Vol. 14 Special Issue (2023) 1-11

Jurnal Riset
Teknologi Pencegahan Pencemaran Industri

Journal homepage : https://www.jrtppi.id

Kementerian Perindustrian
REPUBLIK INDONESIA

Isotherm Study, Adsorption Kinetics and Thermodynamics of Lead Using Combination Adsorbent of Chitosan and Coffee Ground Activated Carbon

Nisa Nurhidayanti*[1], Aris Dwi Cahyanto[1]

[1] Universitas Pelita Bangsa.

ARTICLE INFO

Article history:
Received March 11, 2023
Received in revised form July 08, 2023
Accepted September 21, 2023
Available online December 22, 2023

Keywords :
Chitosan
Coffee Ground
Isotherm
Kinetics
Lead
Thermodynamics

ABSTRACT

The presence of lead metal in water naturally, due to its mobility, can cause the nature of water to become toxic and endanger the environmental ecosystem by causing bioaccumulation within the food chain. The purpose of this study was to determine the maximum adsorption capacity through an isotherm model, ascertain the rate of adsorption kinetics when utilizing chitosan and coffee grounds as adsorbents to reduce lead concentrations in industrial wastewater, and analyze its thermodynamic properties. The research method was carried out using experiments in the laboratory followed by quantitative data analysis to determine the isotherm model and adsorption kinetics. The results showed that the adsorption isotherm conforms to the Langmuir isotherm model with a correlation coefficient of 0.9970 with a maximum adsorption capacity of 1.0511 $mg.g^{-1}$ which indicates that chemical adsorption occurs in the mono layer with a homogeneous distribution of adsorption sites with adsorption energy constant, with negligible interactions between lead metal molecules (adsorbate). The kinetics of lead adsorption using chitosan-activated carbon coffee grounds following the Weber-Morris/intra-particle diffusion model with a correlation coefficient of 0.9920 with a diffusion rate of 76.512 $g.mg^{-1}.hour^{-1}$ indicating that intra-particle diffusion is the rate step limiting in the overall biosorption process. Negative ΔG^o values indicate that the adsorption reaction takes place spontaneously, ΔH^o of 0.8130 indicates an endothermic reaction, and ΔS^o of 4.1888 indicates an increase in the randomness of the adsorption process at the adsorbent interface and lead during adsorption.

1. INTRODUCTION

Bekasi Regency is Southeast Asia's largest industrial zone. A preliminary study conducted on a wastewater sample from one of textile industries in the Bekasi district showed a lead metal concentration of 1.02 mg/L. Notably, this concentration of lead metal exceeds the water quality standard limit concentration of 0.1 mg/L as outlined in the 2014 Waste Water Quality Standard Environment Ministry Ordinance Number 5 (Ministry of Environment, 2014). Lead (Pb) is a heavy metal commonly encountered in effluents originating from electronics and silicon semiconductor industries, primarily due to its prevalence as a constituent in these materials. The high concentration of lead in these industries can result in its release into the environment. Lead exhibits natural mobility and can be distributed through various means, including chemical reactions, biological processes, geochemical interactions, volcanic activities, and human activities. Because lead metal is naturally present in water due to its mobility, the toxic nature of the water made it a problem all over the world from the 20th century to his 21st century. With a density of 11.400 kg/m^3, lead is a heavy metal found in nature and typically occurs in the form of bluish minerals alongside elements like oxygen and sulfur. Due to its toxic

*Correspondence author.
E-mail : nisa.kimia@pelitabangsa.ac.id (Nisa Nurhidayanti)

doi : https://10.21771/jrtppi.2023.v14.si.p1-11

Accreditation number : (Ristekdikti) 158/E/KPT/2021

characteristics, lead is recognized as a hazardous metal that can lead to neurocognitive impairments. This is attributed to factors such as its lethal dosage, assimilation rate, and half-life within the human body (M. S. Kim et al., 2014).

Various methods, including chemical precipitation, adsorption, membrane filtration, ion exchange, and coagulation-flocculation, are employed to mitigate the presence of heavy metals in wastewater. Recent research efforts have primarily focused on exploring alternative adsorbents that not only offer cost-effectiveness but also exhibit environmentally friendly attributes, characterized by their ease of operation and high efficiency (H. Kim, Hwang, & Sharma, 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 to reduce heavy metals, but it has the disadvantage of increasing water turbidity, requiring further treatment. Combining chitosan and coffee grounds increases the recyclability of the sorbent, improves the chemical stability and adsorption capacity of the sorbent, and improves the reduction efficiency (Das, Chakraborty, Chatterjee, & Kumar, 2018). The utilization of chitosan and activated carbon derived from coffee grounds as adsorbents has demonstrated effective reduction capabilities for various heavy metals. For instance, cadmium levels were reduced by 74.54%, and nickel levels by 73.43% (Purnama, 2019). Additionally, these adsorbents have been found to efficiently reduce lead metal, achieving an adsorption efficiency of 92.26% and resulting in a final concentration of 0.774 mg/L within a contact time of 120 minutes (Said, 2018). Furthermore, these materials have also been successful in reducing drug contaminants present in wastewater, including metamizole, acetyl salicylic acid, acetaminophen, and caffeine (Lessa, Nunes, & Fajardo, 2018).

