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Synthesis and characterization of magnetic activated carbon from *Ceiba pentandra* fiber for zinc ion removal

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Abstract. One of the heavy metals contained in the electroplating industrial wastewater is zinc. Adsorption is found to be one of the most effective methods for zinc ion removal from aqueous solution due to low cost and simple to operate. The main purpose of this study was to use cotton (*Ceiba pentandra*) fiber as a precursor to developing a magnetic activated carbon (MAC) for zinc ion removal. The activation process was carried out using potassium hydroxide (KOH) by conventional heating using a tubular furnace at a temperature of 500°C for 2 hours under a stream of nitrogen (N₂), while the magnetization process was carried out using co-precipitation method. The adsorption of zinc ion onto MAC was recorded to be 96% at a solution pH of 5 and contact time of 180 min. The adsorption of zinc onto AC is fitted well by the Freundlich isotherm model, while the zinc-MAC system is described well by the Langmuir isotherm model. Meanwhile, the pseudo second order kinetic model is suitable for AC and MAC. Owing to low cost and high efficiency, MAC prepared from *Ceiba pentandra* fiber can be used as an effective adsorbent for zinc ion removal from industrial wastewater.

1. Introduction

Electroplating is a metal coating process on a solid substrate using a direct electric current. One of the heavy metals contained in electroplating industrial wastewater is zinc ion (Zn²⁺) [1]. Zinc removal from the wastewater is an important and challenging task due to its toxicity if the concentration exceeds the recommended limit [2]. Several methods have been developed for zinc removal from wastewater, such as coagulation [3], ion exchange [4], and adsorption [5]. Among them, adsorption using activated carbon (AC) is one of the most effective techniques for zinc removal from wastewater. However, the high cost of AC encourages the researchers to use agricultural products, by-products, and biomass waste as precursors in the AC preparation, including *Ceiba pentandra* fiber waste. *Ceiba pentandra* is a tropical tree of the family Bombacaceae [6]. The tree is cultivated for seed fiber, particularly in Indonesia, and is also known as cotton fiber or kapok fiber [7, 8]. Cotton fiber is formed from pure cellulose (90-95%) and is a biopolymer material that can be used as a precursor in the preparation of activated carbon [9].

Although AC has been widely used for zinc removal from wastewater, the separation of AC from solution is still an important issue. The filtration process using a rotary vacuum filter used after the



adsorption process is uneconomic and time-consuming. The addition of magnetite (Fe_3O_4) to the AC becomes a promising alternative to easily separate AC from the effluent. Therefore, the purposes of this study were to (1) prepare magnetic activated carbon (MAC) from cotton fiber with KOH activation and (2) evaluate the feasibility of MAC to remove Zn^{2+} in aqueous solution.

2. Materials and methods

2.1. Materials

Potassium hydroxide (KOH), hydrochloric acid (HCl), zinc nitrate tetrahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), iron(II) sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in the analytical grade were purchased from Merck (Germany), while Cotton (*Ceiba pentandra*) fiber waste was collected from mattress market in Sukoharjo, Central Java, Indonesia.

2.2. Methods

2.2.1. Activated Carbon Preparation

Cotton fiber was dried in an electric oven (Mettler type UN55, Germany) at 105°C for 24 hours. Then, carbonization was carried out at 500°C in an electric furnace (Model FB131M-33 Thermolyne, Thermo Scientific, USA) for 30 minutes in limited air [10]. The resulting char was then impregnated with 8.75 g KOH and 10 ml distilled water for 24 hours, with an impregnation ratio of 1.75: 1 (g /g) KOH to char [11]. Furthermore, the char was dried in an electric oven at 105°C for 24 hours. The activation process was carried out in a tubular furnace at 500°C for 2 hours under a stream of nitrogen (N_2) gas with a flow of $100 \text{ cm}^3/\text{min}$ [11]. The sample was then washed with 0.1 N HCl and distilled water until the pH was neutral. The sample was then dried at 105°C until the weight was constant.

