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The Adsorption Isotherm and Kinetics Studies of Cu(II) and Cr(III) Metal Ions from Aqueous Solutions on Activated Biosorbent of Coffee Pulp Waste

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ABSTRACT

Heavy metals such as copper and chromium are toxic even trace levels in contaminated water can be harmful to humans. Heavy metals removal from wastewater using low cost technology, resulting in high efficiency and being environmentally friendly, is still a research concern. The purpose of this study is to investigate the possibility of using activated coffee pulp biosorbent to evacuate Cu(II) and Cr(III) heavy metal ions from an aqueous solution. Coffee pulp powder was activated with sodium hydroxide at different ratios of biosorbent to activator. The numerous framework, such as exposure time, initial concentrations of Cu(II) and Cr(III), isotherms as well as kinetic adsorption behaviors, were investigated through a batch adsorption technique. The results revealed the weight ratio of coffee pulp powder to NaOH for the favorable condition for Cu(II) and Cr(III) adsorption was 1:3.75, with their maximum adsorption capacities being 3.7319 ± 0.0058 and 3.3255 ±0.0129, respectively. The optimum operating conditions were obtained at 60 minutes of contact time, 70 mg/L, and 100 mg/L concentrations for Cu(II) and Cr(III) metal ions, with the adsorption capacity being 2.9155 mg/g and 4,1278 mg/g, respectively. The adsorption behavior of Cu(III) and Cr(III) onto the NaOH-activated coffee pulp biosorbent surface follows the Freundlich isotherm model and correspond to pseudo-second-order. This study proves that biosorbents derived from agricultural waste, such as activated coffee pulp, can be used as an alternative and effective adsorbent to remove Cu (II) and Cr (III) from aqueous solutions.

Keywords: adsorption kinetic, biosorbent, coffee pulp, NaOH-activator, heavy metals.

INTRODUCTION

Environmental pollution problems require special attention, both from environmental authorities and society itself. One of the environmental issues related to land and water is heavy metal pollution due to its toxic properties and persistence in the environment. Rapid industrial development, livestock waste, industrial sludge, textile effluent, and the large-scale use of synthetic fertilizers and pesticides are factors that cause an increase in heavy metals in the environment [Jadaa et al., 2023; Wang et al., 2022; Haghighizadeh et al., 2024]. Overuse of heavy metals in anthropogenic activities has resulted in heavy metal contamination, which poses a danger to the environment, from soil and water pollution to ecosystem disorder [Li et al., 2023]. Several heavy metals, such as Ni, Cd, Hg, Cu, Cr, As, Pb, and Zn, are often found in large quantities in agricultural soil and have a negative impact on plants [Toth et al., 2016]. Through soil and water, these heavy metals have the capability to enter the food chain and accumulate in the bodies of humans and animals [Mitra et al., 2022; Angon et al., 2024].

Copper and chromium are two of the most hazardous metal pollutants, predominantly originating from mining sites, deposits, and industrial wastewater effluents [Okewale and Grobler., 2023; Dermentzis et al., 2011; Liu et al., 2023]. Both heavy metals can come into the human body via a variety of activities and pose a high risk to humans [Irshad et al., 2023]. Copper is a microelement in the human body that is needed for enzymatic reactions in cellular metabolism [Garza et al., 2023]. As a transition metal, copper functions as a vital cocatalyst for a number of redox enzymes involved in energy and iron metabolism, as well as immune function [Bost et al., 2016]. However, excessive intake of copper is often connected with cell damage that causes Wilson disease [Tchounwou et al., 2008], insomnia, and liver disease and other stomach problems in humans [Rahman et al., 2014]. Likewise, the chromium occurs in nature and is generally found in Cr(III) and Cr(VI) forms. Chromium enters the body through the ingestion of chromium-containing food and water. Chromium is very toxic and can cause lung carcinoma, nasal congestion, immune system disorders, nervous system disorders, and respiration disorders [Shrivastava et al., 2022]. The WHO states that the permissible concentrations of copper and total chromium in industrial wastewater are 1.00 and 0.50 mg/L, respectively, while in soil they are 10.00 and 1.60 mg/kg, respectively. Generally, the concentration of copper in wastewater ranges from 2.5 mg/L to 10.000 mg/L (Liu et al., 2023), whereas the total chromium content in wastewater is approximately 0.1–6.28 mg/L [Mayzarah et al., 2018]. In addition, Indonesian government regulation No. 22 of 2021 about water quality standards has adjusted the permissible limits for copper and total chromium in freshwater to a maximum of 0.02 and 0.05 mg/L, respectively. Therefore, copper and chromium in wastewater must be reduced to an acceptable concentration level before being discharged into the environment.

