mgL^{-1} was treated for 30 minutes with 0.3 g of MNP. All Cu (II) ions adsorption studies were performed by batch technique.

All batch adsorption were investigated in aqueous solution for an initial Cu (II) ions concentration of 11 mgL^{-1} . First, the effect of contact time was examined to find the suitable contact time at which the nanoparticles are saturated and the adsorption is at equilibrium. The contact time used were 5, 10, 15, 20, 25, 30 minutes. The copper stock solution was treated with 0.3 g of MNP at room temperature with different periods of contact times. The initial and final concentrations of the sample solutions have been identified by using AAS. The quantity of Cu (II) ions at equilibrium, q_e (mgg^{-1}) can be determined using Eq. (1):

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

where q_e (mgg^{-1}) is the adsorption capacity of nanoparticles at time t . C_o and C_e are the initial and equilibrium concentrations (mgL^{-1}) of metals in the solutions. V is the volume of the solution in litres, and m (g) is the mass of the MNP used.

III. RESULTS AND DISCUSSION

A. Structure Characterization

Fig. 1. displays the XRD pattern of MNP after milled for 3, 5 and 7 h. As the milling time increase, the crystalline peak of magnetite is broader. This is due to the particle size decrease and increases the lattice strain. The ball powder jar surface collision causes big stress in the powder particles [22]. Apart from that, as the milling time increases, the peak intensity decreases which lead to more refinement of magnetite particle and reduction in crystallinity with milling.

During the milling process, the powder was collided with the steel balls and milled in the vial. The energy of the collision between the balls and vial transferred to the powders and heating the powder continuously. By prolonging the milling time, the more heat transferred to the powder. Continue collisions in the milling process produce heat generation during the milling process. Hence, the particle size increases as milling time increases [23].

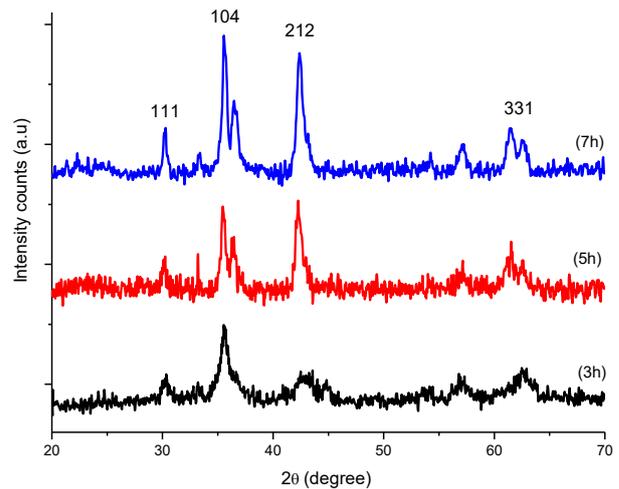
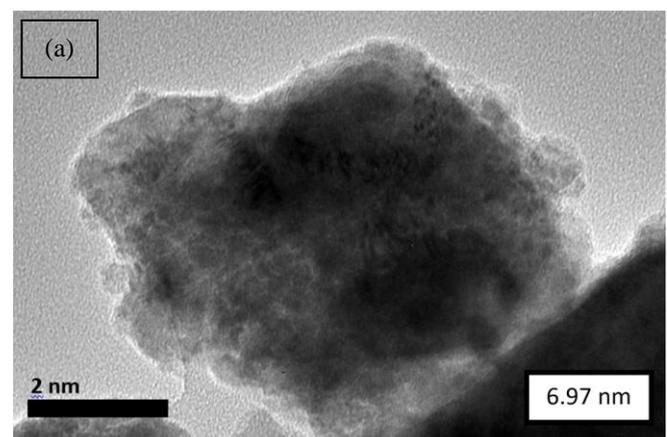


Fig. 1. XRD spectra of MNP milled for 3, 5 and 7 h.

