

AUSTRALIAN PINE CONES-BASED ACTIVATED CARBON FOR ADSORPTION OF COPPER IN AQUEOUS SOLUTION

MUSLIM A.

Process Technology Laboratory, Department of Chemical Engineering, Syiah Kuala University, No.7 Jalan Tgk. Syech Abdul Rauf, Darussalam, Banda Aceh, Indonesia
E-mail: abrar.muslim@che.unsyiah.ac.id

Abstract

The Australian Pine cones (APCs) was utilised as adsorbent material by physical and chemical activation for the adsorption Cu(II) in aqueous solution. FTIR and SEM analysis were conducted to obtain the active site and to characterise the surface morphology of the APCs activated carbon (APCs AC) prepared through pyrolysis at 1073.15 K and alkaline activation of NaOH. The independent variables effect such as contact time, Cu(II) initial concentration and the activator ratio in the ranges of 0-150 min, 84.88-370.21 mg/l and 0.2-0.6 (NaOH:APCs AC), respectively on the Cu(II) adsorption capacity were investigated in the APCs activated carbon-solution (APCs ACS) system with 1 g the APCs AC in 100 mL Cu(II) aqueous solution with magnetic stirring at 75 rpm, room temperature of 298.15 K (± 2 K), 1 atm and pH 5 (± 0.25). As the results, Cu(II) adsorption capacity dramatically increased with increasing contact time and Cu(II) initial concentration. The optimal Cu(II) adsorption capacity of 26.71 mg/g was obtained in the APCs ACS system with 120-min contact time, 340.81 mg/l initial Cu(II) and 0.6 activator ratio. The kinetics study showed the Cu(II) adsorption kinetics followed the pseudo-second-order kinetics with 27.03 mg/g of adsorption capacity, 0.09 g/mg.min of rate constant and 0.985-R². In addition, the Cu(II) adsorption isotherm followed the Langmuir model with 12.82 mg/g of the mono-layer adsorption capacity, 42.93 l/g of the over-all adsorption capacity and 0.954-R².

Keywords: Australian pine cones, Activated carbon, Adsorption, Copper.

1. Introduction

Heavy metals are hazardous pollutants in the environment, which are non-biodegradable and can be bio-accumulated in the food chain. Heavy metals can be found in the industrial wastewater streams of many industrial processes including

petroleum refining, mining, smelting, electroplating, pulp and paper making and rubber processing [1-5]. Among others, copper is one of the most hazardous heavy metals contained in the aqueous waste from chemical, electrical and mining industries [6]. It can accumulate in the tissues of the human body, and cause very bad effect in all the biological system and organ of human body [7, 8]. Therefore, it is necessary to remove copper from copper-contaminated wastewater before it is discharged to the environment.

Many processes have been studied and proposed for heavy metal removal from inorganic effluent [9], and adsorption is one of promoting and effective processes to apply [10]. Renewable natural resources modified agriculture and biological wastes have been chosen as an alternative raw material of regenerable adsorbents. This selection was based on economic considerations, the amount of raw materials are abundant and the impact on the environment is highly preferred. Various renewable lignocellulosic adsorbents had been investigated on the adsorption of copper in aqueous solutions which were utilised from Brazil nut shells, Cassava peel, tea, green tea and coarse tea, and the adsorption capacity was obtained to be 19.4, 52, 11.35, 6.37 and 7.36 mg/g, respectively [11-13]. Swedish Pine cones, European Black Pine cones and South African Pine sawdust and Canadian pine were utilised as activated carbon to adsorb ammonia, lead(II) ions, phenol and acyclovir, respectively [14-17].

Renewable natural resources modified forestry wastes especially the Australian Pine cones (APCs) has not been used as adsorbent raw material. The Australian Pine which is commonly known as *Casuarina* or *Casuarina equisetifolia L.* is fast-growing tree, and it has been introduced to more than 60 countries across Asia, Africa, America, Europe and Oceania [18]. This species widely planted for wood production, erosion control, the reclamation of coastal and the production of timber, tannin, dye and pulp [19-21]. The leaves have been employed to utilise active carbon for chromium removal [22], and the needles and cones were used to remove methyl violet 2B (MV) and anionic dye Congo red from aqueous solutions, respectively [23-24]. However, the dried APCs has not been used for heavy metal adsorption especially Cu(II) after the dried APCs falling to the ground of forest following the seeds wind dispersing, and after the seeds collection by man for plantation [25-26]. Meanwhile, the APCs is believed to consist of several kinds of fibers including alpha cellulose, hemicellulose and lignin for a very economical raw material to be utilised as adsorbent.

Therefore, this study generally aimed to utilise new material of APCs as adsorbent by physical and chemical activation for Cu(II) adsorption. The specific objectives of this study were to quantify the chemical functional groups of the raw APCs and APCs activated carbon, and to investigate the independent variables effect such as contact time, Cu(II) initial concentration and the mass ratios of NaOH and APCs activated carbon on the Cu(II) adsorption capacity of the APCs activated carbon in the APCs activated carbon-solution system. In an optimal condition, the Cu(II) adsorption kinetics of the APCs activated carbon including the kinetics constant were worked out, and the Cu(II) adsorption isotherm of the APCs activated carbon and the adsorption capacity were obtained.

2. Materials and Method

2.1. Adsorbent utilisation

Utilisation of the APCs activated carbon and all the adsorption experiments were conducted in the Process Technology Laboratory at Department of Chemical Engineering, Syiah Kuala University. An atomic absorption spectrometer (AAS) Shimadzu AA 6300 was used to determine the Cu(II) concentration in aqueous solution, which is available in the Chemical Analysis Laboratory at the Faculty of Mathematics and Science, Syiah Kuala University.

