

EFFECT OF CONCENTRATION ON KINETICS AND THERMODYNAMICS PARAMETER IN THE Cu (II) REMOVAL BY ACTIVATED ZEOLITE

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Abstract

Adsorption is a commonly used technique for removing heavy metals, particularly Cu (II), due to its efficiency, cost-effectiveness, simple operation, high stability, and excellent selectivity. This study aims to investigate the impact of varying Cu (II) concentrations on the kinetic and thermodynamic parameters during the adsorption process. The adsorption of Cu (II) by activated zeolite was conducted in several batches, using various initial concentrations (20-120 mg/L) and for varied operating time (30-180 minutes). Various kinetic models have been used to evaluate kinetic rate parameters and maximum adsorption capacity, calculated using linear regression equations. Thermodynamic studies were conducted at different temperatures (303-318 K). The study's results indicate that the concentration has a comparable impact on Cu (II) adsorption by activated zeolite, suggesting a pseudo-second-order equation. As the concentration of Cu (II) increases, so do the adsorption capacity (q_e) and adsorption rate. At a Cu (II) concentration of 120 mg/L, the adsorption capacity and rate were the maximum, with $q_e = 5.6054$ mg/g, $k_2 = 64.2279$ g.mg⁻¹.min⁻¹, and Coefficient Correlation value (R^2) = 0.9998. The ΔG° value suggests that the adsorption process happens spontaneously and through physical adsorption. On the other hand, the ΔH° value reveals that it happens endothermic.

Keywords: Adsorption; Cu (II); Kinetics; Thermodynamics; Zeolite

1. INTRODUCTION

Many hazardous substances are being introduced into aquatic ecosystems through various rapidly growing Industrial processes, including metal processing, pigment and textile manufacture, fertilizer and pesticide production, paper production, and battery fabrication. Heavy metals are hazardous substances that predominantly accumulate in aquatic ecosystems (El-Kammah et al., 2022). The existence of process-induced pollutants, such as antibiotics, in environmental systems underscores the increasing complexity of mitigating their potential impacts on ecosystems and public health (Mohamad Yusop et al., 2024). One among them is heavy metals, hazardous substances that collect largely in aquatic environments. Heavy metals are non-biodegradable and can adversely affect human health, contingent upon their type, concentration, and mechanism of action. They can enter into the surrounding system, leading to harm

when present in sufficient quantity (El-Kammah et al., 2022; Wang et al., 2019).

Copper is one of the most regularly encountered heavy metal contaminants. It is emitted due to industrial activity and can be considered one of the most toxic and harmful heavy metals, even in deficient concentrations. This makes it imperative to remove this particular heavy metal (Ali Babeker et al., 2024; El-Kammah et al., 2022; Elver et al., 2024). Recently, techniques for removing heavy metals from wastewater have been rapidly developed. An expansive number of technologies have been developed to remove numerous kinds of heavy metals, including adsorption, chemical oxidation and reduction, membrane separation, phytoremediation (Haeril et al., 2024), coagulation (Pangeran et al., 2023), and others (Ali Babeker et al., 2024; Gupta et al., 2017; Hokkanen et al., 2016). One method of Cu(II) removal that is cost-effective, straightforward to implement, and highly effective is adsorption. This method is a very widely

used physicochemical method for removing heavy metal compounds, which does not require high operating temperatures and can remove multiple pollutants simultaneously (Melliti et al., 2023). In addition, adsorbents made of various materials found in nature, such as zeolite, can be developed. This is a prevalent physicochemical method used to remove heavy metal compounds. It does not require high operating temperatures but can remove multiple contaminants simultaneously. The application of such methods has been studied by El-Kammah et al. (2022), who utilized by-products from conventional coagulation/filtration processes to be used as adsorbents and then studied their adsorption ability in removing inorganic pollutants, including Cu (II). Equilibrium between liquid and solid phases happened rapidly after 120 min. nWTR was shown to have superior adsorption capability for Cu(II). From the Langmuir isotherm, the adsorption capacity for Cu(II) was 71.9 mg g⁻¹, roughly 3.7 times greater than that of WTR bulk particles. A high elimination percentage (91%) was recorded after five reuse cycles of nWTR, demonstrating that the sorbent can be used more than four times.