A previous study demonstrated that the reduction of lead concentration in industrial wastewater using natural chitosan and activated carbon from coffee grounds as sorbents resulted in a reduction of 90.86%, yielding a final concentration of 0.09 mg/L (Nurhidayanti, Ilyas, & Suwazan, 2021). Previous research has explored the isothermal model and reaction kinetics of metallic arsenic reduction (Nurhidayanti & Nugraha, 2022), as well as the reaction kinetic analysis and adsorption isotherms of chicken egg shells, membranes, and synthetic dyes (Hevira & Gampito, 2022). 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 & Nurhidayanti, 2022; Suwazan, Nurhidayanti, Fahmi, & Riyadi, 2022). The purpose of this study is to explore 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 investigate its thermodynamic ascpects.

2. METHODS

This study was conducted at PT. Tuv Nord Indonesia and Pelita Bangsa University from June to December 2022. The research employed laboratory experiments followed by quantitative data analysis to determine isothermal models, adsorption kinetics, and thermodynamics. The materials utilized in this study included chitosan, $ZnCl_2$ p.a solution 0.1 N (Merck), HCl p.a solution 0.1 N (Merck), NaOH p.a solution 0.1 N (Merck), lead stock solution 1000 mg/L, and coffee grounds obtained from coffee shops as waste. The tools employed for this study comprised beakers, an 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-Infrared (FT-IR) Perkin-Elmer UATR Spectrum Two, and Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX) JEOL JSM-6510LA. The Research procedure in this study follows the flowchart as presented in Figure 1.

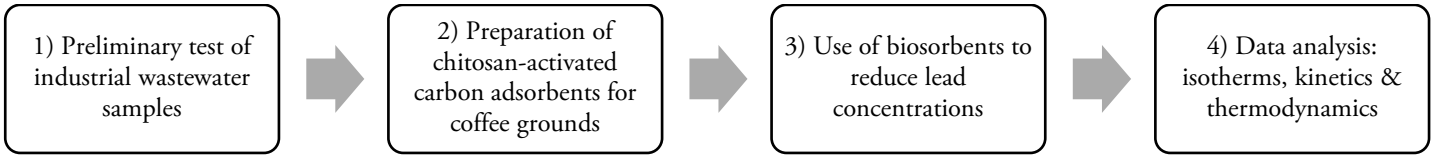


Figure 1. Research procedure

The research process from stages 1 to 3 has been carried out in 2021 (Nurhidayanti et al., 2021). The operational conditions employed included pH control, mass variation ranging from 0.6 to 1.4 grams, activated carbon particle size of 160 mesh, initial lead concentration of 1.02 mg/L, stirring speed of 100 rpm, contact time spanning from 5 to 25 minutes, and a temperature range of 25 to 55°C. 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, Ramakul, Phatanasri, & Pancharoen, 2020).

$$q = \frac{(C_i - C_t)x\,V}{m} \quad (1)$$

Where q is biosorption capacities (mg/g), Ci is the initial concentration of lead (mg/L), Ct is the concentration of lead at time t (mg/L), V is volume of lead solution, and m is mass of adsorbent used in the reaction mixture (g).

Data analysis was performed using final lead concentration data that underwent an adsorption process using the adsorbent chitosan charcoal coffee powder with mass change (from 0.6 grams to 1.4 grams) to obtain the maximum adsorption capacity. The results of this analysis are reflected in the isotherm equations.

Biosorption equilibrium data were fitted to linear Langmuir, Freundlich, Temkin, and Dubinin-Raduskevich isotherms (D-R). The Langmuir isotherm equation has the nonlinear form (Wang & Guo, 2020a):

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

where q_e is the equilibrium biosorption capacity (mg/g), C_e is the concentration of at equilibrium (mg/l), qm is the maximum biosorption capacity (mg/g) and KL is the Langmuir equation constants (L/mg) that can to 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):

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

Where KF is the Freundlich constant, and 1/n is the biosorption intensity. The value 1/n < 0 indicates the reaction takes place irreversible. If 0 < 1/n < 1, the biosorption reaction is desired, while if 1/n > 1, the biosorption reaction is not desired. Plotting C_e versus Q_e can solve the Freundlich model in equation (3). The determination of KF and qm 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):

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

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

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

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

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 biosorption.

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):

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

where qe is equilibrium biosorption capacities (mg/g) and qt is the amounts of lead adsorbed on the adsorbent at time

(mg/g), t is time, and k1 is the pseudo-first-order rate constants (min-1)

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

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

where k2 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):

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

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):

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

Where ki 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 ki.

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.

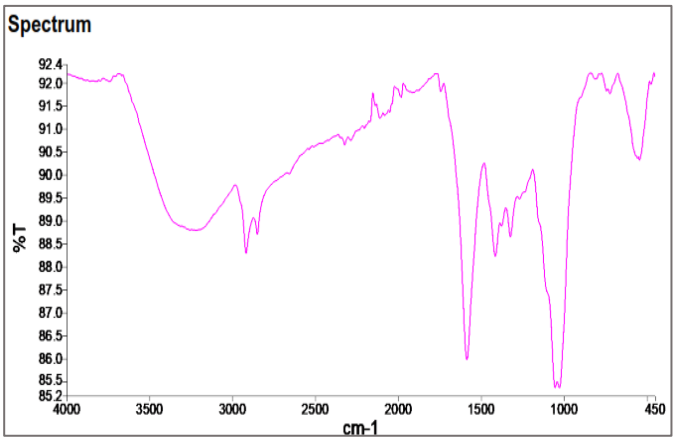
The thermodynamic behavior of the biosorption of lead on adsorbent can be described by the thermodynamic parameters, including the change in free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o), which were calculated based on the following equation (Sunsandee et al., 2020).

