

Impregnation of Magnetic Particles on Oil Palm Shell Activated Carbon for Removal of Heavy Metal Ions from Aqueous Solution

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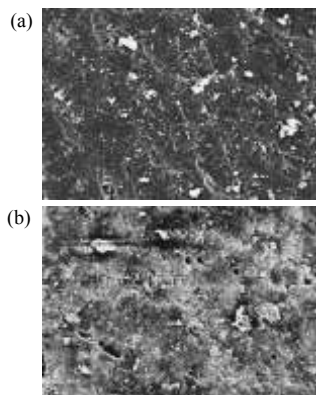
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Graphical abstract



FESEM images of (a) CAC (b) CAC-MP

Abstract

Oil palm shell activated carbon magnetic particle (CAC-MP) was prepared for adsorption of metal ions (Zn^{2+} , Pb^{2+} , Cu^{2+}). Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), surface area and pore analysis (BET, BJH and t-plot method), field emission scanning electron microscopy (FESEM), vibrating sample magnetometer (VSM), and X-ray diffraction (XRD) were used to characterize CAC-MP. Its properties were compared with the parent activated carbon (CAC). The CAC-MP, with a high surface area ($1007 \text{ m}^2/\text{g}$), was used to study metal ions removal at different pH, adsorbent dosage, and contact time. The removal efficiency of metal ion increased with increasing pH, dosage, and time until equilibrium was reached. The optimum condition for maximum removal efficiency was at pH 6 and adsorbent dosage of 0.5 g. Kinetic studies were also performed and the best kinetic model was fitted by pseudo-second-order model.

Keywords: Heavy metal, activated carbon, magnetic particle, adsorption, metal removal

Abstrak

Karbon teraktif tempurung kelapa sawit (CAC-MP) telah disediakan untuk penjerapan ion logam (Zn^{2+} , Pb^{2+} , Cu^{2+}). Spektroskopi inframerah transformasi Fourier (FTIR), analisis termogravimetrik (TGA), analisis luas permukaan dan liang (kaedah BET, BJH dan plot-t), mikroskopi medan pancaran pengimbas elektron (FESEM), magnetometer sampel getaran (VSM), dan belauan sinar-X (XRD) telah digunakan untuk mencirikan CAC-MP. Sifatnya dibandingkan dengan karbon aktif induk (CAC). CAC-MP yang mempunyai luas permukaan tinggi ($1007 \text{ m}^2/\text{g}$) telah digunakan untuk mengkaji penyingkiran ion logam pada pH, dos jerapan, dan masa yang berbeza sehingga mencapai kesetaraan. Keadaan optimum bagi penyingkiran efektif maksima ialah pada pH 6 dan dos jerapan 0.5 g. Kajian kinetik telah dijalankan dan model kinetik terbaik diwakili oleh model kinetik pseudo-tertib-kedua.

Kata kunci: Logam berat, karbon aktif, zarah bermagnet, penjerapan, penyingkiran logam

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1.0 INTRODUCTION

Heavy metals in wastewater are referred to metal ions that are dissolved in water and require treatment process for removal. Wastewater from plating plant, mining, metal finishing, welding, and alloy manufacturing contains heavy metal compounds which can cause environmental pollution, serious symptoms of poisoning, and thus becomes an important problem in water purification.^{1,2} Many technologies have been proposed for removal of metal ions from effluents and aqueous solutions, including ion exchange, reduction flocculation, membrane filtration, precipitation, electrochemical, filtration and reverse osmosis.³ All the processes have been implemented to remove the heavy metal, and adsorption process become one of the solutions that have been applied. The simplicity, convenience and efficiency of adsorption process have attracted considerable

attention as one of the most popular methods for treatment process.² Therefore, proper methods in managing or removing the heavy metals are required to preserve the environment and life.

