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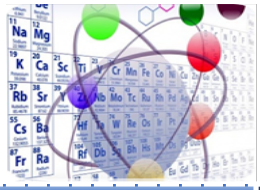

Kinetics and Equilibrium Properties of Fe(II) Adsorption Using Modified Empty Palm Oil Bunches Activated Carbon

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ABSTRACT

The increasing palm oil production in Indonesia contributes to higher agricultural waste, particularly Empty Fruit Bunches (EFB). This waste can be processed into activated carbon as an adsorbent to remove Fe(II) ions from Palm Oil Mill Effluent (POME). This study reviews two EFB-based adsorbents: Fe-Cu modified activated carbon and a composite of activated carbon with Copper-TAC Metal Organic Frameworks ($Cu(TAC)_2$). Adsorption kinetics data show that the pseudo-second-order model fits best, with the highest regression coefficient ($R^2 = 0.99637$) found in the $Cu(TAC)_2$ composite, indicating a chemisorption mechanism. Adsorption equilibrium analysis using Freundlich isotherm revealed that while all materials fit the model, plain activated carbon had an unfavorable 1/n value (>1), suggesting weak interaction between adsorbent and adsorbate. Based on kinetic and isotherm analysis, the $Cu(TAC)_2$ composite was more effective for Fe(II) adsorption than Fe-Cu or unmodified activated carbon.

Keywords: Adsorption Fe(II), EFB, Activated Carbon, $Cu(TAC)_2$, Pseudo-Order Two, Freundlich Isothermal

1. INTRODUCTION

The increase in palm oil production in Indonesia in 2024 rose by 9.96% compared to the previous year, with North Sumatra ranking fourth in Indonesia for palm oil production, reaching around 5 million tons in 2023. This increase has led to a rise in waste generated from palm oil production, including solid, liquid, and gaseous waste. One such solid waste is empty fruit bunches (EFB), which, if left untreated, can cause air pollution due to the release of methane gas. Each 1 ton of palm oil produces approximately 23%–30% or 230–300 kilograms of EFB waste, yet the utilization of EFB remains suboptimal. In addition to solid waste, palm oil production also generates liquid waste that contains hazardous substances such as siloxanes, FAME, phenol and phenolic compounds, and heavy metals including lead (Pb), cadmium (Cd), nickel (Ni), iron (Fe), copper (Cu), zinc (Zn), chromium (Cr), and aluminum (Al).[1] Solid and liquid wastes contain hazardous substances that can negatively impact the surrounding environment. Therefore, these wastes are processed into more useful materials. For example, solid waste such as empty fruit bunches (EFB) can be utilized as an adsorbent

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material capable of removing harmful metals like Fe(II), which is commonly found in palm oil mill effluent (POME).[2] EFB (Empty Fruit Bunches) can also be converted into activated carbon, which is effective in adsorbing heavy metals due to its large surface area, pore size, and surface chemical properties. Activated carbon has been widely used in research; however, to enhance its surface area and porosity, modifications are necessary. Several modifications have been carried out, including metal-modified activated carbon aimed at improving its adsorptive properties—for example, modification with Fe-Cu metals, which has been shown to effectively adsorb Fe(II) heavy metal.[3] It can also be developed into a composite of EFB-based activated carbon with Metal–Organic Frameworks $Cu(TAC)_2$, which is capable of adsorbing various metals, particularly Fe(II).[4]

2. EXPERIMENTAL

The research conducted has several stages in common, including the preparation stage, carbonization, activation, adsorption process and the same carbon base material, namely empty oil palm bunches. The difference lies in the modification of Fe-Cu and $Cu(TAC)_2$. This literature review aims to analyze the three materials, namely activated carbon, AC-Fe-Cu, and AC-$Cu(TAC)_2$ which are the best in their adsorption process such as absorption efficiency, adsorption equilibrium and adsorption kinetics.

2.1. Tools and Materials

The tools and materials used in this study are glass equipment, staves and clamps, 3 neck flasks, 250 ml, analytical balances, hot plates, ovens, furnaces, 200 mesh sieves, thermometers, *Atomic Absorption Spectrophotometer (AAS).* The materials used are Empty Bunches of Palm Oil, metal $FeSO_4.7H_2O$, H_3PO_4, TAC (Terephthalate Acid), HF (Fluoride Acid), HNO_3 (Nitric Acid), $Cu(NO_3)_2$ (Copper(II) Nitrate), H_2O.