2.2.2. Magnetization Process

MAC was prepared via a co-precipitation method. First, 0.0375 mol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.025 mol $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ each dissolved in 25 ml of distilled water. The solutions were then mixed, stirred, and heated at 55°C . Furthermore, 15 g of AC was added and stirred for one hour while gradually dropping 1 M NaOH solution gradually until the pH reached 12. After cooling, the MAC obtained was then washed with distilled water until the pH was neutral and dried in an oven at 105°C for 6 hours.

2.2.3. Characterization of Adsorbent

The char, AC, and MAC were analyzed to determine the surface morphology using Phenom Pro X Desktop Scanning Electron Microscope (UK). Fourier Transform Infrared (FTIR) spectrometer (Perkin Elmer, USA) recorded between $400\text{-}4000 \text{ cm}^{-1}$ with KBr disc method was used to determine the functional groups on the surface of activated carbon. Thermogravimetric analysis (TGA) (TGDTA7300, Japan) with a scanning temperature of $30\text{-}900^\circ\text{C}$ was used to analyze the decomposition of cotton fibers.

2.2.4. Adsorption Studies

The Zn^{2+} solution was prepared by dissolving $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with distilled water to a certain concentration. The adsorption experiments were carried by adding 0.4 g of activated carbon to 50 ml of Zn^{2+} solution (concentration of 10-500 mg/L) in Erlenmeyers (100 mL size). The pH was adjusted with the addition of HCl (0.1 N) or NaOH (0.1 N) to an appropriate pH. In this sense, the pH of solution was varied, namely 1, 3, 5, 7, 9, 11. The Erlenmeyers were sealed and shaken with a speed of 120 rpm for 10, 20, 40, 60, 120, and 180 minutes. Afterward, the suspended solid was filtered, and the filtrate was analyzed for residual Zn^{2+} using atomic absorption spectrophotometry (AAS) (Perkin Elmer-PinAAcle 900F, USA). The percentage of Zn^{2+} adsorbed can be calculated by Eq. (1), while the amount of Zn^{2+} adsorbed per unit mass of AC or MAC at equilibrium, q_e (mg/g) can be expressed by Eq. (2) [11]:

$$\text{Zn}^{2+} \text{ adsorbed (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 (mg.L^{-1}) is the initial concentration of Zn^{2+} , C_t (mg.L^{-1}) is the concentration of Zn^{2+} in solution at time t , C_e (mg.L^{-1}) is the concentration of Zn^{2+} in solution at equilibrium, V (L) is the volume of Zn^{2+} solution, and m (g) is the adsorbent mass.

3. Result and discussion

3.1. Characterization Adsorbent

Fig. 1 describes the SEM micrographs of char, AC, and MAC. The surface of char appears dense (Fig. 1(a)). Meanwhile, after the activation process (Fig. 1(b)), the pores are created, leading to the increase of porosity. It may be due to the diffusion of potassium compounds into the internal structure of the carbon matrix, followed by the reaction of a fraction of carbon with potassium compounds [11]. When magnetite (Fe_3O_4) was loaded to the AC (Fig. 1(c)), the surface appears to be covered by a layer of Fe_3O_4 .

