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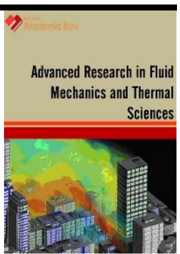

# Preliminary Study of Novel Coal Spills-based Physical Activated Carbon for Copper ions Adsorption in Aqueous Solution: Kinetics and Isotherms

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Dadang Ramadhan[1], Mahidin[2], Abrar Muslim[2,*], Sri Aprilia[2], Nasrul Arahman[1], Saiful[3], Maizirwan Mel[4]

[1] Graduate School of Environmental Management, Postgraduate Program, Universitas Syiah Kuala, Darussalam, Banda Aceh, Indonesia
[2] Department of Chemical Engineering, Faculty of Engineering, Universitas Syiah Kuala, Darussalam, Banda Aceh, Indonesia
[3] Department of Chemistry, Faculty of Mathematics and Science, Universitas Syiah Kuala, Darussalam, Banda Aceh, Indonesia
[4] Department of Biotechnology Engineering, Faculty of Engineering, International Islamic University, Malaysia

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**ABSTRACT**

This study proposed a novel activated carbon which was prepared from coal spills by physical activation. It was activated in tube furnace at 500 °C with nitrogen injection. Based on Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy analyses, the coal spills-based activated carbon (CSFAC) was expected to have more pores and cavities compared to the untreated coal spills (UCS). This preliminary study focused on adsorption kinetics and isotherms by investigating separately the effects of two independent variables i.e. contact time and initial Cu(II) ions concentration. The temperature of ion solution was set at 30 °C (1 atm) and initial pH 5. The Cu (II) ions adsorbed onto the CSFAC and USC had best fitting to the pseudo-second-order kinetics model with $R^2$ being 1.000 and 0.978, respectively. The Cu(II) ions equilibrium adsorption capacity and adsorption rate of the CSFAC were 90.909 mg/g and 0.093 g/mg.min respectively and they tracked well Freundlich adsorption isotherms with $R^2$ being 0.811 and 0.917, respectively. The Freundlich-based pore volume and adsorption intensity were 3.861 L/mg and 1.132 respectively. The Brunauer-Emmett-Teller surface area and total pore volume of the CSFAC were approximately 50.848 $m^2/g$ and 0.018 cc/g respectively. Based on this research, CSFAC was found to be a good potential candidate to be used in water treatment in the near future.

***Keywords:***
Coal spills; activated carbon; adsorption; copper; kinetics; isotherms

## 1. Introduction

The existence of heavy metals ions in the surface water and groundwater creates a pollution problem in the environment. Undegradable and very toxic heavy metals can affect water quality and cause serious problems on the bodies of animals and humans [1]. Heavy metals can accumulate in

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[*] *Corresponding author.*
*E-mail address: abrar.muslim@che.unsyiah.ac.id (Abrar Muslim)*

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the human body through the food chain leading to a continuous increase of the ions concentration. Copper is one of the heavy metals which results in human health problem when exceeding the required concentrations limits. It can cause malfunction of organs and tissues such as kidney damage, stomach distress, anemia and even death [2-4]. Copper is mostly widespread in the environment due to human activity. It is used in electroplating, electrical conductor and circuit wires production, chemical reagents, pigments and paint industries, fertilizer industry, refining of petroleum, agricultural and mining operations [5-8]. Several process technologies and methods such as ion exchange, precipitation, solvent extraction, oxidation [9], neutralization [10], separation using membrane [11], bioremediation [12] and adsorption [13] have been proposed to reduce Cu(II) concentration in its solution. Adsorption is the better one because it is an inexpensive and simple process and less energy use [14-16].

In general, the activated carbon (AC) has a great specific surface area. Due to its high grade of microporosity, it has been used widely for industrial applications and medical uses. Its global consumption increased and it is expected to reach approximately 2.8 million tons by 2022 [17]. Most of activated carbon has been produced commercially using coal as raw material [17] which had been developed in the twentieth century [19- 23]. Low cost organic solid waste has been used as the AC raw material such as agricultural wastes. Among others, hazelnut husks and shell [24,25], pecan shell [26], Tunisian date stones [27], cassava peel [28], corncob [29], Australian pine cones [30], *Myristica fragrans* and *Pithecellobium jiringa* shell [31,32] and areca catechu stem [33] had been proposed as an AC raw material for copper adsorption.