The APCs were collected from the ground of an Australian Pine (*Casuarina*) plantation area for the coastal reclamation of Tsunami at Alue Naga in Banda Aceh, Indonesia. The APCs of 1 kg was washed thoroughly using tap water then distilled water, and dried under the sun for 2 d at an average temperature of 303.15 K and average relative humidity of 12%. The dried APCs were crushed to a powder using a cleaned rice mill. Physical activation was conducted by coating the dried APCs with four layers of aluminum foil in a furnace (Nabertherm, More Than Heat 30-3000 °C, made in Germany) at 1073.15 K for 3 h to let the pyrolysis taking place. The APCs carbon was chemically activated in 500-mL of beaker glass consisting of 250 g distilled water, 25 g the APCs carbon and 5 g NaOH (97% pure from Merk) with a constant stirring speed of 75 rpm for 3 h. The APCs activated carbon was washed with distilled water and decanted to remove the excess basic, and it was filtered using vacuum filter.

The chemical activation was conducted for the mass ratios of NaOH and the APCs activated carbon in the range of 0.2-0.6. The APCs activated carbon with the varying activator composition of NaOH were separately dried in an oven (Memmert, NN-ST342M, made in Germany) at 383.15 K for 2 h to remove the excess water, and sieved to obtain a uniform size of 100 mesh. The APCs activated carbon was then ready to use.

2.2. Characterization of the APCs activated carbon

The chemical functional groups on the raw APCs and activated carbon were identified using Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra were obtained between 400 and 4000 cm^{-1} using a Shimadzu IR Prestige 21 Spectrophotometer (Shimadzu Co. Kyoto, Japan). KBr pellets (0.1% sample) were used to obtain the transmission spectra of the samples. Meanwhile, the physical morphology of the APCs powder and activated carbon surface was identified using a Scanning Electron Microscopy (SEM) of HITACHI TM3000 (Tokyo, Japan) with an accelerating voltage of 500VA 1 phase, 50/60Hz. The samples were dried in an oven at 283.15 K for about 15 min prior to the SEM analysis.

2.3. Stock solution of Cu(II)

The aqueous solution of Cu(II) was prepared by dissolving 2 g (± 0.001) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (99% pure from Aldrich) in 1000 mL distilled water in 1000-mL Erlenmeyer flask. The sample of 5 mL was taken and analysed using Atomic Absorption Spectrophotometer (AAS) to determine the concentration of stock solution. The stock solution was taken using a variable volume pipette, and

diluted with distilled water into the predetermined concentration of aqueous solution using general dilution formula for both experiments of kinetics and isotherm adsorption.

2.4. Adsorption experiments

2.4.1. Experiments of adsorption kinetics

To determine the equilibrium time of the Cu(II) adsorption on the APCs activated carbon, an experiment of Cu(II) adsorption was carried out in batch mode using the same procedure mentioned in previous work [27]. The APCs activated carbon of 1 g was placed into a 200-mL erlenmeyer flask, and it was mixed with 100 mL of Cu(II) aqueous solution with the predetermined initial concentration of 340.81 mg/L based on the AAS reading, and was stirred using a magnetic stirrer at 75 rpm, room temperature of 298.15 K (± 2 K), 1 atm and pH 5 (± 0.25). The sample of 1 mL was taken using a variable volume pipette at the predetermined contact time of 0, 15, 30, 45, 60, 75, 90 and 120 min whereas stirring was stopped for 1 min for sampling. Each sample was added to 10 mL of distilled water in a separated 20-mL vial. The dilution objective is to avoid losing adsorbate when filtering using syringe filters. The filtrate was placed in 10-mL vial for the AAS analysis. The dilution factor was taken into account to determine the concentration from the AAS reading. Based on the preliminary experiment, the adsorption reached equilibrium at 110 min of contact time. However, 120-min contact time was taken into account for all the experiments for 15-min constant time step.

The adsorption kinetics of Cu(II) on the APCs activated carbon was investigated on the optimal adsorption capacity of the APCs activated carbon in terms of Cu(II) initial concentration. Therefore, a set of experiments for obtaining adsorption capacity was conducted with the predetermined varying initial concentration of Cu(II) in the range of 84.88-370.21 mg/L based on the AAS reading, and the activator ratios of 0.2-0.6. Based on the best initial concentration of Cu(II) and activator ratio in which the optimal adsorption capacity was obtained, the same procedure of preliminary adsorption kinetics experiment was taken into account to deal with the adsorption kinetics of Cu(II) on the APCs activated carbon. All the experiments results were presented in average values of the results of duplicated each experiment with the correlation coefficients of the values being higher than 0.85.

2.4.2. Experiments of adsorption isotherm

The APCs activated carbon of 1 g was placed into a 200-mL erlenmeyer flask. To start an experiment of adsorption isotherm, Cu(II) aqueous solution of 100 mL with the predetermined varying initial concentration of Cu(II) in the range of 84.88-370.21 mg/L and the best activator composition of NaOH was put into the erlenmeyer flask and stirred using a magnetic stirrer at 75 rpm, room temperature of 298.15 K (± 2 K), 1 atm and pH 5 (± 0.25). The experiment was stopped at 119 min contact time for sampling. The samples of 1 mL were placed in a 20-mL vial and diluted with 10 mL distilled water, and filtered using a syringe filter. The filtrate was placed in 10-mL vial for the AAS analysis. Dilution factor was taken into account to determine the concentration Cu(II) in the samples from the AAS

reading. All the experiments results were presented in average values of the results of duplicated each experiment with the correlation coefficients of the values being higher than 0.85.

3. Results and Discussion

3.1. Chemical functional groups of the APCs activated carbon

The raw material of the dried APCs is shown in Fig. 1(a), and the APCs activated carbon is shown in Fig. 1(b). As can be seen in Fig. 1(a), the APCs is woody material. The APCs activated carbon is arranged in clusters with 10-20 mm in diameter.



Fig. 1. Photographs of (a) the dried APCs raw material and (b) the APCs activated carbon.

