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# Kinetics and Equilibrium Properties of Cu(II) Adsorption Using Modified Activated Carbon from Empty Oil Palm Fruit Bunches

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**ABSTRACT**

Oil palm empty fruit bunch (EFB) is a biomass waste containing lignocellulose that has the potential to be used as activated carbon to adsorb heavy metals such as Cu(II). This study aims to compare the adsorption performance of Cu(II) ions from three types of TKKS-based adsorbents, namely pure activated carbon (A.C), Fe-Cu metal modified activated carbon (A.C-Fe-Cu), and activated carbon composite with $Cu(TAC)_2$ (A.C-$Cu(TAC)_2$). Data were obtained from two previous studies and analyzed using first- and second-order pseudo-kinetic models, as well as Langmuir and Freundlich isotherm models. Results showed that all adsorbents followed a two-order pseudo-kinetic model with $R^2 \geq 0.998$, indicating a chemisorption mechanism. A.C-Fe-Cu showed the highest maximum adsorption capacity (389.47 mg/g) and the best fit to both isotherm models, while A.C-$Cu(TAC)_2$ showed suboptimal results. Thus, the modification of TKKS with Fe-Cu metal synergistically increases the effectiveness of adsorption on Cu(II) ions and has potential for wastewater treatment applications.
Keywords: Activated carbon, TKKS, Cu(II), Fe-Cu, $Cu(TAC)_2$, adsorption, kinetics, isotherm.

## 1. INTRODUCTION

Indonesia is the largest producer of palm oil (CPO) in the world, which can be seen from the increase in the area of new plantations. In 2024, palm oil output in Indonesia reached 52.76 thousand tons. Meanwhile, North Sumatra is fourth in terms of palm oil production, with around 5 million tons in 2023. The increase in palm oil production has resulted in an increase in the amount of waste generated. Waste generated by the palm oil industry consists of solid waste, liquid waste, and gas waste. Empty palm bunches are solid waste generated by the palm oil processing industry. Empty palm bunches contain lignocellulose between 55-60% of dry weight, which has the ability to absorb heavy metals due to the presence of active groups -COOH and -OH. In addition to solid waste, there is also liquid waste, which is the most generated type of waste compared to other types of waste, which is around 60% of the total



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100% fresh fruit bunch processing. In general, liquid waste from oil palm contains heavy metals such as copper (Cu), nickel (Ni), silver (Ag), zinc (Zn), iron (Fe), and lead (Pb). These solid and liquid wastes are very dangerous if disposed of directly into the environment, as they can cause pollution and are harmful to living things. Therefore, these wastes are processed into more useful materials. One type of solid waste, oil palm empty fruit bunches (EFB), can be used as an effective sorbent to remove harmful metals such as Cu(II). TKKS can also be used as activated carbon, which is effective in absorbing heavy metals due to its large surface area, pore size, and surface chemical properties. Modifications are made to enlarge its surface area and increase its porosity. Various modifications have been applied, including metal-modified activated carbon, which aims to improve its adsorption properties. For example, modification with Fe-Cu metal has been shown to be effective in adsorbing heavy metal Cu(II). Furthermore, it can be developed into a composite of activated carbon from TKKS with Metal-Organic Frameworks Fe(TAC) which is able to adsorb various types of metals, especially Cu(II) metal.

## 2. EXPERIMENTAL

This research uses data from previous research conducted in 2021 and 2022. This research has the same stages consisting of preparation, carbonization, activation, synthesis process and adsorption stage with the same carbon material. The difference between these two studies lies in the type of adsorbent material applied. In the research conducted in 2021, activated carbon produced from oil palm empty fruit bunches (TKKS) that has been modified with Fe-Cu metal is used. Meanwhile, in the 2022 study, a composite adsorbent material consisting of TKKS-based activated carbon and MOF $Cu(TAC)_2$ was used to adsorb Cu(II) metal.

This literature review aims to analyze which material from the two studies shows better adsorption performance, including a comparative analysis of isotherms and kinetics in the Cu(II) metal adsorption process.

