

Original Article

Phosphoric Acid Activated Coffee Pulp Waste for Cu and Cr Adsorption

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Abstract - Adsorption is a method that is used widely to overcome heavy metal pollution. Adsorption can be carried out using some natural materials, one of which is coffee pulp. This study aims to determine the adsorption capacity of phosphoric acid-activated coffee pulp on Cu and Cr adsorption as well as their reaction kinetics. The activated coffee pulp adsorbent was characterized by determining its surface area using the methylene blue method and the surface acidity by the acid-base titration method. The study included the determination of the maximum amount of activator, contact time, isotherm and adsorption kinetics. The results showed that the optimum mass ratio of coffee pulp powder and phosphoric acid for the optimum adsorption of Cu and Cr was 1:3.75. The surface acidity of phosphoric acid-activated coffee pulp adsorbent was 1.2801 ± 0.0061 mmol/g with active sites as much as 7.7086×10^{20} molecules/g, and the surface area was 36.5363 - 37.0249 m²/g. The contact time in the adsorption process for both metals was 60 minutes, with adsorption capacities of Cu and Cr of 2.5054 mg/g and 3.7277 mg/g, respectively. The adsorption process of Cu and Cr metals by phosphoric acid-activated coffee pulp adsorbent followed the Langmuir isotherm pattern and the kinetics reaction of the second order.

Keywords - Activated adsorbent, Coffee pulp, Cu and Cr adsorption, Phosphoric acid.

1. Introduction

Adsorption is one method that is widely used to overcome environmental problems such as heavy metal pollution. This method can be used to adsorb heavy metal pollutants or other harmful pollutants by using a material called adsorbent. An adsorbent can be prepared from a variety of biomass coming from agricultural residues, one of which is coffee pulp [1, 2]. Coffee pulp is a by-product in coffee production containing carbohydrates, proteins, minerals, tannins, polyphenols and caffeine [3]. Coffee pulp has been reported to be a sustainable alternative to be used as an adsorbent for the removal of Cr (VI) [4]. This material can be chemically and thermally modified to improve its physical and chemical condition as well as improve its sorption capacities. The modification causes substantial changes in its chemical configuration as well as its physical structure. Significant changes are noted in the point of zero charge, functional group number, lignin cellulose, and hemicellulose content, which allow the capture and removal of Cu and Pb [5]. Copper and chromium are among the heavy metals that are very hazardous. These metals are basically used in industries such as paints and pigment tanneries, fertilisers and many more. Ingestion of higher concentrations of copper continuously may cause Wilson disease, liver damage, insomnia, and renal damage. In contrast, chromium can cause cancer in the digestive tract, headache, diarrhoea, nausea, vomiting, lung tumour/cancer,

and haemorrhage vomiting. Chromium may exist in Cr(III) and Cr(VI) forms. The toxicity of Cr(VI) is very high, and it is carcinogenic [6]. Coffee pulp without any chemical modification could decrease the level of Mn by 53.40% with an adsorption capacity of 8.01 mg/g [7] and could decrease Cr(III) and Cr(VI) in synthetic wastewater with removal efficiencies of 93.26% and 74.80%, respectively. Adsorbent from coffee pulp is also proven to be a good material for investigating the possible interfering factors that affect the adsorption process through desorption studies [8]. The content of Pb²⁺ and Cd²⁺ in industrial wastewater could also be removed by the adsorption method using coffee pulp as the adsorbent. In that study, it was evident that the biosorption of Cd and Pb ions on the adsorbents was described well by the Freundlich model and the second-order kinetics model [9]. Another metal that can be removed by adsorption method using Arabica coffee pulp as the biosorbent is Ni²⁺. The removal fulfilled the Langmuir isotherm model with a biosorption capacity (Q₀) of 18.86 mg/g [10]. The kinetic data for the adsorption of Ni²⁺ ions usually followed the pseudo-second-order kinetic model, and the adsorption process was endothermic and spontaneous in most cases [11]. Some parameters in adsorption kinetics give information on adsorption capacity, adsorption rate and amount of adsorbate removed at equilibrium and at any given time. Moreover, adsorption gives information about the type of layer formed