The development of the metal processing industry in the Morowali industrial area has resulted in heavy metal pollution, especially Cu(II). research conducted by Delly (2021) shows that the Cu(II) content in the mining port area is 0.05 mg/L, which is above the established standard of 0.008 mg/L. In addition, previous research conducted by Utomo (2021) shows that heavy metal Cu(II) pollution has affected the river and marine ecosystems in the Morowali industrial area. This was obtained based on the research results showing the Cu(II) content in fish samples, ranging from 0.06-0.18 mg/kg (Delly et al., 2021). Subsequently, this factor became a crucial aspect of conducting this research.

This research comprises the kinetics and thermodynamics analysis of the adsorption process with activated zeolite as an adsorbent medium and studies initial Cu(II) concentration factors. Similar earlier investigations conducted by Avelino Abin-Bazaine et al., 2019; Georgiev et al., 2012; Panayotova, 2001; and Turan & Ergun, 2009 studied the adsorption process of Cu (II) by zeolite is assessed using kinetic models including Pseudo-First Order (PFO), Pseudo-Second Order (PSO), Elovich, and Intraparticle Diffusion (IPD), which are commonly employed to evaluate the adsorption capacity of natural zeolite for Cu (II) removal. In this work, the author presents various kinetic models, including the Avrami and Bangham models, which will then be compared with other previously established models. The Avrami kinetic model elucidates phase change kinetics and applies to adsorption, detailing intricate processes related to surface coverage and heterogeneous adsorption mechanisms. In contrast to PSO kinetics, which posits chemisorption as the exclusive rate-limiting phase, the Avrami model accommodates multiple or non-linear processes, offering a superior fit for systems characterized by time-dependent

adsorption mechanisms. The Bangham kinetic model emphasizes the pore diffusion mechanism in adsorption, particularly when diffusion within micropores considerably influences the adsorption rate. Intra-particle diffusion models concentrate on general particle diffusion, whereas Bangham's is concerned explicitly with pore-level diffusion dynamics. The PFO and PSO models presume uniform adsorption across accessible sites, potentially oversimplifying diffusion-limited systems.

The main objective of this research is to identify the most efficient concentration for removing Cu (II) from aqueous solutions, which is explained by various kinetics and thermodynamics models. This research can also become a reference for reducing Cu(II) contamination in industrial areas.

2. MATERIALS AND METHOD

2.1 Materials

The primary raw material employed in this research is natural zeolite purchased at the marketplace from Bandung, Indonesia. CuCl₂·5H₂O 99%, Merck), a 25% ammonia solution (Merck), and aquadest are other materials utilized.

2.2 Methods

2.2.1 Adsorbent preparation

The zeolite adsorbent was prepared through physical activation. Initially, the zeolite adsorbent was subjected to a size reduction of 60 mesh to enhance the contact surface area. Subsequently, the drying process was conducted using an oven for 4 hours, with the temperature at 105°C. Next, the dried adsorbent was placed in a furnace and calcinated at 550°C for 4 hours.

2.2.2 Batch adsorption

The adsorption process was conducted in a batch approach by adding 1 gram of zeolite adsorbent into an Erlenmeyer flask. The observation took 30-180 minutes at room temperature, around 28°C. A Cu(II) solution was formed by dissolving a specific quantity of solid CuCl₂·5H₂O in distilled water. The resulting filtrate was further examined using visible spectrophotometry (ICEN IN-B046) at a wavelength of 620 nm, following the previously conducted process by Sirotiak et al. (2014). The effectiveness of the Cu(II) adsorption process can be determined by equation (1).

$$\% \text{ Cu(II) removal} = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (1)$$

C₀ represents the initial concentration of Cu(II) in milligrams per liter (mg/L), while C_t refers to the concentration of Cu(II) at certain times in milligrams per liter (mg/L). This research also identified the value of adsorption capacity (qt) using equation (2).

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

The V value is the volume of the sample containing Cu(II) (L), and the m value is the mass of the zeolite adsorbent utilized (g).

