Adsorption of Cu(Ii) Ions in Aqueous Solution Onto Limonia Acidissima Shellbased Activated Carbon: Kinetic and Isotherm Studies

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Adsorption of Cu(Ii) Ions in Aqueous Solution Onto *Limonia Acidissima* Shell-based Activated Carbon: Kinetic and Isotherm Studies

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Abstract

Adsorption of Cu(II) ions from aqueous solution using activated carbon prepared from *Limonia acidissima* fruit shell (LAFS-AC) was conducted in batch mode experiments at pH 5 (±0.15), 100 rpm and 1 atm. The effects of contact time, initial Cu(II) ions concentration, KOH concentration, and adsorption temperature on Cu(II) ions adsorption capacity were investigated. Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy analyses were performed to investigate the active site and surface morphology of the LAFS-AC, respectively. The Cu(II) ions adsorption was fitted very well (R^2 = 0.94 on average) to the pseudo second-order adsorption kinetic with the adsorption capacity and rate being 25.58 mg/g and 0.07 g/mg.min, respectively at 27 °C by the LAFS AC activated using 0.5 M KOH. It was 26.88 mg/g and 0.15 g/mg.min, respectively at 60 °C. The Cu(II) ions adsorption followed the Langmuir adsorption isotherm model (LAIM) (R^2 = 0.98 on average). The LAIM adsorption capacity and constant were 26.67 mg/g and 0.03 L/g, respectively at 27 °C. It increased dramatically to 0.09 L/g at 60 °C. The optimal adsorption condition obtained was the 0.5 M KOH activated LAFS-AC, initial Cu(II) concentration of 509.81 mg/L and 120-min contact time at 60 °C with the Cu(II) ions adsorption capacity of 26.95 mg/g.

Abstract

Adsorpsi Ion Cu(Ii) di dalam Larutan Berair menggunakan Karbon Aktif Berbasis Kulit Buah *Limonia acidissima*: Studi Kinetika dan Isotermal. Adsorpsi ion Cu(II) dari larutan berair menggunakan karbon aktif yang dibuat dari kulit buah *Limonia acidissima* (LAFS-AC) dilakukan pada percobaan dengan sistem *batch* pada pH 5 (± 0,15), 100 rpm dan 1 atm. Efek waktu kontak, konsentrasi awal ion Cu(II), konsentrasi KOH, dan suhu adsorpsi pada adsorpsi ion Cu (II) diselidiki. Analisis spektroskopi FTIR dan SEM dilakukan untuk menyelidiki morfologi bagian aktif dan permukaan LAFS-AC. Adsorpsi ion Cu(II) memiliki kemiripan (R2 rata-rata = 0,94) terhadap kinetika adsorpsi pseudo orde kedua dengan kapasitas adsorpsi dan laju masing-masing 25,58 mg/g dan 0,07 g/mg.min pada suhu 27 °C pada LAFS-AC aktif menggunakan 0,5 M KOH. Pada suhu 60 °C, nilainya menjadi 26,88 mg/g dan 0,15 g/mg.min. Adsorbsi ion Cu(II) mengikuti model adsorpsi isotherm Langmuir (LAIM) (R2 = 0,98 rata-rata). Kapasitas adsorpsi LAIM dan konstanta masing-masing bernilai 26,67 mg/g dan 0,03 L/g pada suhu 27 °C. Pada suhu 60 °C, nilainya meningkat secara dramatis menjadi 0,09 L/g. Kondisi adsorpsi optimal yang diperoleh adalah 0,5 M KOH pada LAFS-AC aktif, konsentrasi awal Cu(II) 509,81 mg/L dan waktu kontak 120 menit pada suhu 60 °C dengan kapasitas adsorpsi ion Cu(II) sebesar 26,95 mg/g.

Keywords: activated carbon, isotherm, kinetic, limonia acidissima shell

1. Introduction

Heavy metal ions can enter the environment by uncontrolled waste water released from mining practise, petroleum and metallurgical processes, agricultural industries and even chemical laboratories in university [1]-[6]. Among heavy metal ions, Cu(II) ions are the most toxic ions to the human body because these ions can break the tissues and organs [7],[8]. Cu(II) ions may be found in the untreated waste water of chemical, and mining and electrical industries [9]. To treat heavy metal ions in waste water, many processes have been

applied. However, adsorption is the simpler, effective and more economics one compared to others [10-12].