B. Transmission Electron Microscopy (TEM) Analysis

Fig. 2. (a) shows TEM micrograph of the MNP. The micrograph demonstrates sphere-morphological shape particles that favor the technique of ceramic processing [24]. The TEM micrographs also revealed that the particles were agglomerated even before the TEM measurement through a sonication process was performed. It might be due to the huge surface area of the MNP nanoparticles. These agglomerations also contribute to cold welding and alloying process between the particles. In Fig. 2. (b) the histogram shows the particle size distributions of MNP nanoparticles after 7 h of milling, nano-sized particles were obtained in the range of 5- 10 nm on average.



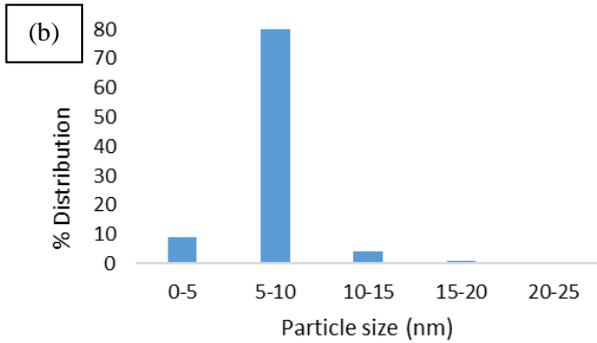


Fig. 2. (a) Transmission electron microscope (TEM) micrograph at 20 nm and (b) scale bar of particle size distributions of MNP after milling at 7 h.

C. BET Analysis

Fig. 3 shows the N_2 adsorption and desorption isotherm curve of MNP. Nitrogen adsorption using Brunauer–Emmett–Teller (BET) has been applied to characterize the porous and surface area property of MNP. The nitrogen adsorption-desorption isotherms were determined over the range of relative pressure. The specific surface area observed are 4.9, 6.3 and 5.4 m^2/g at milling time of 3, 5 and 7 h, respectively. The pore size observed are 77.1, 75.2 and 80.1 Å; with the pore volume of 0.009, 0.012 and 0.011 cm^3/g for of 3, 5 and 7 h milling time, respectively. The BET graph shows the MNP is type III mesoporous with the pore size between 20-500 Å [25],[26]. Mesoporous offers more available sites for adsorption and plays an important role as a transportation channel that allows adsorbate molecules to diffuse from bulk into adsorbent [27]. This indicates that MNP in 7 h milling time is a more promising adsorbent. Furthermore, it can be separated quickly from aqueous solution and achieved its regeneration better.

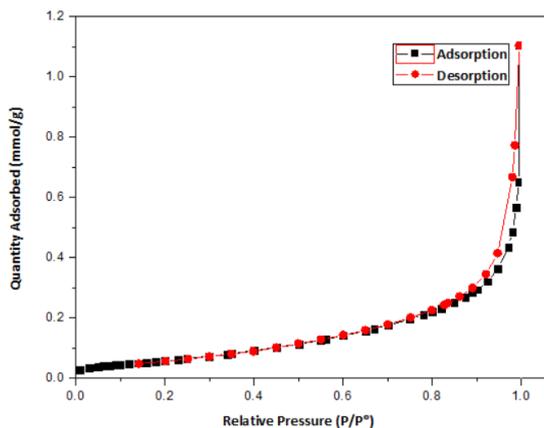


Fig 3. N_2 adsorption and desorption isotherm curve of MNP milled for 7 h.

D. Adsorption Properties

Effect of Milling Time

Fig. 4. illustrates the effect of milling time on the percentage removal of Cu (II) ions. The milling hours are varied at 3, 5 and 7 h. As the milling hour increase, the particle size decreases hence the percentage removal increases. The smaller particle size exhibits greater surface area and greater availability of the adsorption site of Cu (II) ions. The percentage of removal can be deduced by applying Equation 2 :

$$Removal \% = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

where C_o and C_e (mgL^{-1}) are the initial and equilibrium concentrations (mgL^{-1}) of metals in the solutions.

