

Adsorption, Kinetic and Thermodynamic Studies for the Adsorption of Cadmium onto Combination of Chitosan and Coffee Ground Activated Carbon

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Abstrak

Kehadiran kadmium dalam air akibat mobilitas alamnya dapat menyebabkan sifat air menjadi racun dan mengancam ekosistem sekitar bila terakumulasi dalam rantai makanan. Tujuan dari penelitian ini adalah untuk mengetahui kapasitas adsorpsi maksimum menggunakan model isothermal, mengetahui laju kinetika adsorpsi menggunakan adsorben kitosan dan bubuk kopi dalam menurunkan konsentrasi kadmium pada air limbah industri, dan mengetahui besaran termodinamikanya. Metode penelitian yang diterapkan adalah eksperimen laboratorium yang dilanjutkan dengan analisis data kuantitatif untuk menentukan model isothermal dan kinetika adsorpsi. Hasil penelitian menunjukkan bahwa isotherm adsorpsi mengikuti model isotherm Langmuir dengan koefisien korelasi sebesar 0,9970 dan kapasitas adsorpsi maksimum sebesar 0,7546 mg.g⁻¹ yang menunjukkan bahwa adsorpsi kimia terjadi pada monolayer, dimana lokasi adsorpsi terdistribusi secara homogen dengan energi adsorpsi. Interaksi permanen dan dapat diabaikan antara molekul kadmium (adsorbat) dan adsorben. Dengan demikian model kinetika orde dua semu merupakan cara yang lebih baik untuk menjelaskan laju reaksi kadmium dalam kombinasi kitosan dan karbon aktif bubuk kopi. Nilai ΔG° yang negatif menunjukkan bahwa reaksi adsorpsi berlangsung secara spontan, ΔH° sebesar 0,3467 menunjukkan reaksi endoterm, dan ΔS° sebesar 3,5296 menunjukkan adanya peningkatan keacakan proses adsorpsi pada antarmuka adsorben dan kadmium selama adsorpsi.

Kata Kunci : kapasitas adsorpsi, kadmium, kitosan, bubuk kopi

Abstract

The presence of cadmium in water due to its natural mobility can cause the nature of the water to become toxic and threaten the surrounding ecosystem when it accumulates in the food chain. The aim of this study was to investigate the maximum adsorption capacity using an isothermal model, to determine the rate of adsorption kinetics using chitosan and coffee powder adsorbents in reducing cadmium concentrations in industrial wastewater, and to investigate its thermodynamic magnitude. The research method was applied with laboratory experiments followed by quantitative data analysis to determine the isothermal model and adsorption kinetics. The results showed that the adsorption isotherm follows the Langmuir isotherm model with a correlation coefficient of 0.9970 and a maximum adsorption capacity of 0.7546 mg.g⁻¹, which indicates that the chemical adsorption occurs in a monolayer, where the adsorption sites are homogeneously distributed with the adsorption energy. Permanent and negligible interactions between cadmium molecules (adsorbate) and adsorbent. Thus the pseudo second order kinetic model is a better way to explain the reaction rate for cadmium in combination chitosan and coffee ground activated carbon. Negative ΔG° values indicate that the adsorption reaction takes place spontaneously, ΔH° of 0.3467 indicates an endothermic reaction, and ΔS° of 3.5296 indicates an increase in the randomness of the adsorption process at the adsorbent interface and cadmium during adsorption.

Key words : adsorption capacity, cadmium, chitosan, coffee ground

INTRODUCTION

The United States Environmental Protection Agency published a list of pollutants threatening human health and living organisms, which included such heavy metals as cadmium, chromium, zinc, mercury, lead, copper, and nickel. Among them, cadmium ion is a very toxic heavy metal that can enter the environment from various man-made sources, such as plastic factories, plating processes, nickel-cadmium batteries, pesticides and fertilizers, paint pigments, metal alloy production, and mining, smelting, welding and refining processes. The toxicological effects of cadmium on the human body have been widely confirmed, including kidney damage, respiratory failure, hypertension, cancer, gastrointestinal diseases and also osteoporosis. Because of the irreparable damage that cadmium can cause to the human body, it must be properly removed from water sources and industrial effluents. Several abiotic techniques such as ion

exchange, chemical precipitation, reverse osmosis, electrochemical treatment, coagulation and surface adsorption are used to remove heavy metals is often used. Recently, adsorption methods have also been introduced as a good alternative to remove toxic substances from wastewater. Adsorption methods are simpler, more effective and cheaper for the removal of heavy metals because they are cheap, short working time, high efficiency, do not produce toxic compounds and are environmentally friendly (Dirbaz & Roosta, 2018).