Heavy metals romoval, including copper and chromium, from wastewater can be accomplished by several methods, such as physico-chemical and biological methods. The various physico-chemical treatments for heavy metals include coagulation, electrocoagulation [Novia et al., 2023; Smiri and Elarbaouli., 2023; Setyawan et al., 2024], membrane separation, and sorption [Ayub et al., 2020; Su et al., 2024], while the biological methods include the use of bacteria and microalgae consortia [Tangahu et al., 2020; Suyasa et al., 2024]. Adsorption stands out among the available methods due to its relatively low cost, simplicity of operation, environmental friendliness, high removal efficiency, and reusability after regeneration [Gupta et al., 2021; Badran et al., 2023].

Adsorption is the mass transfer process of pollutants present in the aqueous phase and accumulated on the surfaces of solid materials. The capacity of adsorption is strongly affected by several factors, such as the initial pH medium, adsorbent dosage, contact time, and the adsorbent properties that involve active sites, porosity, and surface area [Sahu et al., 2024; Fouda-Mbanga et al., 2024]. Commercial adsorbents such as graphene, carbon nanotubes, metal-organic frameworks, activated carbon, and dendritic polymers have proven effective in removing pollutants from water but have high production costs [Cusioli et al., 2023; Tariq et al., 2024]. At present, the research is directed towards a less expensive process using natural and renewable adsorbents, namely eggshell, zeolite, hydroxyapatite, biomass of khamir, and biosorbents from agricultural waste [Ozcan et al., 2018; Abdelwahab and Thabet., 2023; Brazdis et al., 2021; Sukarta et al., 2021]. Among natural adsorbents, agricultural waste-based biosorbents such as coconut leaf stalk, rice straw, and sawdust have received great attention from researchers for their use in removing contaminants from water due to their plentiful availability, renewable nature resources, and relatively low cost [Sudiana et al., 2022; Badhoria et al., 2022; Karic et al., 2022; Zhou et al., 2023]. Active groups such as hydroxyl and phenolic groups of cellulose, hemicellulose, and lignin contained in agricultural waste interact with heavy metals in wastewater. However, generally, biosorbents from agricultural waste have limitations such as low adsorption capacity, so activation treatment is carried out before use. Therefore, in this study, an effort has been made to increase the adsorption capacity of coffee pulp biosorbents through surface activation with sodium hydroxide (NaOH). The activation process of the adsorbent surface using NaOH has three advantages: a lower dosage is required, it is low-cost, and the corrosion rate is lower compared to KOH [Hafizuddin et al., 2021].

The research aimed to investigate the adsorption capacity, isotherm, and kinetic adsorption patterns of NaOH-activated coffee pulp biosorbents for Cu^{2+} and Cr^{3+} metal ions in an aqueous solution.

MATERIALS AND METHODS

Materials

The main substances used in this research include coffee pulp waste from a coffee-producing area in Pupuan-Tabanan village, $Cu(NO_3)_2 \cdot 3H_2O$, $Cr(NO_3)_3$ solution, distilled water and Whatman No.12 filter paper. All chemicals used have a high level of purity.

Biosorbent preparation

Samples of coffee pulp were properly cleaned with tap water and then rinsed with distilled water. Next, the coffee grounds are cut into small pieces and dried in an oven at 105 °C for 24 hours, and the results are weighed. Drying and weighing are carried out repeatedly until a constant weight is obtained. After drying, the coffee pulp is turned into a fine powder using a blender, then sieved with sieve sizes of 150 µm and 250 µm.