Solid separation from liquid product requires a good filtration process, high operating cost, and required a proper maintenance and observation for the effectiveness of the process. The development of magnetic particles technology has encouraged many researches to come out with new innovative ideas by providing new applications or improving available applications. Currently, the synthesis of magnetic particles has been explored in adsorption process to provide an effective removal and easy separation. Adsorbent with presence of magnetic particle required a simple magnetic process for solid separation from solution after the adsorption process.

Accordingly, in this study, oil palm shell activated carbon was modified with magnetic particles through impregnation

method for adsorption of metal ions. The resultant activated carbon magnetic particles were characterized and the effects of pH solution, amount of dosage, and contact time on adsorption capacity and removal efficiency of Pb^{2+} , Cu^{2+} , Zn^{2+} ions are investigated. The adsorption kinetic was also studied to comprehend the mechanism of metal ions adsorption onto the adsorbent surface.

2.0 EXPERIMENTAL

2.1 Material

All chemicals used in this study were commercially available and mainly purchased from QRec, New Zealand. The chemicals used in this study were iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ammonium hydroxide (NH_4OH , 28-30%), sodium hydroxide (NaOH), acid hydrochloric (HCl, 95-97%) and sodium chloride (NaCl). Lead nitrate ($Pb(NO_3)_2$), copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), and zinc nitrate hexahydrate, ($Zn(NO_3)_2 \cdot 6H_2O$) are used for preparing metal ions solution.

The oil palm shell activated carbon (CAC), was purchased from Multi Filter Sdn. Bhd, Malaysia for making adsorbent. CAC was then washed with distilled water for several times, dried at 105 °C for 24 h, crushed and sieved for particles size of 0.2-0.4 mm.

2.2 Preparation Of Activated Carbon Magnetic (CAC-MP) Adsorbent

The activated carbon magnetic adsorbent was prepared by impregnation of CAC with synthesized magnetic particles (MP). A solution of Fe^{2+}/Fe^{3+} with molar ratio of 0.5 in 80 mL of deionized water was stirred and 10 mL of ammonium hydroxide was added slowly at 80 °C to precipitate the solution. Then, 10 g of CAC was added instantly to the precipitated solution to ensure the growth of magnetic particle on carbon precursor. The reaction was carried out for 30 at constant temperature and stirring. The resulting CAC-MP was washed repeatedly to remove excess unreacted chemical. Next, the sample was dried under vacuum.

2.3 Characterization

The surface area and pore (BET, BJH and t-plot) of CAC and CAC-MP were characterized using Quantachrome Autosorb-1 instrument according to standard nitrogen adsorption and desorption at 77 K. The morphology of product was observed through FESEM (JSM-6701F) at 1000X and 10kV. XRD analysis was evaluated using a Bruker D8 Advance diffractometer system (Cu K α radiation, 40 kV, 30 mA) for angle 2 θ between 10° to 80°. FTIR (Perkin-Elmer Spectrum) was used to detect the chemical bonding for adsorbent using KBr pellet for IR range of 400 to 4000 cm^{-1} . VSM (Lake Shore 7400) was used to study the magnetization, coercivity and remanent value of the magnetic adsorbent.

2.4 Adsorption Experiment

The stock solution of Pb (II), Zn (II) and Cu (II) were prepared by dissolving $Pb(NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Cu(NO_3)_2 \cdot 3H_2O$ in distilled water for a 30 mg/L concentration. Batch adsorption process were performed by using 50 ml of metal ions solution. The range of independent variables were: pH from 2 to 10, adsorbent dosage of 0.05 to 12 g and equilibrium time for adsorption between 5 and 120 min. The adsorption experimental

work was conducted at room temperature with constant stirring speed. The sample was separated by using a magnetic rod and solutions were analyzed by atomic adsorption spectrometer (AAS).

The equations for adsorption capacity and removal efficiency of heavy metal ions are expressed as:¹

$$\text{Adsorption Capacity, AC (mg/g)} = (C_i - C_f) \times V / W_g \quad (1)$$

$$\text{Removal Efficiency, RE (\%)} = (C_i - C_f) / C_i \times 100 \quad (2)$$

where, C_i (mg/L) and C_f (mg/L) are concentration of heavy metal ions before and after adsorption process, respectively. V (L) is the volume of heavy metal ions solution, and W_g (g) is the dosage of adsorbent.