$$\Delta G^o = -RT \ln Keq \quad (11)$$

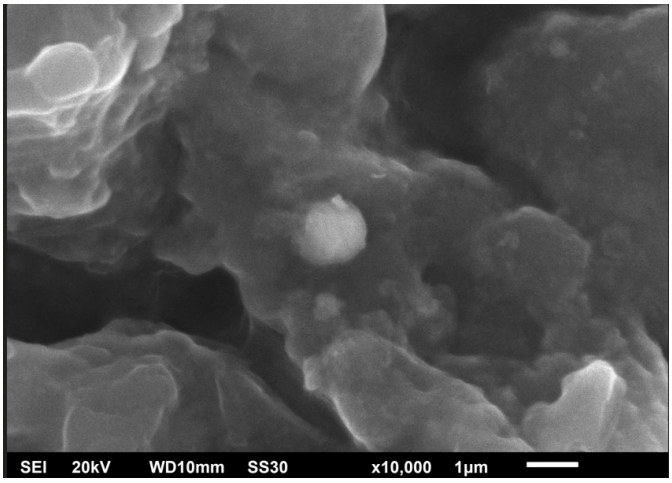
Where R is the universal gas constant (8.314 J/mol K), T is the temperature (K) and K_D is the equilibrium constant.

3. RESULTS AND DISCUSSION

The results of the FT-IR and SEM-EDX analysis with operating conditions pH, mass variation of 0.6-1.4 gram, activated carbon particle size of 160 mesh, the ratio of chitosan activated carbon and coffee grounds is 50:50 , initial lead concentration of 1.02 mg/L, stirring speed (100 rpm), contact time of 5-25 minutes, and the temperature used 25-55°C are presented in Figures 2a and 2b.



(a)



(b)

Figure 2. a) Results of FT-IR spectrum and b) SEM-EDX from biosorbent

The FT-IR analysis result showed the presence of various functional group in the biosorbent, including CH (as an alkane), NH (possibly as a secondary/primary amine and amide), N=O (nitro), CO (possibly as an alcohol/ether/ester/carboxylic acid/ anhydride), CN (amine) C-Cl (chloride), and N=O (nitro). This indicates that the interaction between activated carbon from coffee and chitosan involves both physical interaction and a chemical reaction that results in the formation of a nitro group (NO_2) in the activated carbon made from coffee grounds as part of the chitosan biosorbent. The introduction of the nitro functional group enhances adsorption capacity due to electrostatic interaction with lead metal cations, thereby increasing the adsorption ability of the chitosan-activated carbon composite (Nurhidayanti,

Ilyas, Suwazan, & Fajar, 2022). The results of SEM-EDX consistent with previous research that adding activated carbon from coffee grounds to chitosan can improve the biosorbent active site and open up more surface pores, which increasing the absorption of cadmium and lead metals in PXI industrial effluent (Sahu, Singh, & Koduru, 2021). In comparison to using chitosan adsorbent or coffee grounds activated carbon individually, the combination of the two is more efficiently employed as an adsorbent due to the increase in pore size and quality of the adsorbent. The adsorption capacity of an adsorbent is positively correlated with its surface area, signifying greater efficiency in adsorbing target contaminants (Joshi, Kataria, Garg, & Kadirvelu, 2020).

The use of chitosan coffee grounds sorbent to reduce lead concentrations in industrial wastewater is shown in Figure 3.

The figure above shows that the highest reduction in lead metal concentration was in the use of chitosan adsorbent with a coffee grounds activated carbon mass of 1.4 grams to 0.09 mg/L. This implies that as the mass of coffee grounds activated carbon, in conjunction with chitosan, increases during the adsorption process, there is a corresponding enhancement in the reduction of lead concentration. This correlation can be attributed to the amplified adsorption capacity, which is directly proportional to the augmented active absorption sites on the biosorbents. The increased mass of activated carbon consequently leads to a higher potential for the removal of lead metal from wastewater due to the heightened availability of active sites for adsorption (Naga Babu, Reddy, Kumar, Ravindhranath, & Krishna Mohan, 2018).

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

No.	Langmuir	Freundlich	Dubinin-Raduskevich	Temkin
1	K_L=40.204	K_F=0.1869	q_{mD-R}=3.7123	b_T=0.0057
2	Q_m=1.0511	1/n=-3.8425	ε=8x10^{-9}	B=0.0199
3	R_L=2.3805	R^2=0.9732	R^2=0.9433	R^2=0.9815
4	R^2=0.9970			