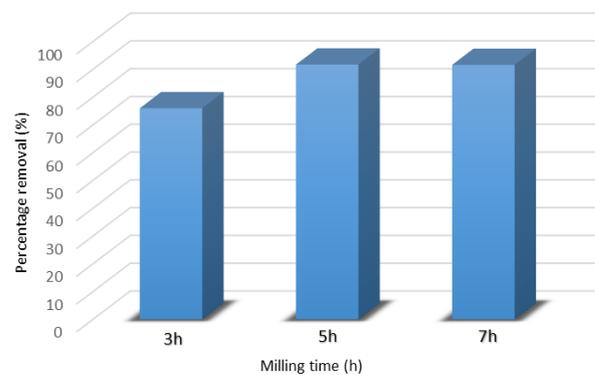


Fig. 4. Removal percentage of 11 mgL^{-1} Cu (II) ions solution treated at 3, 5 and 7 h milling time for 30 min contact time.

Effect of Contact Time

Fig. 5. indicates the effect of contact time on the removal of Cu (II) ions by MNP. It was revealed that the rate of adsorption for removing Cu (II) ions is significantly quicker at the beginning of the process. Then slowed down as equilibrium achieved. Consequently, the adsorption takes place faster in the active external sites that are readily available and slowly in the internal sites which are less available [28]. Approximately 93% of the adsorption capacity was achieved in 30 minutes for 3 milling hours.

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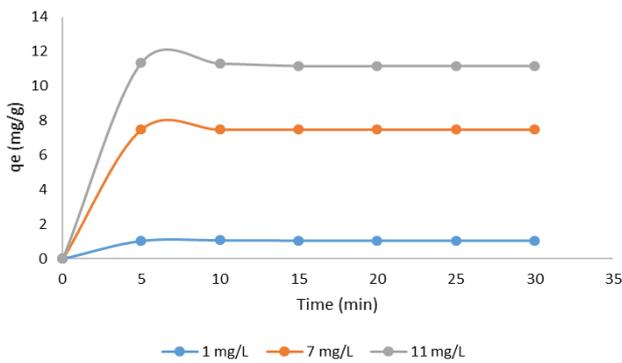


Fig. 5. Effect of contact time of Cu (II) ions onto MNP on the adsorption equilibrium.

Effect of the Initial Concentration of Cu (II) ions

The effect of the initial Cu (II) ions concentration on the adsorption capacity of MNP are 1,7,11 mgL⁻¹. The adsorption capacity rises from 1.02 mgg⁻¹ to 11.36 mgg⁻¹ when the initial metal concentration rises from 1 mgL⁻¹ to 11 mgL⁻¹ until a steady state is reached in which more metal ion could be discarded [29]. The adsorption capacity vs contact time at different concentration is presented in Fig. 6.

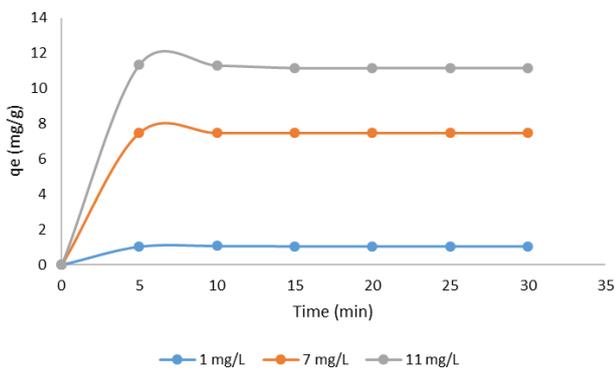


Fig. 6. Effect of initial concentration on the equilibrium adsorption capacity of Cu (II) ions on the adsorbent.

E. Adsorption Isotherm

Langmuir Isotherm

The Langmuir isotherm model rev the presence of monolayer coverage over a homogenous sorbent surface of the sorbate molecules [26]. The linear form of Langmuir adsorption isotherm model and its separation factor R_L as in Eq. (3) and Eq. (4):

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \quad (3)$$

$$R_L = \frac{1}{1+bC_i} \quad (4)$$

where q_e (mgg⁻¹) is the equilibrium adsorbed, C_e (mgL⁻¹) is the adsorbate concentration at equilibrium, q_{max} (mgg⁻¹) is the maximum monolayer adsorbed, b (Lmg⁻¹) represent the adsorption-related Langmuir constant. Langmuir constant q_{max} and b were computed from the slope and intercept of the linear plot of C_e/q_e versus C_e .