Zero point charge (PH_{zpc}) for CAC-MP was determined using a method proposed by Panneerselvam et al. (2011).³ PH_{zpc} was determined by using 50 mL of 0.01M NaCl prepared solution in conical flasks with different pH in the range of 2 -12. Then, 0.25 g of sample was added into each flask and kept for 48 h. The initial and final pH was measured using pH meter and finally plotted as pH_{final} versus $pH_{initial}$.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Adsorbent

The FTIR spectra of CAC and CAC-MP for studying surface chemistry of the samples through bonding structure are exhibited in Fig. 1. The peak for C-O stretching and -C-C- group was detected around 1000 to 1200 cm^{-1} , while C=O vibration band was detected around 1625 cm^{-1} in both CAC and CAC-MP. However, for CAC-MP, O-H stretching vibration was detected around 3400 cm^{-1} which is assigned to the functional group on the surface of magnetite. A new peak was detected from 500 to 700 cm^{-1} corresponding to Fe-O intense bonding after impregnation with magnetic particles.

The TG and DTG curves of CAC and CAC-MP are depicted in Fig. 2. The initial loss, observed around 100 °C, indicated volatilization of the sample moisture. As for TG curve, CAC-MP has small difference in weight loss compared to CAC. The weight differences were ~5% for these two samples in the temperature range between 200 and 850 °C. The thermal stability of sample was increased after impregnation as the percentage weight loss reduced.

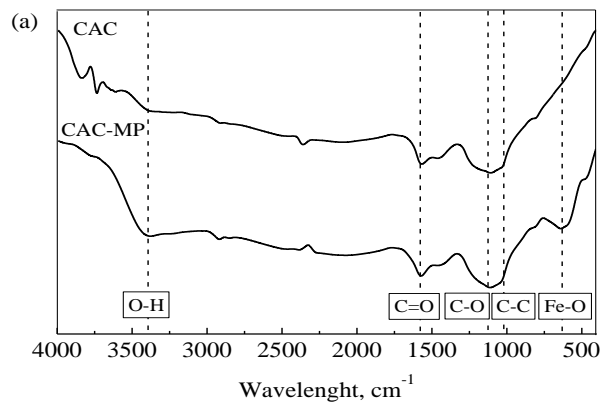


Figure 1 FTIR spectra of CAC and CAC-MP

The surface area and pore analysis for CAC and CAC-MP are listed in Table 1. The total surface area was 731 and 1,007 m²/g for CAC and CAC-MP, respectively. The pore volume for CAC-MP was 0.4 cm³/g compared to 0.29 cm³/g for CAC. The diameter of meso and micropore for CAC and CAC-MP was 3.25 and 3.59 nm and 0.5 and 0.8 nm, respectively. Previous studies have also reported increment in surface area after impregnation of magnetic particles.³⁻⁴ This may be due to the high dispersion of magnetic particle with a specific surface area on the surface of the activated carbon. Besides, there is possibility the activated carbon have been treated with the precipitation of the iron oxide and hot solution which gives some effect on the pore structure and surface area. The pore volume and pore diameter also increased with the increasing of surface area after the impregnation process. The impregnation of magnetic particles has affected the pore structures and enlarged the surface area especially mesoporous area. The CAC-MP showed some magnetic properties and was confirmed through VSM.

The FESEM images for CAC and CAC-MP is shown in Fig. 3. The difference between the CAC and CAC-MP can be seen through the images. Based on Fig. 3b, magnetic particles are highly dispersed on CAC-MP surface. The dispersed magnetic particles on the carbon surface have specific surface area which gives an effect on the total surface area of CAC-MP as previously reported⁵.