Biosorbent activation

The biosorbent of coffee pulp was activated by a chemical process using sodium hydroxide (NaOH) solution. Coffee pulp powder and NaOH were mixed with the weight ratios of the coffee pulp powder to NaOH used were 1:1.25, 1:2.5, 1:3.75, 1:5.0, and 1:6.25, respectively. These mixtures were left for 24 hours while stirring using a magnetic stirrer, then filtered and washed with water until a neutral pH was achieved. Finally, all of the obtained coffee pulp biosorbent were dried at 105 °C in an oven until they attained a constant weight. Each activated biosorbent of coffee pulp powder was analysed for its adsorption capacity, for Cu(II) and Cr(III) metal ions from aqueous solution.

The adsorption experiment studies

The heavy metal ions Cu(II) and Cr(III) removed from an aqueous solution using the activated coffe pulp biosorbent were carried out through batch technique. A coffee pulp biosorbent activated by NaOH at a biosorbent to NaOH ratio of 1:3.75, which has the highest adsorption capacity, was selected and used in this treatment. Each 1.0 g of activated biosorbent was placed in two 250 mL Erlenmeyer flasks to be filled with 50 mL of a 100 mg/L Cu(II) and Cr(III) metal ion solution. The different parameters such as the effect of contact time and metals ions concentration are investigated. The adsorption capacity was determined using the following equation:

$$Adsorption\ capacity\ (mg/g) = \frac{Co - Ct}{W} \times V \quad (1)$$

where: W is the weight of the biosorbent (g), V is the volume of metal ions (mL), and Co and Ct are heavy metal ion concentrations (mg/L) before and after treatment, respectively.

Effect of contact time

In this treatment, 50 mL of Cu(II) solution at a concentration of 100 mg/L in an Erlenmeyer flask was added with 1.0004 g of NaOH-activated biosorbent.The mixture was left for 90 minutes while stirring slowly with a magnetic stirrer. After the treatment process, the mixture was filtered using Whatman No. 12 filter paper, and then the concentration of copper contained in the filtrate was measured using an atomic absorption spectrophotometer (AAS) at a wavelength of 324.7 nm. In the same way, the Cu(II) adsorption treatment was conducted at various contact times, namely 20, 40, 60, 90, and 120 minutes. The same procedure was also applied to Cr(III) solution adsorption treatment. The chromium content in the filtrate was measured using AAS at a wavelength of 267.7 nm.

Effect of metal ions concentration

In this treatment, 1.0012 g of NaOH-activated biosorbent was conveyed into a 250-mL Erlenmeyer flask with 50 mL of Cu(II) metal ion solution at a concentration of 50 mg/L. The adsorption process is carried out at the optimum contact time obtained from the previous treatment. The same treatment was also conducted at various concentrations of Cu(II) solution, including 10, 30, 50, 70, 100, and 120 mg/L. Furthermore, the same procedure was applied at variations in Cr(III) solution concentration, including 10, 30, 50, 70, 100, and 120 mg/L. The concentration of Cu(II) and Cr(III) metal ions in each filtrate was determined using AAS at wavelengths of 324.7 nm and 267.7 nm, respectively.

The adsorption isotherms studies

Adsorption isotherm studies were conducted to describe the equilibrium behavior of copper (Cu) and chromium (Cr) adsorption on NaOH-activated coffee pulp biosorbent. The Langmuir and Freundlich isotherm models were applied to investigate the adsorption capacity of NaOH-activated coffee pulp biosorbent for Cu and Cr. The Langmuir isotherm model express adsorbate adsorption takes place on a monolayer of metal ions on the adsorbent surface, while the Freundlich adsorption models describes a multilayer adsorption with a heterogeneous surface. The Langmuir equation is displayed as follows:

$$\frac{Ce}{qe} = \frac{Ce}{q_{max.}} + \frac{1}{K_L\, q_{max.}} \quad (2)$$

where: Ce is the metal ion concentration at equilibrium (mg/L), qe is the metal ion adsorbed at equilibrium (mg/g), $q_{max.}$ is the maximum adsorption capacity (mg/g), and K_L is the Langmuir adsorption equilibrium constant (L/mg).

The equation for the Freundlich isotherm is expressed as follows:

$$\ln qe = \ln K_F + \frac{1}{n} \ln Ce \quad (3)$$

where: K_F is the constant for Freundlich isotherm (L/mg), n is a representation of the adsorption effectiveness.

