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Adsorption of Heavy Metal Cu(II) in Wastewater Using Adsorbents from Empty Oil Palm Bunches

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ABSTRACT

Heavy metal pollution has increased with increasing industrialization. To overcome this contamination, carried out by using the adsorption method. The adsorbents used are activated carbon and porous polymer composite carbon Cu(TAC). in liquid waste, one of which is Cu metal. This is evidenced by the existence of data showing the efficiency of activated carbon and porous polymer composite carbon Cu(TAC) above 90%. In addition, activated carbon and porous polymer composite carbon Cu(TAC) have an adsorption isotherm equation that is suitable for Cu(II) adsorption is the Langmuir isotherm with linear regression values of 0.9045 and 0.8912.

Keywords: Adsorption, Isotherm, Copper (Cu), Wastewater

1. INTRODUCTION

Oil palm is a group of plantation crops that have an important position in the agricultural and plantation sectors. This is because oil palm produces the largest economic value per hectare of the many plants that produce oil or fat in the world [1]. According to the Oil Palm Plantation Sector Data Base in Indonesia, the area of oil palm plantations in 2022 will be 15.38 million hectares, an increase of 4.5% from 2021. Meanwhile, oil palm production will increase by an average of 3% per year. The increase in area was factored in by the relatively stable nominal CPO price on the international market and providing income for producers, especially for farmers. The distribution of oil palm in several provinces in Indonesia contributes to the production of oil palm plants which is quite large. The number of oil palm plantations spread across various regions in Indonesia is 26 provinces. North Sumatra Province has an area of 1.29 million hectares with a production of 5.2 tons [2].

Empty palm fruit bunches are included in the most common type of solid waste from the processing of palm oil mills. In this case, it can be seen that every 1 hectare of oil palm plantation will produce around 1.5 tons of empty palm oil fruit bunches [3]. Lignocellulose is the main component of empty palm oil fruit bunches at 55-60% dry weight [4] which has the ability to absorb heavy metals because it contains active groups such as -COOH and –OH [5]. In addition to producing solid waste, palm oil mills also produce liquid waste which is waste from processing fresh fruit bunches into CPO, which is around 60% of liquid waste produced from every 100% processing of fresh fruit bunches. Generally, industrial wastewater contains heavy metals such as Pb, Cd, Fe, Cu, Cr, Zn, Mn and so on [6 7].

Heavy metals are substances that are harmful to living things, especially to human health. Heavy metals can be found in the form of dissolved ions [8]. Heavy metal pollution increases with increasing industrialization [9]. Heavy metal pollution is caused by industrial and household activities which can cause environmental problems faced by almost all countries today [10]. Heavy metal-producing industrial environment, including the Printing Industry, Garment, Stainless Steel, etc. Waste from inorganic industries is more difficult to handle and has a greater potential hazard [9]. Industrial activities produce liquid waste with the category of hazardous and toxic chemicals such as heavy metals Cr, Cd, Zn, Pb, and Cu [10].

Copper is found in our environment naturally, but the metal can also be the result of (non-natural) human activities. Natural events such as the erosion of mineral rocks that occur are one of the factors for the presence of copper naturally in the environment. Copper dust and/or airborne particles carried by rainwater are also natural sources of copper in the environment. Non-natural sources of copper are mostly the result of human activities. An example is the result of industrial waste that uses copper in its production process, such as the shipbuilding industry, wood processing industry, and household waste.

Copper is toxic to some degree to the human body. Metal poisoning can be acute or chronic. Acute poisoning causes symptoms such as nausea, vomiting, abdominal pain, hemolysis, neutropenia, convulsions, and can result in death. During chronic poisoning, copper accumulates in the liver and causes hemolysis. Hemolysis occurs because H_2O_2 accumulates in red blood cells resulting in oxidation of the cell lining which causes the cell to burst. Hemolysis can cause anemia and stunted growth [11]. The maximum allowable limit for copper set by the USEPA is 1.3 mg/L [12].

Various methods that have been developed for the separation of heavy metals are chemical precipitation methods, ion exchange, membrane media, electrochemical technology and adsorption filtration. The adsorption method is the safest method compared to other methods, because this method does not give side effects that affect human health, the equipment and maintenance used are also simple, and the operation is easy both in batch and continuously. Biomass adsorbent in the adsorption process is an excellent choice because it is cheap and easy to obtain and is available in large and varied quantities [10].

Metal-organic frameworks (MOFs) are a new class of porous crystalline solids assembled from single metal ions or clusters thereof, coordinated by organic linkers with strong bonds [13]. Organic linkers are generally mono-, di-, tri-, or tetravalent ligands. The combination of metal types together with the linker determines the characteristics and properties of the MOF. The application of MOFs in wastewater treatment is no exception. Although the synthesis method is simple and easy, MOF has superior adsorption and regeneration ability, with large surface area and adjustable pores at low temperature, which is suitable for wastewater treatment processes [13][14]. Moreover, the convertible nature of the organic linker, by changing the geometry of the MOF, length, ratio, and functional groups, makes it a potential candidate for removing pollutants from wastewater [13].