2.2. Research procedure

2.2.1. Activated Carbon

This research was carried out by washing EFB thoroughly and smoothing up to 200 mesh. Then, it is baked at 500°C for 2 minutes and activated with 10% H_3PO_4 for 24 hours. Next, an adsorption process was carried out with a mass variation of 1 gr, 2 gr, 4 gr, 6 plus 100 mL of Fe(II) solution with a concentration of 20 ppm, in the strirer for 15 minutes at a speed of 125 rpm. The adsorption results were filtered and the filtrate was taken which was then analyzed with the AAS instrument. The results of the analysis were followed by concentration variations (20,60,100,140,180) ppm with the optimum mass stirred for 15 minutes at a speed of 125 rpm. The filtrate is filtered and taken for AAS analysis. The results of the analysis were followed by time variations of 15, 30, 45, 60, 75 minutes with optimal mass and optimum concentration stirred at a speed of 125 rpm and the adsorption results were analyzed with the AAS instrument.

2.2.2. Activated Carbon and Fe-Cu

In this study, sample preparation was also carried out by cleaning and mashing up to 200 mesh and activated with 10% H_3PO_4 and left for 24 hours, the results were washed with aquades to neutral pH and dried in the oven, then modified with Fe metal and Cu metal in a ratio of 1:1 and then reflux for 6 hours. The results are washed with aquades to neutral pH and dried in an oven at 105°C for 60 minutes. Followed by the adsorption of Fe(II) metal with a mass variation of 0.5 g, 1 g, 2 g, 4 g, 6 g plus 30 mL of Fe(II) solution with a concentration of 6 ppm, stirred for 45 minutes at a speed of 125 rpm. Each adsorption result is filtered and

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its filtrate is taken which is then analyzed with the AAS instrument. Then continued with concentration variations of 2, 4, 6, 8, 10 ppm with the optimum mass stirred for 45 minutes at a speed of 125 rpm. Time variations of 15, 30, 45, 60, 75 minutes with optimum mass and optimum concentration are stirred at a speed of 125 rpm.

2.2.3 Activated Carbon and MOFs $Cu(TAC)_2$

The procedure in this study is almost the same as the previous procedure the difference is in the modification of activated carbon with $Cu(TAC)_2$ MOFs. The synthesis of activated carbon composites and $Cu(TAC)_2$ MOFs was carried out by means of a solution with a composition of 0.315 g $Cu(NO_3)_{2.3}H_2O$; 0.544 g terephthalate acid; 0.2 mL HF; 0.19 mL HNO_3; 20 mL H_2O mixed and refluxed at 105°C for 9 hours using the reflux method. The composite results were carried out an adsorption process by adding a 20 ppm Fe(II) metal solution of 100 ml for each mass variation (1,2,3,4) g stirred for 15 minutes, filtered and the filtrate analyzed with AAS. Followed by a variation of concentration (20,60,100,140,180) ppm of 100 mL of Fe(II) ions, stirred at 125 rpm for 15 minutes and the adsorption results were analyzed with the AAS instrument. The optimal results obtained at the concentration variation were followed by time variations of 15, 30, 45, 60, 75 minutes and the adsorption results were filtered and the filtrate was taken which was then analyzed with the AAS instrument.

3. RESULTS AND DISCUSSION

3.1. Adsorption Efficiency to Mass Variation

The highest efficiency value of the three adsorbent materials is A.C-$Cu(TAC)_2$, followed by A.C-Fe-Cu and the lowest is activated carbon. This can happen because activated carbon depends on a larger amount of its mass so that the adsorption process takes place less than optimally. A.C-$Cu(TAC)_2$ and A.C-Fe-Cu have active sites, this can increase the efficiency of adsorption that occurs where the more mass of the adsorbent increases, the more area of the adsorbent surface will be, so that there is an increase in the active field in the adsorbent which causes a lot of metals to be absorbed.[5] Can be seen in figure 1:

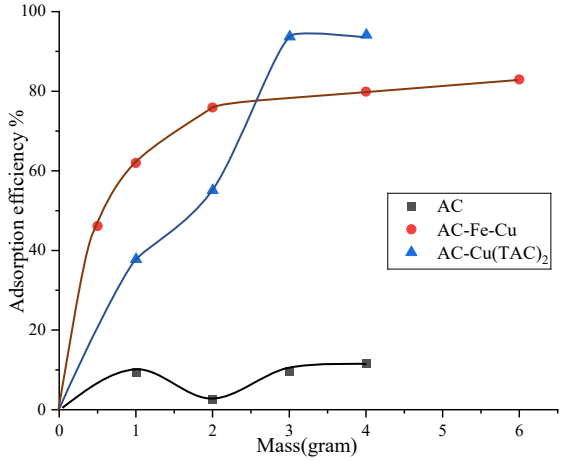

Figure 1. Adsorption efficiency at Mass variation

3.2. Adsorption Efficiency against Concentration Variations

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In concentration variations, the efficiency of activated carbon increased to 57.8% at a concentration of 60 ppm, then decreased drastically. This indicates activated carbon has a limited capacity that when the surface is saturated, increased concentration reduces efficiency. In AC-Fe-Cu, the highest concentration at the concentration of 8 ppm was 97.26% and decreased at the concentration of 10 ppm. However, AC-Fe-Cu is particularly effective at low concentrations because the active site fills up quickly, but is not able to withstand excess ions at high concentrations. For AC-Cu(TAC)$_2$, it shows relatively stable high efficiency with two significant peaks (approximately 49.2% at 20 ppm and 68% at 100 ppm). This indicates that AC-Cu(TAC)$_2$ has a more diverse active site and multilayer adsorption capabilities, so its performance is more consistent than other adsorbents. It can be seen in figure 2:

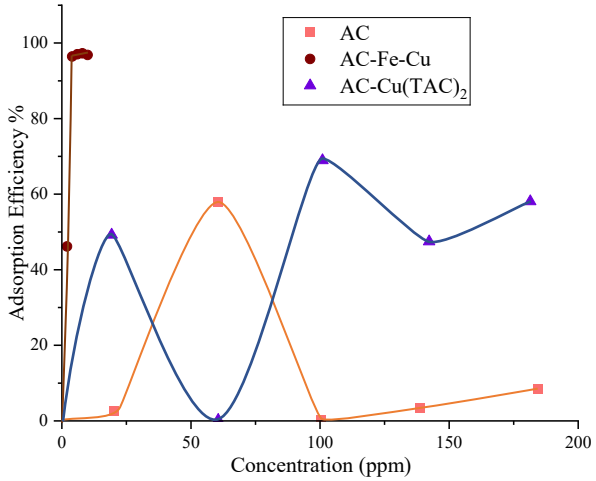

Figure 2. Adsorption Efficiency at Concentration Variations

3.3. Adsorption Efficiency against Time Variations

Consider figure 3. The following shows the efficiency of adsorption against time variations:

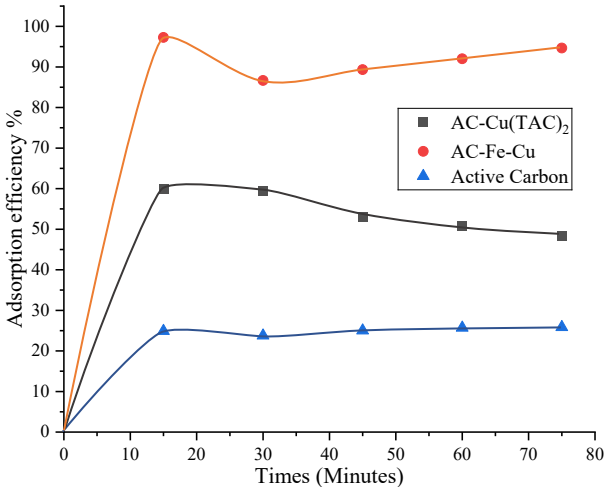

Figure 3. Adsorption Efficiency Against Time Variations

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Figure 3. Shows the relationship between contact time and adsorption efficiency % for the three materials. In AC-Fe-Cu the efficiency is highest at 97% in the first 15 minutes, and decreases in 30 minutes, and begins to increase again in 45 to 75 minutes with a value of 94%. This indicates rapid adsorption (fast kinetics) at the beginning of time because many active sites are available, then there is little desorption or redistribution. In AC-Cu(TAC)$_2$ the efficiency increases rapidly at 15 minutes and decreases slowly and tends to be stable at around 50-55%. This shows that the adsorption process occurs quickly at first, then approaches equilibrium. As for activated carbon, the increase in efficiency is much slower, only reaching 20-25% after 70 minutes. This shows that the adsorption ability of AC is much lower compared to modified adsorbents.