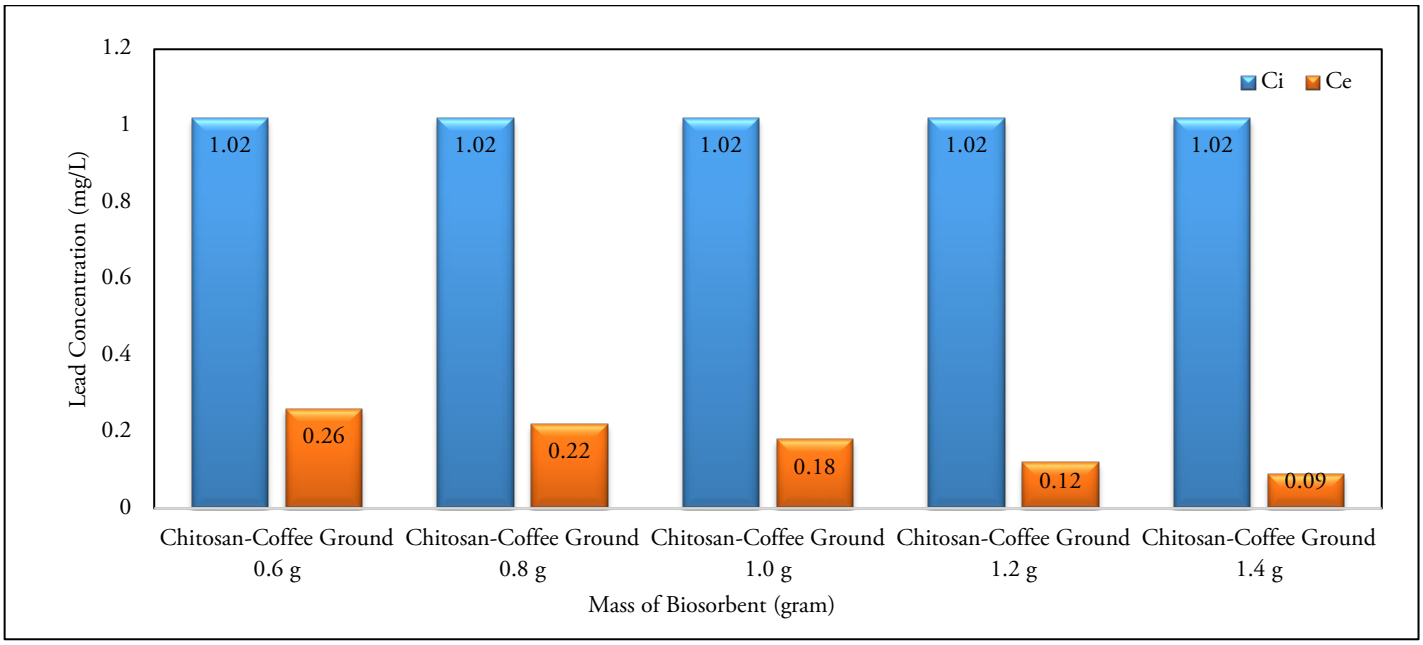


Figure 3. Reduction in lead concentration at various concentrations of biosorbents