during adsorption. Adsorption kinetics and isotherms can be applied to adsorption processes, especially those that involve variations in time of interaction and concentration of adsorbate [12]. Pujungan, which is one of the coffee-producing areas in Bali-Indonesia, produces a lot of coffee pulp waste. This biomass waste has the potential to be used as an adsorbent to deal with the problem of pollution by heavy metals. Based on the reasons above, in this study, the coffee pulp waste, which was activated with phosphoric acid, was used as an adsorbent for Cu and Cr adsorptions. The capacity of an adsorbent prepared from coffee pulp waste, as well as some parameters that affect the adsorption of Cu and Cr, were investigated. Moreover, the isotherm and the kinetics of the adsorption for both metals were also established. From this research, it can be scientifically known, the nature and ability of the adsorbent from coffee pulp waste for Cu and Cr in solution adsorptions that can be applied to environmental samples.

2. Materials and Methods

2.1. Research Materials and Equipment

The chemicals used in this study were of reagent grade consisting of H_3PO_4 , $CuSO_4 \cdot 5H_2O$, $CrCl_3 \cdot 6H_2O$, $C_{16}H_{18}ClN_3S$, $C_2H_2O_4 \cdot 2H_2O$, HNO_3 , phenolphthalein and distilled water. The raw material for making the adsorbent was the coffee pulp waste obtained from a coffee plantation in the Pujungan area, Tabanan-Bali, Indonesia. The equipment used in this study were glass tools, balances, magnetic stirrers, oven, desiccator, 150 μm and 250 μm sieves, Whatman filter paper no. 12, Atomic Absorption Spectrophotometer (AAS) Simadzu AA 7000 and UV-Vis Spectrophotometer.

2.2. Adsorbent Preparation

The coffee pulp waste sample was washed with tap water and then rinsed several times with distilled water. Then, the sample was dried in an oven at 105°C to a constant mass. After that, the dried sample was mashed using a blender and then sieved using 150 μm and 250 μm sieves. Hereinafter, this powder was called an adsorbent.

2.3. Determination of the Optimum Amount of H_3PO_4 for Adsorbent Activation

Into six Erlenmeyer flasks, each was filled with 6 grams of adsorbent and then added with 150 mL of phosphoric acid with various concentrations, namely 5, 10, 15, 20 and 25 %. These mixtures resulted in the mass ratio of adsorbent and phosphoric acid of (1:1.25); (1:2.5); (1:3.75), (1:5), and (1:6.25), respectively, then were labelled with A1, A2, A3, A4, and A5, respectively. These mixtures were stirred well and left for 24 hours, then filtered and rinsed with distilled water until the pH was neutral. The activated adsorbents formed were dried to constant mass and then used for Cu and Cr adsorptions. Into five Erlenmeyer flask, each was filled with one gram of activated adsorbent, then 50 mL of the mixture of 100 mg/L of Cu and Cr solutions were added into the flask. The mixtures were stirred with a magnetic stirrer for 60 minutes at room temperature. After that, the mixtures were

filtered, and the filtrates were collected for Cu and Cr measurements with an Atomic Absorption Spectrophotometer, with Cu at 324.7 nm and Cr at 357.9 nm. The adsorbent that showed maximum adsorption capacity for both metals was then labelled as Aopt and used for further work. A control, which was only the adsorbent without activation, was also carried out for Cu and Cr adsorptions, and this was labelled as A0.

2.4. Adsorbent Surface Area Determination

As much as 0.1 gram of Aopt and A0 adsorbents were put into 250 mL beaker glass separately and were added with 20.0 mL of 50 mg/L methylene blue solution. Then, the mixtures were stirred with magnetic stirrers at a contact time of 5, 10, 15, 20, 40 and 60 minutes. After that, the mixtures were filtered, and the filtrate was collected for UV-Vis spectrophotometer measurement at the maximum wavelength of methylene blue, which is 665 nm.