Bekasi Regency is the largest industrial area in Southeast Asia. Preliminary studies that have been conducted on samples of wastewater from one of the textile industries in Bekasi Regency showed a concentration of cadmium metal of 1.15 mg/L. The concentration of cadmium metal has exceeded the quality standard concentration stipulated in the Minister of Environment Regulation Number 5 of 2014 concerning Wastewater Quality Standards, namely 0.05 mg/L (Menteri Lingkungan Hidup, 2014). Therefore it is necessary to conduct research on industrial wastewater treatment using appropriate methods.

The focus of research in recent years has focused on the use of alternative adsorbents to reduce the cost of using adsorbents and are more environmentally friendly because of their easy operation and high efficiency (Kim et al., 2014). Chitosan (β -1,4,2-amino-2-deoxy D-glucose) is an organic material derived from chitin obtained through a deacetylation process at high temperatures using a strong base (Nuryono et al., 2020). Chitosan has been used as an adsorbent in reducing heavy metals but has the disadvantage of increasing turbidity in water, so further processing is required. The combination of chitosan with coffee grounds can increase the recycling potential of the adsorbent, can increase the chemical stability and adsorption capacity of the adsorbent to increase the reduction efficiency (Das et al., 2018). Utilization of chitosan and activated carbon from coffee grounds as adsorbents can reduce levels of cadmium metal by 74.54%, and nickel by 73.43% (Purnama, 2019), and reducing lead metal with an adsorption efficiency of 92.26% and a final concentration of 0.774 mg/L at a contact time of 120 minutes (Said, 2018) and reducing drug contaminants in wastewater such as metamizole, acetyl salicylic acid, acetaminophen and caffeine (Lessa et al., 2018).

Previous research results showed that the effectiveness of using natural adsorbents from chitosan and coffee grounds activated carbon in reducing cadmium concentrations in industrial wastewater was 90.86% with a final concentration of 0.07 mg/L (Nurhidayanti et al., 2021). Previously, the isotherm model and kinetics of arsenic metal in reducing arsenic metal (Nurhidayanti & Nugraha, 2022), kinetic analysis and adsorption isotherm of chicken egg shells and membranes against synthetic dyes (Hevira & Gampito, 2022), kinetic analysis and adsorption isotherm of cadmium onto microalgae *Parachlorella* sp (Dirbaz & Roosta, 2018) had been studied. However, the proper lead metal adsorption isotherm model has not been studied to determine the adsorption capacity of the use of chitosan and coffee grounds adsorbents in reducing lead concentrations in industrial wastewater (Nurhidayanti et al., 2021; Suwazan et al., 2022; Suwazan & Nurhidayanti, 2022). The purpose of this study was to study the maximum adsorption capacity through an isotherm model, to determine the rate of adsorption kinetics in the use of chitosan and coffee grounds adsorbents in reducing lead concentrations in industrial wastewater and to study its thermodynamic magnitude.

RESEARCH METHOD

This research was conducted at the Laboratory of PT. Tuv Nord Indonesia and Pelita Bangsa University from June to December 2022. The research method was carried out using experiments in the laboratory followed by analysis of quantitative data to determine isotherm models, adsorption kinetics and thermodynamics. All treatments and measurements in the experiment were carried out in triplicate.

The materials used in the study were chitosan, Cadmium solution, $ZnCl_2$ p.a solution (Merck), HCl p.a solution (Merck), NaOH p.a solution (Merck) and coffee grounds which were coffee waste from coffee shops. The tools used in this study consisted of beakers, analytical balance, filter paper, volume pipette, funnel, porcelain cup, universal indicator, oven, spatula, acrylic plate, hot plate, sieve, furnace, desiccator, rubber suction/bulb, aluminum foil, ball mill, magnetic stirrer, vacuum, Fourier Transform-Infra Red (FT-IR) and Scanning Electron Microscopy- Energy Dispersive X-Ray (SEM-EDX). The Research procedure in this study follows the flowchart as presented in Figure 1.