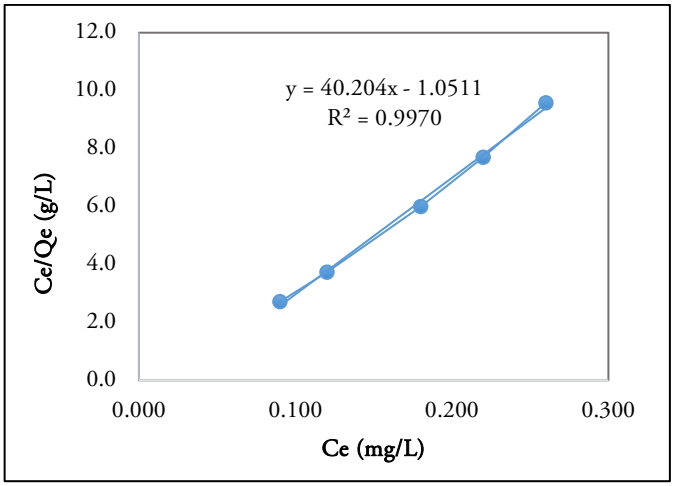


Figure 4. Plot Ce vs Ce/Qe on the Langmuir isotherm model

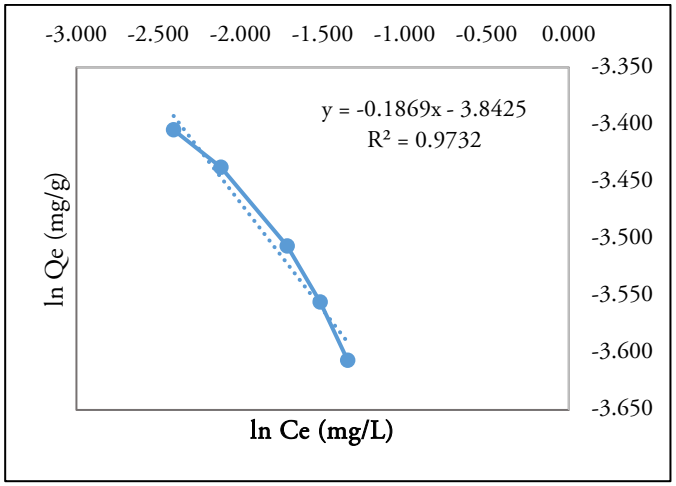


Figure 5. Plot Ln Ce vs Ln Qe on the Freundlich isotherm model

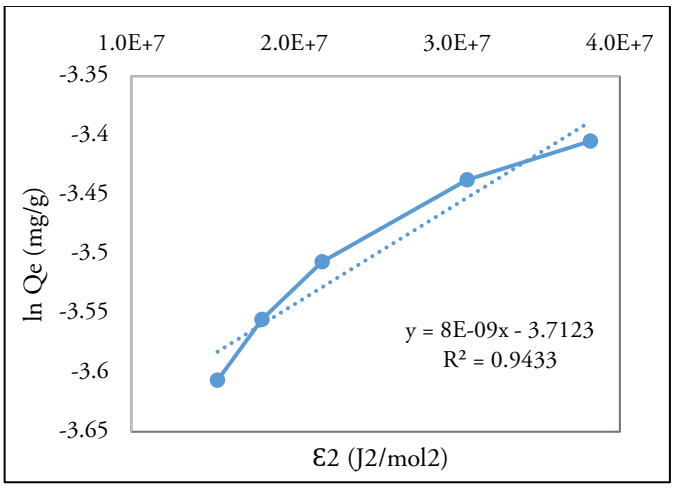


Figure 6. Plot Ce vs Ce/Qe on the Dubinin-Raduskevich (D-R) isotherm model

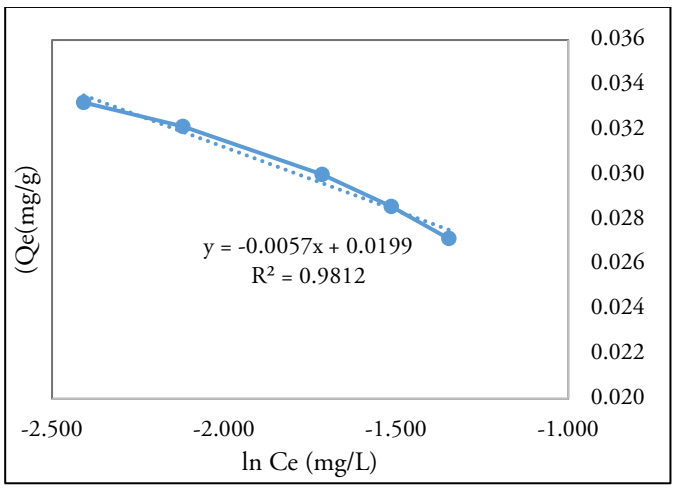


Figure 7. Plot Ln Ce vs Qe on the Temkin isotherm model

The results of data analysis performed using Microsoft Excel on several isotherm equations are presented in Figures 4 to 7.

The figure above shows that the correct isotherm model for the adsorption process of lead metal using chitosan-activated carbon coffee grounds is the Langmuir model because the highest correlation coefficient is 0.9970. This is later followed by the models of Temkin, Freundlich and Dubinin-Raduskevich. The magnitude of the adsorption isotherm parameters is presented in Table 1.

The table above shows the calculated data regarding several adsorption isotherm parameters, namely the Langmuir constant which is 40.204 with a maximum adsorption capacity of 1.0511 mg/g and a separation factor (RL) value of 2.3805 which means that adsorption is favorable (RL>1) (Khalil et al., 2020). The Freundlich equation shows that there is a Freundlich constant (KF) of 0.1869 and a biosorption intensity (1/n) of -3.8425 (<0), which means that the adsorption reaction takes place in irreversible (Pagalan et al., 2020). Consequently, it is feasible to conclude that the significant lead adsorption on biosorbent that has been chemically activated by phosphoric acid verifies the presence of enhanced porosity and a high specific surface. The laboratory-produced active carbon has a strong affinity for this heavy metal. (Benyekkou, Ghezzar, Abdelmalek, & Addou, 2020).

The Dubinin Raduskevich isotherm equation shows that there is a maximum adsorption capacity (q_{mD-R})

of 3.7123 mg.g^{-1}, the biosorption potential based on Polanyi potential theory (ε) is 8x10^{-9} kJ/mol. The Temkin isotherm equation shows that the Temkin constant associated with the heat of biosorption is 0.0199 J/mol. In this equation, bT is referred to as the Temkin harmony constant, which is linked to the highest binding energy. On the other hand, B is essential to characterize the heat of adsorption. The Temkin constant, denoted as b, is associated with the heat of adsorption measured in kJ/mol. As per the Temkin adsorption isotherm, direct fittings were achieved by plotting qe against ln Ce at the experimental temperatures (RT–298K), as depicted in Figure 6. These linear relationships facilitate the examination of the Temkin adsorption isotherm parameters bT and B. The overall heat of adsorption diminishes with an increase in adsorption due to the interaction between lead and the adsorbent surface. The values of the Temkin adsorption constants bT, B, and R2 are presented in Table 1. According to the data extracted from the fittings and included in Table 1, it is evident that the Temkin adsorption isotherm model aligns well in comparison to the Freundlich and Dubinin Raduskevich isotherm models (Sultana et al., 2022).