2.5. Adsorbent Surface Acidity Determination

As much as 1.0 grams of Aopt was put into a 250 mL Erlenmeyer, then added with 15.0 mL of 0.1 M NaOH and stirred with a magnetic stirrer for 15 minutes. A few drops of 1% phenolphthalein were added to the mixture and then titrated with 0.1 M HCl until the color changed from pink to colourless.

2.6. Contact Time Determination

Into six 250 mL Erlenmeyer flasks, each was filled with 1.0 gram of Aopt and then added with 50 mL of the mixture of 100 mg/L Cu and Cr solution. The mixture was stirred with a magnetic stirrer for 5, 10, 20, 40, 60, 90 and 120 minutes at room temperature, followed by filtration and metals measurement with Atomic Absorption Spectrophotometer. The contact time that resulted in the optimum Cu and Cr adsorption capacity was then chosen as the optimum contact time and then applied for further work.

2.7. Adsorption Capacity and Adsorption Isotherm of Adsorbent Determination

Into six 250 mL Erlenmeyer flasks, each was filled with 1.0 gram of Aopt, then added with 50 mL of the mixture of Cu and Cr solutions with concentrations of 10, 30, 50, 70 mg/L 100 mg/L and 120 mg/L. Furthermore, the mixture was stirred for the optimum contact time at room temperature and then filtered followed by Cu and Cr measurement with Atomic Absorption Spectrophotometer.

2.8. Adsorption Kinetics of the Adsorbent Determination

As much as 1.0 grams of Aopt was put into 8 Erlenmeyer flasks separately, then added with 50 mL of Cu and Cr solutions with adsorption isotherm concentrations. The mixture was then stirred with a magnetic stirrer for 0, 5, 10, 20, 30, 40, 60 and 120 minutes at room temperature. After that, the solution was filtered, and the filtrates were collected for metal measurement with an Atomic Absorption Spectrophotometer.

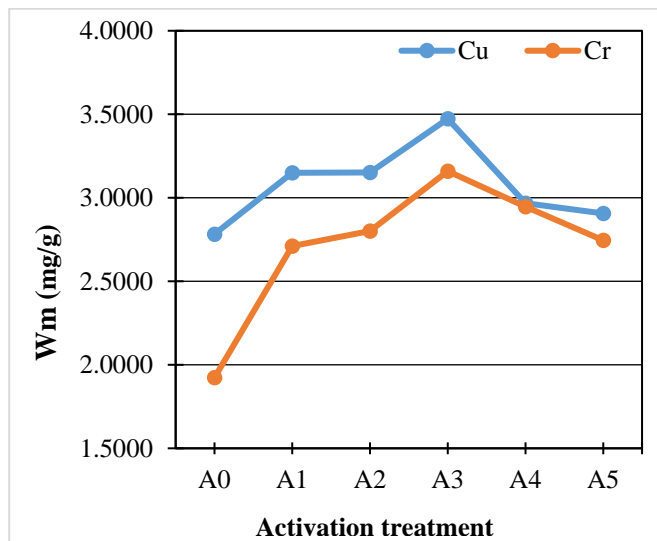
3. Results and Discussion

3.1. Determination of the Optimum Amount of H₃PO₄ for Adsorbent Activation

The results obtained in determining the optimum amount of activator in the absorption of Cu and Cr metals can be seen in Figure 1. The figure shows the relationship between the adsorption capacities of coffee pulp at various mass ratios of adsorbent and phosphoric acid to Cu and Cr adsorption. The figure clearly shows that activation with phosphoric acid could increase the adsorption capacity of both metals.

Generally, the adsorption capacities for both metals increased after activation, in which the adsorption capacity to Cu was higher than that of Cr. The activation dissolves impurities on the surface of the adsorbent so that the pores become open, which ultimately increases the surface area. Based on the figure, it can be seen that there was an increase in the adsorption capacity from A1 to A3.