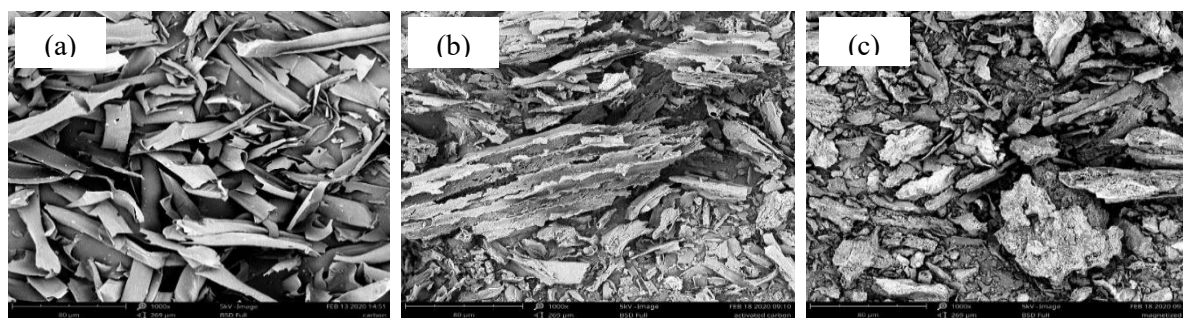


Figure 1. SEM micrographs of (a) char, (b) activated carbon (AC), and (c) magnetic activated carbon (MAC)

The FTIR analysis was conducted to confirm the presence of functional groups in the char, AC, and MAC surface. The results were shown in Fig. 2. The stretching vibration of hydroxyl ($-\text{OH}$) group in the char is detected through the existence of the absorption peak around $3400\text{-}3700\text{ cm}^{-1}$ [12]. The peak observed 2927.50 cm^{-1} and 2856.50 cm^{-1} is assigned to the C-H vibration [13]. The band at 1593.47 cm^{-1} may be attributed to the C=C stretching vibrations. The absorption band at 1060.36 cm^{-1} indicates the presence of C-O of carboxylate group [14]. After the activation process, the position and intensity of some peaks being changed. Peak around $3400\text{-}3700\text{ cm}^{-1}$ became shallower, which suggested the decrease of $-\text{OH}$ group. The peak around $600\text{-}700\text{ cm}^{-1}$ indicating Fe-O vibrations of Fe_3O_4 appears after the magnetization process [15].

The TGA (Thermogravimetric analysis) of cotton fibers is shown in Fig. 3. The TGA curve shows the change in the sample weight of cotton fibers at different temperatures scanning, ranging from 30°C to 900°C . The first decomposition is indicated by a weight loss at a temperature of 110.7°C , leading to the evaporation of substances having a low boiling point such as water. The second decomposition is detected through a drastic weight loss at a temperature around 220°C to 350°C , indicating the loss of lignin and hemicellulose. The third decomposition at a temperature around 350°C to 550°C shows the degradation of non-cellulose substances, including lignin. Lastly, at temperatures above 550°C , it appears a horizontal line and no significant change in weight. It may be due to the cotton fibers have formed crystals.

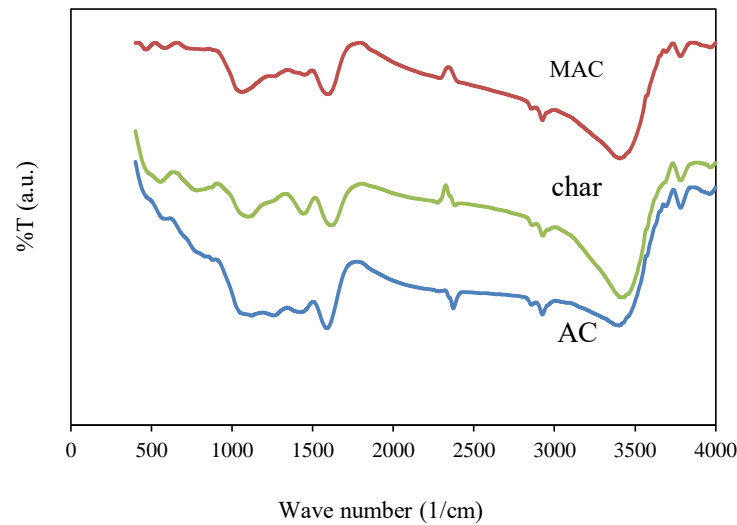


Figure 2. FTIR spectra of (a) char, (b) activated carbon (AC), and (c) magnetic activated carbon (MAC)