The adsorption kinetic studies

To identify the rate of adsorption, two typical adsorption kinetic models were applied to simulate the removal rate for Cu(II) and Cr(III) metal ions onto NaOH-activated coffe pulp biosorbent, namely pseudo-first-order and pseudo-second-order. The equation for the pseudo-first-order kinetic model is exhibited by the formula:

$$\ln qe - qt = \ln qe - k_1 t \quad (4)$$

While the equation for pseudo-second-order kinetic model is expressed as follows:

$$\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{t}{qe} \quad (5)$$

where: qe and qt are the metal ions adsorbed at equilibrium and a certain time (mg/g), respectively, k_1 and k_2 susessively represent the rate constants for pseudo-first-order model (1/min.) and pseudo-second-order models (g/mg/min.) and t is the contact time (min.).

RESULTS AND DISCUSSIONS

Adsorption capacity of activated biosorbents with various ratios of NaOH

An activated biosorbent from coffee pulp was prepared to remove dirt and other impurities. The concentration of activating agent is an essential factor influencing the biosorbent capacity of the biosorbent. The results of the calculation of adsorption capacity for Cu(II) and Cr(III) metal ions at various ratios of biosorbent to NaOH are listed in Table 1. As seen in Table 1, the adsorption capacity increases with increasing the coffee pulp biosorbent to sodium hydroxide weight ratio from 1:1.25 to 1:3.75. However, the adsorption capacity tend decreased after the biosorbent to sodium hydroxide ratio increased. The optimum adsorption capacity was retrieved when the treatment ratio of the biosorbent to the NaOH activator was 1:3.75 by weight, with the adsorption capacities for Cu(II) and Cr(III) being 3.7319 ±0.0058 and 3.3255 ±0.0129, respectively. The function of the activator is to open the pores of the biosorbent by removing hydrocarbons present on the biosorbent surface. The more activator (NaOH) used, the more pores are opened until a certain amount of NaOH is achieved. Once the optimum state is reached, increasing the amount of NaOH actually decreases the adsorption capacity, indicating that the number of open pores is reduced. According to Maneerung et al. (2016) and Shokry et al. (2019), the alkaline treatment of biosorbents can also be associated with the enhanced hydroxyl groups (-OH) on the surface of the biosorbent, where these hydroxyl groups can increase the adsorption capacity of positively charged metal ions. In addition, the electrostatic attraction causes positive charge metal ions to adsorb on negative charged adsorbents (hydroxyl or other functional group) surfaces.

Effect contact time on adsorption capacity

The equilibrium adsorption study of Cu(II) and Cr(III) at concentration of 100 mg/L in an

Table 1. The adsorption capacity of activated coffee pulp biosorbent

Weight ratio of biosorbent to NaOH (w/w)	Adsorption capacity for Cu (mg/g) ± SD	Adsorption capacity for Cr (mg/g) ± SD
1:1.25	3.2862 ± 0.0028	2.3124 ± 0.0161
1: 2.50	3.3014 ± 0.0064	2.4902 ± 0.0295
1: 3.75	3.7319 ± 0.0058	3.3255 ± 0.0129
1: 5.00	2.9015 ± 0.0014	2.8980 ± 0.0156
1: 6.25	3.2680 ± 0.0029	3.0025 ± 0.0129

aqueous solution using NaOH-activated coffee pulp biosorbent was set with a contact time range of 20–120 min. The relationship between contact time and adsorption capacity for both metal ions is displayed in Figure 1.

Figure 1 presents the adsorption capacity of Cu(II) and Cr(III) metal ions, which can be significantly increased by extending the contact period from 20 to 60 min. and further decreased at contact times of 90 to 120 min. because of the absence of active sites reaching saturation after this time. Initially, this increase in adsorption can be associated with the presence of free and highly unsaturated sites of the adsorbent. Subsequently, over time, these sites gradually become saturated and eventually reach equilibrium, so that no further increase in metal ion adsorption occurs (Ullah et al., 2023; Basem et al., 2024). The adsorption capacity of Cu(II) and Cr(III) metal ions on NaOH-activated biosorbents with a contact time of 20 minutes was 3.3115 mg/g and 2.9589 mg/g, respectively, then increased to 3.9986 mg/g and 3.1891 mg/g at a contact time of 60 minutes. This finding is consistent with the results obtained by Taheri et al. (2023), who state the amount of adsorption rises with the lengthening of the contact time between the adsorbent and the metal ions because the adsorbent makes more contact with the ions. In addition, Adsorption can decrease if the contact time is longer because the adsorbent has reached maximum efficiency in adsorption and the desorption process will begin (Ullah et al., 2023).