In the beginning, where the concentration of phosphoric acid was low, Cr increased rapidly, then increased slower until the ratio reached A3. Obviously, the higher the concentration of the activator, the greater the ability of the adsorbent to adsorb both metals. However, in the A4 and A5 treatments, there was a decrease in adsorption capacity due to the fact that the adsorbent had reached a saturation state, causing the adsorption capacity to decrease. This indicates that at the mass ratio of 1:3.75, the reaction of the adsorbent and adsorbate occurred the most intense; however, the higher ratio damaged or burnt the adsorbent pore [13].



Caption:

A0: control

A1: Adsorbent : H₃PO₄ = 1 : 1.25

A2: Adsorbent : H₃PO₄ = 1 : 2.5

A3: Adsorbent : H₃PO₄ = 1 : 3.75

A4: Adsorbent : H₃PO₄ = 1 : 5

A5: Adsorbent : H₃PO₄ = 1 : 6.25

Fig. 1. Adsorption Capacity of Coffee Pulp to Cu and Cr at Various Mass Ratios of Adsorbent and Phosphoric Acid

3.2. Adsorbent Surface Area Determination

The adsorption of methylene blue allows the determination of the specific surface area of an adsorbent. The results of measuring the surface area of the coffee pulp adsorbent can be seen in Table 1. The table shows that the Aopt had an average surface area of 36.7927 ± 0.1993 m²/g, while the adsorbent without activation (Acon) was 36.0447 ± 0.1397 m²/g. It was evident that by activation with phosphoric acid, the surface area of the adsorbent increased.

Table 1. Surface area of coffee pulp adsorbent

Stirring Time (minutes)	Without activation (m ² /g) ± SD	With activation (m ² /g) ± SD
5	35.9224	36.5565
10	36.0066	36.8803
15	36.2266	36.8976
20	36.1628	37.0249
40	35.8644	36.8607
60	36.0851	36.5363
Average	36.0447 ± 0.1397	36.7927 ± 0.1993

From the table, it can be seen that the coffee pulp adsorbent activated by phosphoric acid has a larger surface area compared to the coffee pulp adsorbent without activation. This is in accordance with the theory which states that the greater the surface area of an adsorbent, the greater its absorption power. The increase in the surface area of the adsorbent is due to the phosphoric acid activator being able to dissolve impurities covering the pores of the adsorbent so that the pores become more open and can increase the active site of the adsorbent [14,15].

3.3. Adsorbent Surface Acidity Determination

The surface acidity of the adsorbent was obtained from the calculation result between the difference in the amount of HCl for blank titration and the amount of HCl for adsorbent titration. At the same time, the number of active sites can be calculated by multiplying the surface acidity by Avogadro's number. The results of determining surface acidity and the number of active sites are presented in Table 2. The data in the table above shows that the surface acidity of the coffee pulp adsorbent is 1.2801 ± 0.0061 mmol/g, and the number of active sites is 7.7086 × 10²⁰ ± 0.0369 molecules/gram.

Table 2. Surface acidity and number of active sites on phosphoric acid activated coffee pulp adsorbents

Repetition	Surface Acidity (mmol/g) ± SD	Active sites (molecules/gram) ± SD
I	1.2773	7.6919 × 10 ²⁰
II	1.2758	7.6829 × 10 ²⁰
III	1.2871	7.7509 × 10 ²⁰
Average	1.2801 ± 0.0061	7.7086 × 10²⁰ ± 0.0369

The greater the surface acidity value of the adsorbent, the greater the absorption power, which is caused by the increasing number of active sites from the adsorbent. The

greater the number of active sites on the adsorbent, the more metal ions can be adsorbed because, in the adsorption process, the active site acts as a proton donor (Bronsted acid), where metal ions will replace the protons in the active site.