Fourier transform infrared spectroscopy (FTIR) in the spectra range of 400 and 4000 cm^{-1} was used to obtain the chemical functional groups of the raw APCs and APCs activated carbon. The FTIR spectras are shown in Fig. 2. As can be seen in Fig. 2, there are seven major absorption bands obtained from the raw APCs spectra. The first band is at 3500-3700 cm^{-1} of wavenumber with the intense band at approximately 3643.53, presenting alcohols and phenols in the O-H stretching group [28]. The second band indicates the C-H stretching of aldehyde with the band at 2700-2980 cm^{-1} and 2 peaks. The intense bands in this wide band is at approximately 2924.09 and 2858.51 cm^{-1} . The third band is the range of 1720-1740 cm^{-1} with the peak at approximately 1732.08 cm^{-1} which is assigned to the C=O stretching of aldehyde [29]. The fourth band is very weak band presenting C=C stretching at 1570-1580 cm^{-1} with the intense band at approximately 1577.77 cm^{-1} and the transmittance of 91.64%. The fifth band is associated with the C-H asymmetrical and symmetrical bendings with the band at 1317-1450 cm^{-1} [30] and the multiple intense band at approximately 1321.24, 1369.46 and 1448.54 cm^{-1} . The sixth band is at 1000-1260 cm^{-1} , refers to C-O stretching of volatile species and carboxyl acids [31] with 2 peaks at approximately 1039.63 and 1238.30 cm^{-1} . The last band is also weak indicating the C-C stretching at 400-700 cm^{-1} [30] with the peak at 462.91 cm^{-1} and the transmittance of 89.97%.

From the FTIR spectras shown in Fig. 2, it is clear that the intermolecular hydrogen bonded of O-H stretching in the raw APCs decreased due to the physical and chemical activation, and it decreased by approximately 32.72% from

the transmittance of 105.83 to 71.19% in the APCs ACS system with the activator ratio of 0.4. Moreover, increasing the activator ratio to 0.6 obviously resulted in more reduction of O-H stretching by approximately 39.29%. The activation of the raw APCs also removed a considerable amount of hydrogen from the C-H stretching the band at 2700-2980 cm^{-1} indicated by the decrease in the transmittance from approximately 93.05% to 72.96 and 66.19% for the activator ratio of 0.4 and 0.6, respectively.

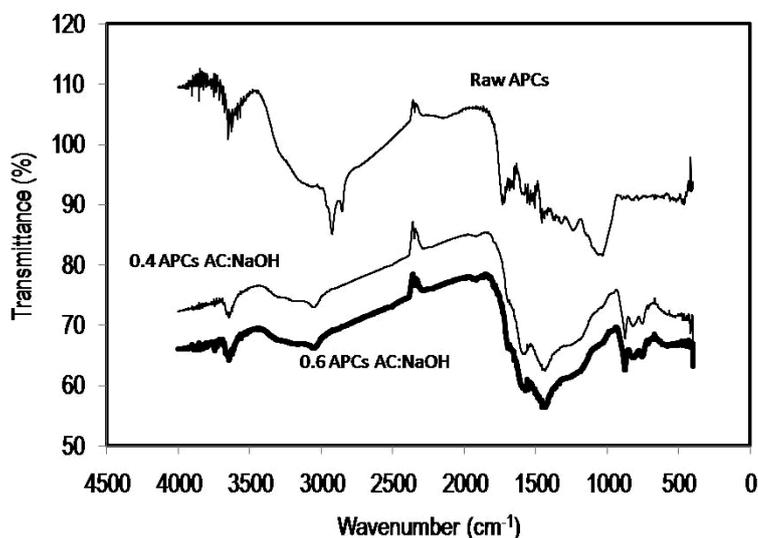


Fig. 2. The FTIR spectra of the raw APCs and the APCs activated carbon with the activator ratios of 0.4 and 0.6.

Interesting to note that the raw APCs band at 1720-1740 cm^{-1} with the peak at approximately 1732.08 cm^{-1} was absent in the APCs activated carbon, as can be observed in Fig. 2. This result indicated that favorable and volatile compounds eliminated due to the physical and chemical activation leading to breaking the C=O stretching of aliphatic and aromatic molecules [30]. The elimination of volatile species and carboxylic acids also took place during the activation, and it caused C-O stretching band being absent in the APCs activated carbon. The band of C-H asymmetrical and symmetrical with the multiple intense band was decreased in the amount of intense band and the wavenumber due to the activation. There was only one band of C-H asymmetrical and symmetrical left with the intense band of 1440.82 and 1433.11 cm^{-1} for the activator ratios of 0.4 and 0.6, respectively with the transmittance decreased to approximately 62.55 and 56.35%, respectively. Meanwhile, the transmittance of multiple intense band in the raw APCs were approximately 86.86, 87.64 and 87.84%. It means that the activation of raw APCs enabled to remove a significant amount of hydrogen.

As can be seen in Fig. 2, the weak band assigned to the C-C stretching become more clear to obtain in the FTIR spectras of APCs activated carbon especially with the activator ratio of 0.6. The band peaks of APCs activated carbon aromatic stretching are 586.36 and 574.79 cm^{-1} with the transmittance being decreasing from 89.97% in the raw APCs to 71.79 and 66.64% in the APCs activated carbon

for 0.4 and 0.6 activator ratios, respectively. The C=C stretching in the FTIR spectras of APCs activated carbon is also much more clear to observe, the band peaks are at 1581.63 and 1581.54 cm^{-1} with the transmittance being decreasing to 65.14 and 59.52% for the activator ratios being 0.4 and 0.6, respectively from 91.64% for the C=C stretching in the raw APCs. In general, activation reduces the hydrogen functional groups that attack OH ion in the solution of APCs ACS system. Thus the FTIR results have confirmed the presence of more hydroxyl functional group on the APCs activated carbon that could be the potential adsorption site for interaction with Cu(II).

3.2. Surface morphology of the APCs activated Carbon

Figures 3(a), (b), (c) and (d) show the SEM micrographs (1000-2500X) of the surface morphology of the raw APCs, the APCs carbon, the 0.4 NaOH:APCs AC and the 0.6 NaOH:APCs AC, respectively. As can be seen in Figs. 3(a) and (b), the physical activation of pyrolysis at 1073.15 K for 3 h changed the pores being almost full with substance on the raw APCs to the bubbly surface on the APCs carbon. It indicates that the physical activation does not enable lift up all the favorable and volatile compounds to leave the APCs carbon surface. In this stage, more cavities were formed under the APCs carbon surface as shown by the cracked cross section area shown by the small figure in Fig. 3(b).