The results in Fig. 4 indicate very small coercivity and remanent present in CAC-MP. The saturated magnetization value was 9.01emu/g. The high remanent value show that the material behaved magnetically at zero magnetic field which formed a permanent magnet. For paramagnetic material usually they are attracted to a magnetic field if external magnetic field is applied. The paramagnetic does not retain the magnetic properties after the magnetic field is removed. Small magnetic particles are referred as superparamagnetic since the particles are attracted to magnetic field and zero magnetization appear in the absence of external magnetic field. Thus, this result suggested that the CAC-MP has superparamagnetic behavior since the coercivity and remanent value is very small. Tural et al. (2009) have stated that the aggregation of magnetic particles resulted in small remanent and coercivity product with nanoparticles size are expected to be superparamagnetic.⁶

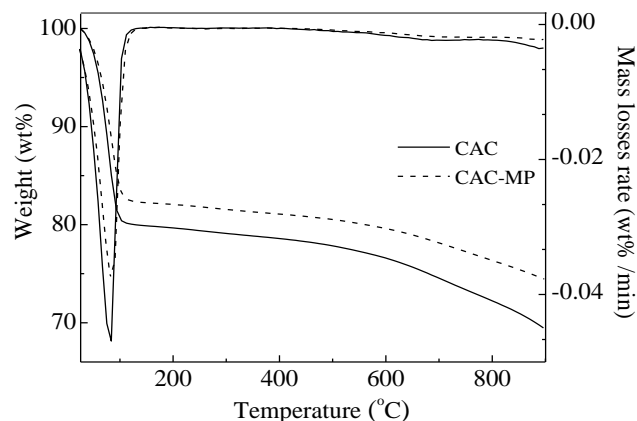


Figure 2 TG-DTG curve of CAC and CAC-MP

The XRD patterns of CAC and CAC-MP are illustrated in Fig.5 exhibited the diffraction peaks characteristic of carbon and

magnetic phase. The formation of amorphous phase of carbon can be seen in Fig. 5a and new diffraction peaks for magnetic phase as shown in Fig. 5b. The magnetic phase referred to the formation of magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃). Tural et al. (2009) stated that Fe₃O₄ or γ-Fe₂O₃ are usually used as magnetic materials.⁶ Based on previous study, the result showed that the production of Fe₃O₄ and γ-Fe₂O₃ is difficult to distinguish by using this analysis.⁷ Both iron oxide can have same peak in XRD analysis but their properties can be accepted since both have magnetic phase.

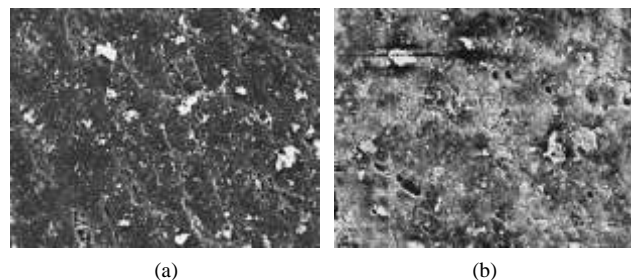


Figure 3 FESEM images (1000X, 10kV) of (a) CAC (b) CAC-MP.

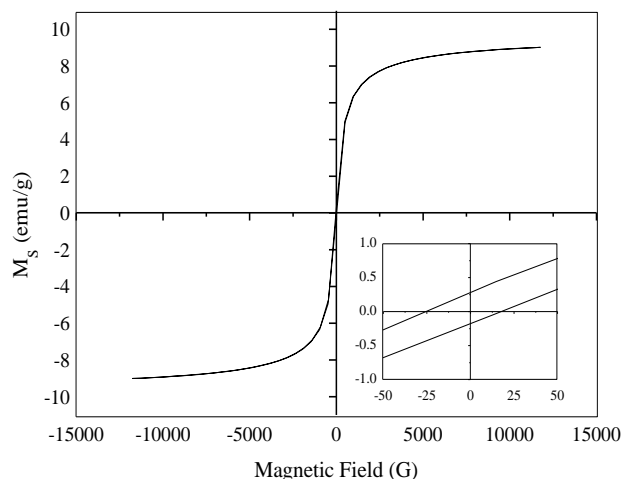


Figure 4 Magnetization curve of CAC-MP.