3.4. Adsorption Kinetics Analysis

The adsorption capacity of a material is influenced by several key factors, including the type and surface area of the adsorbent, which can be enhanced through physical or chemical activation methods. These treatments improve the porosity and surface characteristics, enabling better interaction with the adsorbate. Other influential factors include the type and concentration of the adsorbate, which affect the extent of adsorption, as well as the contact time, which determines the rate and equilibrium of the process. Adsorption kinetics play an important role in evaluating how quickly an adsorbate is taken up by the adsorbent. This is essential for designing time-efficient and effective adsorption systems, particularly in applications such as wastewater treatment. In addition, adsorption kinetics help to identify whether the adsorption mechanism is dominated by physisorption (weak physical interactions) or chemisorption (strong chemical bonding). This can be determined by comparing the fit of experimental data to kinetic models such as the pseudo-first-order and pseudo-second-order models. The model with the highest coefficient of determination (R^2) indicates the dominant adsorption mechanism. A better fit to the pseudo-first-order model typically suggests physisorption, while a better fit to the pseudo-second-order model indicates chemisorption.[6]

The equations for adsorption kinetics and isotherms can be seen in Table 1:

Table 1. Adsorption Kinetics and Adsorption Isotherms

Type of Model	Equation	
Adsorption Kinetic Model	Pseudo-first-order	$log\ (q_e - q_t) = log\ q_e - \frac{K_1}{2.303} t$
	Psesudo-second-order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}\ t$
Adsorption Isotherm Model	Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_{max}}\ C_e + \frac{1}{q_{max} b}$
	Freundlich	$lnq_e = ln\ K_f + \frac{1}{n} ln\ C_e$

Keterangan:

$q_t\ (mg.g^{-1})$: Amount of adsorbate removed at time t.
$q_e\ (mg.g^{-1})$: equilibrium adsorption
$K_1\ (min^{-1})$: adsorption rate constant of first order.

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K_2 $(g\ mg^{-1}min^{-1})$: adsorption rate constant of second order.
C_e $(mg.L^{-1})$: equilibrium concentration of adsorbate in solution.
q_e $(mg.g^{-1})$: amount of adsorbate removed at equilibrium.
$(q_{max}(mg.g^{-1})$: maximum adsorption capacity.
b $(L.g^{-1})$: Langmuir constant.
$K_F(mg/g)/(mg/L)^{1/n}$: Adsorption capacity.
n: heterogeneity factor [5]
It can be seen in Table 2:

Table 2. Kinetic Models for Fe(II) Adsorption

Kinetic Model			
Pseudo-First Order			
	A.C	A.C-Fe-Cu	A.C-Cu(TAC)$_2$
q_e (mg/g)	-71,8	-74,6	34,02
K_1 (min^{-1})	-0,0002	-0,00018	0,0004
R^2	0,935	0,959	0,725
Pseudo-First Order			
q_e (mg/g)	4,055	0,455	10,70
$K_2(g\ mg^{-1}min^{-1})$	12,54	1,537	-0,439
R^2	0,990	0,996	0,996

Based on Table 2, the most suitable kinetic model for the Fe(II) adsorption process on the three materials is the pseudo-second-order model, as indicated by the highest linear regression coefficients (R^2) for all adsorbent materials, namely activated carbon from empty fruit bunches (EFB), Fe-Cu modified activated carbon, and Cu(TAC)$_2$ composite activated carbon. Among these, the Cu(TAC)$_2$ composite activated carbon shows the highest R^2 value of 0.996.

The pseudo-second-order model suggests that the adsorption process occurs through rapid chemical interaction (chemisorption) between the dissolved metal ions (Fe(II)) and the surface of the adsorbent (Cu(TAC)$_2$ composite activated carbon). This involves the formation of coordination bonds, where Fe^{2+} ions interact with the carboxylate groups ($–COO^-$) of TAC. In this interaction, the oxygen atoms from TAC act as electron donors, while Fe(II) ions serve as electron acceptors, forming a coordination complex. It can be seen in Figure 1, which shows the adsorption kinetics that occur.[6]