2.2.3 Kinetics study

To investigate the variables that affect adsorption steps, like mass transfer and reactions of chemicals. A

few kinetic models analyze kinetic parameters in the Cu(II) adsorption process utilizing zeolite adsorbents, including pseudo-first-order, pseudo-second-order, Elovich, and Avrami. Meanwhile, intra-particle diffusion and Bangham kinetic models have been used to determine the mechanism of adsorption in action. The pseudo-first-order kinetic model presented by Lagergen (Benjelloun et al., (2021) and Qiu et al. (2009) can be observed in equation (3).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

The q_e value is the adsorption capacity at equilibrium (mg/g), q_t is the adsorption capacity value at time t (mg/g), and k_1 is the rate constant value for pseudo-first-order (minute^{-1}). The pseudo-second-order kinetic model can be observed in equation (4) (Varank et al., 2012; Yazdani et al., 2014).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

The k_2 value is the rate constant for pseudo-second-order (g/mg/minute), q_e is the adsorption capacity at equilibrium (mg/g), and q_t is the adsorption capacity value at time t (mg/g). The Elovich kinetic model is given by the equation (5). (López-Luna et al., 2019; Musah et al., 2022).

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln(t) \quad (5)$$

α is the initial adsorption rate (mg/g/minute), and β is the number of sites available for the adsorption Model. Equation (6) shows Avrami's kinetic model (Oladoja, 2016).

$$\ln \ln \left(\frac{q_e}{q_e - q_t} \right) = n_{Av} K_{Av} + n_{Av} \ln t \quad (6)$$

The K_{Av} represents the rate constant in the Avrami model, while n_{Av} represents the order of the Avrami model. Equation (7) represents the Bangham Kinetic Model (Inyinbor et al., 2016).

$$\log \log \left(\frac{C_0}{C_0 - m q_t} \right) = \log \left(\frac{K_B m}{2.303 V} \right) + \alpha \log t \quad (7)$$

Where the K_B value is the constant rate of Bangham models, m is the adsorbent mass (g/L), and V is the adsorbate volume (L). The intra-particle diffusion kinetics model can be observed in equation (8) (Ersali et al., 2013; Simonin & Boute, 2016).

$$q_t = K_{int} \cdot t^{1/2} + C \quad (8)$$

K_{int} is the value of the intra-particle diffusion rate constant, and C is the constant value of the thickness of the boundary layer.

2.2.4 Thermodynamics study

Thermodynamic evaluates were conducted using 50 mL samples containing Cu(II) (40–120 mg/L) with a zeolite adsorbent mass of 1 g for 2 hours at numerous variations in temperatures (303, 308, 313, and 318 K). The effect of temperature changes is utilized to analyze the Cu(II) adsorption process on zeolite adsorbents utilizing thermodynamic parameters (ΔG° , ΔH° , and ΔS°) to discover whether the process happens spontaneously. Enthalpy (ΔH°), Gibbs free energy (ΔG°), and entropy (ΔS°) can be determined using equation (9–11) (Sakin Omer et al., 2018; Xiyili et al., 2017; Yang et al., 2020):

$$\Delta G^\circ = -RT \ln K_C \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (10)$$

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

$$K_C = e^{\frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}} \quad (12)$$

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

3. RESULTS AND DISCUSSION

3.1 Effect of Concentration

Cu(II) concentration can affect the ability of the zeolite adsorbent. The success rate of the adsorption process is related to the number of active sites available on the adsorbent surface. The influence of Cu(II) concentration on the zeolite adsorption capacity value may be shown in Figure 1.

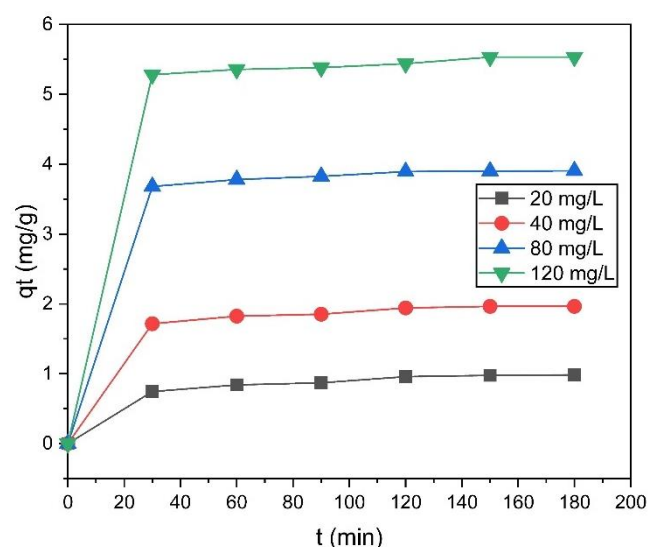


Figure 1. Adsorption capacity at various initial concentration of Cu(II)