Some adsorbent was prepared from low cost lignocellulosic solid waste such as rice husks [13], water melon [14], coffee bean husks [15], Brazil nut shells and tea [16], and areca catechu shell [17] for Cu(II) ions adsorption. Lignocellulosic materials have been also investigated for raw material of activated carbon to answer the world consumption of approximately 2 billion tons in this year [18]. Among others, pecan shells [19], Cassava peel [20], biomass residue from gasification [21], hazelnut shell and husks [21],[22], Tunisian date stones [23], corn cob [24] and Casuarina equisetifolia cones [25]. Other lignocellulosic solid waste for adsorbent is *Limonia acidissima* fruit shell (LAFS). *Limonia acidissima* tree is native to India, Sri Lanka, Pakistan, Bangladesh, Myanmar, Thailand, Malayseia and Indonesia. As edible uses, the fruit contains fruit acids, minerals and vitamins [26], and the leaves contain an essential oil and tannin for medical [27]. The LAFS can be used as raw material for biosorbent because it contains as much as 51,62% carbon and used to absorb malachite green dye [28]. It was also used for activated carbon to adsorb Cr(VI) [29]. However, this material has not been investigated for raw material of activated carbon for Cu(II) ions adsorption.

To improve metal ions adsorption capacity, several methods of carbon active preparation and adsorption condition have been proposed [30]. In general, two ways to produce activated carbon which are called as physical and chemical activation. In the physical activation, the raw material carbonization has occurred in a furnace at the temperature being less than 700 °C in an oxygen-free environment which is also called as pyrolysis, and the product is charcoal. Then, it is then converted to physical activated carbon in a furnace at the temperature being less than 800-1000 °C in oxidizing gases such as CO_2, SO_2, sulphur vapors, chlorine, ammonia air and steam [14,31]. In the chemical activation, oxidizing chemicals like NaOH, KOH, H_3PO_4 or $ZnCl_2$ is mixed with uncarbonized in a furnace at being less than 400 °C, and then is carbonized in an oxygen-free environment at 400-1000 °C for pyrolysis [31]. A simpler and economics method of physical and chemical activation was proposed. The physical activation of raw material coated with four layers of aluminum foil has occurred in a furnace at 800 °C for 3 h, and the chemical activation of carbon has occurred in solid (carbon) and liquid (NaOH solution) phases for 3 h at room temperature [25].

The research aim is to prepare activated carbon from *Limonia acidissima* fruit shell (LAFS-AC). The effects of contact time, initial Cu(II) ions concentration, KOH-activator concentration and adsorption temperature on adsorption capacity were investigated. The chemical functional groups was analyzed by Fourier Transform Infrared Spectroscopy (FT-IR), and the structural surface was analyzed by Scanning Electron Microscopy (SEM). The optimal conditions for maximum Cu(II) ions adsorption on the LAFS-AC were reported based on kinetic and isotherm parameters.

2. Materials and Methods

Preparation of Activated Carbon. *Limonia acidissima* fruit shell (LAFS) waste was collected from Rujak Aceh Garuda shop in Banda Aceh, Aceh Province. The same procedure of preparation of activated carbon in the previous study was taken into account [25]. The LAFS waste of 2 kg was rinsed in tap water. Then, the rinsed LAFS waste was dried under the sun at 30 °C (± 2 °C) on average for 4 days. The dried LAFS was grinded in a cleaned dry spice ginder, and the LAFS powder was then sieved into 40–60 mesh. Pyrolysis of the LAFS powder was taken place in a tube furnace (type TF-80/120/160, 300-1500 °C, Human Lab Instrument Co., made in Korea) with the heating rate at 45 °C/min for 65 min. Nitrogen was injected into the tube furnace at 7 mL/min to limit oxygen in the pyrolysis. Initial and final temperature of system was 30 and 450 °C, respectively. Physical activation at 500 °C for 1 h without oxidizing gases was conducted as a new method proposed in the current study to save energy and oxidizing gases consumption. The LAFS carbon of 25 g was activated using 250 mL of 0.25 M KOH (99% pure, Aldrich) in 500-mL beaker glass at 100-rpm stirring speed (Hotplate Stirrer, IKA, C-MAG HS 7) for 24 h at 27 °C (± 1 °C). The LAFS activated carbon (LAFS-AC) was thoroughly washed many times using tap water and distilled water at the end until a neutral pH of 6.8 (± 0.2) of the rest washing water was obtained. The LAFS-AC was filtered vacuum, and it was dried in an oven drier (Memmert-NN-ST342M, Western Germany) at 120 °C (±1 °C) for 3 h to remove the excess water. Finally, it was stored in a sealed bottle for adsorption experiment. The above procedure was repeated to prepare the LAFS-AC with different concentration of KOH (0.5 and 0.75 M).