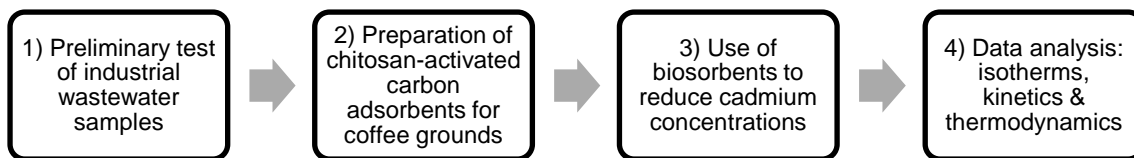


Figure 1. Research Procedures

The research process from stages 1 to 3 has been carried out in 2021 (Nurhidayanti et al., 2021). The scope of this research is at point 4 of the framework in the picture above. The isotherm models used in this study are Langmuir, Freundlich, Dubinin Raduskevich (D-R) and Temkin isotherms. Determination of the adsorption capacity (q) uses equation 1 (Sunsandee et al., 2020).

$$q = \frac{(C_i - C_t) \times V}{m} \dots \dots \dots (1)$$

Where q is adsorption capacities (mg/g), C_i is the initial concentration of cadmium (mg/L), C_t is the concentration of cadmium at time t (mg/L), V is volume of cadmium solution, and m is mass of adsorbent used in the reaction mixture (g). Data analysis was carried out using final lead concentration data which had gone through an adsorption process using adsorbent chitosan-activated carbon coffee grounds with mass variations (0.6 gram to 1.4 gram) to obtain maximum adsorption capacity. The results of this analysis are then entered into the isotherm equation.

Adsorption equilibrium data were fitted for linear Langmuir, Freundlich, Temkin and Dubinin-Raduskevich (D-R) isotherms. The Langmuir isotherm equation has the following non-linear forms (Wang & Guo, 2020a) :

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \dots \dots \dots (2)$$

Where q_e is the equilibrium adsorption capacity (mg/g), C_e is the concentration of at equilibrium (mg/l), q_m is the maximum adsorption capacity (mg/g) and K_L is the Langmuir equation constants (L/mg) that can be determined by $\frac{C_e}{q_e}$ vs based on the linear plot of C_e . The Freundlich isotherm equation has the following non-linear forms (Wang & Guo, 2020a) :

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \dots \dots \dots (3)$$

Where K_F is the Freundlich constant, and $1/n$ is the adsorption intensity. The value $1/n < 0$ indicates the reaction takes place irreversible. If $0 < 1/n < 1$, the adsorption reaction is desired, while if $1/n > 1$, the adsorption reaction is not desired. Plotting C_e versus Q_e can solve the Freundlich model in equation (3). The determination of K_F and q_m is generated from the slope and intercept resulting from the regression equation. This D-R isotherm model is expressed by the following equation (Wang & Guo, 2020a):

$$q_e = q_{mD-R} e^{-K_{DR} \varepsilon^2} \dots \dots \dots (4)$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \dots \dots \dots (5)$$

Where q_{mD-R} (mg/g) is the maximum adsorption capacity ; $[-K_{DR}$ is the activity coefficient (mol^2/J^2); ε (kJ/mol) is the adsorption potential based on Polanyi potential theory. The Temkin isotherm model is expressed in the following equation (Wang & Guo, 2020a):

$$q_e = \frac{RT}{b} \ln(AC_e) \dots \dots \dots (6)$$

Where R is the universal gas constant, T is the temperature; A (L/g) is the equilibrium constant and b (J/mol) is the Temkin constant related to the heat of adsorption. To investigate the mechanism of the adsorption process, pseudo-first-order adsorption, pseudo-second-order adsorption models, Elovich and Webber Morris were used to test the adsorption data. The pseudo-first-order model (Wang & Guo, 2020b) is expressed by Equation (7):

$$\ln(q_e - q_t) = \ln(q_t) - k_1 t \dots \dots \dots (7)$$

where q_e is equilibrium adsorption capacities (mg/g) and q_t is the amounts of lead adsorbed on the adsorbent at time (mg/g), t is time, and k_1 is the pseudo-first-order rate constants (min^{-1})

The pseudo second-order index model (Wang & Guo, 2020b) is given in Eq. (8):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots \dots \dots (8)$$

where k_2 is the constant of the pseudo-second-order rate (g/mg/min), which is obtained by plotting $\frac{t}{q_t}$ versus t . The Elovich model has been expressed in Equation (9):

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t) \dots \dots \dots (9)$$

Then a graph of the relationship q_t versus $\ln t$ is made which will produce slope as a value of $1/b$ and an intercept as a value of $1/b \ln(ab)$.