3.4. Contact Time Determination

The optimum contact time can be determined by making a curve between contact time vs. the amount of Cu and Cr metal adsorbed by each gram of adsorbent. The curve of the amount of Cu and Cr adsorbed by Aopt against the interaction time can be seen in Figure 2. Based on Figure 2, it can be seen that at a contact time of 20 minutes to 60 minutes there was an increase in adsorption capacity and reached a maximum capacity at 60 minutes. Then, at 90 minutes, the amount of adsorbed Cu and Cr decreased due to the adsorption capacity of the active sites on the surface of the adsorbent being saturated.

There was an equilibrium between the metal concentrations in the adsorbent and its environment so that if the contact time were increased, it would cause a desorption process to occur. Optimum contact time is required so that the adsorbent can adsorb metal optimally. In contrast, the longer the contact time, the more metal is adsorbed because there are more opportunities for adsorbent particles to interact with the metal. However, if the adsorbent is saturated, the contact time will not affect the adsorption capacity of an adsorbent.

In Figure 2, it can be seen that at 60 minutes, the adsorption capacities of the coffee pulp adsorbent on Cu and Cr metals were 3.8361 and 3.0900 mg/g, respectively. These results indicate that the adsorption capacity of the coffee pulp adsorbent on Cu is greater compared to Cr. This is because the ionic radius of Cu is smaller than that of Cr, where the smaller the ionic radius of a metal, the greater the ionization energy, making it more difficult to remove electrons and causing weaker metal bonds, which causes the metal to be easily absorbed by the adsorbent [16].

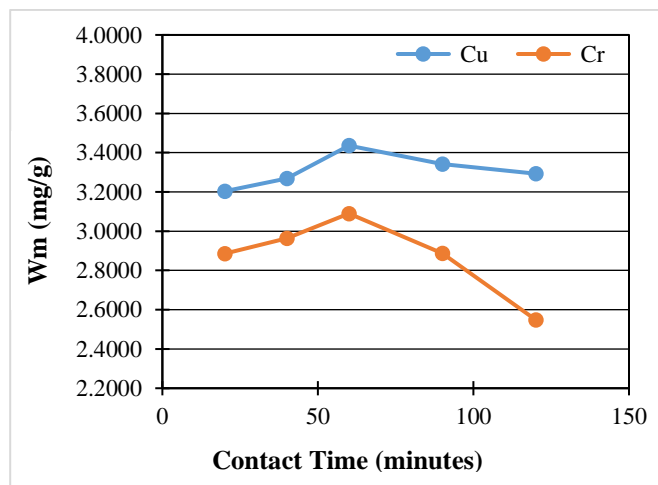


Fig. 2 Adsorption capacity of activated Coffee Pulp (Aopt) to Cu and Cr at Various contact times

3.5. Adsorption Capacity and Adsorption Isotherm of Adsorbent Determination

Determination of adsorption isotherms was carried out to determine the amount of Cu and Cr metals that could be adsorbed by phosphoric acid-activated coffee pulp. In this study, the adsorption isotherm was determined by varying the Cu and Cr mixture solutions with concentrations of 10, 30, 50, 70, 100 and 120 mg/L. Then, the metal solution will be adsorbed by the activated coffee pulp adsorbent for an equilibrium time of 60 minutes at room temperature. The results of measuring the adsorption capacities of Cu and Cr metals at various metal concentrations can be seen in Figure 3. The absorption of Cu and Cr metals increased with increasing solution concentration, as shown in the figure. This increase in adsorption capacity was due to the fact that the adsorbents that interact with Cu and Cr solutions had not yet reached saturation. Hence, the higher the concentration of metal ions, the more metal ions are adsorbed. The figure shows that the maximum concentration of Cu and Cr absorption by phosphoric acid-activated coffee pulp occurred at a concentration of 70 mg/L with an adsorption capacity For Cu and Cr of 2.5054 mg/g and 3.7277 mg/g, respectively. When the coffee pulp adsorbent reaches its maximum concentration, the adsorption capacity decreases because the adsorbent used in the adsorption process has begun to saturate, where the high concentration of metal in solution was not proportional to the particles contained in the adsorbent so that a desorption process occurs. The adsorption capacity of Cu metal by the coffee pulp adsorbent was smaller than the adsorption capacity of Cr metal. This is inconsistent with the theory, which states that the adsorption capacity will be affected by the ionic radii, where the smaller the ionic radius, the greater the adsorption capacity produced [16]. Cu metal has a smaller ionic radius compared to Cr, so Cu metal has a greater adsorption capacity. However, the results of this study showed different results, which might be due to the functional groups present in the coffee pulp adsorbent in this study, which binds Cr metal more easily than Cu.