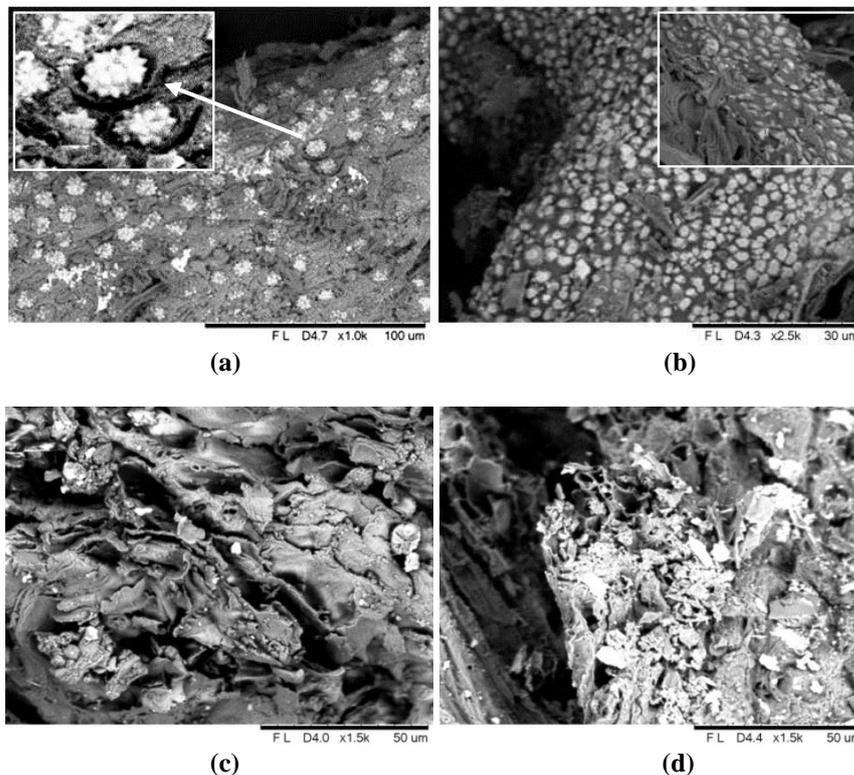


Fig. 3. The SEM micrographs of (a) the raw APCs, (b) the APCs carbon, (c) the 0.4 NaOH:APCs AC and (d) the 0.6 NaOH:APCs AC.

In contrast, it seems that the chemical activation can crack the APCs carbon surface by breaking C-H, C-O, C=O, C-C and C=C stretchings. As a result, the surface matrix of the APCs carbon was changed leading to the formation of irregular pores on and under the APCs AC surface, as shown in Fig. 3(c). In addition, the more the activator ratio, the higher porosity on the internal and external surface were formed, as revealed in Fig. 3(d), and the more Cu(II) should be adsorbed on the APCs AC.

3.3. Equilibrium concentration of Cu(II) on the APCs AC system

A preliminary experiments of Cu(II) adsorption on the APCs activated carbon were conducted to obtain a contact time where Cu(II) adsorption on the APCs activated carbon reaching an equilibrium condition. The amount of Cu(II) adsorbed on the APCs activated carbon can be calculated from the decrease of Cu(II) concentration in solution.

Figure 4 shows the Cu(II) concentration in solution versus adsorption time in the APCs activated carbon-solution (APCs ACS) system. In an equilibrium condition, there should be no more decrease of Cu(II) concentration in solution. As shown in Fig. 4, Cu(II) concentration in solution during 90 min of adsorption changes dramatically from approximately 340.81 mg/L at 0-min contact time for the three activator ratios. It increases moderately from approximately 233.48 and 21.25 mg/L for the activator ratios of 0.2 and 0.4, respectively at 105-min contact time to 249.12 and 217.25 mg/L for the activator ratios of 0.2 and 0.4, respectively at 120-min contact time. Then, it decreases moderately from approximately 80.54 mg/L at 105-min contact time to 73.76 mg/L at 120-min contact time for the activator ratio of 0.6. However, as clearly shown in Fig. 4, Cu(II) concentration in solution for the three activator ratios reach approximately constant values at time beyond 120 min. Therefore, the contact time of 120 min was taken into account for equilibrium of Cu(II) adsorption on the APCs activated carbon for all the rest experiments in the APCs ACS system.

3.4. Effect of contact time on Cu(II) adsorption

Contact time dramatically affects Cu(II) mass on the APCs activated carbon in the APCs ACS system. As highlighted in Fig. 5, the amount of Cu(II) adsorbed per 1 g of APCs activated carbon sharply increases in the beginning 15-min contact time from 0 to approximately 20.06, 23.06 and 25.88 mg/g for the activator ratios of 0.2, 0.4 and 0.6, respectively. However, Cu(II) adsorption capacity sharply decreases during the following 30-min contact time to 7.58 and 11.54 mg/g for the activator ratios of 0.2 and 0.4, respectively. In contrast, it slowly decrease to 25.31 for 0.6 activator ratio. Then, it increases moderately over the rest contact time until reaching the equilibrium Cu(II) adsorption of 9.17, 12.36 and 26.71 mg/g for the activator ratios of 0.2, 0.4 and 0.6, respectively.

Cu(II) adsorption capacity is approximately 9.17, 12.36 and 26.71 mg/g for the activator ratios of 0.2, 0.4 and 0.6, respectively. This significant increase of adsorption capacity for gradual increase of the activator ratios is reasonable according to the FTIR spectras, because the transmittance of the C=C stretching significant decreased from 65.59% to 65.14 and 59.52% for gradual increase of

the activator ratios from 0.2 to 0.4 and 0.6, respectively. Overall, Cu(II) adsorption capacity of the APCs activated carbon with 0.6 activator ratio is much higher than the one with 0.2 and 0.4 activator ratios. In addition, the Cu(II) adsorption capacity over contact time is more stable for the activator ratio of 0.6 compared to 0.2 and 0.4. These results justified that 0.6 activator ratio is the best in terms of maximum Cu(II) adsorption capacity of the APCs activated carbon.