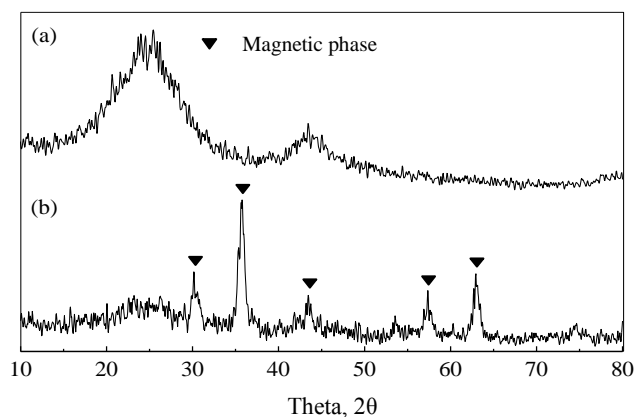


Figure 5 XRD pattern of (a) CAC (b) CAC-MP.

Table 1 Surface area, pore volume and size, and magnetic properties

Sample	Surface Area (m ² /g)			Volume (cm ³ /g)		Diameter (nm)		Magnetic Properties	
	Total	Micro	Meso	Micro	Meso	Micro	Meso	Value (emu/g)	Coercivity (G)
CAC	731	622	109	0.25	0.04	0.50	3.25	n.a	n.a
CAC-MP	1,007	728	279	0.30	0.10	0.80	3.59	9.01	21.535

n.a - not available

3.2 Adsorption Studies Of the CAC-MP For Metal ions

The pH_{zpc} of CAC-MP was studied to determine the maximum point of pH that can be applied for adsorption. The pH_{zpc} for CAC-MP was 6.84 as can be seen in Fig. 6a. The pH_{zpc} means the point the removal will achieve equilibrium after which there is no significant change in adsorption capacity and removal efficiency. The pH_{zpc} indicates the electrical neutrality of adsorbent and surface which becomes an important parameter in order to achieve optimum removal.³

The adsorption of metal ions was investigated at pH 2 to 10 to study the effect of pH (Fig. 6b). The evaluation on pH effect would determine the optimum pH value. The removal efficiency increased gradually but remained constant after pH 6.

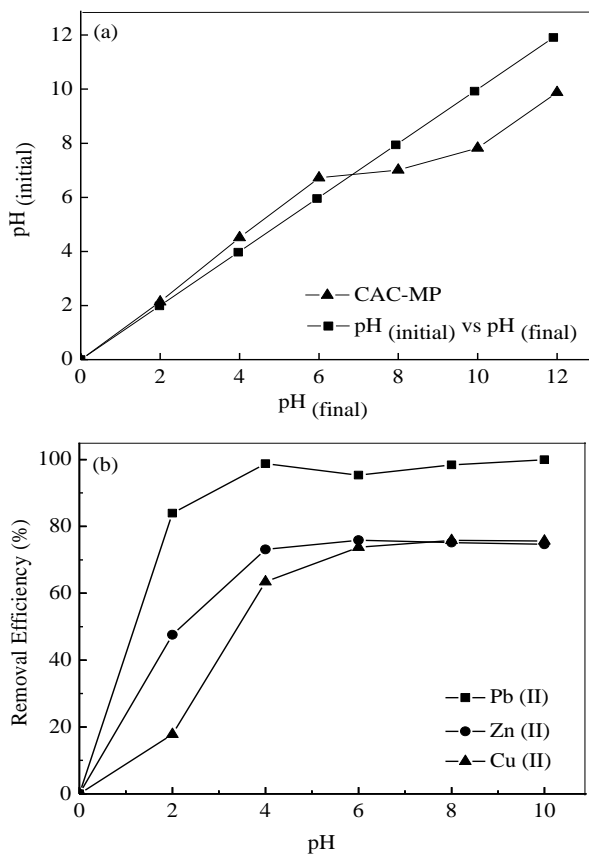


Figure 6 (a) Point zero charge (pH_{zpc}) plot and (b) effect of pH on metal ions removal by CAC-MP (30 min, 5 g)