The Webber Morris model has been expressed in Equation (10):

$$q_t = k_i t^{1/2} \dots \dots \dots (10)$$

Where k_i is the intra-particle diffusion constant. Then graph the relationship between q_t versus $t^{1/2}$ which will produce the slope as the value of k_i . Determination of the appropriate isotherm model and adsorption kinetics was carried out based on the correlation coefficient with the largest R^2 value close to 1.0 using Microsoft excel software. The thermodynamic behavior of the adsorption of cadmium on adsorbent can be described by the thermodynamic parameters, including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), which were calculated based on the following equation (Sunsandee et al., 2020). Where R is the universal gas constant (8.314 J/mol K), T is the temperature (K) and K_D is the equilibrium constant. To strengthen the research results, tests were also carried out One-way ANOVA statistics to determine the effect of variations in chitosan-coffee grounds mass.

$$\Delta G^\circ = -RT \ln K_{eq} \dots \dots \dots (11)$$

RESULTS AND DISCUSSION

The use of chitosan-coffee grounds adsorbent in reducing cadmium concentrations in industrial wastewater is presented in Figure 2, shows that the highest reduction in cadmium metal concentration was in the use of chitosan adsorbent with a coffee grounds activated carbon mass of 1.4 grams to 0.07 mg/L. Which means that the greater the mass of coffee grounds activated carbon combined with chitosan in the adsorption process, the greater the decrease in cadmium concentration produced, because the increase in adsorption capacity along with the increase in activated carbon mass is related to the increase in the active absorption sites of biosorbents in the absorption of cadmium metal in wastewater. In this case, the presence of activated carbon from coffee grounds in the bioadsorbent causes an increase in organic compound components in the form of n-hexadecanoic acid and n-octadecanoic acid which can increase the absorption capacity of chitosan (Lessa et al., 2018). The results of the one-way ANOVA test showed showed p of 8.28×10^{-9} ($p < 0.05$) and F calculated of 599.17, F table of 5.32 (F calculated $>$ F table), which means that there was an influence of variations in the mass of coffee grounds added on reducing the concentration of cadmium metal.

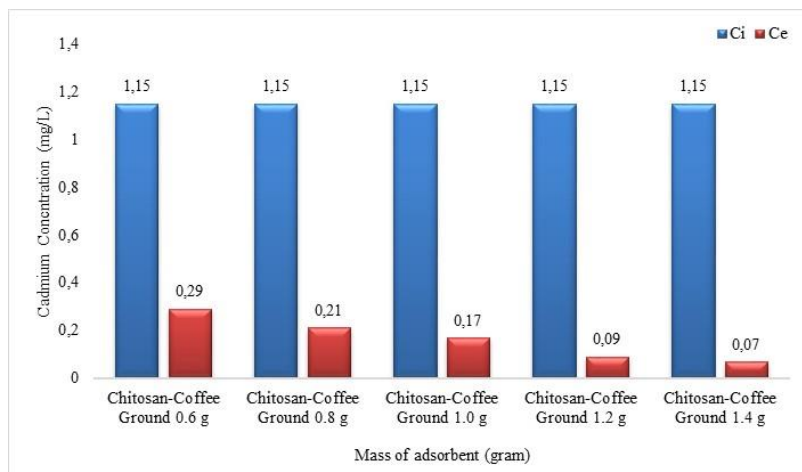


Figure 2. Graph of Cadmium Concentration in Wastewater at various masses of adsorbent

Figure 3 shows that the reduction efficiency of cadmium metal in chitosan bioadsorbent and 0.6 gram coffee grounds activated carbon was 74.57%, in chitosan bioadsorbent and 0.8 gram coffee grounds activated carbon was 81.87%, in chitosan bioadsorbent and 1.0 gram coffee grounds activated carbon was 85.54%, chitosan bioadsorbent and 1.2 gram coffee grounds activated carbon was 91.85% and chitosan