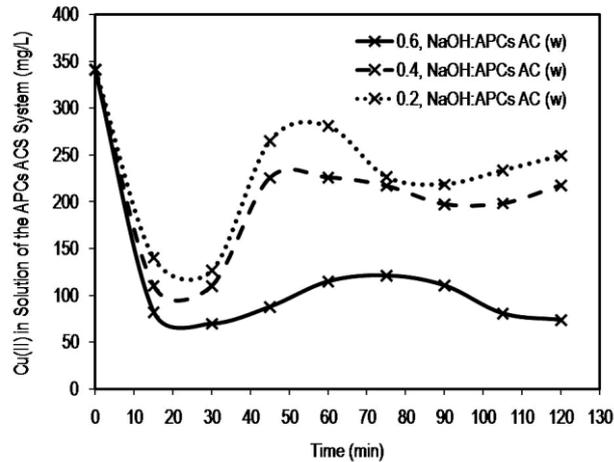


Fig. 4. Cu(II) concentration in solution versus adsorption time for determining the equilibrium time in the APCs ACS system with 1 g the APCs AC and 100 mL aqueous solution of initial Cu(II) concentration being 340.81 mg/L, the mass ratios of NaOH and APCs activated carbon being in range of 0.2-0.6, magnetic stirring at 75 rpm, room temperature of 298.15 K (± 2 K), 1 atm and pH 5 (± 0.25).

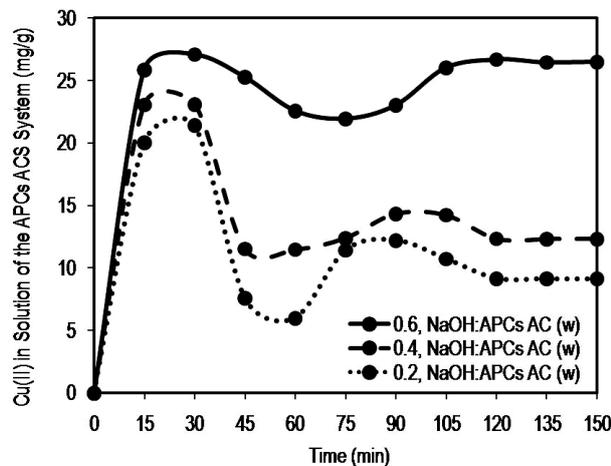


Fig. 5. Adsorption time versus Cu(II) adsorption capacity of the APCs activated carbon in the APCs ACS system with 1 g the APCs AC and 100 mL aqueous solution of initial Cu(II) concentration being 340.81 mg/L, the mass ratios of NaOH and APCs activated carbon being in range of 0.2-0.6, magnetic stirring at 75 rpm, room temperature of 298.15 K (± 2 K), 1 atm and pH 5 (± 0.25).

3.5. Effect of Cu(II) initial concentration

The experiments with a wide range of predetermined initial concentration of Cu(II) were conducted to investigate the effect of Cu(II) initial concentration on the adsorption capacity of the APCs activated carbon as adsorbent in the APCs ACS system. The results of APCs activated carbon-solution system with varying initial concentration of 84.88-370.21 mg/L and the best mass ratio of NaOH and APCs AC being 0.6 are shown in Fig. 6.

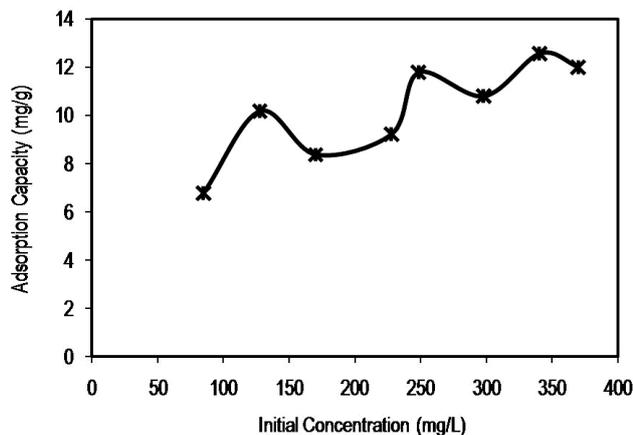


Fig. 6. Effect of initial Cu(II) concentration in solution on the adsorption capacity of the APCs ACS system with 1 g the APCs AC and 100 mL aqueous solution of initial Cu(II) concentrations in range of 84.88-370.21 mg/L, the best activator ratio of NaOH and APCs activated carbon being 0.6, magnetic stirring at 75 rpm, room temperature of 298.15 K (± 2 K), 1 atm and pH 5 (± 0.25).

As can be seen in Fig. 6, the Cu(II) adsorption capacity of the APCs activated carbon oscillatory increases leading to an exponential growth over Cu(II) initial concentration in solution. It is approximately 6.79, 10.18, 8.37, 9.23, 11.79, 10.80, 12.58 and 12.01 mg/g for the Cu(II) initial concentration of 84.88, 127.82, 170.41, 228.01, 248.62, 298.21, 340.81 and 370.21 mg/L, respectively. As a result, the Cu(II) initial concentration in solution of 340.81 is the best initial concentration of Cu(II) in range of 84.88-370.21 mg/L which yields the highest adsorption capacity of Cu(II) on the APCs activated carbon.

3.6. Cu(II) adsorption kinetics on the APCs activated carbon

Adsorption kinetics of Cu(II) represent the amount of Cu(II) adsorbed by the APCs activated carbon per unit of time. It can be obtained by measuring the change in Cu(II) adsorption capacity of the APCs activated carbon over time, which is presented in a rate constant of Cu(II) adsorption. The pseudo-first-order model [32] and the pseudo-second-order model [33] shown by Eqs. (1) and (2), respectively were taken into account to obtain the rate constant of Cu(II) adsorption by the APCs activated carbon:

$$\frac{dq_t}{dt} = k_L (q_e - q_t) \quad (1)$$

$$\frac{dq_t}{dt} = k_H (q_e - q_t)^2 \quad (2)$$

where q_t (mg/g) denotes the Cu(II) adsorption capacity at the time of t (min), q_e (mg/g) represents the adsorption capacity in equilibrium, k_L is the pseudo-first-order rate constant (min^{-1}), and k_H is the pseudo-second-order rate constant ($\text{g/mg}\cdot\text{min}$). Taking integration of Eqs. (1) and (2) with the initial conditions $q_t = 0$ mg/g at $t = 0$ s and $q_t = q$ mg/g at $t = t$ s, Eqs. (1) and (2) can be defined as Eqs. (3) and (4), respectively:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_L t}{2.303} \right) \quad (3)$$