Preparation of Cu(II) Aqueous Solution. The Cu(II) ions aqueous solution of 510 mg/L was made by dissolving 2.023 g (±0.001) $CuSO_4.5H_2O$ (99% pure, from Aldrich) in 1000 mL distilled water in 1000-mL volumetric flask. The 2 mL sample was taken and mixed with 10 mL distilled water in 15 mL vial for Atomic Absorption Spectrophotometer (AAS, AA-6300 Shimadzu made in Japan) analysis to obtain the Cu(II) ions concentration in the vial [25]. Meanwhile, the real Cu(II) concentration of stock solution was calculated by multiply the AAS-based Cu(II) ions concentration with the dilution factor of 6. The desired concentration of Cu(II) ions for each run of adsorption experiment was

made by taking the stock solution, and adjusted by diluting it with distilled water.

Characterization of the LAFS-AC. A spectrophotometer (Shimadzu, IR Prestige 21 made in Japan) was used to obtain the chemical functional groups in the LAFS powder and LAFS-AC by Fourier Transform Infrared Spectroscopy (FT-IR) analysis at the spectra of 400–4000 cm⁻¹. KBr pellets (0.1% sample) was used to obtain the the LAFS powder and LAFS-AC transmission spectra. Scanning Electron Microscopy (SEM) (TM-3000, 500VA, 1 phase 50/60Hz, Hitachi made in Japan) was used to show the LAFS powder and LAFS-AC surface micrographs [17,25].

Experiments of Cu(II) Adsorption. The same procedure of Cu(II) ions adsorption in the previous study [25] was conducted in batch mode for the current study. The LAFS-AC of 1 g was contacted with 100 ml Cu(II) solution of 509,81 mg/L (based on the AAC analysis) in a 100-mL erlenmeyer flask. The system was stirred at 100-rpm, 27 °C and 1 atm. The 2-mL samples of Cu(II) ions solution were taken with time series (0, 20, 40, 60, 80 and 120 min), and it was added with 10 mL distilled water in 15 mL vial. The Cu(II) ions concentration of filtrate was quantified by the AAS, and the real Cu(II) ions concentration at each contant time was calculated by multiply the AAS-based Cu(II) ions concentration with the dilution factor of 6.

The effect of contact time, initial Cu(II) ions concentration, KOH-activator concentration and adsorption temperature on the Cu(II) ions adsorption capacity of the LAFS-AC were investigated. The effect of intial pH in the system was not investigated. However, pH 5 (±0.15), was taken into account for the current study because the maximum Cu(II) ions adsorption capacity of activated carbon was moslty found at the pH 5 [24],[32]. The contact time, initial Cu(II) ions concentration, KOH concentration and temperature of adsorption were in the range of 0–120 min, 24.45–509.81 mg/L and 27–60 °C (± 1 °C), respectively. The highest adsoprtion temperature is 10 °C higher then the previous study [33]. The Cu(II) solution pH was adjusted by dropping HCl and KOH at the range concentration of 0.01-0.2 M. Hot Plate Magnetic Stirrer (Thermo Scientific, Cimarec-Sp131635) was used to set the temperature of system. Each the AAS reading of each experiment was done in duplicate with the standard deviation value being 0.4-0.5 for the average value taken. The parameters of Cu(II) ions adsorption kinetic and isotherm were obtained based on the experimental data and the adsorption kinetic and isotherm equations.

3. Results and Discussion

The functional groups of samples. The FT-IR transmission spectra of the LAFS powder as the raw material

is shown by the bottom graph in Figure 1. The spectra for the LAFS-AC with 0.5 M KOH activator is shown by the top graph, and the spectras for the LAFS-AC with 0.25 and 0.75 M KOH are shown by the middle graphs in Figure 1. As shown in Figure 1, There were two bands at 3851–3698 cm⁻¹ with the peaks at 3738 and 3705 cm⁻¹ which was signed to first functional group of the O-H stretch of hydroxyl groups [25,32,34]. As clearly shown in Figure 1, transmittance of O-H stretch increased because of chemical actvation, which was from 78.36% (the LAFS powder) to 82.37 % (the 0.25 M KOH LAFS-AC) and 93.32% (the 0.5 M KOH LAFS-AC). This also comfirmed that increased KOH concentration from 0.25 to 0.5 M resulted in more hydroxyl compounds in the LAFS-AC. However, increasing it from 0.5 to 0.75 M brought back it to the almost the 0.25 value which is shown by the coincided graphps of the 0.25 and 0.75 M KOH LAFS-AC.