bioadsorbent and 1.4 gram coffee grounds activated carbon was 94.35%. This shows that the higher the dose of coffee grounds activated carbon combined with chitosan will further increase the absorption efficiency of cadmium metal in wastewater. The results of the one-way ANOVA test showed p of 1.01×10^{-8} ($p < 0.05$) and F count of 569.43, F table of 5.32 (F count > F table) which means that there is an influence of variations in the mass of coffee grounds added to the percent removal of cadmium metal concentration. This is due to the presence of active sites as evidenced by SEM characterization results which show that the surface of the chitosan-activated carbon bioadsorbent of coffee grounds consists of several pore sites with very rough and wavy edges. This indicates the availability of a significant active surface for the adsorption process of cadmium heavy metal contaminants in wastewater (Ahmadi et al., 2017). The results of the EDX characterization of the bio-adsorbent chitosan and 1.4 gram coffee grounds showed the presence of 74.30% carbon; 18.29% Oxygen; 0.88% Sodium; 0.34% Magnesium; 2.99% tin, 0.51% zirconium; 0.53% copper; 0.46% zinc; 0.46% chlorine; 0.42% potassium; 0.34% phosphorus; 0.27% calcium; 0.15% silicon and 0.06% aluminum. The results of data analysis performed on several isotherm equations are presented in Figures 4 to 7.

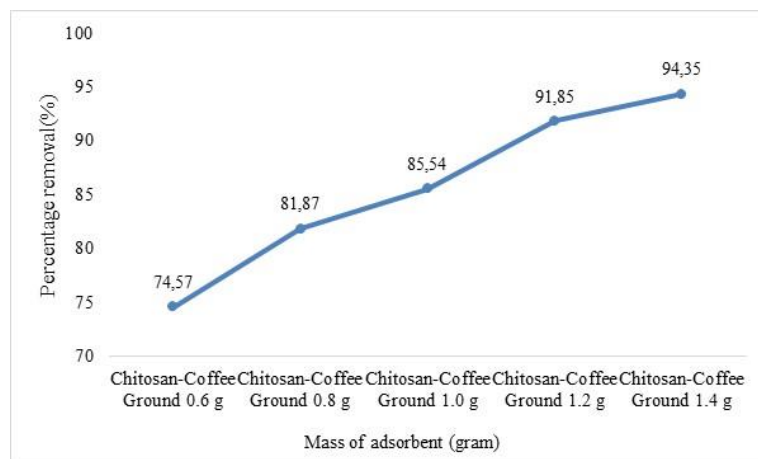


Figure 3. Percent removal of Cadmium Concentration in Wastewater at various masses of adsorbent

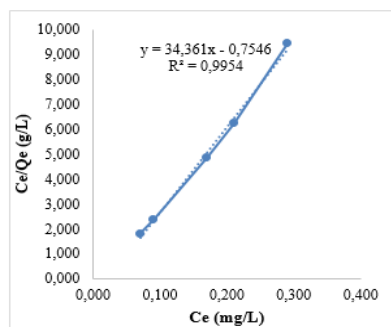


Figure 4. Plot Ce vs Ce/Qe on the Langmuir isotherm model

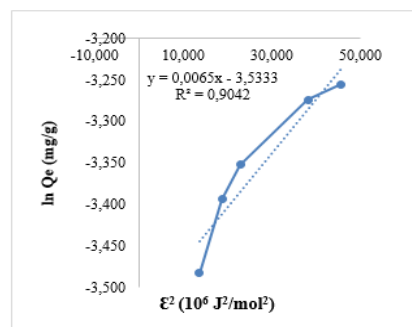


Figure 6. Plot ln Qe vs E² on the Dubinin-Raduskevich (D-R) isotherm model

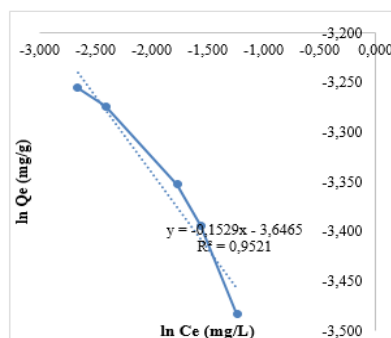


Figure 5. Plot ln Ce vs ln Qe on the Freundlich isotherm model

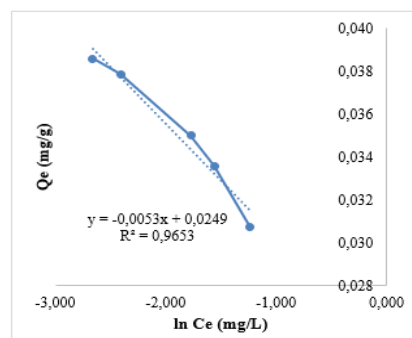


Figure 7. Plot ln Ce vs Qe on the Temkin isotherm model

Figures 4-7 above show that the correct isotherm model for the adsorption process of cadmium using chitosan-activated carbon coffee grounds is the Langmuir model because the highest correlation coefficient is 0.9954; later followed by the models of Temkin, Freundlich and Dubinin-Raduskevich. The magnitude of the adsorption isotherm parameters is presented in Table 1.