The reported effect of the initial concentration of Cu (II) in the current study ranged from 20 to 120 mg/L. The experimental results obtained in Figure 1 demonstrate that the larger the Cu (II) concentration, the greater the adsorption capacity value. A more significant initial concentration seems to supply more energy in the mass transfer process from the liquid phase to the solid phase on the surface of the adsorbent. In addition, the decrease in adsorption capacity at a smaller initial concentration might be due to the presence of unoccupied active sites on the surface of the zeolite adsorbent. At lower concentrations of Cu, the number of active sites on the adsorbent surpassed the concentration of Cu(II) ions in the solution. As a result, the adsorption capacity will be slightly reduced. Conversely, at increasing concentrations of Cu(II) ions, there will be more intense competition among the ions to occupy the active sites on the adsorbent. In these situations, Cu(II) metal ions can transcend the limitations of mass transfer on the surface, allowing a more significant amount of Cu(II) metal ions to be adsorbed by a given quantity of adsorbent. Consequently, the quantity of adsorption sites on the

surface of the zeolite adsorbent is effectively reduced. Therefore, the overall removal efficiency percentage reduced as the concentration of Cu(II) metal ions in the water expanded. The interaction between Cu(II) and zeolite is enhanced by increasing the initial Cu(II) concentration due to the concentration gradient. The zeolite exhibited Cu(II) removal rates of 98.45% at a concentration of 20 mg/L, 98.27% at 40 mg/L, 97.62% at 80 mg/L, and 88.34% at 120 mg/L.

The observation results also reveal the effect of contact time on zeolite's Cu(II) adsorption capacity, which shows that the longer the contact time, the more directly proportional the adsorption capacity value. There are still many active sites at the beginning of the adsorption process when the first interaction occurs between the adsorbent and the adsorbate molecules, causing the adsorption process to run very quickly in the first 30 minutes, which then slows down as the active sites on the surface of the adsorbent begin to fill with Cu (II) molecules. as an adsorbate, which subsequently interacts between one molecule and another, hence limiting the availability of active sites on the surface of the adsorbent. The interaction between Cu (II) molecules as an adsorbate will result in repulsive forces between each other and the molecules that have been adsorbed. When the conditions on the adsorbent surface reach a maximum point, the adsorption capacity value will be at the saturation point and no longer rise. The zeolite adsorbent reached equilibrium after 120 minutes for every initial Cu (II) concentration, resulting in a removal percentage of 90%.

3.2 Kinetics Study

3.1.1 Pseudo-first-order (PFO)

The pseudo-first-order kinetic model suggests that the first contact adsorption process rate correlates to the difference in concentration between the liquid phase and the adsorbent surface (Afandy & Sawali, 2024; Galamini et al., 2020). The parameters determined based on the PFO kinetic model can be shown in Table 1. The parameters of the PFO kinetic model are produced using the linear regression approach between $\log(q_e - q_t)$ vs. t (Fig. 2a) according to equation (3), which may be checked using the correlation coefficient (R^2). The parameters obtained are based on the PFO kinetic model, which produces poor outcomes. These results are indicated by comparing the experimental q_e and the calculated q_e , which tend to have significant differences. The q_e and k_1 parameters at various initial Cu(II) concentrations indicate findings that are not too varied, and the R^2 values derived based on the PFO kinetic model tend to lower. So, the PFO kinetic model is inappropriate for describing the kinetics of Cu(II) adsorption by zeolite.

3.1.2 Pseudo-second-order (PSO)

The pseudo-second-order kinetics concept indicates that distinct adsorption sites on a solid substrate randomly collide with each other at a rate-limiting mechanistic step. In other words, the adsorption process comprises interactions between

adsorbate molecules and numerous locations on the adsorbent surface (Cazetta et al., 2011; Kristianto et al., 2022; Ying, 2019). PSO kinetic model parameters can be derived using linear regression between t/q_t vs. t (Fig. 2b). The PSO parameter values can be seen in Table 1. Based on the results obtained from this research, the q_e value will increase as the initial Cu(II) concentration increases, providing a reasonably good comparison between calculated q_e and experimental q_e data. Similar results were also obtained for the Cu(II) adsorption rate parameter (k_2), which rose more rapidly with increasing adsorbate concentration. The kinetic rate, directly proportional to the Cu(II) concentration, reveals that the interaction between Cu(II) ions and the active sites on the zeolite surface will be faster. A higher Cu(II) concentration might decrease the attraction force between Cu(II) molecules and enhance the attraction force between Cu(II)