All three materials follow a pseudo-order-two model because the adsorption mechanism is dominated by chemosorption, where the adsorption rate is affected by the number of active sites on the adsorbent surface and chemical interactions. Pure activated carbon (AC) still has functional groups such as –OH and –COOH, AC-Fe-Cu has metal sites Fe and Cu that strengthen metal ion interactions, while AC-Cu(TAC)$_2$ has a carboxylate group ($–COO^-$) capable of forming a coordinating bond with Fe^{2+}. In addition, the adsorption rate depends on the equilibrium capacity, so the closer it gets to equilibrium, the adsorption rate slows down as per the assumptions of the pseudo-order-two model. This is supported by an R^2 value of > 0.99 which on all materials, shows a high suitability with the model compared to the pseudo-order-one, indicating that the interaction that occurs is not only physical diffusion but involves chemical reactions. In AC-Fe-Cu and AC-Cu(TAC)$_2$, Fe^{2+} forms a coordinating bond with a metal or functional group through an electron donor, whereas

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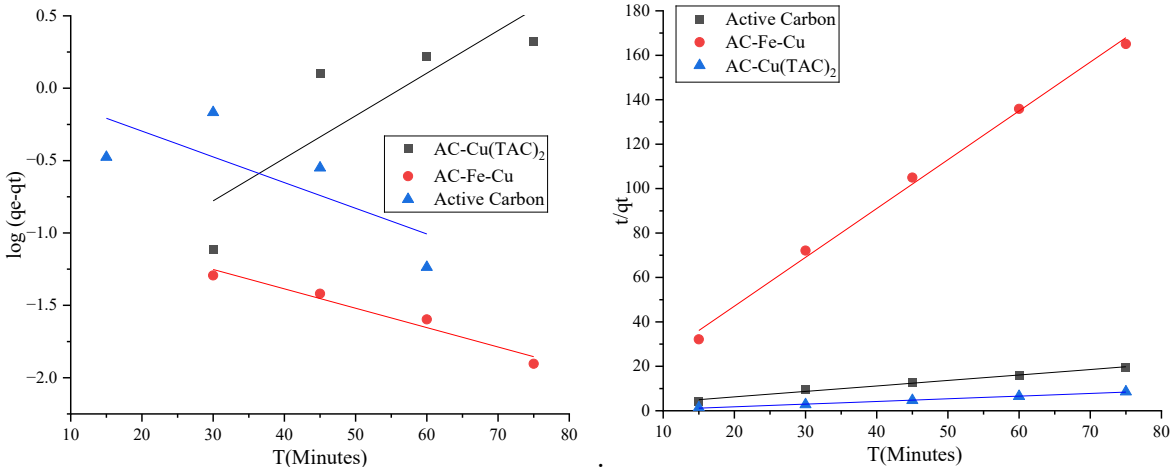
in pure AC this interaction is weaker but still possible through the polar group on its surface. A pseudo-order one and pseudo-order two graphs can be seen in figure 4:



(a) (b)

figure 4. (a) Pseudo-First-Order and (b) Pseudo-Second-Order

3.4. Adsorption equilibrium.

Adsorption equilibrium can be mathematically predicted through isotherm modeling, primarily using the Langmuir and Freundlich models. The Langmuir isotherm model describes chemical adsorption (chemisorption) that forms a monolayer on the surface of the adsorbent. In this model, all adsorption sites are assumed to be identical, there is no interaction between adsorbate molecules, and adsorption occurs on a fully covered surface. Its main functions are to calculate the maximum adsorption capacity and the adsorption energy constant, as well as to represent homogeneous adsorption behavior on the adsorbent surface.On the other hand, the Freundlich isotherm model describes physical adsorption on a heterogeneous surface. It is suitable for non-ideal and multilayer adsorption systems. The main purpose of this model is to evaluate the adsorption intensity and surface heterogeneity, as well as to determine the relative adsorption capacity (Kf) and the nature of the interaction between the adsorbate and adsorbent through the exponential parameter (1/n).[6]

The following are the adsorption equilibrium data for activated carbon, Fe-Cu modified activated carbon, and Cu(TAC)₂ composite activated carbon, as shown in Table 3.