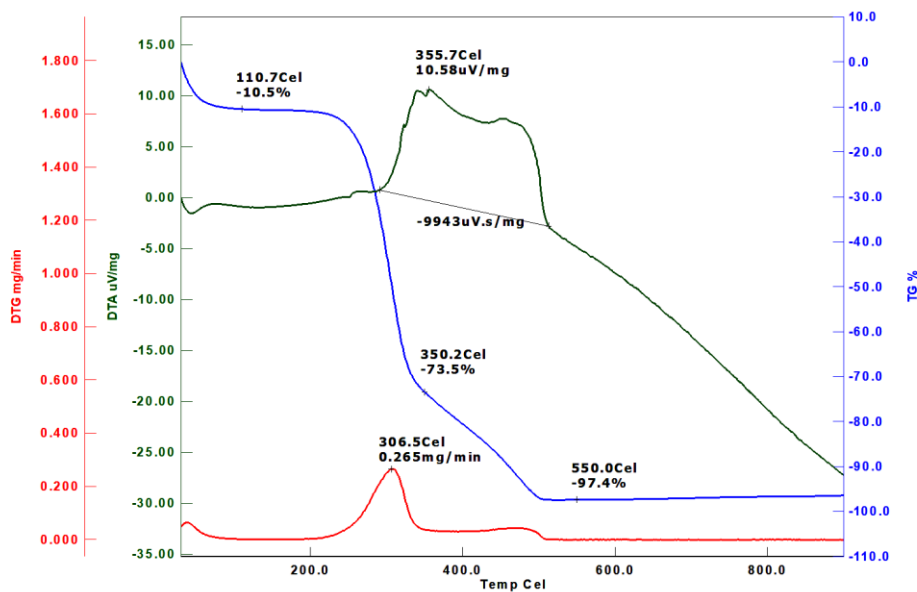


Figure 3. TGA Curve of Cotton Fibers

3.2. Adsorption of Zinc

The effect of solution pH on the adsorption of Zn^{2+} onto AC and MAC is shown in Fig. 4(a). It is clear that the increase in pH leads to an increase in the amount of Zn^{2+} adsorbed. It may be due to deprotonation of phenolic groups, resulting in an electrostatic interaction between Zn^{2+} with the negative charge of the adsorbent surface. Furthermore, the increase of pH from 5 to 11 leads to a decrease in the Zn^{2+} adsorbed due to the formation of hydroxide complexes of Zn^{2+} , including $ZnOH^+$ and $Zn(OH)_2$. Thus, further experiments were conducted at pH 5. Fig. 4(b) describes the effect of contact time toward the amount of Zn^{2+} adsorbed onto AC and MAC. The adsorption of Zn^{2+} increases rapidly at the first 10 minutes, and thereafter, it gradually slows down until 180 minutes, indicating the

equilibrium is reached. It is because a large number of vacant sites are available to adsorb Zn^{2+} ions during the initial stage. The effect of initial concentration on the Zn^{2+} adsorption is illustrated in Fig. 4(c). It is clear that the increase in the initial concentration leads to an increase in the amount of Zn^{2+} adsorbed.