The same trend and even more contrast was shown by the second functional group of the C–H stretching of alkenes and alkanes with the weak bands at 3099–32845 cm⁻¹ and the peaks at 3055 and 2951 cm⁻¹, respectively [25],[35]. It existed in the three samples whereas the 0.5 M KOH slightly increased alkenes and alkanes compounds in the LAFS-AC, as can be seen in Figure 1. This was shown by the samples' transmittance being increased to 107.57% (the 0.5 M KOH LAFS-AC) from 79.07% (the LAFS powder) and 87.79% (the 0.25 and 0.7 M KOH LAFS-AC). Insignificant increase happened to the other functional groups as the result of 0.5 M KOH activation. The functional groups are the C=O stretch of carbonyls (a strong band at 1732–1636 cm⁻¹ with the peak at 1697 cm⁻¹, the C–C stretch of aromatics (a weak band at 1630–11373 cm⁻¹ with the 2 peaks at 1566 and 1436 cm⁻¹), the C–O stretch of esters (a weak band at 1116–989 cm⁻¹ with the peak at 1031 cm⁻¹), and the C–H "oop" stretch of aromatics (at 980–684 cm⁻¹ with the 3 peaks at 852, 804 and 684 cm⁻¹) [25,36].
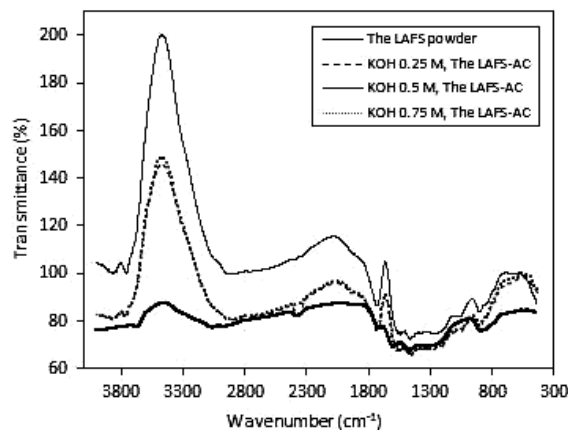

Figure 1. The FT-IR Spectra of the LAFS Powder and the LAFS-AC

Overall, the transmittance of functinal groups in the the 0.5 M KOH LAFS-AC especially the O-H and the C–H stretching was higher than the one in the 0.25 and 0.75 M KOH LAFS-AC. This condition would lead more Cu(II) ions being adsorbed by the active site of the 0.5 M KOH LAFS-AC compared to the the 0.25 and 0.75 M KOH LAFS-AC, and chemical sorption could control the adsorption of Cu(II) ions onto the 0.5 M KOH LAFS-AC.

Surface morphology of samples. Figures 2(a) and (b) show the SEM analysis result for the 0.25 M KOH LAFS-AC and 0.5 M KOH LAFS-AC, respectively.

As shown in Figure 2, the 0.5 M KOH LAFS-AC surface has more macroprous compared to the 0.25 M KOH LAFS-AC surface. The porous wall of the 0.5 M KOH LAFS-AC also consisted of more small macroporous compared to the porous wall of the 0.25 M KOH LAFS-AC. In addition, transport pores were likely also can be seen in the 0.5 M KOH LAFS-AC surface. The more porous formed in the surface of activated carbon caused more active sites on the activated carbon [25], and there should more functional groups on the 0.5 M KOH LAFS-AC surface to be active sites. Therefore, Cu(II) ions should be adsorbed more onto the 0.5 M KOH LAFS-AC compared to the other.

Effect of contact time on adsorption capacity. Cu(II) ions adsorption capacity at the certain contact time (qt), and contact time influenced the amount of Cu(II) ion being adsorbed onto the LAFS-AC at different temperature

(a)