Effect metal ions concentration on adsorption capacity

The Cu(II) and Cr(III) metal ions at various concentrations ranging from 10 to 120 mg/L were added to as much as 1.00 g of active biosorbent and left for 60 minutes while stirring at a speed of 100 rpm. The adsorption capacity for Cu(II) and Cr(III) metal ions at various concentrations against NaOH-activated coffee pulp biosorbents is given in Figure 2.

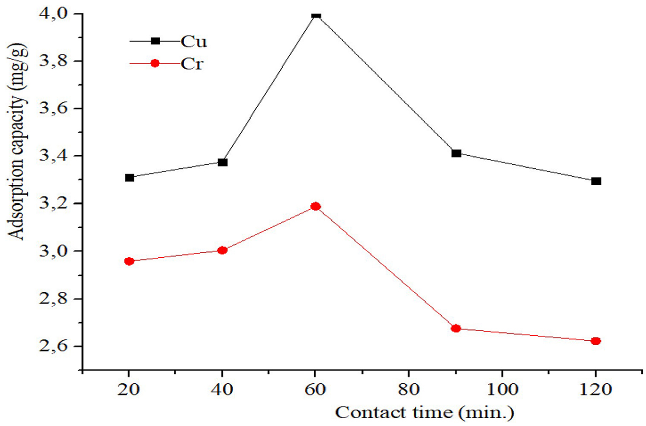

Figure 1. The adsorption capacity of Cu(II) and Cr(III) onto activated coffee pulp biosorbent at different contact times.

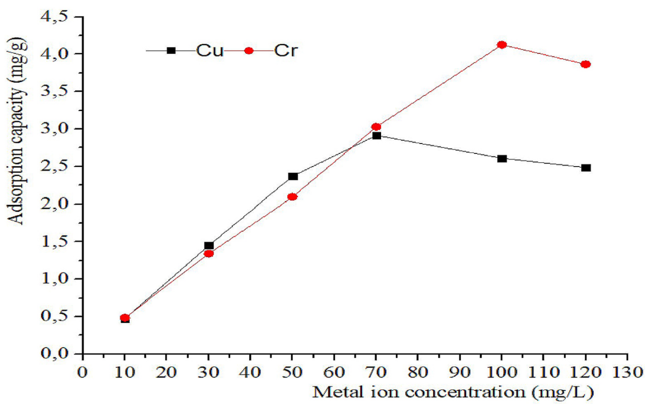

Figure 2. The adsorption capacity of different Cu(II) and Cr(III) metal ion concentrations onto activated coffee pulp biosorbent.

As clearly seen in Figure 2, the adsorption efficiency decreases with increasing concentrations of Cu(II) and Cr(III) metal ions. In the 60-minute treatment, the adsorption efficiency of Cu(II) and Cr(III) with a concentration of 30 mg/L reached 1.4531and 1.3432 mg/g, respectively, but became 2.853 mg/g and 3.8655 mg/g at a concentration of 120 mg/L. This finding aligns with Khedr et al. (2024), who reported that the adsorption percentage of Cu, Cr, Zn, and Pb metal ions on modified iron magnetic nanocomposites decreased with higher early concentrations of metal ions. The adsorption of heavy metals using agrowaste biosorbents (moringa, lupinus, sugarcane straw, and tea residue), carried out by Ahmed et al. (2023), also found a decrease in the efficiency of adsorption of Cu, Pb, Se, Zn, and Cr ions as the concentration of treated heavy metals increased. Our study found that the optimum concentration for removing Cu(II) and Cr(III) from aqoueus solution for 60 min. of contact time using NaOHactivated coffee pulp biosorbent was 70 mg/L and 100 mg/L, respectively, with adsorption capacities of 2.9155 mg/g and 4.1278 mg/g.