Table 1. Parameters of cadmium adsorption isotherm using chitosan-activated carbon of coffee grounds

No.	Langmuir	Freundlich	Dubinin-Raduskevich	Temkin
1	$K_L=34.3610$	$K_F=0.1529$	$q_{mD-R}=3.5333$	$b_T=0.0053$
2	$Q_m=0.7546$	$1/n=-3.6465$	$\epsilon=7 \times 10^{-9}$	$B=0.0249$
3	$R_L=2.468$	$R^2=0.9521$	$R^2=0.9042$	$R^2=0.9653$
4	$R^2=0.9954$			

The table above shows the calculated data regarding several adsorption isotherm parameters, namely the Langmuir constant which is 34.3610 with a maximum adsorption capacity of 0.7546 mg/g and a separation factor (RL) value of 2.468 which means that adsorption is favorable ($RL > 1$) (Khalil et al., 2020). The Freundlich equation shows that there is a Freundlich constant (KF) of 0.1529 and a adsorption intensity ($1/n$) of -3.6465 (< 0), which means that the adsorption reaction takes place in irreversible (Pagalan et al., 2020). The Dubinin Raduskevich isotherm equation shows that there is a maximum adsorption capacity (q_{mD-R}) of 3.5333 mg.g^{-1} , the adsorption potential based on Polanyi potential theory (ϵ) is 7×10^{-9} kJ/mol. The Temkin isotherm equation shows that the Temkin constant associated with the heat of adsorption is 0.0199 J/mol. Based on the data analysis carried out, the correlation coefficient of the Langmuir model > Temkin > Freundlich > D-R. This shows that the adsorption isotherm follows the Langmuir isotherm model with a correlation coefficient of 0.9954 with a maximum adsorption capacity of 0.7546 mg.g^{-1} which indicates that chemical adsorption occurs in the mono layer with a homogeneous distribution of adsorption sites with adsorption energy constant and negligible interactions between cadmium molecules (adsorbate). The results of data analysis on several kinetics equations are presented in Figures 8 to 11. The magnitude of the adsorption kinetics parameters is presented in Table 2.