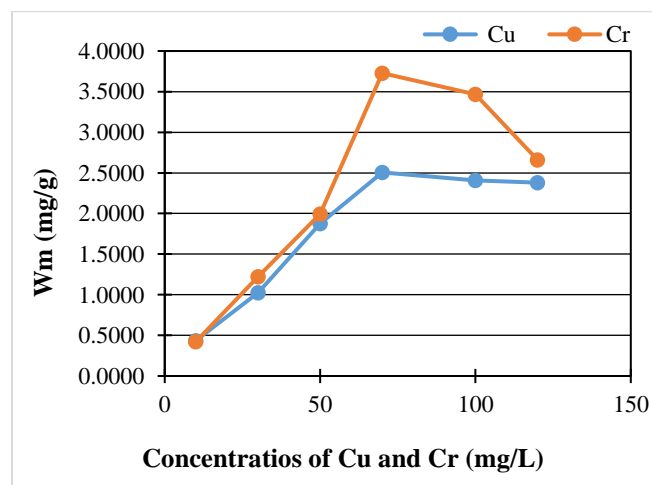


Fig. 3 Adsorption capacity of coffee pulp adsorbent for Cu and Cr metals at various concentrations of metals solution

Furthermore, the determination of the adsorption isotherm pattern of coffee pulp adsorbent was carried out to study the mechanism of the reaction that occurred. Determination of the adsorption isotherm pattern of coffee pulp adsorbent for Cu and Cr metals can be identified by making a curve. The Langmuir isotherm pattern was determined by making a relationship curve between C_e and C_e/q_e .

In contrast, the Freundlich isotherm pattern was determined by making a relationship curve between $\log C_e$ and $\log q_e$. The pattern of Langmuir isotherms for Cu and Cr can be seen in Figure 4, while the Freundlich isotherms for both metals are shown in Figure 5. Figure 4 shows the R^2 values for the Langmuir isotherm for Cu and Cr were 0.9951 and 0.8126, respectively, while in Figure 5 for the Freundlich isotherm, the R^2 values for Cu and Cr were 0.7424 and 0.9073, respectively.