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

A rate constant of Cu(II) adsorption kinetics in the APCs ACS system was determined using the data presented in Fig. 5 whereas the highest Cu(II) adsorption capacity of the APCs activated carbon was obtained in the APCs ACS system with the best activator ratio of 0.6 and Cu(II) initial concentration of 340.81 mg/L. The rate constants, k_L and k_H of Cu(II) adsorption kinetics were worked out by taking the slope of straight lines in Figs. 7 and 8, respectively. As the results, the rate constants, k_L and k_H of Cu(II) adsorption kinetics is approximately 0.018 min^{-1} and $0.09 \text{ g/mg}\cdot\text{min}$, respectively. The Cu(II) adsorption capacity of the APCs activated carbon, q_e being approximately 5.99 and 27.03 mg/g for the pseudo-first-order and the pseudo-second-order kinetics, respectively with the correlation coefficients, R^2 of 0.43 and 0.98, respectively. The R^2 values imply that the Cu(II) adsorption kinetics on the APCs activated carbon follows the pseudo-second-order kinetics.

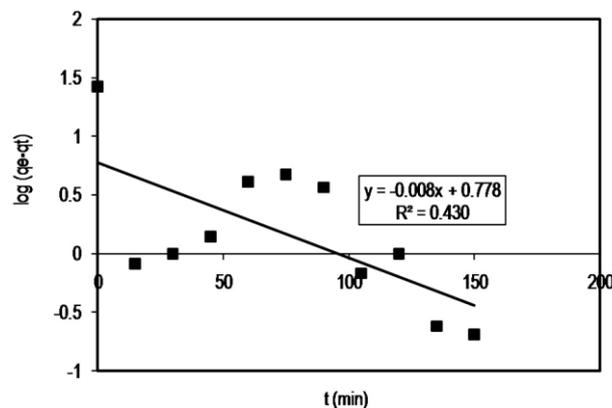


Fig. 7. Pseudo-first-order kinetics of Cu(II) adsorption on the APCs activated carbon in the APCs ACS system with 1 g the APCs AC and 100 mL aqueous solution with the best initial Cu(II) concentration of 340.81 mg/L, the best activator ratio of NaOH and APCs activated carbon being 0.6, magnetic stirring at 75 rpm, room temperature of 298.15 K (± 2 K), 1 atm and pH 5 (± 0.25).

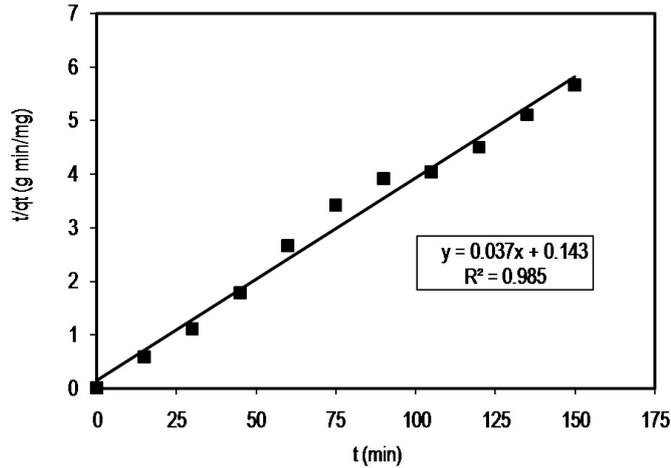


Fig. 8. Pseudo-second-order kinetics of Cu(II) adsorption on the APCs activated carbon in the APCs ACS system with 1 g the APCs AC and 100 mL aqueous solution with the best initial Cu(II) concentration of 340.81 mg/L, the best activator ratio of NaOH and APCs activated carbon being 0.6, magnetic stirring at 75 rpm, room temperature of 298.15 K (± 2 K), 1 atm and pH 5 (±0.25).

3.7. Cu (II) adsorption isotherm

The adsorption isotherm models of Langmuir and Freundlich were taken into account to investigate the adsorption isotherm of Cu(II) on the APCs activated carbon. The data of Cu(II) adsorption were fitted to the models in order obtain of the maximum capacity of Cu(II) presented in the adsorption isotherm constants. The Langmuir model [34] is linearized to Eq. (5):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \tag{5}$$

where C_e (mg/L) denotes as the equilibrium concentration of Cu(II) in solution, q_e (mg/g) represents the adsorption capacity in equilibrium, q_m (mg/g) is the monolayer adsorption capacity, and K_L (l/g) is the Langmuir over-all adsorption capacity. Plotting C_e / q_e versus C_e for the adsorption isotherm of Cu(II) results in a straight line with the slope, $1 / q_m$ and the intercept, $1 / (q_m K_L)$ as can be obtained from Fig. 9. Meanwhile, the linear form of the Freundlich model [35] (Freundlich 1906) is expressed as Eq. (6):

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \tag{6}$$

where K_F (l/g) is the Freundlich over-all adsorption capacity, $1/n$ denotes as the adsorption intensity. By plotting $\log q_e$ against $\log C_e$ for the adsorption isotherm of Cu(II) results in a straight line with the slope, $1/n$ and the intercept, $\log K_F$ as can be obtained from Fig. 10.

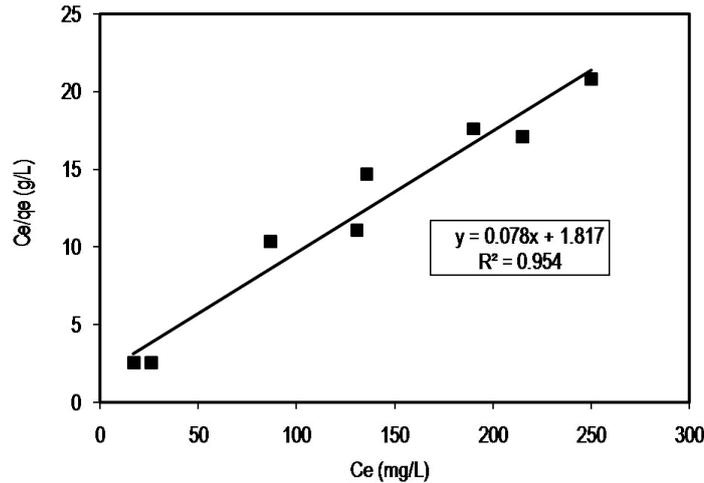


Fig. 9. Langmuir isotherm for Cu(II) adsorption in the APCs ACS system with 1 g the APCs AC and 100 mL aqueous solution of initial Cu(II) concentrations in range of 84.88-370.21 mg/L, the best activator ratio of NaOH and APCs activated carbon being 0.6, magnetic stirring at 75 rpm, room temperature of 298.15 K (± 2 K), 1 atm and pH 5 (± 0.25).