Coal spills created an environmental impact not only on the aquatic ecosystems and marine environment but also the coastal areas. The spills can cause hundreds to thousands of tons of coal to be deposited in coastal rivers and areas. For example, approximately 1,500 tons of coal spilled into the Magdalena river in 1995 [34], 5,400 tons of coal spills in Colombia marine [35], 17,000 and 100,000 tons of unburnt coal into the marine environment of Spain, Italy and South Africa [36], and 7,000 tons of coal into the Sumatera coast of Aceh [37]. It was rejected to use, and it became solid waste in the coastal areas. It would be valuable and environmentally friendly to use coal spills as a raw material of activated carbon and there has not been any study on this matter being published.

Therefore, the novel in the present study is the use of coal spills to prepare activated carbon by physical activation. Its chemical functional groups and morphology structure were analyzed using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM), respectively. Nova Station C (Quantachrome Instruments 11.0, USA) was used to obtain its Brunauer-Emmett-Teller (BET) surface area and total pore volume. This preliminary study focuses on adsorption kinetics and isotherms by investigating separately the effects of two independent variables i.e. contact time and initial Cu(II) ions concentration solution. The results were compared to Cu(II) adsorption using an untreated coal spills conducted in the present study and other results of Cu(II) adsorption using organic solid waste in the previous studies.

## 2. Methodology

### *2.1 Material Preparation*

Coal spills (CS) which was polluting Lampuuk Beach in Aceh Besar district, Aceh Province (Figure 1) was collected. 3 kilograms of coal spills were rinsed thoroughly using tap water and finally using distilled water. After that, they were dried under the sun for 7 days at 30 °C (± 1 °C) on the average [31]. 0.5 kg of CS was milled in a ball mill and sieved into 100-120 mesh. To pyrolyze, 100 g of dried coal spills in a tube furnace (TF80/120/160, 300-1500 °C, Human Lab Inc. made in Korea) was heated with 5 ml/min of nitrogen injection and heating rate of 45 °C/min [33]. After 10 min 27 sec of pyrolysis, it reached the final temperature of 500 °C (± 1 °C) and had been kept for 30 min of physical activation. Finally, the coal spills-based physical activated carbon (CSFAC) was washed using reverse osmosis (RO) water. The CSFAC was filtered and dried using an oven at 110 ° C until the CSFAC mass being constant. The other 100 g of coal spills was untreated of physical activation. It was dried using an oven drier (NN-ST342M, Memmert, Western Germany) at 110 ° C until the untreated coal spills (UCS) mass being constant. Both the CSFAC and UCS were stored in two sealed bottles separately for sample analysis and adsorption experiments. The chemical functional groups and structure of samples were analyzed and characterized using the FTIR and SEM, respectively. The surface area and total pore volume of samples were analyzed using Nova Station C (Quantachrome Instruments 11.0, USA).

**Fig. 1.** Coal spills (CS) of 7,000 tons was polluting Lampuuk Beach in Aceh Besar district, Aceh Province. The photo was taken by Abrar Muslim on August 7th 2018

A stock Cu(II) aqueous solution of 500 mg/L was made by dilution 2.02 g (±0.01) $CuSO_4.5H_2O$ (Aldrich, 99% pure) into one liter of distilled water in one liter glass beaker [30]. The 5 mL sample was pipetted for analysis using Atomic Absorption Spectrophotometer (AAS, Shimadzu AA 6300, Japan) to quantify the Cu(II) ions stock solution concentration. The desired initial Cu(II) ions concentration for the adsorption experiment was prepared by dilution [31].

### *2.2 Experiments of Cu(II) Ions Adsorption*

Batch mode of Cu(II) adsorption experiments were carried out based on the previous studies [30,32]. The CSFAC adsorption systems consisted of 100 mL Cu(II) ions aqueous solution, 1 g of the CSFAC in a 200-mL glass beaker. It was stirred at 100-rpm, 30 °C (± 1 °C), 1 atm and initial pH 5 (±0.25) [30]. The Cu(II) adsorption capacity of the CSFAC was attained over contact time in the range of 0-60 min and the initial Cu(II) ions concentration of 5.001–500.100 mg/L based on the AAS analysis. The adsorption kinetics and isotherms of Cu(II) ions were determined based on the contact time and initial Cu(II) ions concentration, respectively.