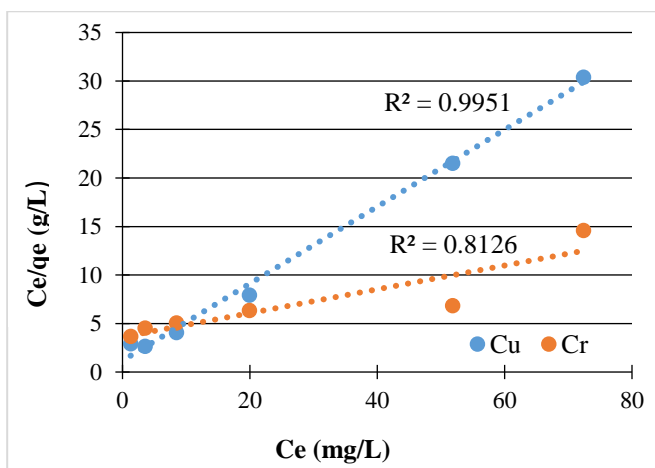


Fig. 4 Isotherm Langmuir for Cu and Cr

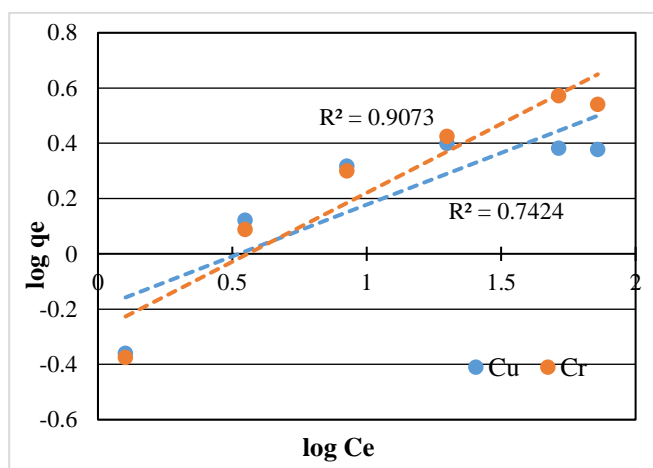


Fig. 5 Isotherm Freundlich for Cu and Cr

Based on this, it can be concluded that the adsorption of Cu with coffee pulp adsorbent activated by phosphoric acid followed the Langmuir isotherm pattern. The Langmuir

isotherm pattern states that the adsorbent surface is homogeneous, and the adsorption energy for each adsorption site is equivalent. In the Langmuir isotherm pattern, the interaction of the active site of the adsorbent with the adsorbed substance only occurs in a single absorption layer (monolayer) on the surface of the adsorbent cell wall which is referred to as chemical adsorption. The results of this study were in line with research on the adsorption of methylene blue by the coffee pulp adsorbent following the Langmuir isotherm pattern [17]. From the R^2 values for Cr, which were close to each other, it can be concluded that the adsorption of Cr metal by phosphoric acid-activated coffee pulp adsorbent followed the pattern of the Langmuir and Freundlich isotherms but tended to follow the Langmuir isotherm.

The adsorption process of coffee pulp adsorbent on Cr metal occurred chemically (monolayer) and physically (multilayer). Chemical adsorption occurs because of the interaction between the active site of the adsorbent and the adsorbed substance occurring on single adsorption on the surface of the adsorbent cell wall. Physical adsorption allows bonds between metal ions in solution to occur in addition to their bonds with the adsorbent, where the two bonds are bound by van der Waals forces so that the adsorbate bonds with the adsorbent are weak, which causes multilayer adsorption.

3.6. Adsorption Kinetics of the Adsorbent Determination

Determination of adsorption kinetics was carried out to determine the rate of absorption of an adsorbent on the adsorbate. The adsorption capacity of an adsorbent can be seen from the rate of adsorption carried out by determining the order of the reaction experimentally. Determination of kinetics was carried out by interacting the coffee pulp adsorbent with 70 mg/L Cu and Cr (adsorption isotherm concentration) for 0, 5, 10, 20, 30, 40, 60 and 120 minutes at room temperature. Then, the adsorption kinetics can be established by plotting a curve between $\ln C_e$ with time variation for the first order and a curve between $1/C_e$ and time variation for second order kinetics. The first-order adsorption kinetics curves for Cu and Cr can be seen in Figure 6, while the second-order adsorption kinetics for Cu and Cr can be seen in Figure 7. The k value, which can be seen in Table 3, was also calculated to determine the adsorption rate of the coffee pulp adsorbent.

In Figure 6, it can be seen that the R^2 values for the absorption of Cu and Cr in the first-order kinetics are 0.9111 and 0.9467, respectively, while in Figure 7, the R^2 values for the absorption of Cu and Cr in the second-order are 0.9677 and 0.9656, respectively. The R^2 values for both metals in the second-order kinetics model are greater than in the first-order kinetics. This indicates that the uptake of the metals by phosphoric acid-activated coffee pulp adsorbent follows the second-order kinetic model with an adsorption kinetic constant of 0.0034 $\text{min}^{-1} \text{ppm}^{-1}$ for Cu and 0.00041 $\text{min}^{-1} \text{ppm}^{-1}$ for Cr.