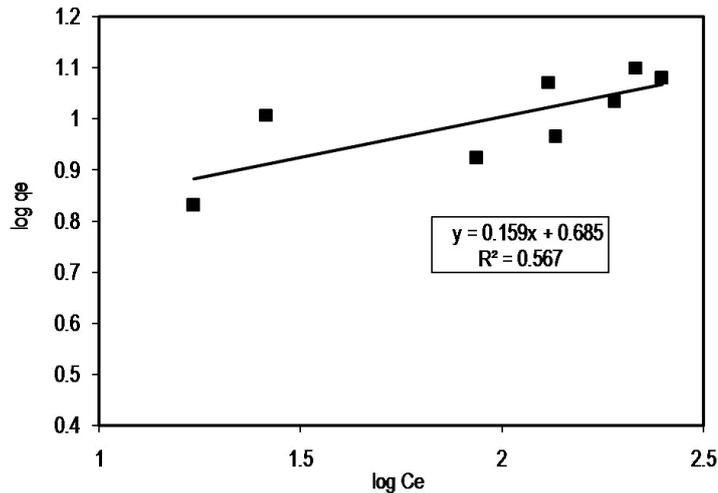


Fig. 10. Freundlich isotherm for Cu(II) adsorption in the APCs ACS system with 1 g the APCs AC and 100 mL aqueous solution of initial Cu(II) concentrations in range of 84.88-370.21 mg/L, the best activator ratio of NaOH and APCs activated carbon being 0.6, magnetic stirring at 75 rpm, room temperature of 298.15 K (± 2 K), 1 atm and pH 5 (± 0.25).

As highlighted in Figs. 9 and 10, the correlation coefficients (R^2) of the Cu(II) adsorption isotherm linear plot is approximately 0.95 and 0.57 for the Langmuir and Freundlich models respectively. The parameters in the Langmuir model were obtained, and the q_m and K_L values were 12.82 mg/g and 42.93 l/g, respectively. Meanwhile, the parameters in the Freundlich model were calculated, and the n and

K_F values were worked out to be 6.29 and 4.84 l/mg, respectively. Overall, the adsorption isotherm of Cu(II) on the APCs activated carbon follows the Langmuir model. Overall, the APCs AC adsorption capacity of 12.82 mg/g in this work is less than the Brazil nut shells adsorbent capacity (19.4, 52 mg/g), and more than the adsorbent capacity prepared from Cassava peel (11.35 mg/g), green tea (6.37 mg/g) and coarse tea (7.36 mg/g) [11-13].

4. Conclusions

The Australian Pine is fast-growing tree which has been planted around the world. The Australian Pine cones (APCs) is promoting renewable natural resource of forestry wastes, and can be utilised as adsorbent material. The APCs activated carbon (APCs AC) was prepared by pyrolysis at 1073.15 K and the APCs carbon was chemically activated using NaOH. The surface morphology of the APCs AC was successfully characterised using FTIR and SEM. The effect of independent variables on the Cu(II) adsorption capacity were investigated by conducting experiments on the APCs activated carbon-solution (APCs ACS) system with varying contact time in the range of 0-150 min, Cu(II) initial concentration in the range of 84.88-370.21 mg/L, and the mass activator ratio (NaOH:APCs AC) in the range of 0.2-0.6 respectively. The system consisted of 1 g the APCs AC and 100 mL Cu(II) aqueous solution with magnetic stirring at 75 rpm, room temperature of 298.15 K (± 2 K), 1 atm and pH 5 (± 0.25). The results showed that Cu (II) adsorption capacity dramatically increased over the increasing contact time and Cu(II) initial concentration. An optimum condition was obtained for the highest Cu (II) adsorption capacity of 26.71 mg/g in the APCs ACS system whereas, 120-min contact time, 340.81 mg/L initial Cu(II), and 0.6 activator ratio were applied. As the result of kinetics study, the pseudo-second-order kinetics was reliable model to represent the Cu(II) adsorption kinetics on the APCs AC with the adsorption capacity and kinetics rate constant being 27.03 mg/g and 0.09 g/mg.min, respectively with the correlation coefficient, R^2 of 0.985. Moreover, the Cu(II) adsorption isotherm followed the Langmuir model with the mono-layer adsorption capacity and over-all adsorption capacity being 12.82 mg/g and 42.93 l/g, respectively with the correlation coefficient, R^2 of 0.954.

References

1. Hawkes, S.J. (1997). What is a heavy metal? *Journal of Chemical Education*, 74(11), 1374-1380.
2. Srivastava, N.K.; and Majumder, B.C. (2008). Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. *Journal of Hazardous Materials*, 151(1), 1-8.
3. Bala, M.; Shehu, R.A.; and Lawal, M. (2008). Determination of the level of some heavy metals in water collected from two pollution - Prone irrigation areas around Kano Metropolis. *Bayero Journal of Pure and Applied Sciences*, 1(1), 6-38.
4. Yan-Biao, G.; Hong, F.; Chong, C.; Chong-Jian, J.; Fan, X.; and Ying, L. (2013). Heavy metal concentrations in soil and agricultural products near an industrial district. *Polish Journal of Environmental Studies*, 22(5), 1357-1362.