## **3. Results and discussion**

### *3.1 The Transmission Spectra of the UCS and CSFAC*

Figure 2 shows the transmission spectra of the UCS and CSFAC at wavenumber 400–4000 $cm^{-1}$. As can be seen by the UCS spectrum in Figure 2, a strong band at a wavenumber range of 3515-3694 cm$^{-1}$ with an intense band at 3650 cm$^{-1}$ was associated with O-H stretch (hydroxyl groups) [30,38]. A band at 2810-2985 cm$^{-1}$ with 2 peaks at 2850 and 2900 cm$^{-1}$ were linked to C–H stretch (alkenes). The NCO stretch (cyanate) was at a weak band of 2341-2398 cm$^{-1}$ with an intense band at 2370 cm$^{-1}$. Multiple bands of the C-O and C=C strechs at 1032-1657 cm$^{-1}$ were associated to ether and aromatic rings respectively with the peaks at 1050, 1520 and 1621 cm$^{-1}$ [31,39]. The last one is C-H 'oop' stretch (aromatics) a bands at 682-897 cm$^{-1}$ with an intense band at 825 cm$^{-1}$. The UCS transmittance of O-H stretch, C–H stretch, C=C stretch, C-O stretch and C-H 'oop' stretch was approximately at 71.86, 64.74, 56.37, 55.93, and 59.29 % respectively. Meanwhile, the CSFAC transmittance was 86.60, 87.83, 76.56, 78.49 and 79.03 % respectively. As clearly shown by the CSFAC spectrum in Figure 2, except for the NCO stretch, all the transmittance of chemical functional groups increased after physical activation. Moreover, the NCO stretch was not apparent in the CSFAC. It means that physical activation almost removed all volatile matter in the UCS leading to more pores and cavities on the CSFAC, which has the same expectation with the previous studies [30,31]. It was expected that the total surface area and pore volume of the CSFAC should be higher than the UCS ones, and the CSFAC should adsorb Cu(II) ions more than the UCS.

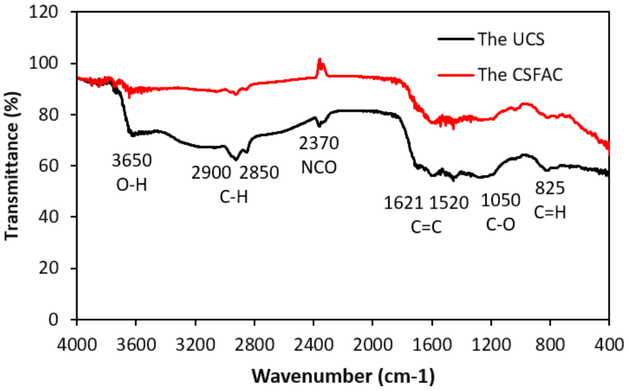
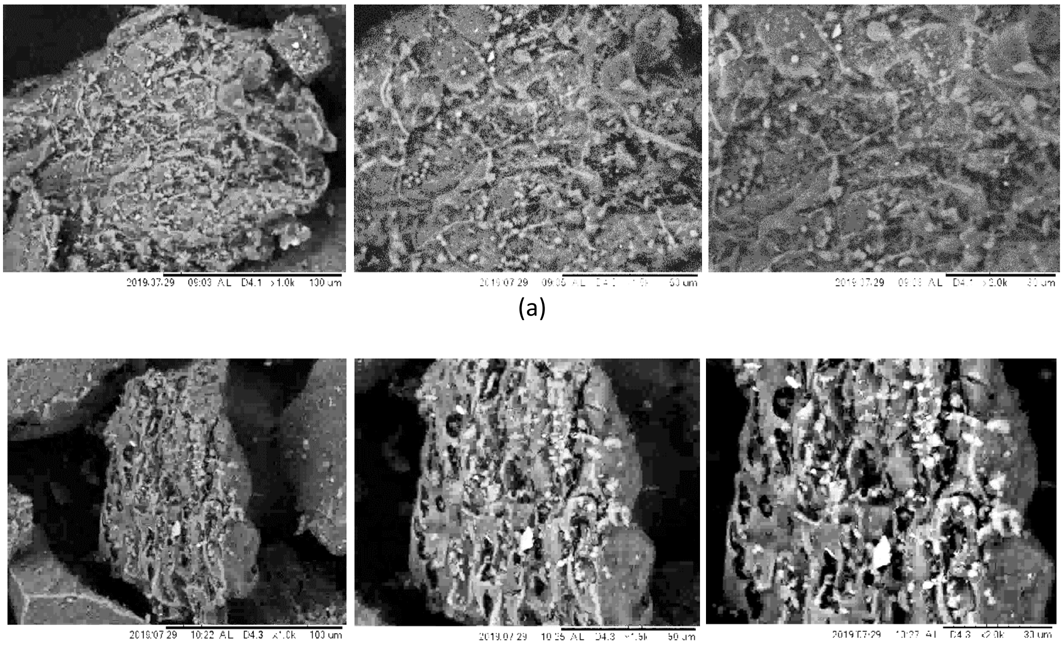