## 3. RESULTS AND DISCUSSION

### *3.1. Adsorption Kinetics Analysis*

Most pollutants are difficult to degrade by natural biochemical decomposition. However, pollutants can be treated by adsorption on a suitable medium through various treatments. Adsorption is a surface phenomenon in which a mixture of gases or liquids (multicomponent) is attracted to the surface of a solid adsorbent and forms bonds through physical or chemical bonds. The adsorption capacity of a material is influenced by various important factors, including the type and surface area of the adsorbent. A high specific surface area can enhance adsorption efficiency by providing more active sites for interaction with the adsorbate. Other factors affecting the adsorption process include the type and concentration of the adsorbate, as well as the contact time between the adsorbent and adsorbate. These parameters determine the adsorption rate and the achievement of system equilibrium. Adsorption kinetics studies play a crucial role in understanding the mechanisms and rates of the adsorption process. Kinetic information is essential for designing time-efficient and performance-optimized adsorption systems, particularly in practical applications such as wastewater treatment. Kinetic analysis can also provide insights into the dominant type of adsorption mechanism, whether it is physisorption (involving weak physical forces) or chemisorption (involving the formation of chemical bonds). This can be identified through modeling of experimental data using kinetic approaches, such as the pseudo-first-order model and the pseudo-second-order model. The model with the



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highest coefficient of determination ($R^2$) is considered the most representative in describing the mechanism. Fitting with the pseudo-first-order model generally indicates that the process is dominated by physisorption, while fitting with the pseudo-second-order model suggests a tendency toward chemisorption mechanisms. The equations for adsorption kinetics and isotherms can be seen the table below:

**Tabel 1.** Adsorption Kinetics and Adsorption Isotherms

| Type of model | Equation | |
|---|---|---|
| **Adsorption kinetic model** | Pseudo-First-order | $\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$ |
| | Pseudo-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 | $\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$ |

seen in the table below:

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.

$K_2\ (g\ mg^{-1} min^{-1})$: : 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

The following table presents the literature review results from both studies.

**Table 2.**kinetic models for Cu(II) Adsorption

| Pseudo-First Orde | | | |
|---|---|---|---|
| | $q_e$ (mg/g) | $K_1 (min^{-1})$ | $R^2$ |
| A.C | | | |
| A.C-Fe-Cu | 1,01094 | -0,000295 | 0,95758 |
| A.C $Cu(TAC)_2$ | 0,32324 | -0,000165 | 0,44557 |
| Pseudo-second order | | | |
| | $q_e$ (mg/g) | $K_2 (g\ mg^{-1} min^{-1})$ | $R^2$ |
| A.C | 9,62245 | -0,08565 | 0,99999 |
| A.C-Fe-Cu | 2,13311 | 0,00598 | 0,99887 |
| A.C $Cu(TAC)_2$ | 9,92575 | 0,03995 | 0,99997 |



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Table 2 shows that adsorption kinetics were analyzed using two models, namely pseudo-first order and pseudo-second order. The parameters that must be considered include equilibrium adsorption capacity (qe), rate constants (k1 and k2), and the coefficient of determination ($R^2$), which is used as an indicator of model suitability.

In the pseudo-first-order model, the $R^2$ value is relatively low compared to the pseudo-second-order model, indicating that this model is less accurate in describing the adsorption kinetics in the system. The highest $R^2$ value recorded was 0.95758 for activated carbon modified with Fe-Cu metal, while the lowest value reached 0.32324 for $Cu(TAC)_2$ activated carbon composite. On the other hand, this model cannot be applied to unmodified activated carbon. This indicates that the adsorption mechanism is not dominated by physical diffusion, which is the basic assumption of the first-order model.

In the pseudo-second-order model, there is a much better fit with a very high $R^2$ value (≥ 0.99887) for all types of adsorbents. Activated carbon shows the highest value with $R^2$ = 0.99999. This indicates that the adsorption process is more likely to follow a chemisorption mechanism, which involves chemical bonding between the adsorbate and the adsorbent surface. Additionally, the adsorption capacity (qe) values obtained from the pseudo-second-order model are more accurate and stable. Activated carbon and K. A $Cu(TAC)_2$ exhibit the highest values (qe > 9 mg/g), while K. A-Fe-Cu shows slightly lower values (qe ≈ 2 mg/g), yet still demonstrates a strong correlation with the pseudo-second-order model. Therefore, the pseudo-second-order kinetic model provides a better fit to the experimental data compared to the pseudo-first-order model, based on the high $R^2$ value and consistency in adsorption capacity. This indicates that the primary adsorption process in this system is chemisorption, not physisorption.