molecules and the zeolite surface. The R^2 value of >0.997 suggests a suitable model appropriateness for PSO in describing the adsorption process between the zeolite adsorbent surface and Cu (II) ions. This research suggests that the examined process is best described by PSO when compared with PFO kinetics, based on the assumption that the rate-barrier phase may be valence force-related chemisorption processes via electron sharing and exchange. The PSO kinetic model demonstrates that the ion exchange process enhances adsorption, while activated zeolite performs as an adsorbent due to its excellent capacity for cation exchange, attributed to its negatively charged aluminosilicate structure. Various cations inside the zeolite framework can swap Cu (II) ions, including Na^+ , K^+ , and Ca^{2+} (Velarde et al., 2023; Wang et al., 2019). The adsorption of Cu (II) by activated zeolite could also happen by surface complexation facilitated by hydroxyl groups on the zeolite surface, which can form complexes with Cu (II) ions. This process involves coordinating Cu (II) ions with the specified surface areas (Finish et al., 2023).

3.1.3 Elovich

The Elovich adsorption kinetics model assumes that adsorption occurs at different active sites and that adsorption energy increases as surface coverage increases. Additionally, it suggests that the adsorption process occurs across multiple surfaces. During the adsorption process, the concentration of the adsorbate remains constant. The Elovich kinetic model, specifically the rate at which a molecule can interact, is applicable for describing the kinetics of adsorption with the surface of the adsorbent (Edet & Ifealebuegu, 2020; López-Luna et al., 2019). The parameters of the Elovich kinetic model can be determined by linear regression analysis of $\ln t$ and q_t (Fig. 2c). The values of these parameters are presented in Table 1. The results indicate that the concentration of Cu (II) does not have a significant impact on the initial rate parameters (α) of the adsorbate molecules attached to the adsorbent surface in the process of Cu (II) adsorption by zeolite. This result appears from the fluctuation in the α value, which corresponds to the rise in the initial

Table 1. Kinetics parameters

Kinetics Models	Initial Concentration			
	20 mg/L	40 mg/L	80 mg/L	120 mg/L
Pseudo-first-order:				
q _e (mg/g)	1.1984	1.1460	1.3036	1.2769
k ₁ (minute ⁻¹)	0.0244	0.0267	0.0246	0.0156
R ²	0.9653	0.9330	0.9619	0.8859
Pseudo-second-order:				
q _e (mg/g)	1.0697	2.0429	3.9667	5.6054
k ₂ (g.mg ⁻¹ .minute ⁻¹)	0.0783	1.2371	23.2450	64.2279
R ²	0.9977	0.9995	0.9999	0.9998
Elovich:				
α (mg/g.minute)	7.1276	6.7797	7.5700	6.8120
β (g/mg)	0.9289	554.8042	5.7845 x 10 ⁹	1.7768 x 10 ¹³
R ²	0.9712	0.9676	0.9751	0.9207
Avrami:				
n _{av}	0.7153	0.6038	0.4711	0.3123
K _{av} (minute ⁻¹)	3.1145	2.4133	1.3613	0.1873
R ²	0.9199	0.8939	0.9285	0.7972
Intra-particle diffusion:				
K _{int} (mg. g ⁻¹ minute ^{-1/2})	0.0314	0.0328	0.0292	0.0337
C (mg/g)	0.5858	1.553	3.5427	5.0876
R ²	0.9598	0.9477	0.9380	0.9571
Bangham:				
α	0.1658	0.0819	0.0356	0.0278
K _B (g)	0.6127	0.3990	0.3172	0.3250
R ²	0.9749	0.9689	0.9749	0.9240

concentration of Cu(II). The activation energy parameter (β) in the Cu(II) adsorption process indicates a direct correlation between the results and the initial concentration of Cu(II). As the adsorbate concentration increases, the value of β also increases. The higher β value suggests a stronger Cu(II) adsorption process on the surface of the zeolite.