5. Dimple, L. (2014). Adsorption of heavy metals: A review. *International Journal of Environmental Research and Development*, 4(1), 41-48.
6. Minamisawa, M.; Minamisawa, H.; Yoshida, S.; and Takai, N. (2004). Adsorption behavior of heavy metals on biomaterials. *Journal of Agricultural and Food Chemistry*, 52(18), 5606-5615.
7. Theophanides, T.; and Anastassopoulou, J. (2002). Copper and carcinogenesis. *Critical Reviews in Oncology/Hematology*, 42(1), 57-64.
8. Carl, L.K.; Harry, J.M.; and Elizabeth, M.W. (2003). *A review: The impact of copper on human health*. New York: International Copper Association Ltd.
9. Eccles, H. (1999). Treatment of metal-contaminated wastes: Why select a biological process? *Trends in Biotechnology*, 17(12), 462-465.
10. Leung, W.C.; Wong, M.F.; Chua, H.; Lo, W.; Yu, P.H.F; and Leung, C.K. (2000). Removal and recovery of heavy metals by bacteria isolated from activated sludge treating industrial effluents and municipal wastewater. *Water Science and Technology*, 41(12), 233-240.
11. Basso, M.C.; Cerrella, E.G.; and Cukierman, A.L. (2002). Lignocellulosic materials as potential biosorbents of trace toxic metals from wastewater. *Industrial and Engineering Chemistry Research*, 41(15), 3580-3585.
12. Moreno-Pirajan, J.C.; and Giraldo, L. (2010). Adsorption of copper from aqueous solution by activated carbons obtained by pyrolysis of cassava peel. *Journal of Analytical and Applied Pyrolysis*, 87(2), 188-193.
13. Baquero, M.C.; Giraldo, L.; Moreno, J.C.; Suárez-García, F.; Martínez-Alonso, A.; and Tascón, J.M.D. (2003). Activated carbons by pyrolysis of coffee bean husks in presence of phosphoric acid. *Journal of Analytical and Applied Pyrolysis*, 70(2), 779-784.
14. Birbas, D. (2011). *Preparation of activated carbon: Forest residues activated with phosphoric acid and zinc sulfate*. Master Thesis. Sweden: Department of Chemical Engineering, Royal Institute of Technology.
15. Momčilović, M.; Purenović, M.; Bojić, A.; Zarubica, A.; and Randelović, M. (2011). Removal of lead(II) ions from aqueous solutions by adsorption onto pine cone activated carbon. *Desalination*, 276(1-3), 53-59.
16. Mukosha, L.; Onyango, M.S.; Ochieng, A.; and Kasaini, H. (2013). Development of better quality low-cost activated carbon from South African pine tree (*Pinus patula*) sawdust: Characterization and comparative phenol adsorption. *International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering*, 7(7), 228-238.
17. Jain, S.; Kumar, P.; Vyas, R.K.; Pandit, P.; and Dalai, A.K. (2014). Adsorption optimization of acyclovir on prepared activated carbon. *The Canadian Journal of Chemical Engineering*, 92(9), 1627-1635.
18. Julissa, R.S.; and Pedro, R.S. (2013). *Datasheet: Casuarina equisetifolia (casuarina)*. Washington DC: Botany-Smithsonian NMNH.
19. Elfers, S.C. (1988). *Element stewardship abstract for casuarina equisetifolia Australian pine*. Virginia: The Nature Conservancy.
20. Snyder, S.A. (1992). *Casuarina spp. In: Fire effects information system*. Rocky Mountain: U.S. Department of Agriculture, Forest Service.
21. Swearingen, J.M. (1997). *Australian pine*. Washington DC: National Park

- Service, Plant Conservation Alliance, Alien Plant Working Group.
22. Ranganathan, K. (2000). Chromium removal by activated carbons prepared from *Casuarina equisetifolia* leaves. *Bioresource Technology*, 73(2), 99-103.
 23. Dahri, M.K.; Kooh, M.R.R.; and Lim, L.B.L. (2013). Removal of methyl violet 2b from aqueous solution using *Casuarina equisetifolia* needle. *Environmental Chemistry*, 2013, Article ID 619819.
 24. Dawood, S.; Sen, T.K.; and Phan, C. (2013). Synthesis and characterisation of novel-activated carbon from waste biomass pine cone and its application in the removal of Congo red dye from aqueous solution by adsorption. *Water, Air, & Soil Pollution*, 225:1818.
 25. Pinyopusarerk, K.; Kalinganire, A.; Williams, E.R.; and Aken, K.M. (2004). *Evaluation of international provenance trials of Casuarina equisetifolia*. Canberra: Australian Centre for International Agricultural Research.
 26. Global Invasive Species Database (2005). *Casuarina equisetifolia (tree)*. New Zealand: the Invasive Species Specialist Group (ISSG).
 27. Muslim, A.; Zulfian, Ismayanda, M.H.; Devrina, E.; and Fahmi H. (2015). Adsorption of Cu(II) from the aqueous solution by chemical activated adsorbent of areca catechu shell. *Journal of Engineering Science and Technology*, 10(12), 1654-1666.
 28. Yang, T.; and Lua, A.C. (2003). Characteristics of activated carbons prepared from pistachio-nut shells by physical activation. *Journal of Colloid and Interface Science*, 267(2), 408-417.
 29. Yagmur, E.; Ozmak, M.; and Aktas, Z. (2008). A novel method for production of activated carbon from waste tea by chemical activation with microwave energy. *Fuel*, 87(15-16), 3278-3285.
 30. Hesas, R.H.; Niya, A.A.; Daud, W.M.A.W.; and Sahu, J.N. (2003). Activated carbon sorbent. *Bio Resources*, 8(2), 2950-2966.
 31. Silverstein, R.M.; Bassler, G.C.; and Morrill, T.C. (1981). *Spectrometric identification of organic compounds*. 4th ed. New York: John Wiley and Sons.
 32. Lagergren, S. (1989). About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademies Handlingar*, 24(4), 1-39.
 33. Ho, Y.S.; Wase, D.A.J.; and Forster, C.F. (1996). Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat. *Environmental Technology*, 17, 71-77.
 34. Langmuir, I. (1918). The adsorption of gases on plane surface of glass, mica and platinum. *Journal of the American Chemical Society*, 40(9), 1361-1403.
 35. Freundlich, H. (1906). Adsorption in solution. *The Journal of Physical Chemistry*, 57, 384-410.