(b)
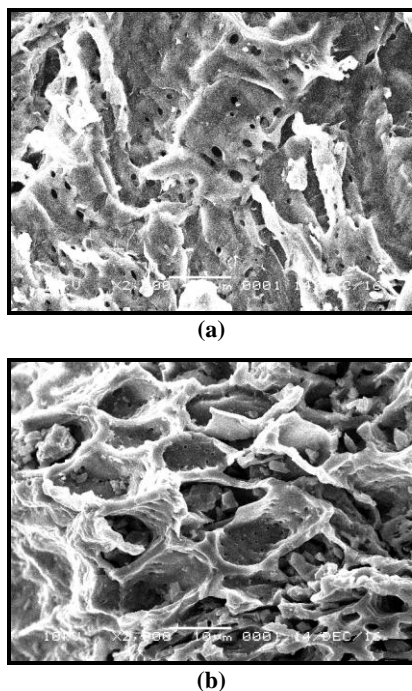
**Figure 2. The SEM Micrographs of (a) the 0.25 M KOH LAFS-AC and (b) the 0.5 M KOH LAFS-AC**
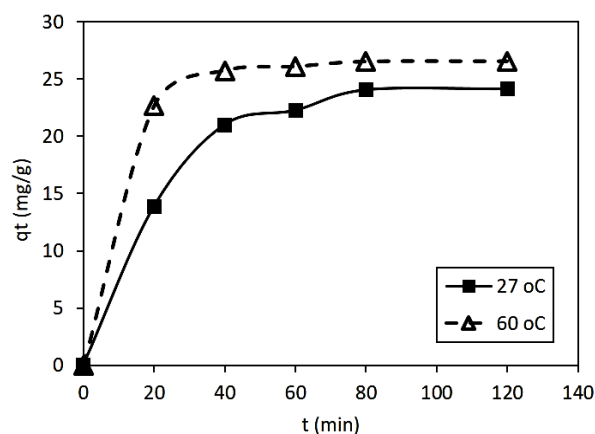
Figure 3. Effect of Contact Time on Adsorption Capacity of the LAFS-AC. Experimental Condition: 100 mL Cu(II) Ions Aqueous Solution at 509.81 mg/L, 1 g of the 0.5 M KOH LAFS-AC, 27 and 60 °C (± 1 °C), 100-rpm, pH 5 and 1 atm
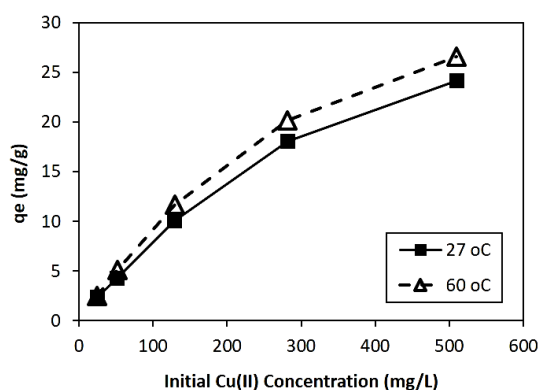
of adsorption, as revealed in Figure 3. It sharply increased at beginning of 40 min from 0 to approximately 13.88 and 21.02 mg/g at 20 and 40 min, respectively at 27 °C. Then, it slowly increased to 24.06 mg/g at 40-min contact time, and it was 24.14 mg/g at 120-min contact time. It seems that Cu(II) ions adsorption capacity did not change for the contact time of more than 80 min. Almost all the active sites on the LAFS-AC could be occupied by Cu(II) ions at 80-min contact time, and Cu(II) ions in solution was no longer being adsorben by the LAFS-AC after 80-min contact time especially when the equilibrium time was attained [25]. The same trend was also shown by the LAFS-AC at 60 °C, but it reached an equilibrium adsorption capacity faster than at 27 °C. Therefore, 120 min was chosen at the equilibrium adsorption time.

Effect of KOH concentration on adsorption capacity. As expected in the result of FT-IR analysis, the 0.5 M KOH LAFS-AC should adsorbed more Cu(II) ions compared to the 0.25 M KOH LAFS-AC because the higher amount of OH⁻ ions in the activating solution can produce higher amount active sites of hydroxyl functional group on the LAFS-AC surface [36]. As clearly shown in Figure 4, it was 22.61 mg of Cu(II) ions on 1 g of the 0.25 M KOH LAFS-AC, it was 22.14 mg of Cu(II) ions when concentration of activator being increased to 0.5 M. However, increasing KOH concentration to 0.75 M decreased the Cu(II) ions adsorption capacity to 8.99 mg/g. It could be because the higher concentration (0.75 M) of dehydrating agent of KOH can break the C–C stretch producing broken porous in the 0.75 M KOH LAFS-AC. As can be seen in Figure 1, the transmittance of the C–C stretch for the 0.75 m KOH LAFS-AC was lower than the 0.5 M KOH LAFS-AC.
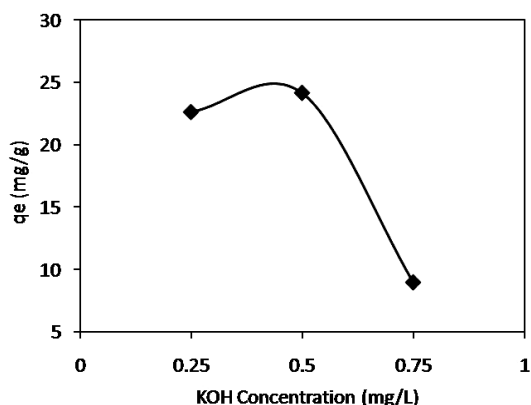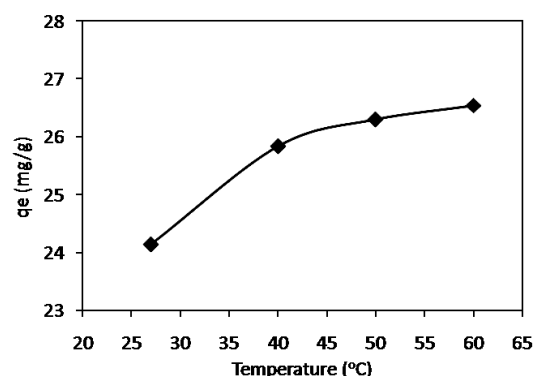
Figure 4. **Effect of KOH Concentration on Adsorption Capacity of the LAFS-AC. Experimental Condition: 100 mL Cu(II) Ions Aqueous Solution at 509.81 mg/L, 1 g of the LAFS-AC, 120-min Contact Time, 27 °C (± 1 °C), 100-rpm, pH 5 and 1 atm**