Adsorption isotherm pattern

The study of adsorption isotherms can give a message about the process of adsorption (monolayer adsorption and multi-layer adsorption) as well as the maximum adsorption capacity, which is important for designing an adsorption system. The Langmuir and Freundlich adsorption isotherm patterns were applied to test the adsorption isotherm patterns of Cu(II) and Cr(III) on NaOH-activated coffee pulp as biosorbents, and the test results are displayed in Figures 3 and 4. Figures 3 and 4 show the Langmuir and Freundlich adsorption models fitting for the NaOH-activated biosorbent of coffee pulp for Cu(II) and Cr(III) metal ions in aqueous solution. The selection of the suitability of the adsorption isotherm to explain the adsorption process

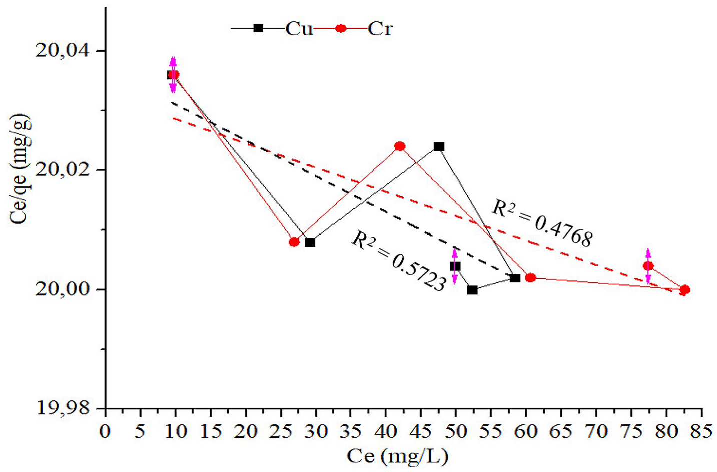

Figure 3. Langmuir adsorption isotherm curve of Cu and Cr onto the biosorbent surface

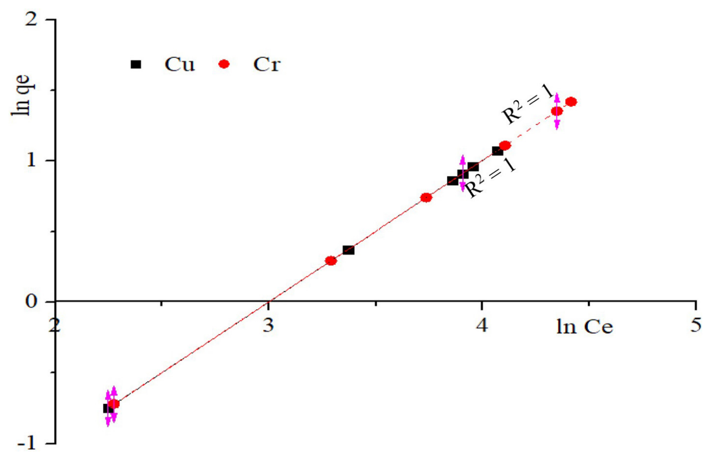

Figure 4. Freundlich adsorption isotherm curve of Cu(II) and Cr(II) onto the biosorbent surface

was assessed based on the determination coefficient (R^2) value. The curves in Figures 4 and 5 show that the Freundlich isotherm is most suitable for defining the adsorption behavior of Cu^{2+} and Cr^{3+} ions on NaOH-activated coffee pulp biosorbents. This is based on the R^2 value for Freundlich being greater than Langmuir. Hence, the adsorption process of the NaOH- activated coffee pulp biosorbent on Cu(II) and Cr(III) ions in solution occurs through multilayer interactions. The same findings were also obtained from research by Bakar et al. (2023), who observed that the process of removing heavy metals ions (Pb^{2+}, Zn^{2+}, and Fe^{2+}) from laundry wastewater using chitosan ceramic beads followed the Freundlich isotherm model.