As mentioned before, the removal will achieve equilibrium above pH_{zpc} and this parameter study inferred no significant change of removal efficiency after pH_{zpc} . This may be due to the presence of

carboxyls in CAC-MP at low pH and the adsorption increased when the alkalinity of solution increased which turn the carboxyls into carboxylate anions. There is no more change in adsorption after the carboxyls completely turned to carboxylate anions.²

Fig. 7 depicts the removal efficiency of metal ions at different dosage. The efficiency increases until it reaches equilibrium after 0.5 g. The optimum dosage was chosen as 0.5 g in the subsequent experiments to synchronize the parameter although the dosage required for Zn(II) ion kept increasing until 1.2 g.

The effects of contact time have been studied and from the results (Fig. 8) the metal ions absorption reached equilibrium at 45 min. The removal efficiency achieved was about 100 %, 79 % and 81 % for Pb(II), Zn(II) and Cu (II) ions, respectively. CAC-MP exhibits higher Pb(II) removal at pH 6, 0.5 g of adsorbent dosage at contact time of 45 min.

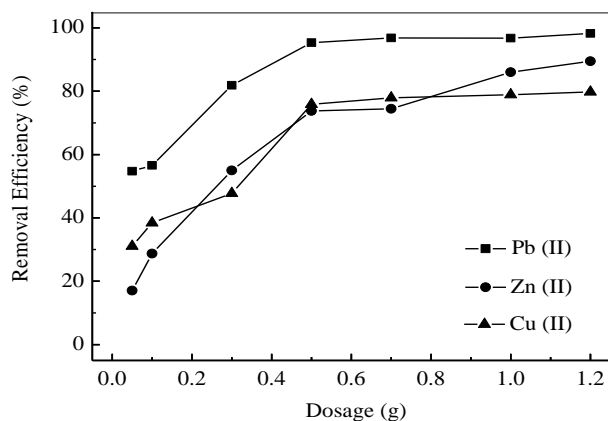


Figure 7 Effect of adsorbent dosage on metal ions removal by CAC-MP (30 min, pH 6)

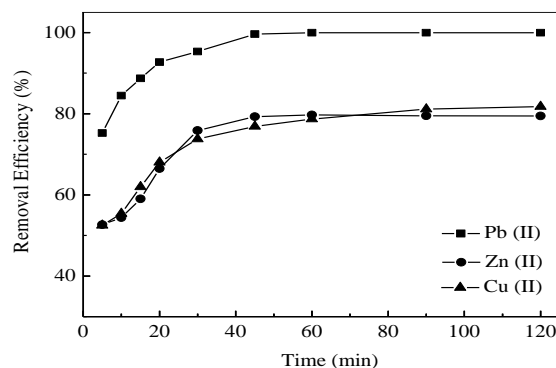


Figure 8 Effect of contact time on metal ions metal ion removal by CAC-MP (0.5 g, pH 6)

Table 2 Kinetic constant for linear kinetic models of metal ions adsorption

Metal Ion	Experiment value, q (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
		q _e	k ₁	R ²	q _e	k ₂	R ²
Pb ²⁺	3.0	0.538	0.058	0.826	3.058	0.180	0.999
Zn ²⁺	2.4	0.593	0.040	0.711	2.488	0.101	0.998
Cu ²⁺	2.8	1.049	0.010	0.825	2.551	0.083	0.999

3.3 Kinetic Studies Of The CAC-MP For Metal Ions Removal

The kinetic study for adsorption of metal ions using CAC-MP provided useful data related to efficiency of adsorption and feasibility for scale-up operations.³ Two kinetic models were considered, namely Lagergren pseudo-first-order and second-order models as written in Eqs. 3 and 4, respectively.²

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (4)$$

where, q_t (mg/g) is the adsorption at time t (min); q_e (mg/g) is the adsorption capacity at adsorption equilibrium; and k₁ (min⁻¹) and k₂ (g/mg.min) are kinetic rate constants for pseudo-first-order and pseudo-second-order models, respectively.