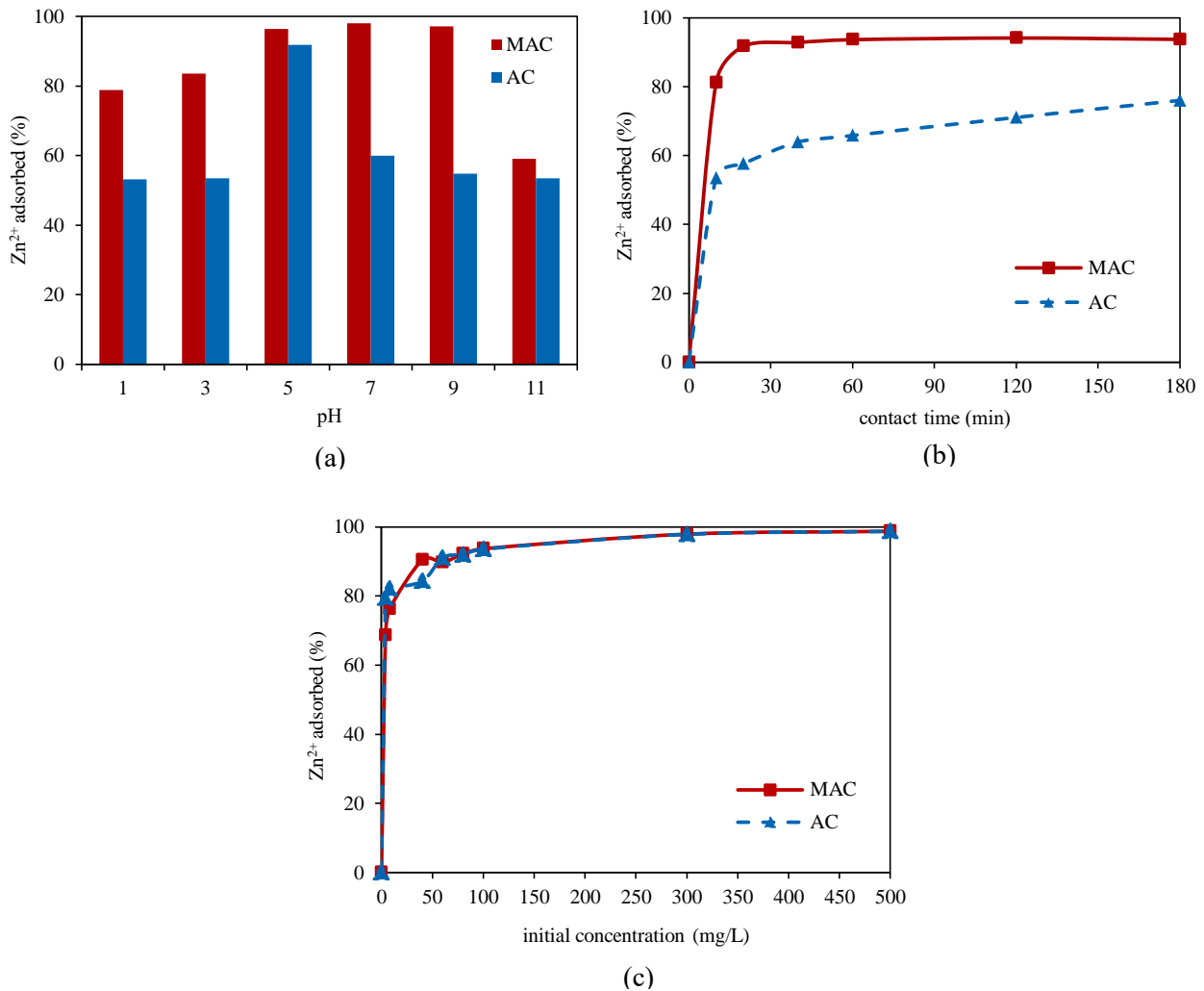


Figure 4. Effect of (a) pH, (b) contact time, and (c) initial concentration on the removal of Zn^{2+} by char, activated carbon (AC), and magnetic activated carbon (MAC).

3.3. Kinetics Studies

The kinetic models used in this study are pseudo first order (PFO), pseudo second order (PSO), and Elovich model. The PFO model expresses pseudo first order to the number of free adsorption sites and zero order to the concentration of adsorbate in the solution, while the PSO model expresses pseudo second order to the number of free adsorption sites and zero order to the concentration of adsorbate in solution. The Elovich kinetic model describes the chemisorption kinetic in a solid-liquid system. The linear form of the kinetic models is expressed by Eq. (3)-(5) [16].