3.1.4 Avrami

The Avrami kinetic model suggests that reactions take place at the active sites on the surface of the adsorbent, which is in a solid state. This kinetic model relies on two parameters: the K_{av} value, which represents the adsorption rate parameter, and the n value, which is associated with the adsorption process (George & Sugunan, 2014). The value of n_{av} can be used to assess potential variations in the adsorption mechanism based on temperature and contact time. Typically, the value of n serves as a criterion for determining the location of a heterogeneous reaction. A n_{av} < 1 suggests that a diffusion process controls adsorption; n_{av} = 1 is generally connected with a monolayer adsorption process and exhibits pseudo-first-order kinetics. n_{av} > 1 suggests that the adsorption mechanism occurs in a multilayer way, and surface reactions control the kinetics. Avrami's kinetic parameters can be determined based on a linear regression between ln(ln(q_e/(q_e-q_t))) vs. ln t (Fig. 2d) and can be seen in Table 1. The results revealed that the k value will drop as the concentration increases, based on the Avrami kinetic model. At lower concentrations, the adsorption rate, according to the Avrami kinetic model, will be controlled by film diffusion. However,

the intra-particle diffusion process will control it at higher concentrations. Based on the n_{av} value derived in the Avrami kinetic model, it demonstrates that the Cu(II) adsorption process by zeolite has been controlled by a diffusion process with a n_{av} < 1. In addition, a n_{av} value < 1 can explain that the current adsorption process has early obstacles caused by the existence of steric obstacles or other obstacles by oxide compounds on the surface of the adsorbent and can also be influenced by heterogeneous features of the surface.

3.1.5 Bangham

In research on kinetics, the Bangham kinetic model is widely used to represent the rate between molecules or substances to be adsorbed and the adsorbent surface and can provide a concept of how the concentration of molecules or substances changes over time. This model suggests that molecules are adsorbed by permanent active sites with the same energy level so that each active site can interact with one adsorbate molecule. In other words, the Bangham kinetic model suggests that one adsorbate molecule will interact separately with the active site on the surface of the adsorbent. The parameters of the Bangham kinetic model could be determined based on linear regression between log(Co/(Co-mqt)) vs log t (Fig 2e) and can be seen in Table 1. The data suggests that the K_B value achieved will decrease as the initial Cu(II) concentration increases. It indicates that according to the Bangham kinetic model, the adsorption rate will become slower as the initial Cu (II) concentration increases. The correlation coefficient (R²) value in the Bangham