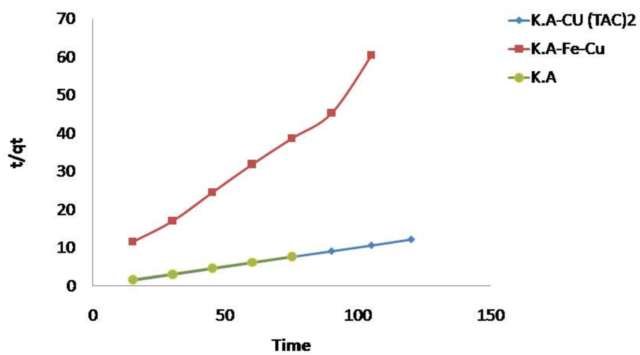


**Figure 1.** Adsorption Kinetics of Cu(II) by Activated Carbon (AC), Activated Carbon-$Cu(TAC)_2$, and Activated Carbon-Fe-Cu Based on the Second-Order Pseudo-Model

**Table 3.** Langmuir and Freundlich Parameters for Cu(II) Adsorption

| Langmuir | | | |
|---|---|---|---|
| | $q_{max}$ | RL | $R^2$ |
| A.C | 5,908298 | 0,002966 | 0,014699 |
| A.C-Fe-Cu | 389,47488 | 0,401722 | 0,9445956 |
| A.C $Cu(TAC)_2$ | 3,6129976 | -0,000395 | 0,063744193 |
| Freundlich | | | |
| | $K_F$ | 1/n | $R^2$ |
| A.C | 4,79473 | 0,28914 | 0,0458447 |
| A.C-Fe-Cu | 13,71343 | 1,09898 | 0,9428570 |
| A.C $Cu(TAC)_2$ | 7,84984 | -0,06645 | 0,0032143 |


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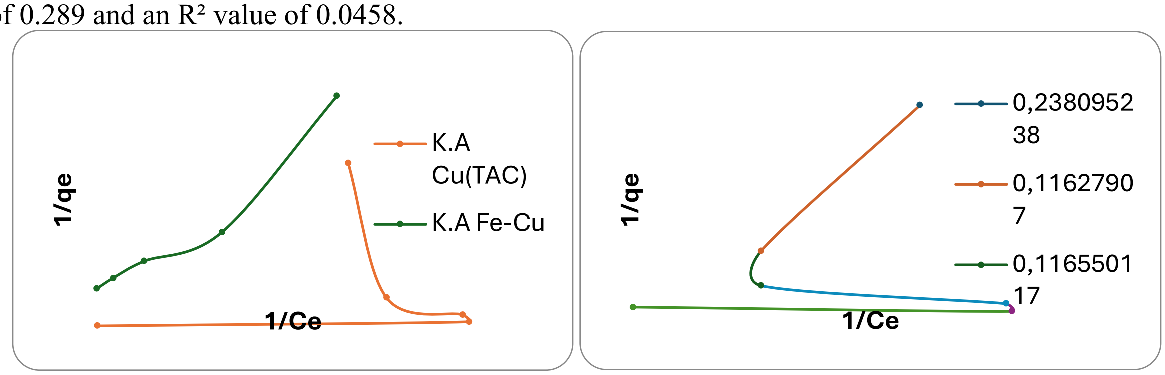
Based on the data in Table 3, the Langmuir and Freundlich isotherm models show significant differences between the three types of adsorbents, namely activated carbon, activated carbon-Fe-Cu, and activated carbon $Cu(TAC)_2$, in terms of Cu(II) metal adsorption capacity and model suitability.