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

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \left(\frac{1}{q_e} \right) t \quad (4)$$

$$q_t = \left(\frac{1}{\beta} \right) \ln (\alpha \beta) + \left(\frac{1}{\beta} \right) \ln t \quad (5)$$

where q_t (mg/g) is the amount of Zn^{2+} adsorbed at time t , k_l (min^{-1}) is the rate constant of pseudo first order model, k_2 (g/mg min) is the rate constant of pseudo-second-order model), α and β are Elovich constants. The parameters of the kinetic models can be obtained from the slope and intercept of the line chart of Eq. (3)-(5), and the result is described in Table 1. Data in Table 1 shows that pseudo second order model is seen in accordance with experimental data due to the correlation coefficient is closer to unity than the others.

Table 1. Kinetic parameters and correlation coefficients for Zn^{2+} adsorption onto AC and MAC

Adsorbent	PFO model	PSO model	Elovich model
AC	$q_e = 0.8$	$q_e = 0.982718$	$\alpha = 9.8043$
	$k_l = 0.4$	$k_2 = 0.7822$	$\beta = 10.607$
	$R^2 = 0.9541$	$R^2 = 0.9987$	$R^2 = 0.9132$
MAC	$q_e = 0.8$	$q_e = 1.1777$	$\alpha = 2.1192$
	$k_l = 0,4$	$k_l = 0.333$	$\beta = 5.6156$
	$R^2 = 0.8826$	$R^2 = 0.9999$	$R^2 = 0.9584$

3.4. Equilibrium Isotherm

The adsorption isotherm is used to describe the adsorption mechanism of adsorbate on the adsorbent surface. In this study, the Langmuir and Freundlich isotherm model is studied. The Langmuir isotherm, based on the fact that the monolayers adsorption occurs in homogeneous sites on the adsorbent surface, is expressed by Eq. (6), while the linear form is defined as Eq. (7). Freundlich isotherm, based on the fact the presence of energetically heterogeneous adsorption sites, is defined as Eq. (4), while the linear form is given by Eq. (8) [17].

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (6)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m k_L} \quad (7)$$

$$q_e = k_F C_e^{\frac{1}{n}} \quad (8)$$

$$\ln C_e = \ln k_F + \frac{1}{n} \ln C_e \quad (9)$$

where q_m (mmol/g) is the maximum adsorption capacity, k_L (L/mmol) is the Langmuir constant, k_F (mmol/g) (L/mmol) $^{-1/n}$ is the Freundlich parameter, which is related to the adsorption capacity, and n is the Freundlich constant. Based on Fig. 5, the adsorption of Zn^{2+} by AC in accordance with the Freundlich isothermal model with the value of R^2 is 0.7745. It indicates that the adsorption of Zn^{2+} by AC takes place on a heterogeneous surface. Meanwhile, Fig. 6 shows that the R^2 of the Langmuir isotherm is more adequate than the Freundlich isotherm model. It indicates that MAC surface has homogeneous energy.