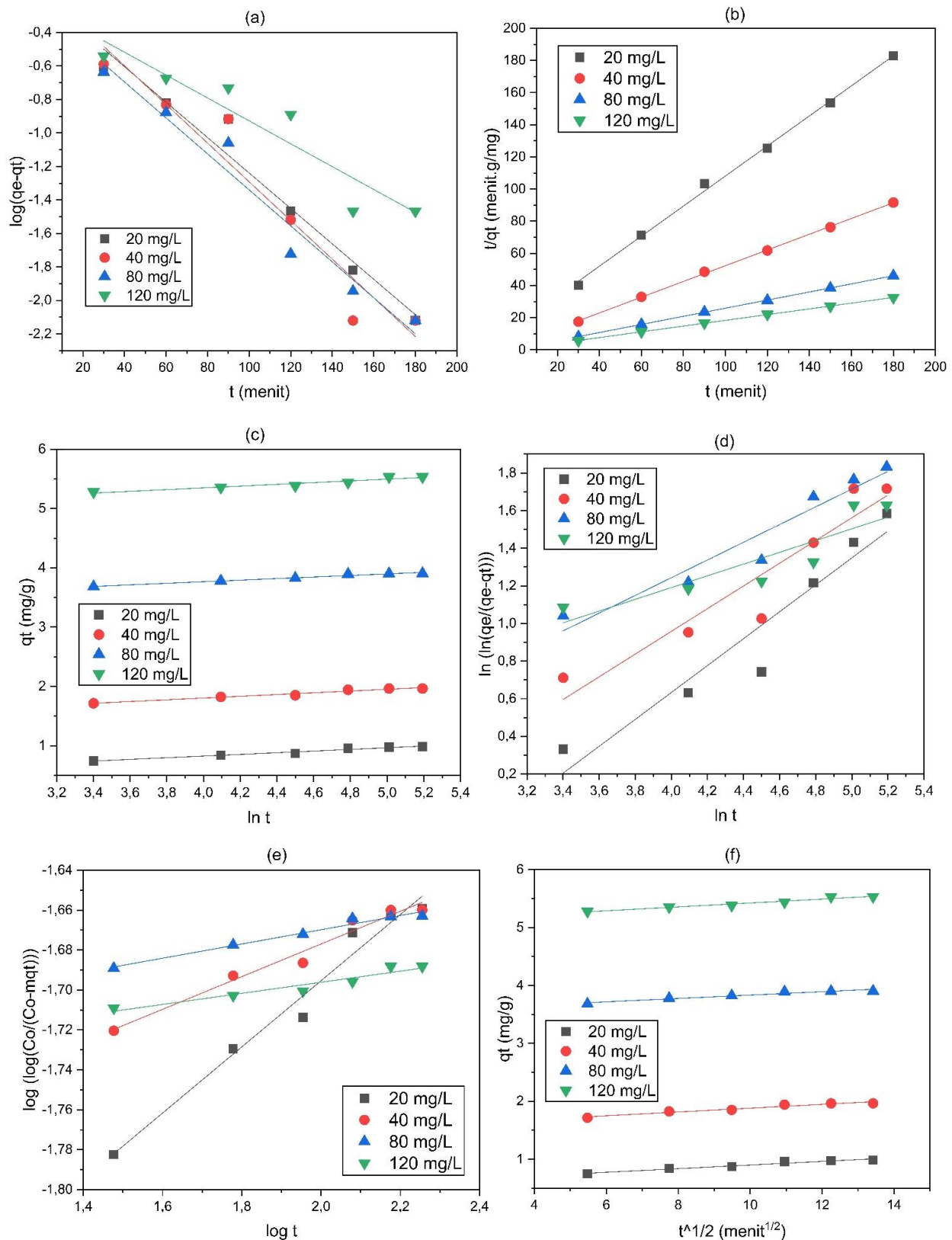


Figure 2. Linear regression of several kinetics models (a) PFO; (b) PSO; (c) Elovich; (d) Avrami; (e) Bangham; and (f) IPD

kinetic model offers a linear relationship for varying initial Cu (II) values. This means the Cu(II) adsorption process on the zeolite adsorbent follows this model. Consequently, it can be concluded that the Cu(II) diffusion into the zeolite influences the adsorption process. The results achieved demonstrate that the

value of $\alpha < 1$ suggests the diffusion process in the adsorbent pores has been slowed down as a result of the effects of obstacles, such as the interaction between Cu(II) as an adsorbate or the interaction between Cu(II) and the pore walls of the adsorbent. The lowering value of α with higher concentrations can be caused by the

larger concentration of Cu(II) in the adsorbate, which will result in the potential for a faster pore-filling process. This can lead to a decrease in the adsorption rate at a later stage, which can be impacted by saturation in the adsorbent pores or changes in the adsorbate concentration gradient in the pores.

3.1.6 Intra-particle diffusion

The intra-particle diffusion (IPD) kinetics model proposes that intra-particle diffusion is a rate-limiting stage throughout adsorption. This model revolves around the diffusion of adsorbate molecules in the adsorbent pores, which is a factor that regulates the adsorption process. (Hong et al., 2014; Hubbe et al., 2019; Wu et al., 2009). The parameters of the IPD kinetic model can be determined using the linear regression approach between $t^{1/2}$ and qt (Fig. 2f) and can be seen in Table 1. The results suggest that the adsorbate concentration has little impact on the intra-particle diffusion constant (K_{int}) rate. A higher K_{int} value indicates a faster intra-particle diffusion process. However, the intra-particle diffusion process is not the only process that plays a role in the adsorption rate. Several other parameters, including external mass transfer and surface reactions, are essential in the adsorption rate. Another parameter that can be obtained is a constant related to the thickness of the boundary layer around the particle (C), where the concentration of Cu (II) as an adsorbate affects the C value. The higher the initial Cu(II) concentration, the greater the boundary layer thickness that Cu(II) molecules can pass through into the solution. This parameter illustrates the impact of the stationary layer containing solute molecules on the intra-particle diffusion rate. The thickness of the boundary layer can affect the efficiency of the adsorption process. Boundary layer thickness is defined as the distance between the adsorbent particle's surface and the surrounding liquid layer. So, at higher concentrations, intra-particle diffusion will play a crucial role.