**Fig. 2.** The FTIR spectra of the UCS and CSFAC

### 3.2 Surface Morphology of the UCS and CSFAC

The SEM micrographs of the UCS and CSFAC are shown in Figure 3. As clearly seen in the figure, there were more pores and cavities on the CSFAC compared to the UCS. This result was supported by the FTIR analysis that all the transmittance of chemical functional groups increased after physical activation. It is implied that the volatile matter such as hydroxyl and aromatic compounds and cyanate left the CSFAC creating more pores and cavities on it [30,31]. In addition, it was also supported based on the BET measurement whereas the BET surface area and total pore volume of the CSFAC were approximately 50.848 m$^2$/g and 0.018 cm$^2$/g respectively. Meanwhile, it was 11.136 m$^2$/g and 0.004 cm$^2$/g respectively for the UCS.



(a)

(b)

**Fig. 3.** The SEM micrographs of (a) the UCS and (b) CSFAC for x1.0k, x1.5k and x2.0k

### *3.3 Effect of Contact Time on Adsorption Capacity*

Figure 4 shows Cu(II) ions adsorption capacity over the contact time for both the UCS and CSFAC with initial Cu(II) ions in an aqueous solution of 1000.21 mg/L. As can be seen in Figure 4, it increased very sharply for the first 2-min contact time, which were approximately 41.42 and 82.02 mg/g for the UCS and CSFAC respectively. The CSFAC one increased very small to 89.36, 89.81 and equilibrium adsorption capacity of 90.11 mg/g at the contact of 10, 20 and 30 min respectively. Meanwhile, the UCS ones were 47.91, 44.02 and 51.05 respectively. Interesting to note that the adsorption capacity of the CSFAC was much more stable than the UCS ones. This stable adsorption on the CSFAC was reasonable because that the activated carbon has more pores and larger surface area leading more active site to adsorb strongly Cu(II) ions. It caused the Cu(II) ions being adsorbed did not desorb into the solution, and it was stable at the rest of the contact times after reaching the equilibrium time to form an exponential trend [39,40,41]. The equilibrium time of 30 min was taken for adsorption isotherms experiments.

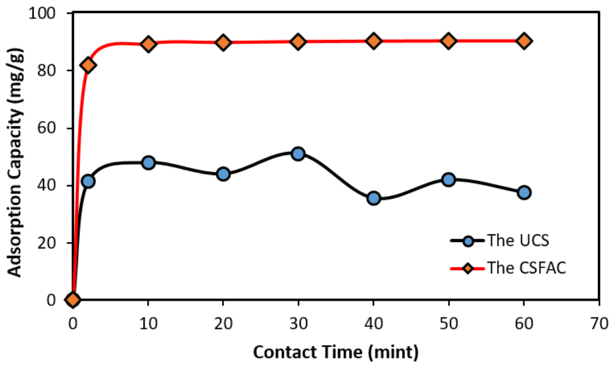


**Fig. 4.** Adsorption capacity over contact time

### *3.4 Effect of Initial Cu(II) Ions Concentration on Adsorption Capacity*

The adsorption capacity of both the UCF and CSFAC were influenced by initial Cu(II) ions concentration in the solution as revealed in Figure 5. For the UFC, it increased linearly with the increase of Cu(II) ions concentration from 5.00 to 500.11 mg/L, and it increased moderately from 500.11 to 1000.21 mg/L. The UCF adsorption capacity for initial Cu(II) ions concentration at 500.11 to 1000.21 mg/L were 38.78 to 51.06 mg/g respectively. It seems that it almost reached its maximum capacity, and it would end up by an exponential trend [41,42]. In contrast, it still increased linearly for the CSFAC and was 90.11 mg/g at 1000.21 mg/L. It revealed that there should be still more available sites on the CSFAC to occupy Cu(II) ions. More Cu(II) ions in solution would be needed to reach the steady-state value [41].