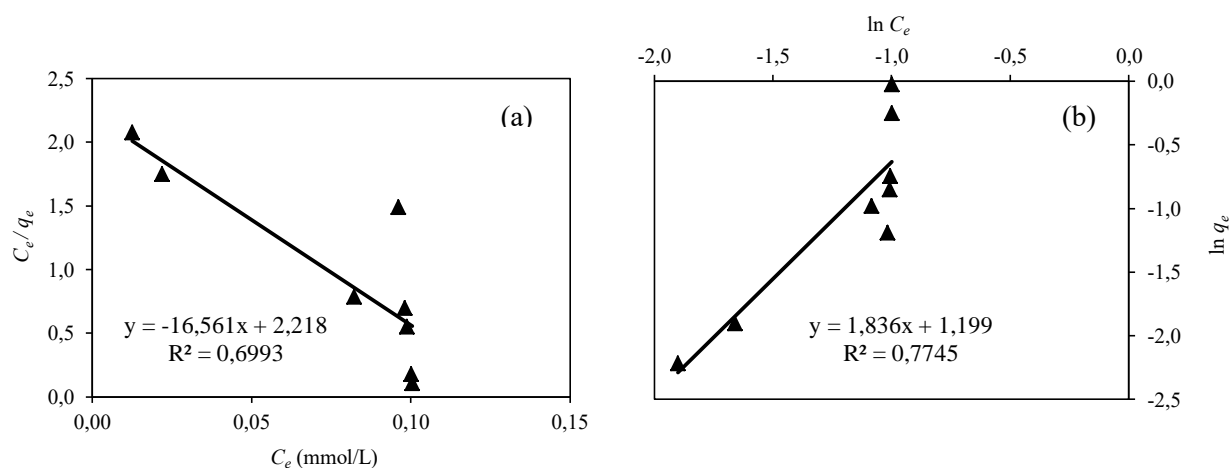


Figure 5. (a) Langmuir, and (b) Freundlich isotherm model for Zn²⁺-AC system

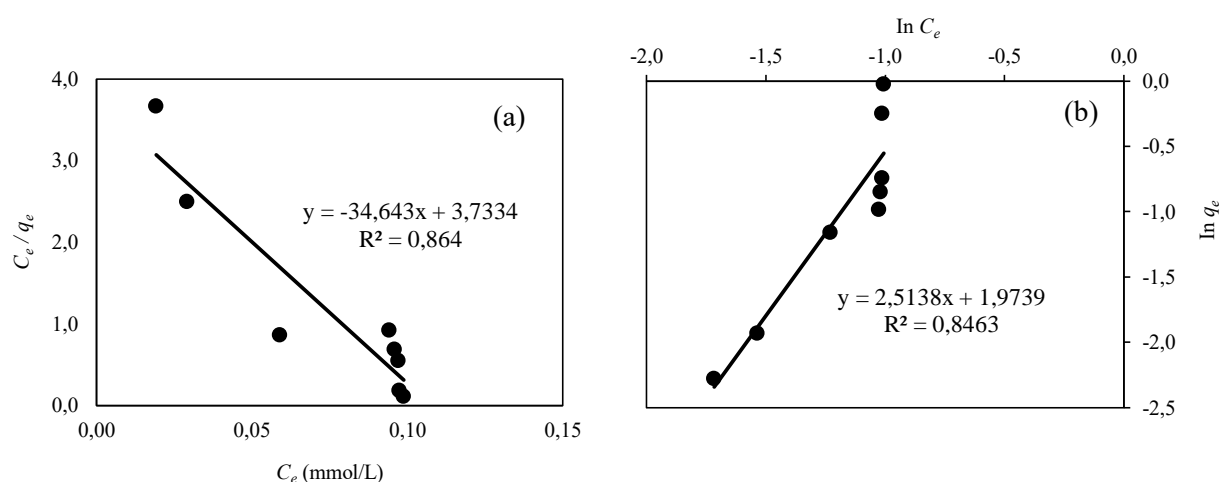


Figure 6. (a) Langmuir, and (b) Freundlich isotherm model for Zn²⁺-MAC system

4. Conclusions

The activated carbon (AC) and magnetic activated carbon (MAC) are successfully produced from cotton fiber. The amount of Zn²⁺ adsorbed by MAC is higher than AC. In this sense, 96% of Zn²⁺ is removed under the optimum conditions (i.e., solution pH of 5, contact time of 180 min, and the adsorbent dose of 0.4 g/50 mL). The adsorption of Zn²⁺ onto AC is fitted well by the Freundlich isotherm model, while the Zn²⁺-MAC system is described well by the Langmuir isotherm model. Meanwhile, the pseudo second order kinetic model is suitable for AC and MAC.