Figure 6. **Effect of Adsorption Temperature on Adsorption Capacity of the LAFS-AC. Experimental Condition: 100 mL Cu(II) Ions Aqueous Solution at 509.81 mg/L, 1 g of the 0.5 M KOH LAFS-AC, 120-min Contact Time, 100-rpm, pH 5 and 1 atm**

Figure 5. **Effect of Initial Cu(II) Ions Concentration on Adsorption Capacity of the LAFS-AC. Experimental Condition: 100 mL Cu(II) Ions Aqueous solution at 24.45-509.81 mg/L, 1 g of the 0.5 M KOH LAFS-AC, 120-min Contact Time, 27 and 60 °C (± 1 °C), 100-rpm, pH 5 and 1 atm**

decreases until attaining the saturation of active sites on the LAFS-AC.

Effect of temperature on adsorption capacity. Temperature affected Cu(II) ions adsorption onto the LAFS-AC, as revealed in Figure 6. The Cu(II) ions adsorption capacity of the LAFS-AC moderately inclined from approximately 24.14 to 25.83 mg/g when temperature of solution being increased from 27 to 40 °C, respectively. Then, it considerately increased to 26.29 and 26.54 mg/g when the temperature being moved to 50 and 60 °C, respectively. It could be reasonable when chemical adsorption was being taking place.

The overall effect of temperature on adsorption capacity can be also evaluated using Le Chatelier's principle to show chemical reaction taken place in a system [37,35] including adsorption process [38, 39]. The activation energy (E) for chemical adsorption was determined using the linear plot slope of $1/T$ versus $\ln q_e$ as given:

$$\ln q_e = q_e - \frac{E}{R}\left(\frac{1}{T}\right) \tag{1}$$

where q_e (mg/g) is Cu(II) ions adsorption capacity at temperature of T (K) presented in Figure 6, R (J/mol K) represents an ideal gas constant is 8.314. The value of T_1, T_2, T_3 and T_4 was 300.15, 313.15, 323.15 and 333.15 K, and the value of T_1, T_2, T_3 and T_4 K was 24.14, 25.83, 26.29 and 26.54 mg/g respectively. As the result, the linear equation obtained was $\ln q_e = 4.15 - 286.92/T$ (R² = 0.90), and the activation energy, E obtained was 2.385 kJ/mol. The E positive sign indicated chemical adsorption and monolayer Langmuir adsorption [39] occured in the Cu(II) ions adsorption onto the LAFS-AC.

Effect of initial Cu(II) concentration. Figure 5 shows the effect of initial Cu(II) concentration in solution on the adsorption capacity of the 0.5 M KOH LAFS-AC for different temperature. Both curves confirmed that the adsorption capacity increased moderately from 2.40 to 24.14 mg/g for the increase in initial Cu(II) concentration ion from 24.45 to 509.81 mg/L, respectively at 27 °C. The same profile was also occured at 60 °C whereas it moderately changed from 2.44 to 26.54 mg/g.