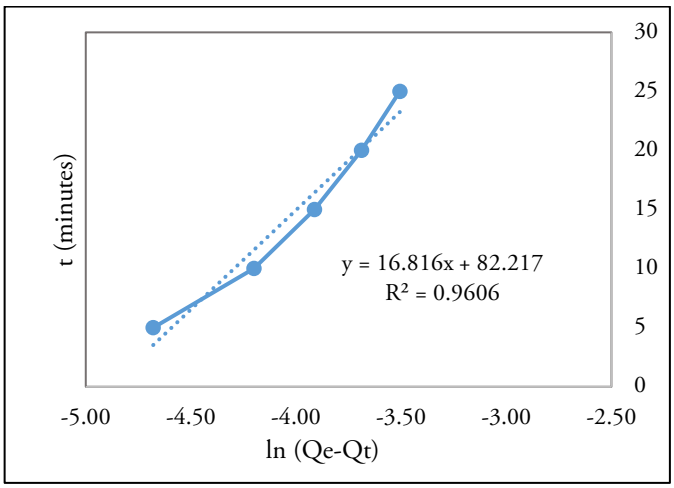


Figure 8. Plot ln(Qe-Qt) vs t on the PFO kinetics model

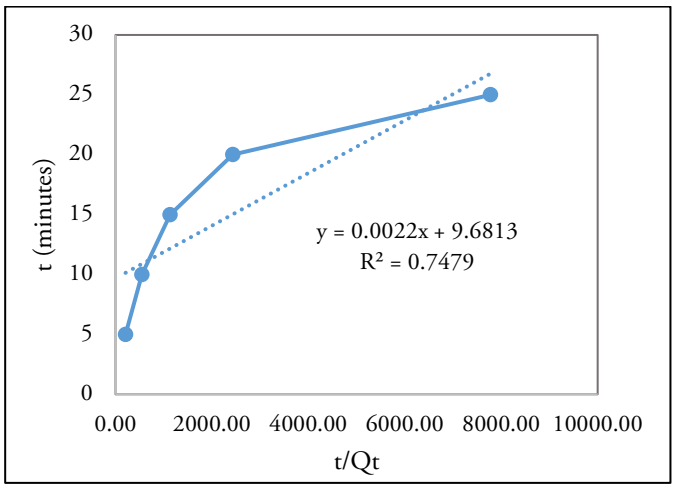


Figure 9. Plot t/Qt vs t on the PSO kinetics model

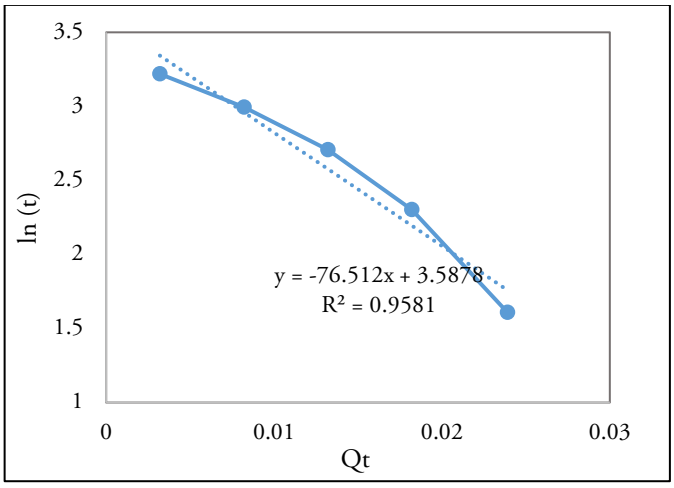


Figure 10. Plot Qt vs Ln t on the Elovich kinetics

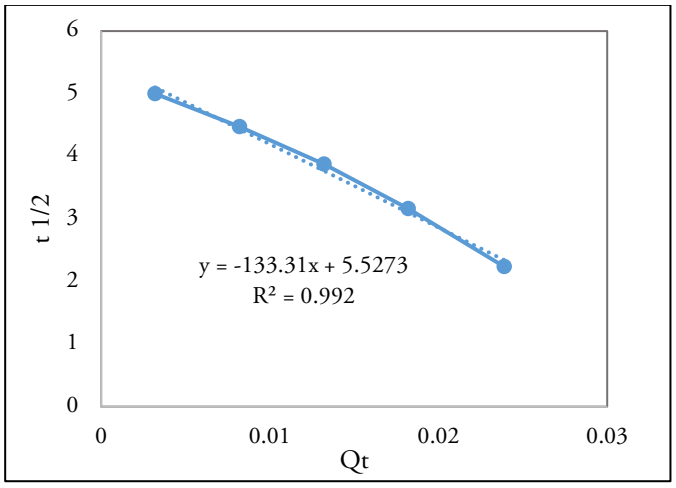


Figure 11. Plot Qt vs t1/2 on the Webber Morris kinetics model model

Based on the data analysis carried out, the correlation coefficient of the Langmuir model> Temkin> Freundlich> Dubinin Raduskevich. This shows that the adsorption isotherm follows the Langmuir isotherm model with a correlation coefficient of 0.9970 with a maximum adsorption capacity of 1.0511 $mg.g^{-1}$ 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 lead metal molecules (adsorbate).

The results of data analysis performed using Microsoft Excel on several kinetics equations are presented in Figures 8 to 11.

The magnitude of the adsorption kinetics parameters is presented in Table 2.

The table above shows the calculated data regarding several adsorption kinetic parameters, namely the PFO constant of 82.217 $mg.g^{-1}$ with an adsorption capacity based on weight at equilibrium of 16.816 $mg.g^{-1}$. The PSO equation shows that there is a PSO constant of 9.6813 $mg.g^{-1}.hour^{-1}$ with an adsorption capacity based on weight at equilibrium of 0.0022 $mg.g^{-1}$. The Elovich equation shows that there is an Elovich constant of 76.512 $mg.g^{-1}$. The intra-particle diffusion equation shows the Weber Morris constant of 133.31 $mg.g^{-1}$. By plotting Q_t against $t^{1/2}$ a straight line was found as displayed in Fig. 11 and the magnitudes of k and q_e were estimated from the intercept and slope of the straight line, respectively. The calculated values of q_e, C and R^2 are displayed in Table 2. The constant, k was found to be 133.31 $mg.g^{-1}$ which indicates that the boundary layer thickness is inversely proportional to the internal mass transfer possibility (Sultana et al., 2022). However, the probability of the internal mass transfer is increased with the increase of the boundary layer. The correlation coefficient factor (R^2) is measured as 0.9920 which reveals that the adsorption rate kinetics is an intra–particle diffusion process. The rate constant (k_i) is 76.512 $g.mg^{-1}.h^{-1}$ and the linear form of the plot indicates that the as developed chitosan and coffee grounds adsorbent is suitable for the uptake of the lead from the aqueous solution. Based on the data analysis conducted, the correlation coefficient for the kinetic model of intra-particle diffusion is greater than that of PFO, Elovich, and PSO. This suggests that the adsorption kinetics follow the intra-particle diffusion kinetics model, with a correlation coefficient of 0.9920 and a diffusion rate of 76.512 $g.mg^{-1}.h^{-1}$. This indicates that intra-particle diffusion is the rate-limiting step in the overall biosorption process and is influenced by the biosorption half-life obtained under these conditions (Park et al., 2019).