References

- [1] Martín-Lara M A, Blázquez G, Trujillo MC, Perez A, Calero M 2014 New treatment of real electroplating wastewater containing heavy metal ions by adsorption onto olive stone *Journal of Cleaner Production* **81** 120–129
- [2] Kenawy I M, Hafez MA, Ismail MA, Hashem MA 2018 Adsorption of Cu(II), Cd(II), Hg(II), Pb(II) and Zn(II) from aqueous single metal solutions by guanyl-modified cellulose *International Journal of Biological Macromolecules* **107** 1538–1549
- [3] Xu L, Huang Q, Xu X, Cao G, He C, Wang Y, Yang M 2017 Simultaneous removal of Zn²⁺ and Mn²⁺ ions from synthetic and real smelting wastewater using electrocoagulation process: Influence of pulse current parameters and anions *Separation and Purification Technology* **188** 316–328

- [4] Zewail T M and Yousef N S 2015 Kinetic study of heavy metal ions removal by ion exchange in batch conical air spouted bed *Alexandria Engineering Journal* **54** 83–90
- [5] Adebisi GA, Chowdhury ZZ, Alaba PA 2017 Equilibrium, kinetic, and thermodynamic studies of lead ion and zinc ion adsorption from aqueous solution onto activated carbon prepared from palm oil mill effluent *Journal of Cleaner Production* **148** 958-968
- [6] Astuti W, Sulistyaningsih T, Maksiola M 2017 Equilibrium and kinetics of adsorption of methyl violet from aqueous solutions using modified ceiba pentandra sawdust *Asian Journal of Chemistry* **29** 133-138
- [7] Astuti W, Sulistyaningsih T, Maksiola M 2016 Chemically modified kapok sawdust as adsorbent of methyl violet dye from aqueous solution *Jurnal Teknologi* **78** 35-42
- [8] Astuti W, Sulistyaningsih T, Maksiola M 2018 Removal of methyl violet dye via adsorption using activated carbon prepared from Randu sawdust *IOP Conf. Ser.: Earth Environ. Sci.* **167** 012013
- [9] Martínez-Sanz M, Pettolino F, Flanagan B, Gidley MJ, Gilbert EP 2017 Structure of cellulose microfibrils in mature cotton fibres *Carbohydrate Polymers* **175** 450–463
- [10] Duan X, Srinivasakannan C, Xin W, Wang F, Liu X 2017 Synthesis of activated carbon fibers from cotton by microwave induced H₃PO₄ activation *Journal of the Taiwan Institute of Chemical Engineers* **70** 374–381
- [11] Astuti W, Sulistyaningsih T, Kusumastuti E, Thomas GYRS, Kusnadi RY 2019 Thermal conversion of pineapple crown leaf waste to magnetized activated carbon for dye removal. *Bioresource technology* **287** 121426
- [12] Astuti W, Fatin DM 2017 Adsorption of methyl violet dye by thermally modified Ceiba pentandra sawdust *Jurnal Alam Terbarukan* **6** 183-189
- [13] Ekpete OA, Marcus AC, Osi V 2017 Preparation and characterization of activated carbon obtained from plantain (*Musa paradisiaca*) fruit stem *Journal of Chemistry* **2017** 8635615
- [14] Astuti W, Hermawan RA, Mukti H, Sugiyono NR 2017 Preparation of activated carbon from mangrove propagule waste by H₃PO₄ activation for Pb²⁺ adsorption *AIP Publishing* **1788** 030082
- [15] Astuti W, Sulistyaningsih T, Prastiyanto D, Purba BSA, Kusumawardani R 2020 Synthesis of magnetically separable activated carbon from pineapple crown leaf for zinc ion removal *Materials Science Forum* **1007** 71-75
- [16] Astuti W, Zulaechah LS, Kristian L 2019 Teak leaf-based activated carbon for phosphate removal *Jurnal Bahan Alam Terbarukan* **8** 52-58