Adsorption kinetics model

Principally, adsorption kinetics describes the rate at which a solute is adsorbed on the solid surface. The rate sorption of Cu(II) and Cr(II) metal ions onto NaOH-activated coffee pulp biosorbent is tested using pseudo-first-orde and pseudo-second-orde kinetic models, and the test results are given in Figures 5 and 6. The pseudo-second-order pattern is the best fit to describe the adsorption rate behavior of Cu(II) and Cr(III) metal ions on the NaOH-activated coffee pulp biosorbent surface, with the highest determination coefficient (R2) of 0.9992 for Cu(II) and 0.9977 for Cr(III), as well as the reaction rate constant (k2) for Cu(II) and Cr(III) being 0.2608 $menit^{-1}$ ppm^{-1} and 0.00459 $menit^{-1}$ ppm^{-1}, respectively. Several researchers have reported that heavy metal adsorption also follows the pseudo-second-order kinetic model, such as Pb(II) adsorption by using carbonized sludge activated with NaOH and carbonized sludge activated with KOH (Felia et al., 2024), Cu metal ion adsorption from aqueous solutions using banana leaves activated carbon (Darweesh et al., 2022), biosorption of Pb (II) and Fe (II) ions using agricultural waste materials of dennettia tripetala (Silas et al., 2023).

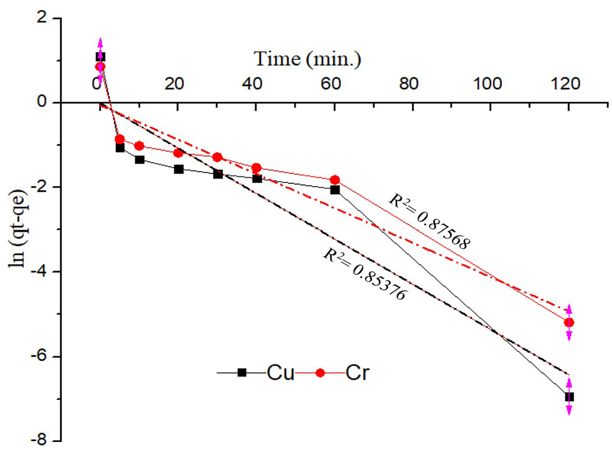

Figure 5. Pseudo-first-order adsorption kinetic pattern for Cu(II) and Cr(II) onto activated coffee pulp biosorbent surface

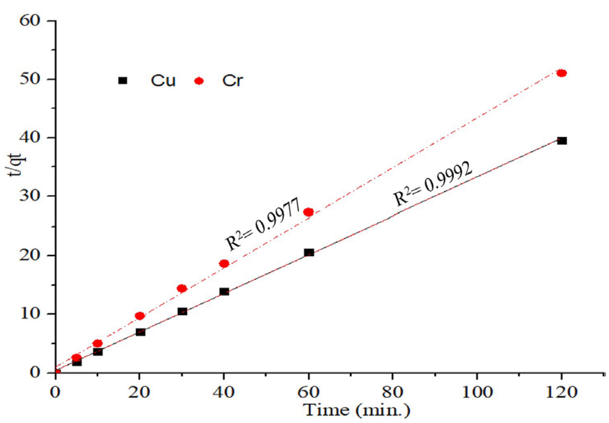

Figure 6. Pseudo-second-order adsorption kinetic pattern for Cu(II) and Cr(III) onto activated coffee pulp biosorbent surface

CONCLUSIONS

Based on the findings obtained in this study, it can be concluded that the optimum mass ratio of coffee pulp powder to NaOH for the adsorption of Cu and Cr metals was 1:3.75, with the highest adsorption capacities being 3.7319 mg/g for Cu(II) and 3.3255 mg/g for Cr(III). The the optimum concentration for eliminating Cu(II) and Cr(III) from aqoueus solution for 60 min. of contact time using NaOH-activated coffee pulp biosorbent was 70 mg/L and 100 mg/L, respectively, with the adsorption capacities of 2.9155 mg/g and 4.1278 mg/g. The removal of Cu(II) and Cr(III) onto coffee pulp biosorbents follows Freundlich isotherm pattern, while their adsorption kinetics tend to fit a pseudo-second-order kinetic model. Biosorbent-derived agricultural waste, such as coffee pulp, has the potential to be an efficient and sustainable biosorbent for heavy metal removal from aqueous solutions.

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