The percentage of Cu (II) ions removal was investigated by optimized adsorbent dosage parameters of 1g/L, the particle size of 6.97 nm, pH of 5, and contact time of 30 minutes at a different concentration. The experimental results are obeyed to the Langmuir isotherm model as illustrated in Fig. 7, the regression R^2 obtained for temperature 301 K is 0.9987.

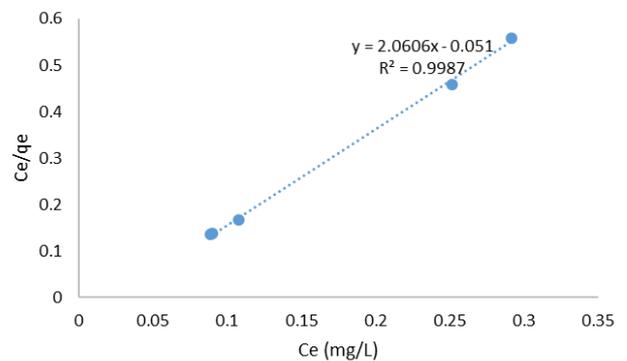


Fig. 7. Langmuir isotherm of Cu (II) ions adsorption onto MNP. Dashed line corresponds to the best linear fit to the experimental results.

F. Kinetic study

Fig. 8 shows the pseudo-second-order of the kinetic study. The calculated q_e values are in agreement with the theoretical values and the graph shows good linearity with R^2 above 0.772. Therefore, the adsorption kinetics of MNP obeys the pseudo-second-order model. The adsorption kinetic represented involving the donation or ions exchange between adsorbate and adsorbent.

The pseudo-second-order is described as in Eq. (5) [27]-[30].

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where q_t and q_e are the adsorption capacity (mgg⁻¹) at any t (min) and at the equilibrium. k_2 is the adsorption rate constant (g/mgh).

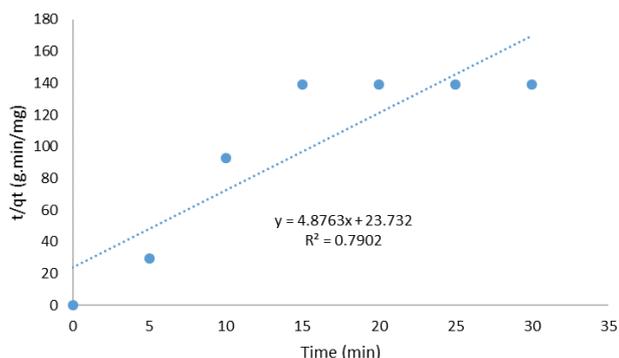


Fig. 8. Sorption kinetics of Pseudo-second-order of Cu (II) ions species at 11 mgL⁻¹ onto MNP.

IV. CONCLUSION

In this study, the high content of iron magnetite in mill scale waste indicated significant advantages for removing Cu (II) ions. The best milling hour of adsorption capacity is 7 h and the maximum adsorption capacity was 11.36 mgg⁻¹. Therefore, the adsorption behaviour was well fitted with the Langmuir isotherm model. The results also evidenced the magnetite is an excellent adsorbent for treating the Cu (II) ions. Further study probably involving several metal ions and real wastewater application to make MNP are more feasible for industrial wastewater treatment.

ACKNOWLEDGEMENT

The authors are thankful for grants from Universiti Putra Malaysia (UPM), Inisiatif Putra Berkumpulan (IPB) GPB/2017/9541600, GP/2018/ 9628400 and IPS Putra research grant, UPM/ 800-3/3/1/(GP- IPS/2017/9533300, GP-IPS/2017/9539100. The authors also thanks to the Fundamental Research Grant Scheme (FRGS) and Long-term Research Grant Scheme [LRGS/ B-U/ 2013/ UPNM/ Defence & Security-P2], Malaysian Ministry of Higher Education (MOHE).

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