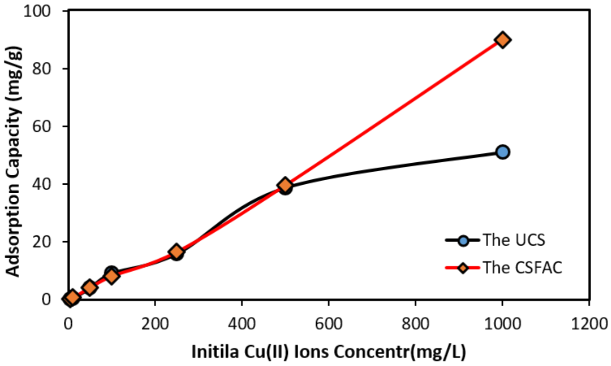


**Fig. 5.** Adsorption capacity over contact time

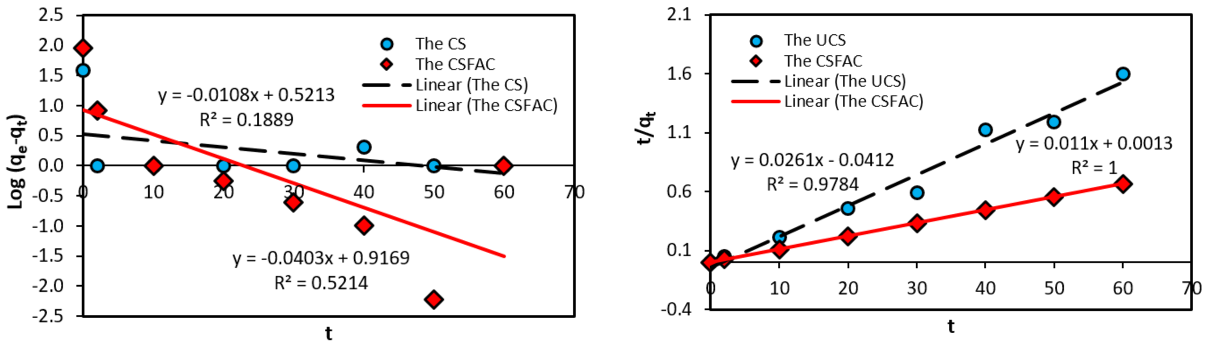
### *3.5 Adsorption Kinetics*

Pseudo-first-order kinetics (PFOK) model by Lagergren [44] and pseudo-second-order kinetics (PSOK) model by Ho *et al.,* [45] are common equations to be used for adsorption kinetics. The linearized formulas are given by Eq. (1)-(2) respectively [31,32,40].

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_L t}{2.303}\right) \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_H q_e^{\ 2}} + \frac{t}{q_e} \tag{2}$$

where $q_t$ is adsorption capacity (mg/g) at any time of $t$ (min), and it becomes $q_e$ (mg/g) at equilibrium time; $k_L$ (/min) is the PFOK rate constant; $k_H$ (g/mg.min) is the PSOK the PFOK rate constant. The data presented in Figure 4 was used for adsorption kinetics, and the results were shown in Figure 6. As shown by correlation coefficients ($R^2$) values in Figure 6(a) and 6(b), it absolutely fitted the PSOK model. Based on the slope and intercept, the $q_e$ and $k_H$ were approximately 38.314 mg/g and 0.016 g/mg.min, respectively for the UCS, and 90.909 mg/g and 0.093 g/mg.min, respectively for the CSFAC. As expected in the FTIR, SEM and BET analyses, the CSFAC equilibrium adsorption capacity is higher than the UCS one, and the Cu(II) ions adsorption by the CSFAC is faster than by the UCS.



(a) (b)