Tabel 1 Langmuir and Freundlich parameters for Fe(II) adsorption

Adsorben	Model Isoterm		
	AC	AC-Fe-Cu	AC-Cu(TAC)$_2$
Langmuir			
q_{max}	0,13	0,06	0,044
RL	1,08	0,676	-0,057
R^2	0,030	0,499	0,070
Freundlich			
K_F	0,14	0,42336	0,75
1/n	0,20	-0,07075	0,176
R^2	0,009	0,539	0,003

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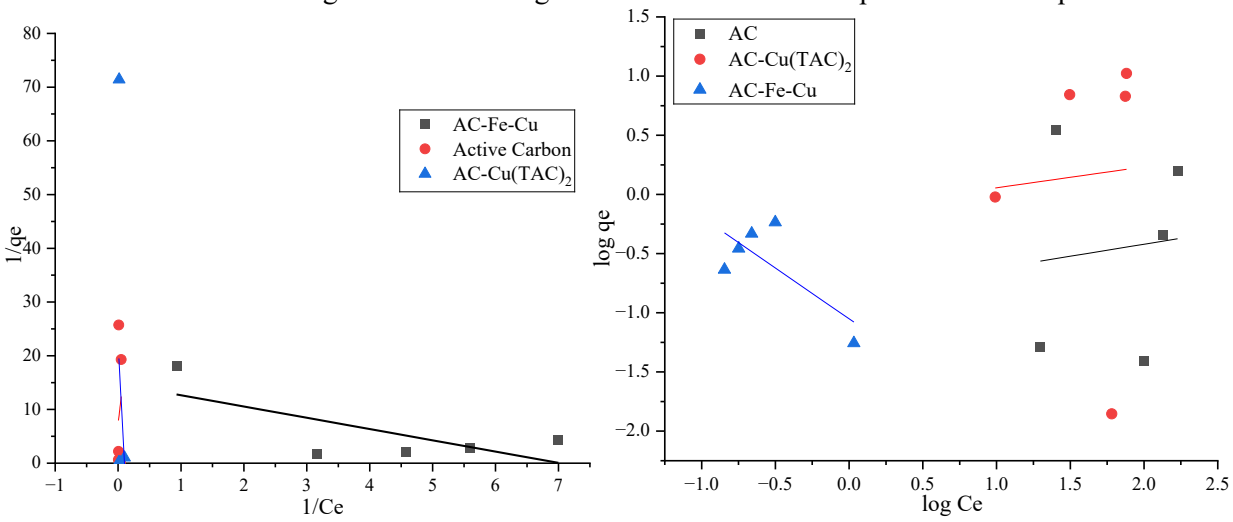
Based on table 3, it shows that the adsorption isotherms that occur in the three materials are Freundlich for AC-Fe-Cu with R2 of 0.539, Langmuir for activated carbon with R2 of 0.030, and AC-Cu(TAC)$_2$ following Langmuir adsorption isotherms with R2 of 0.070. This means that the adsorption process that occurs in activated carbon materials and AC-Cu(TAC)$_2$, experiences the formation of monolayers, with a homogeneous surface, while in AC-Fe-Cu materials there is a formation of multilayers and heterogeneous surfaces.[7]

It can be seen in Figure 2 for the Langmuir and Freundlich adsorption isotherm equilibrium.



(a) (b)

figure 5. (a) Isotherm Langmuir and (b) Isotherm Freundlich

Based on the data trends in Figure 5, it can be seen that AC and AC-Cu(TAC)$_2$ follow the Langmuir isothermal model because the resulting R2 value is greater than that of the Freundlich isothermal model. This shows that the Fe(II) adsorption process is chemical and the distribution of active sites on the adsorbent surface is uniform. This adsorption has an active site on the surface of the adsorbent that is only able to accommodate one adsorbent ion. When all active sites bind to the adsorbate, the adsorption process stops and reaches an equilibrium state, because the interaction between Fe(II) molecules and adsorbents occurs only in one layer or monolayer.[7]

4. CONCLUSION

The process of adsorption of Fe(II) ions is influenced by a variety of factors, including the type and surface area of the adsorbent, the concentration of the adsorbate, and the contact time. The results of kinetic analysis show that the pseudo-order-two model is the most suitable for describing the adsorption rate in AC, AC-Fe-Cu, and AC-Cu(TAC)$_2$. This indicates that the adsorption mechanism occurs through chemissorption, which involves chemical interactions between Fe^{2+} ions and the active group on the adsorbent surface.

From an equilibrium perspective, the Langmuir isothermal model describes the chemical adsorption of a monolayer, while the Freundlich isothermal model is more suitable for multilayer physical adsorption on heterogeneous surfaces. The adsorbents of AC and AC-Cu(TAC)$_2$ follow the Langmuir isothermal model and AC-Fe-Cu follows the Freundlich isothermal model.

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