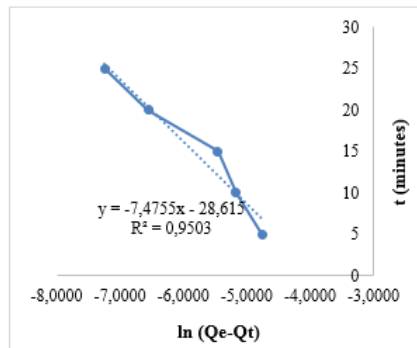


Figure 8. Plot $\ln(Q_e - Q_t)$ vs t on the PFO kinetics model

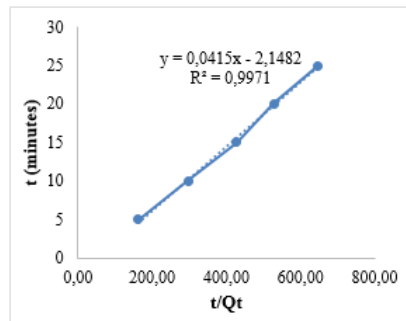


Figure 9. Plot t/Q_t vs t on the PSO kinetics model

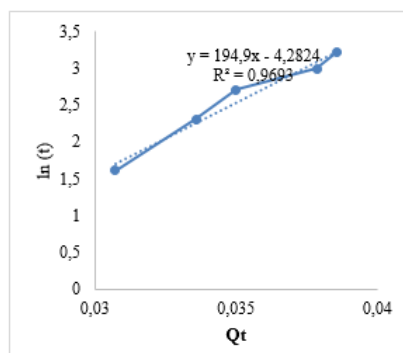


Figure 10. Plot Q_t vs $\ln t$ on the Elovich kinetics model

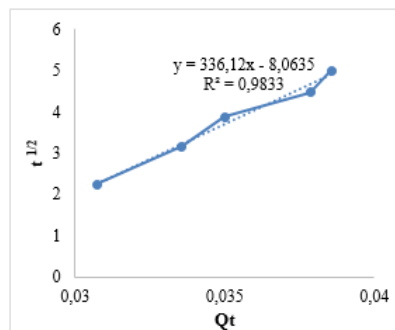


Figure 11. Plot Q_t vs $t^{1/2}$ on the Webber Morris kinetics model

Table 2. The results of rate constant investigated

No	Kinetics	Equation	k	q _e	R ²
1	Pseudo First Order (PFO)	$\ln(q_e - q_t) = \ln q_e - k_1 t$ Rate = $k_1 (q_e - q_t)$	$k_1 = 28.615 \text{ h}^{-1}$	7.4775 mg.g ⁻¹	0.9503
2	Pseudo Second Order (PSO)	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ Rate = $k_2 (q_e - q_t)^2$	$k_2 = 2.1482 \text{ g.mg}^{-1} \cdot \text{h}^{-1}$	0.0415 mg.g ⁻¹	0.9971
3	Elovich	$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t)$ Rate = $a e^{-bq_t}$	$k = 194.9 \text{ mg.g}^{-1}$	-	0.9693
4	Weber Morris/ Difusi Intra Partikel	$q_t = k_i t^{1/2}$	$k_i = 336.12 \text{ mg.g}^{-1}$	8.0635 g.mg ⁻¹ h ⁻¹	0.9833

The table above shows the calculated data regarding several adsorption kinetic parameters, namely the PFO constant of 28.615 mg.g⁻¹ with an adsorption capacity based on weight at equilibrium of 7,4775 mg.g⁻¹. The PSO equation shows that there is a PSO constant of 2.1482 mg.g⁻¹.hour⁻¹ with an adsorption capacity based on weight at equilibrium of 0.0415 mg.g⁻¹. The Elovich equation shows that there is an Elovich constant of 149.9 mg.g⁻¹. The intra-particle diffusion equation shows the Weber Morris constant of 336.12 mg.g⁻¹. Based on the data analysis performed, the correlation coefficient of the kinetic model of PSO > Weber Morris > Elovich > Langmuir. This shows that the adsorption kinetics follows the pseudo second order kinetics model with a correlation coefficient of 0.9971. Thus the pseudo second order kinetic model is a better way to explain the reaction rate for cadmium in combination chitosan and coffee ground activated carbon. These facts indicate that the possible rate-dominant step of Cd sorption is chemisorption, which involves a cation exchange reaction between adsorbate and adsorbent, surface complexation, coordination, and/or chelation. (Yanyan et al., 2018). Negative ΔG° values indicate that the adsorption reaction takes place spontaneously, ΔH° of 0.3467 indicates an endothermic reaction, and ΔS° of 3.5296 indicates an increase in the randomness of the adsorption process at the adsorbent interface and cadmium during adsorption (Table 3).

Table 3. Thermodynamic parameter for adsorption of cadmium onto chitosan coffee ground adsorbent

No.	Temperature (°C)	ΔG° (J/mol)	ΔH°(kJ/mol)	ΔS°(kJ/mol.K)
1	298	-1476.592		
2	318	-2593.167	0.3467	3.5296
3	328	-3698.187		
4	338	-4811.776		

CONCLUSIONS

This study of cadmium adsorption showed that the adsorption isotherm follows the Langmuir isotherm model with a correlation coefficient of 0.9954 with a maximum adsorption capacity of 0.7546 mg.g⁻¹ which indicates that chemical adsorption occurs in the mono layer with a homogeneous distribution of adsorption sites with constant adsorption energy and negligible interactions between cadmium molecules (adsorbate) and adsorbent. This shows that the adsorption kinetics follows the pseudo second order kinetics model with a correlation coefficient of 0.9971. Thus the pseudo second order kinetic model is a better way to explain the reaction rate for cadmium in combination chitosan and coffee ground activated carbon. Negative ΔG° values indicate that the adsorption reaction takes place spontaneously, ΔH° of 0.3467 indicates an endothermic reaction, and ΔS° of 3.5296 indicates an increase in the randomness of the adsorption process at the adsorbent interface and cadmium during adsorption.

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