Negative ΔG^o values indicate that the adsorption reaction takes place spontaneously, ΔH^o of 0.8130 indicates an endothermic reaction, and ΔS^o of 4.1888 indicates an increase in the randomness of the adsorption process at the adsorbent interface and lead during adsorption.

Table 2. The results of rate constant investigated

No	Kinetics Model	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= 82.217 h^{-1}	16.816 $mg.g^{-1}$	0.9606
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=9.6813 $g.mg^{-1}.h^{-1}$	0.0022 $mg.g^{-1}$	0.7479
3	Elovich	$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t)$ $Rate = a\, e^{-bq_t}$	k=76.512 $mg.g^{-1}$	-	0.9581
4	Weber Morris/ Intraparticle diffusion	$q_t = k_i t^{1/2}$	k_i= 133.31 $mg.g^{-1}$	76.512 $g.mg^{-1}.h^{-1}$	**0.9920**

4. CONCLUSION

Study of Lead Metal Adsorption Isotherm and Kinetics Using a Adsorbent Combination of Chitosan and Coffee Ground Activated Carbon showed that the adsorption isotherm follows the Langmuir isotherm model with a correlation coefficient of 0.9970 with a maximum adsorption capacity of 1.0511 $mg.g^{-1}$ 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 lead metal molecules (adsorbate). Study of lead adsorption kinetics using chitosan-activated carbon coffee grounds following the Weber-Morris/intra-particle diffusion model with a correlation coefficient of 0.9920 with a diffusion rate of 76.512 $g.mg^{-1}.h^{-1}$ indicating that intra-particle diffusion is the rate step limiting in the overall biosorption process. Negative ΔG^{o} values indicate that the adsorption reaction takes place spontaneously, ΔH^{o} of 0.8130 indicates an endothermic reaction, and ΔS^{o} of 4.1888 indicates an increase in the randomness of the adsorption process at the adsorbent interface and lead during adsorption.

ACKNOWLEDGMENT

Our thanks go to DIPA DIRJENDIKTI KEMENDIKBUDRISTEK for Fiscal Year 2021 for research funding support that has been provided through grants with research contract number 036/KP/7.NA/UPB/VII/2021 so that research can be completed properly.

REFERENCE

Benyekkou, N., Ghezzar, M. R., Abdelmalek, F., & Addou, A. (2020). Elimination of paracetamol from water by a spent coffee grounds biomaterial. *Environmental Nanotechnology, Monitoring and Management*, *14* (April), 100396. https://doi.org/10.1016/j.enmm.2020.100396

Das, S., Chakraborty, J., Chatterjee, S., & Kumar, H. (2018). Prospects of biosynthesized nanomaterials for the remediation of organic and inorganic environmental contaminants. *Environmental Science: Nano*, *5*(12), 2784–2808. https://doi.org/10.1039/C8EN00799C

Hevira, L., & Gampito. (2022). The Kinetic Analysis and Adsorption Isotherm of Chicken Egg Shells and Membranes Against Synthetic Dyes. *Jurnal Riset Teknologi Pencegahan Pencemaran Industri*, *13*(2), 28–36. https://doi.org/10.21771/jrtppi.2022.v13.no2.p28-36

Joshi, S., Kataria, N., Garg, V. K., & Kadirvelu, K. (2020). Pb2+ and Cd2+ recovery from water using residual tea waste and SiO2@TW nanocomposites. *Chemosphere*, *257*, 127277. https://doi.org/10.1016/j.chemosphere.2020.127277

Khalil, U., Bilal Shakoor, M., Ali, S., Rizwan, M., Nasser Alyemeni, M., & Wijaya, L. (2020). Adsorption-reduction performance of tea waste and rice husk biochars for Cr(VI) elimination from wastewater. *Journal of Saudi Chemical Society*, *24*(11), 799–810. https://doi.org/10.1016/j.jscs.2020.07.001

Kim, H., Hwang, Y. S., & Sharma, V. K. (2014). Adsorption of antibiotics and iopromide onto single-walled and multi-walled carbon nanotubes. *Chemical engineering journal*. Diambil dari https://www.sciencedirect.com/science/article/pii/S1385894714007669

Kim, M. S., Min, H. G., Koo, N., Park, J., Lee, S. H., Bak, G. I., & Kim, J. G. (2014). The effectiveness of spent coffee grounds and its biochar on the amelioration of heavy metals-contaminated water and soil using chemical and biological assessments. *Journal of Environmental Management*, *146*, 124–130. https://doi.org/10.1016/j.jenvman.2014.07.001

Lessa, E. F., Nunes, M. L., & Fajardo, A. R. (2018). Chitosan/waste coffee-grounds composite: An efficient and eco-friendly adsorbent for removal of pharmaceutical contaminants from water. *Carbohydrate Polymers*, *189*(February), 257–266. https://doi.org/10.1016/j.carbpol.2018.02.018