The trend could be an exponential growth whereas continueosly increasing Cu(II) ions concentration in solution from 509.81 mg/L will bring the adsorption capacity to a steady state value. It could be reasonabe because the active site on the LAFS-AC continueosly
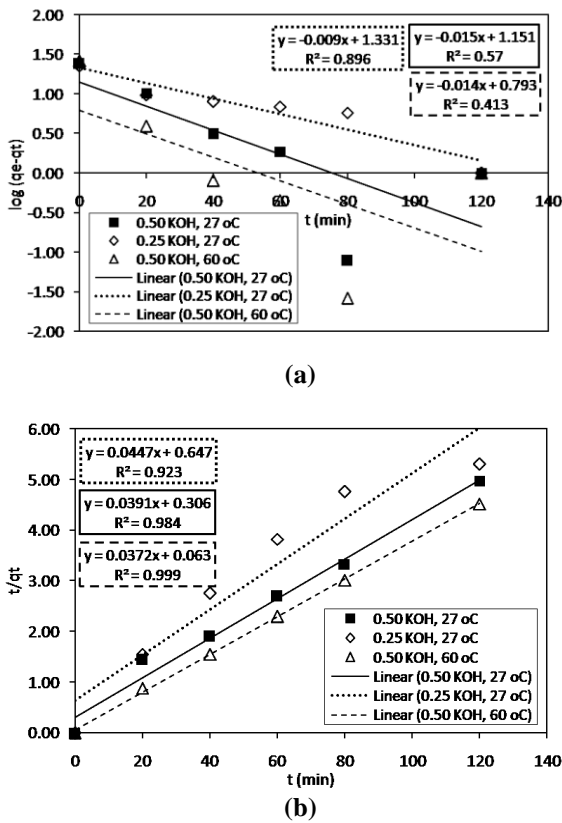
(a)

(b)

Figure 7. (a) The PFOAK and (b) the PSOAK of Cu(II) Ions Adsorption Onto the LAFS-AC. Experimental Condition: 100 mL Cu(II) Ions Aqueous solution at 509.81 mg/L, 1 g of the 0.5 M KOH LAFS-AC, 0-12 min of Contact Time, 100-rpm, pH 5 and 1 atm

Cu(II) adsorption kinetic of the LAFS-AC. The linearised expression of pseudo first-order adsorption kinetic (PFOAK) by Lagergren [40] and pseudo second-order adsorption kinetic [41] (PSOAK) is presented by equations (2) and (3), respectively [17, 23]

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_L t}{2.303}\right) \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_H q_e^2} + \frac{t}{q_e} \qquad (3)$$

where q_t (mg/g) refers tothe Cu(II) ions adsorption capacity at a of t (min), q_e (mg/g) is the adsorption capacity at equilibrium contact time, k_L (/min) and k_H (g/mg.min) denotes as the PFOAK and PSOAK rate constants, respectively.

As shown by the R^2 values in Figure 7, Cu(II) ions adsorption onto the LAFS-AC followed the PSOAK with R^2 value being 0.97 on average. The PSOAK based adsorption capacity for the 0.25 and 0.5 M KOH LAFS-AC obtained at 27 °C was approximately 22.37 and
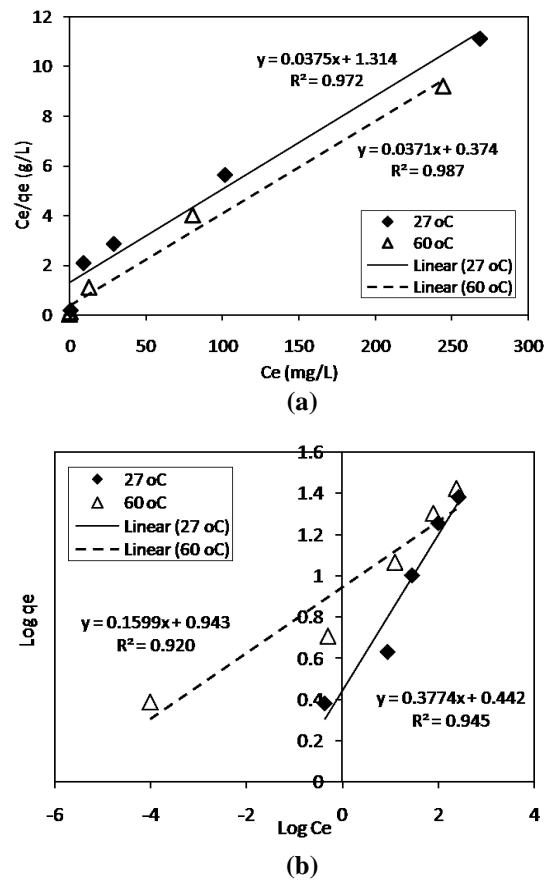

(a)

(b)

Figure 8. (a) Langmuir and (b) Freundlich isotherms of Cu(II) ions adsorption onto the LAFS-AC. Experimental condition: 100 mL Cu(II) ions aqueous solution at 24.45509.81 mg/L, 1 g of the 0.5 M KOH LAFS-AC, 12-min contact time, 100-rpm, pH 5 and 1 atm

25.57 mg/g, respectively with the PSOAK rate constants being 0.06 and 0.07 g/mg.min, respectively. These result show that increasing KOH concentration by 100% from 0.25 M increased the PSOAK based adsorption capacity and rate by 40 and 14.31%, respectively. Meanwhile, the PSOAK based adsorption capacity and rate at 60 °C were approximately 26.88 mg/g and 0.15 g/mg.min, respectively. It means that increasing temperature by 122.22% from 27 °C lifted the PSOAK based adsorption capacity and rate by 5.12 and 114.28%, respectively. Overall, the adsorption kinetic was in line with the Le Chatelier's principle of endothermic adsorption [39].