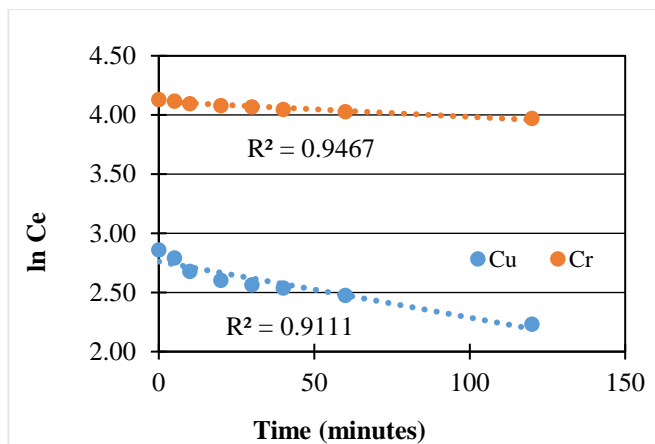


Fig. 6 Adsorption kinetics model curve of the first order for Cu and Cr

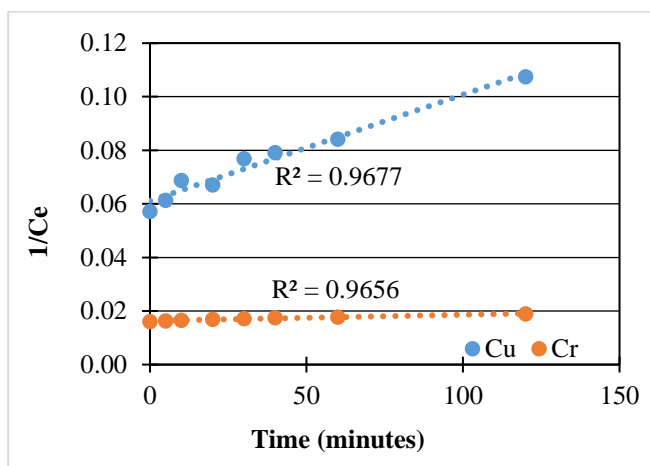


Fig. 7 Adsorption kinetics model curve of second for Cu and Cr

Table 3. Adsorption Kinetic Parameters of Coffee Pulp Adsorbent on Cu and Cr Metals

Metals	Reaction Order	K average	R ²
Cu	1	0.0966 min ⁻¹	0.9111
	2	0.0034 min ⁻¹ ppm ⁻¹	0.9677
Cr	1	0.03169 min ⁻¹	0.9467
	2	0.00041 min ⁻¹ ppm ⁻¹	0.9656

The adsorption process that follows a second-order kinetic model suggests that the adsorption rate of the coffee pulp adsorbent on Cu and Cr metals per unit time is directly proportional to the decrease in concentration.

4. Conclusion

Based on the results of the research that has been done, it can be concluded as follows:

The optimum mass ratio of coffee pulp powder and phosphoric acid (H₃PO₄) for the optimum adsorption of Cu and Cr metals in solution was 1: 3.75. The activated adsorbent resulting in this treatment showed a surface acidity of 1.2801 ± 0.0061 mmol/g with the number of active sites of 7.7086 × 1020 molecules/gram. Its surface area was 36.7927 m²/g, while the adsorbent without activation was 36.0447 m²/g. The optimum contact time for Cu and Cr adsorption by the activated adsorbent was 60 minutes. The adsorption capacity of the coffee pulp adsorbent to Cu metal was 2.5054 mg/g, while to Cr metal was 3.7277 mg/g. The adsorption isotherm for the adsorption process of Cu and Cr followed the Langmuir isotherm pattern. The adsorption kinetics model of the coffee pulp adsorbent on Cu and Cr metals followed the second-order kinetics model.

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