Naga Babu, A., Reddy, D. S., Kumar, G. S., Ravindhranath,

K., & Krishna Mohan, G. V. (2018). Removal of lead and fluoride from contaminated water using exhausted coffee grounds based bio-sorbent. *Journal of Environmental Management*, *218*, 602–612. https://doi.org/10.1016/j.jenvman.2018.04.091

Nurhidayanti, N., Ilyas, N. I., & Suwazan, D. (2021). Efektivitas Kombinasi Kitosan dan Ampas Kopi sebagai Adsorben Alami dalam Menurunkan Konsentrasi Arsen Pada Limbah Cair PT PXI. *Jurnal Tekno Insentif*, *15*(2), 76–87. https://doi.org/10.36787/jti.v15i2.584

Nurhidayanti, N., Ilyas, N. I., Suwazan, D., & Fajar, S. (2022). Effectiveness of Lead and Cadmium Reduction with Adsorption Method using a Combination of Chitosan and Coffee Grounds (Case Study of Industrial Wastewater PT . X Indonesia). *Jurnal Presipitasi*, *19*(1), 11–23.

Nurhidayanti, N., & Nugraha, S. (2022). Kajian Isoterm dan Kinetika Adsorpsi Logam Arsen menggunakan Biosorben Kombinasi Kitosan dan Karbon Aktif Ampas Kopi. *Prosiding SAINTEK: Sains dan Teknologi*, *1*(1), 445–451.

Nuryono, N., Miswanda, D., Sakti, S. C. W., Rusdiarso, B., Krisbiantoro, P. A., Utami, N., … Kamiya, Y. (2020). Chitosan-functionalized natural magnetic particle@silica modified with (3-chloropropyl)trimethoxysilane as a highly stable magnetic adsorbent for gold(III) ion. *Materials Chemistry and Physics*, *255*(February), 123507. https://doi.org/10.1016/j.matchemphys.2020.123507

Pagalan, E., Sebron, M., Gomez, S., Salva, S. J., Ampusta, R., Macarayo, A. J., … Arazo, R. (2020). Activated carbon from spent coffee grounds as an adsorbent for treatment of water contaminated by aniline yellow dye. *Industrial Crops and Products*, *145*(June), 111953. https://doi.org/10.1016/j.indcrop.2019.111953

Park, C. M., Kim, Y. M., Kim, K.-H., Wang, D., Su, C., & Yoon, Y. (2019). Potential utility of graphene-based nano spinel ferrites as adsorbent and photocatalyst for removing organic/inorganic contaminants from aqueous solutions: A mini review. *Chemosphere*, *221*, 392–402. https://doi.org/10.1016/j.chemosphere.2019.01.063

Purnama, F. (2019). *Pembuatan dan Karakterisasi Kitosan-Karbon Aktif dari Ampas Kopi Sebagai Adsorben Untuk Menurunkan Kadar Logam Kadmium dan Nikel*. *Tesis*. Universitas Sumatera Utara.

Sahu, N., Singh, J., & Koduru, J. R. (2021). Removal of arsenic from aqueous solution by novel iron and iron–zirconium modified activated carbon derived from chemical carbonization of Tectona grandis sawdust: Isotherm, kinetic, thermodynamic and breakthrough curve modelling. *Environmental Research*, *200*(May), 111431. https://doi.org/10.1016/j.envres.2021.111431

Said, N. I. (2018). Metoda Penghilangan Logam Berat (As, Cd, Cr, Ag, Cu, Pb, Ni dan Zn) di dalam Air Limbah Industri. *Jurnal Air Indonesia*, *6*(2), 136–148. https://doi.org/10.29122/jai.v6i2.2464

Sultana, S., Islam, K., Hasan, M. A., Khan, H. M. J., Khan, M. A. R., Deb, A., … Rahman, M. W. (2022). Adsorption of crystal violet dye by coconut husk powder: Isotherm, kinetics and thermodynamics perspectives. *Environmental Nanotechnology, Monitoring and Management*, *17*(May 2021), 100651. https://doi.org/10.1016/j.enmm.2022.100651

Sunsandee, N., Ramakul, P., Phatanasri, S., & Pancharoen, U. (2020). Biosorption of dicloxacillin from pharmaceutical waste water using tannin from Indian almond leaf : Kinetic and equilibrium studies. *Biotechnology Reports*, *27*, e00488. https://doi.org/10.1016/j.btre.2020.e00488

Suwazan, D., & Nurhidayanti, N. (2022). Efektivitas Kombinasi Kitosan dan Ampas Teh Sebagai Adsorben Alami dalam Menurunkan Konsentrasi Timbal Pada Limbah Cair PT PXI. *Jurnal Ilmu Lingkungan*, *20*(1), 37–44. https://doi.org/10.14710/jil.20.1.37-44

Suwazan, D., Nurhidayanti, N., Fahmi, A. B., & Riyadi, A. (2022). Pemanfaatan Kitosan dan Karbon Aktif dari

Ampas Teh Dalam Menurunkan Logam Kadmium dan Arsen Pada Limbah Industri PT X, *10*(2), 91–102.

Wang, J., & Guo, X. (2020a). Adsorption isotherm models: Classification, physical meaning, application and solving method. *Chemosphere*, *258*, 127279. https://doi.org/10.1016/j.chemosphere.2020.127279

Wang, J., & Guo, X. (2020b). Adsorption kinetic models: Physical meanings, applications, and solving methods. *Journal of Hazardous Materials*, *390*(January), 122156. https://doi.org/10.1016/j.jhazmat.2020.122156