Table 2 summarizes the result of kinetic data for both kinetic models. The correlation coefficients (R²) for pseudo-second-order model were all higher than the pseudo-first-order model. Thus, the adsorption process was represented by pseudo-second-order kinetic model which refers to the chemisorptions process as the rate-limiting step. Ge et al. (2012) and Shin et al. (2011) reported that chemical adsorption process was dominated for second-order kinetic model.^{2,8} Higher chemisorptions process can occur on material with higher surface area. Thus, good removal and better adsorption can be achieved by a large surface area of the adsorbent. The chemical process occurs between the metal ions and adsorbent through sharing or exchange of electrons.⁸

4.0 CONCLUSION

The adsorption of metal ions by CAC-MP has been investigated. Experimental results indicate that adsorption depends on pH, dosage amount and time. The optimum pH was at 6 with 0.5 g adsorbent dosage and 45 min equilibrium time. Higher amount of Pb(II) ions are removed from the aqueous solution compared to Zn(II) and Cu(II) using CAC-MP. The adsorption kinetic follows second-order kinetic model with high relative coefficient compared to first-order-model. Thus, pseudo-second-order kinetic model can be applied to simulate the metal ions adsorption onto CAC-MP.

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References

- [1] Lo, S.-F., Wang, S.-Y., Tsai, M.-J. and Lin, L.-D. 2012. Adsorption Capacity and Removal Efficiency of Heavy Metal Ions by Moso and Ma Bamboo Activated Carbons. *Chemical Engineering Research and Design*. 90(9): 1397–1406.
- [2] Ge, F., Li, M.-M., Ye, H. and Zhao, B.-X. 2012. Effective Removal of Heavy Metal Ions Cd²⁺, Zn²⁺, Pb²⁺, Cu²⁺ from Aqueous Solution by Polymer-Modified Magnetic Nanoparticles. *Journal of Hazardous Materials*. 211–212(0): 366–372.
- [3] Panneerselvam, P., Morad, N. and Tan, K.A. 2011. Magnetic Nanoparticle (Fe₃O₄) Impregnated onto Tea Waste for the Removal of Nickel(II) from Aqueous Solution. *Journal of Hazardous Materials*. 186(1): 160–168.
- [4] Hu, S., Guan, Y., Wang, Y. and Han, H. 2011. Nano-Magnetic Catalyst KF/CaO-Fe₃O₄ for Biodiesel Production. *Applied Energy*. 88(8): 2685–2690.
- [5] Park, H.J., McConnell, J.T., Boddohi, S., Kipper, M.J. and Johnson, P.A. 2011. Synthesis and Characterization of Enzyme-Magnetic Nanoparticle Complexes: Effect of Size on Activity and Recovery. *Colloids and Surfaces B: Biointerfaces*. 83(2): 198–203.
- [6] Tural, B., Özkan, N. and Volkan, M. 2009. Preparation and Characterization of Polymer Coated Superparamagnetic Magnetite Nanoparticle Agglomerates. *Journal of Physics and Chemistry of Solids*. 70(5): 860–866.
- [7] Zhao, H., Wang, Y., Wang, Y., Cao, T. and Zhao, G. 2012. Electro-Fenton Oxidation of Pesticides with a Novel Fe₃O₄@Fe₂O₃/Activated Carbon Aerogel Cathode: High Activity, Wide pH Range and Catalytic Mechanism. *Applied Catalysis B: Environmental*. 125(0): 120–127.
- [8] Shin, K.-Y., Hong, J.-Y. and Jang, J. 2011. Heavy Metal Ion Adsorption Behavior in Nitrogen-doped Magnetic Carbon Nanoparticles: Isotherms and Kinetic Study. *Journal of Hazardous Materials*. 190: 36–44.