3.3 Thermodynamics Study

The thermodynamic parameters (ΔH° , ΔG° , ΔS°) for the transfer of solute moles from solution to the solid-liquid surface are presented in Table 2. Thermodynamic investigations were conducted at several temperature intervals (303, 308, 313, and 318°K) to assess the Gibbs free energy value obtained from Cu(II) adsorption by zeolite. The outcomes indicate that the adsorption capacity increases at higher operating temperatures, attributed to endothermic processes that occur during Cu (II) adsorption by activated zeolite. When heat is applied to

a system in the adsorption process, it will increase the kinetic energy of the cations in the Cu(II) solution, helping the motion of these cations toward the surface of the active site of the adsorbent. Thermodynamic parameters can be calculated by plotting $\ln K_c$ vs. $1/T$ (Figure 3), creating a linear relationship between ΔH° and ΔS° , which can be evaluated using slope and intercept values as well as ΔG° values determined using equation 10. Thermodynamic parameters of the Cu adsorption process (II) by zeolite can be identified in Table 2.

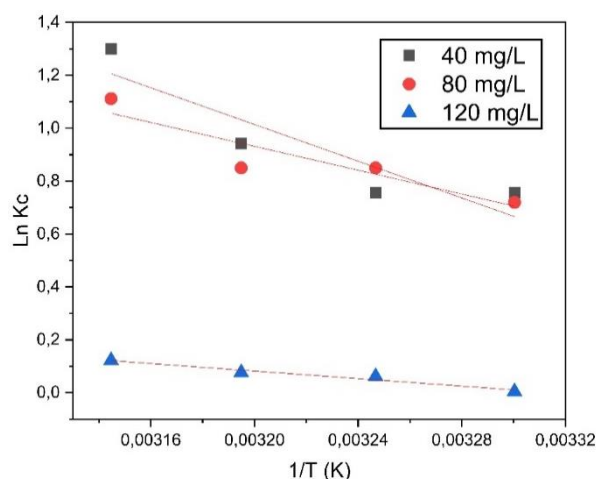


Figure 3. Graph $\ln K_c$ vs $1/T$

The results reveal that the ΔG° values obtained are negative at various concentrations, indicating that the adsorption reaction happens spontaneously. The ΔG° value obtained also illustrates that the adsorption process occurs physically. It occurs when the intermolecular interactions are stronger than the comparatively modest attractive forces between the adsorbate and the adsorbent surface. The ΔG° value for physical adsorption ranges from -20 kJ/mol to 0 kJ/mol. The ΔH° measurement, which gives a positive value (5.9108–28.8546 kJ/mol), indicates that zeolite's Cu(II) adsorption process happens endothermically, where heat is absorbed by the system from its environment. The ΔS° value obtained revealed positive results (0.0087–0.1007 kJ/mol K), indicating a rise in randomness at the solid-solution interface during adsorption. The positive entropy change ($\Delta S^\circ > 0$) indicates the unification of water molecules from hydrated ions into the bulk solution, enhancing the system's volatility. Therefore, the Gibbs free energy (ΔG°) remains negative at higher temperatures, making the process beneficial to the environment and enhancing adsorption efficiency as temperature rises.

Table 2. thermodynamic parameters for adsorption of Cu(II) onto activated zeolite

Co (mg/L)	ΔH° (KJ/mol)	ΔS° (KJ/mol K)	ΔG° (KJ/mol)			
			303°K	308°K	313°K	318°K
40	28.8546	0.1007	-1.6307	-2.1813	-2.6851	-3.1889
80	18.7489	0.0677	-1.7763	-2.1150	-2.4537	-2.7924
120	5.9108	0.0087	-0.0265	-0.1245	-0.2225	-0.3205

4. CONCLUSIONS

Based on the data given in the current study, it appears that the adsorbate concentration impacts the Cu(II) adsorption process by activated zeolite. The pseudo-second-order kinetic model is the most suitable kinetic model to describe the Cu(II) adsorption process by zeolite with k_2 and q_e values that become higher as the Cu(II) concentration rises with a correlation coefficient value ($R^2 = 0.9977-0.9999$). According to thermodynamic studies, it can be proven that the process of adsorption occurs spontaneously and through physical adsorption, as seen from the ΔG° value, and occurs endothermically, as seen from the outcome's ΔH° value.

5. ACKNOWLEDGEMENT

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