Cu(II) adsorption isotherm of the LAFS-AC. The maximum Cu(II) ions adsorption capacity by the 0.5 M KOH LAFS-AC was worked out using the Langmuir adsorption isotherm model (LAIM) [42] which can be expressed as the linear form [17,25,43]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \qquad (4)$$

where C_e (mg/L) denotes the Cu(II) ions concentration in aqueous solution at equilibrium time, q_e (mg/g) is the adsorption capacity at equilibrium time, q_m (mg/g) is the LAIM adsorption capacity, and K_L (L/mg) is the LAIM constant. The values of K_L and q_m were worked out using the slope (1/ q_m) and intercept $1/(q_m \, K_L)$ of the straight line (C_e / q_e versus C_e). The nature of Cu(II) ions adsorption onto the LAFS-AC and the adsorption isotherm type were investigated using a formula of $R_L = 1/(1+ \, K_L C_o)$. C_o (mg/L) represents the higest initial Cu(II) ions concentration in the aqueous solution. The $R_L = 0$, $R_L > 1$, $R_L = 1$, or $0 < R_L < 1$, represent the Cu(II) ion adsorption onto the LAFS-AC being irreversible, unfavorable, linear, or favorable, respectively [44]. Meanwhile, the Freundlich adsorption isotherm model (FAIM) [45], and the linear form [17,25,43] is given:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \qquad (5)$$

where K_F (L/g) is the FAIM constant presenting the FAIM adsorption capacity, and $1/n$ represents the FAIM intensity. The values of K_F and $1/n$ are determined using with the intercept (log K_F) and the slope ($1/n$) of the line of log q_e versus log C_e.

As shown in Figure 8, the LAIM gave the best trendline fitting with the R^2 value being approximately 0.98 confirming that chemical adsorption could be dominant in the Cu(II) ions adsorption onto the LAFS-AC, which was addressed in the previous discussion on the FT-IR analysis and Le Chatelier's principle of temperature effect. The R_L values obtained were 0.12 and 0.06 for 27 and 60 °C, respectively indicating favourable adsorption of Cu(II) ions onto LAFS-AC. The LAIM adsorption capacity and constant were 26.67 mg/g and 0.03 L/g, respectively at 27 °C, and becoming 26.95 mg/g and 0.09 L/g, respectively at 60 °C

Interesting to note that the maximum Cu(II) ions adsorption capacity by the LAFS-AC (26.95 mg/g) was higher than Cu(II) ions adsorption capacity by activated carbon prepared from biomass gasification (23.1 mg/g) [21], hazelnut husks (6.65 mg/g) [22], Australian pine cone (26.71 mg/g) [25], commercial activated carbon of Filtrasorb 200 (15.47 mg/g) [46], apricot stone (22.8 mg/g) [47] and rubber wood sawdust (qm = 5.72 mg/g) [48]. However, it was still lower than Cu(II) ions adsorption capacity by activated carbon prepared from watermelon (31.02 mg/g) [14], Tunisian date stones (31.25 mg/g) [23] and hazelnut shell (58.27 mg/g) [33]. For further research, bamboo-based activated carbon [49] will be considered to compate for adsorption of Cu(II).

4. Conclusion

Activated carbon prepared from *Limonia acidissima* fruit shell (LAFS-AC) was applied for adsorption of Cu(II) ions in batch mode experiments at pH 5 (±0.15), 100 rpm of magnetic stirring and 1 atm. The adsorption capacity was affected by contact time, initial Cu(II) ions concentration, KOH-activator concentration and adsorption temperature. The active site and surface morphology of the LAFS-AC were analyzed by the FT-IR and SEM. The best Cu(II) ions adsorption fitting was obtained using the pseudo second-order adsorption kinetic (R^2 = 0.94 on average), and the equilibrium adsorption capacity and adsorption rate obtained was 25.58 mg/g and 0.07 g/mg.min, respectively at 27 °C by the LAFA-AC activated using 0.5 M KOH. It increased to 26.88 mg/g and 0.15 g/mg.min, respectively at 60 °C. The Cu(II) ions adsorption followed the Langmuir adsorption isotherm model (LAIM) (R^2 = 0.98 on average). The maximum Cu(II) ions adsorption capacity was obtained at 0.5 M KOH for activation of the LAFS carbon, which was 26.95 mg/g with the LAIM constant being 0.09 L/g.

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