In the Langmuir model, the highest maximum adsorption capacity value for Cu(II) was obtained by Fe-Cu activated carbon at 389.47, far exceeding that of pure activated carbon (5.91) and $Cu(TAC)_2$ activated carbon (3.61). This indicates that modification with Fe and Cu metals synergistically enhances surface adsorption capacity. The RL constant value of Fe-Cu activated carbon is also within the 0–1 range, at 0.401, indicating favorable adsorption, while pure activated carbon and $Cu(TAC)_2$ activated carbon also show similar results with RL values of 0.00296 and 0.0637, respectively, although these values are very small. However, the negative Langmuir constant value for activated carbon $Cu(TAC)_2$ (-0.000395) may indicate that the adsorption process does not perfectly follow the ideal Langmuir model.
Meanwhile, in the Freundlich model, the highest correlation coefficient ($R^2$) was shown by activated carbon-Fe-Cu at 0.9428, indicating that the Freundlich model describes the adsorption process very well in this material. The 1/n value of activated carbon -Fe-Cu, which is 1.098, also indicates the presence of physical multilayer adsorption occurring on a heterogeneous surface. In contrast, activated carbon $Cu(TAC)_2$ has a negative 1/n value (-0.06645) and a very low $R^2$ value (0.0032), indicating that this model does not fit the adsorption characteristics of the material. Pure activated carbon shows moderate fit to both models with a 1/n value of 0.289 and an $R^2$ value of 0.0458.




**Gambar 2**. Langmuir Isothermal Model for Cu(II) Adsorption by Activated Carbon, Activated Carbon-$Cu(TAC)_2$, and Activated Carbon-Fe-Cu

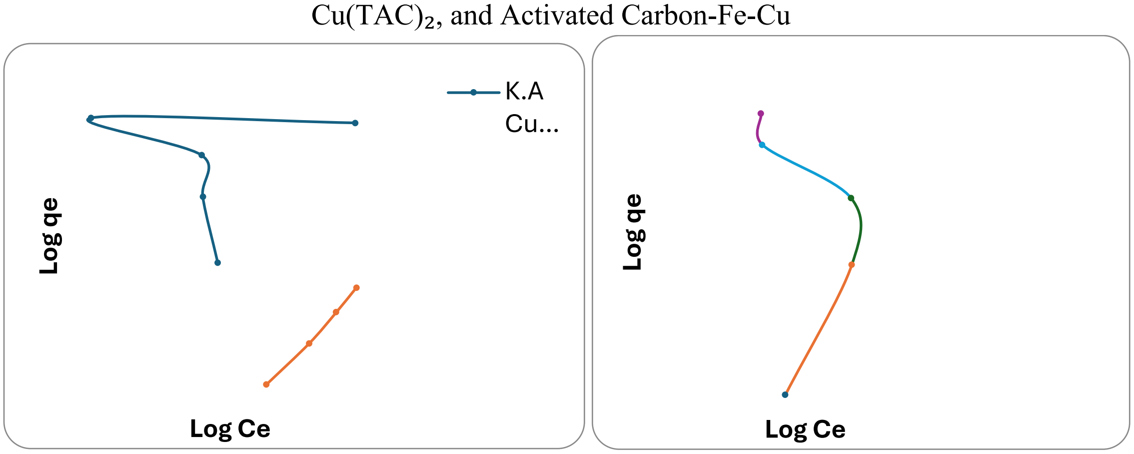



Figure 3. Freundlich Isothermal Model for Cu(II) Adsorption by Activated Carbon, Activated Carbon-$Cu(TAC)_2$, and Activated Carbon-Fe-Cu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Overall, the activated carbon-Fe-Cu adsorbent showed the best performance in both the Langmuir and Freundlich models, indicating that simultaneous activation modification of carbon with Fe and Cu metals produces a material with much higher adsorption capacity and efficiency than pure activated carbon or carbon modified only with $Cu(TAC)_2$ complexes.

## 4. CONCLUSION

Activated carbon modified with Fe-Cu metal exhibits the most superior adsorption performance compared to pure activated carbon or activated carbon modified using $Cu(TAC)_2$. This is demonstrated by high adsorption capacity values, compatibility with the Langmuir and Freundlich isotherm models, and determination coefficient ($R^2$) values indicating the accuracy of the model relative to experimental data. Additionally, the adsorption mechanism generally follows the pseudo-second-order kinetic model, indicating that the adsorption process occurs via chemisorption. These results confirm that the synergistic modification of activated carbon with Fe and Cu metals enhances surface properties and adsorption capacity toward heavy metal Cu(II), making it highly promising for application in the treatment of liquid waste containing heavy metals.

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