**Fig. 6.** Linearized (a) pseudo-first-order kinetics model and (b) pseudo-second-order kinetics models

### *3.6 Adsorption Isotherms*

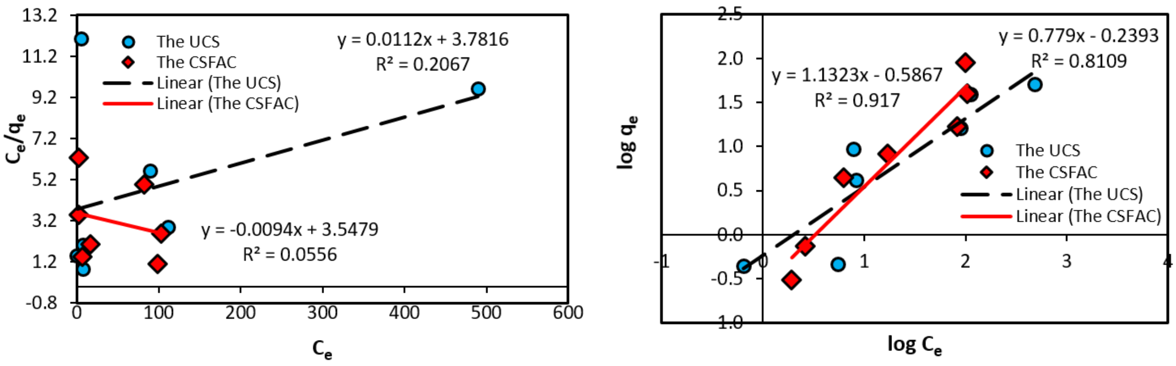
The common Langmuir [46] and Freundlich [47] models were taken for adsorption isotherms study. The linearized expression was written as Eq. (3)-(4) [31,32,40]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \tag{3}$$

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \tag{4}$$

where $C_e$ (mg/L) and $q_m$ (mg/g) are Cu(II) ions concentrations in the solution and the Langmuir adsorption capacity respectively; $K_L$ (L/mg) and $K_F$ (L/mg) refer to pore volumes based on Langmuir and Freundlich isotherms respectively; and $n$ is the Freundlich adsorption intensity. The data presented in Figure 5 was taken, and the results were shown in Figure 7. As can be seen in Figure 7, the UCS and USFCA adsorption isotherms follow the Freundlich model. The $K_F$ and $n$ were approximately 1.734 L/mg and 0.779 respectively for the UCS, and 3.861 L/mg and 1.132 for the CSFAC, respectively.

Table 1 shows Cu(II) ions adsorption capacity of various activated carbon compared to the UCS and CSFAC. As clearly shown in Table 1, Cu(II) ions adsorption capacity of the CSFAC is higher than the ones prepared from the low cost organic solid waste and commercial filtrasorb 200 activated carbon except for *Pithecellobium jiringa.*



(a) (b)

**Fig. 7.** Linearized (a) Langmuir isotherms and (b) Freundlich isotherms models

**Table 1**
A comparison of Cu(II) ions adsorption capacity by various activated carbon

| Raw Material | Activator | T (°C) | pH | $q_m$ (mg/g) | Ref. |
|---|---|---|---|---|---|
| Hazelnut husks | $ZnCl_2$ | 18 | 5.7 | 6.650 | [24] |
| Hazelnut shell | $H_2SO_4$ | 50 | 6 | 58.270 | [25] |
| Tunisian date stones | $H_3PO_4$ | 40 | 5 | 31.250 | [27] |
| Australian pine cone | NaOH | 25 | 5 | 26.710 | [30] |
| Pithecellobium jiringa | NaOH | 27 | 5 | 104.167 | [31] |
| Areca catechu shell | NaOH | 27 | 6.5 | 50.51 | [40] |
| Areca catechu shell | NaOH | 45 | 6.5 | 55.25 | [40] |
| Watermelon | $Ca(OH)_2$ | 30 | 5 | 31.025 | [47] |
| Watermelon | $C_6H_8O_7$ | 30 | 5 | 27.027 | [47] |
| Apricot stone | $H_2SO_4$ | NA | 6.5 | 22.800 | [48] |
| Commercial Filtrasorb 200 | | NA | 4 | 15.470 | [49] |
| Coal Spills (physical activation) | - | 27 | 5 | 90.909 | this study |
| Coal Spills (untreated) | - | 57 | 5 | 38.314 | this study |

## 4. Conclusions

From the results obtained, it can be summarized that coal spills can be utilized to be activated carbon by physical activation in a tube furnace only. Compared to the untreated coal spills (UCS), coal spills-based activated carbon (CSFAC) was expected to have more pores and cavities based on the FTIR, SEM and BET analyses. The BET surface area and total pore volume were approximately 50.848 m²/g and 0.018 cc/g respectively. Cu(II) ions adsorption kinetics of the CSFAC followed very well the second-order kinetics model with correlation coefficient, $R^2$ being 1, and the equilibrium adsorption capacity and adsorption rate of the CSFAC were 90.909 mg/g and 0.093 g/mg.min respectively. Freundlich adsorption isotherms was favorable for Cu(II) ions adsorption kinetics of the CSFAC with $R^2$ being 0.917 respectively and the pore volume and adsorption intensity were 3.861 L/mg and 1.132 respectively.

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