Copper-based porous polymer composites are of particular interest because they can be synthesized with commercially available reagents and have a high surface area. Copper (Cu) was chosen as a classic transition metal which is considered as one of the most attractive elements for use in the preparation of porous polymer composites due to its abundant resources, low cost, non-toxic nature and most importantly high complexation strength. The high and excellent stability of Cu-based porous polymer composites is related to the strong interaction between Cu(II) of metals and -O- of organic ligands which makes these materials stable in aqueous solutions and over a wide pH range. Terephthalic acid as a general ligand has very low toxicity and is easy to obtain where the COOH group can interact strongly with Cu^{2+} cations through coordination interactions. Also, molecules with aromatic rings tend to interact with porous polymer composites due to π-π interactions [16].

Adsorption isotherms are represented as the number of adsorbate molecules per unit mass of adsorbent as a function of the equilibrium concentration in the bulk solution at a constant temperature. The Langmuir model assumes that a fixed number of adsorption sites are available on the surface of the adsorbent; each site can take up one molecule only, that is, monolayer adsorption, and the adsorption energy is constant [17]. The Freundlich isotherm assumes the opposite, which is constructed based on adsorbent surfaces at homogeneous binding energies [18].

2. Experimental

2.1. Activated Carbon Manufacture

Preparation of activated carbon from empty palm oil fruit bunches by incorporating the biosorbent into a porcelain and carbonizing it using a furnace at 500°C for ± 2 minutes. The resulting carbon is activated using phosphoric acid for 24 hours, then washed with distilled water until the carbon pH is neutral. Dry in the oven for 24 hours at 105°C.

2.2. Manufacture of Porous Polymer Composite Carbon Cu(TAC)

Terephthalic acid, ethanol and activated carbon are mixed in a ratio of 1:10:0.6 then the mixture is soaked for 24 hours, then the ethanol is evaporated at 90°C for 24 hours. Then the mixture was mixed with porous polymer composite reagent Cu(TAC) and refluxed at 105°C for 8 hours, cleaned and washed using filter paper and a vacuum pump. The solid obtained was washed until the pH was neutral.

2.3. Adsorption Measurement

a. Determination of Optimum Mass of Adsorbent Against Metal Cu(II)

Put the adsorbent into 5 beakers of 1 gram, 2 grams, 3 grams, 4 grams and 5 grams each. Then 100 mL of Cu ion was added with a concentration of 20 ppm, stirred at 125 rpm for 15 minutes. Then the mixture was filtered using Whatman filter paper no. 42 then the filtrate was analyzed with the AAS instrument.

b. Determination of Optimum Concentration of Adsorbent Against Metal Cu (II)

Put the adsorbent into 5 glass beakers with the optimum adsorbent mass. Then 100 mL of Cu ions were added to the beaker, each with various concentrations of 20 ppm, 40 ppm, 60 ppm, 80 ppm, 100 ppm and 140 ppm, stirred at 125 rpm for 15 minutes. Then the mixture was filtered using Whatman filter paper no. 42 then the filtrate was analyzed with the AAS instrument.

c. Determination of Adsorbent Optimum Contact Time Against Metal Cu (II)

Put the adsorbent into 5 glass beakers with the optimum adsorbent mass. Then 100 mL of Cu ion was added with the optimum concentration, then stirred at 125 rpm with variations of time 15 minutes, 30 minutes, 45 minutes, 60 minutes, 75 minutes. Then the mixture was filtered using Whatman filter paper no. 42 then the filtrate was analyzed with the AAS instrument.

2.4. Adsorption Equilibrium Analysis

Adsorption isotherms for Cu (II) adsorption on activated carbon modified porous polymer composite Cu(TAC) of empty palm oil fruit bunches were determined by varying the concentration of Cu (II) from 20 ppm, 40 ppm, 60 ppm, 80 ppm and 100 ppm. Equilibrium data is determined using Langmuir and Freundlich isotherms.

The data obtained is used to calculate the amount of absorption of equilibrium metal ions (mg/g) which is calculated using the following equation.

$$q = \frac{(C_0 - C)\,V}{m} \qquad (3.1)$$

Where C_0= initial concentration of adsorbent (mg/L), C= adsorption concentration at time t (mg/L), V= volume of standard solution (L), m= mass of adsorbent (g).

a. Langmuir Adsorption Isotherm

The form of the Langmuir adsorption isotherm equation is as follows:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (3.2)$$

Where R_L= separation factor, K_L= Langmuir constant (L/mg), and Co= initial adsorbate concentration (mg/L). Where

b. Freundlich Adsorption Isotherm

The form of the Freundlich adsorption isotherm equation is as follows:

$$Log\ q_e = \log K_f + \frac{1}{n} \log C_e \qquad (3.3)$$

Where q_e= amount of adsorbate in the adsorbent at equilibrium (mg/g), K_F= Freundlich isotherm constant (mg/g)$(dm^3/g)^n$, n= adsorption intensity, and C_e = equilibrium concentration (mg/L).

3. Results and Discussion

Activated carbon produced from the carbonization process at 500°C has a good level of purity [1920] because it is useful for removing volatile substances contained in carbon, thus causing empty spaces on carbon to form a carbon structure. While activation is to increase or expand the pore volume and enlarge the pore diameter that has been formed in the carbonization process, activate the pore side of the carbon and to create several new pores [21]. The choice of chemical activation with H_3PO_4 in this study is that H_3PO_4 has a relatively short activation time, higher carbon end result, and increased adsorption power [20].

Activated carbon modified porous polymer composites is expected to increase porosity, surface area, pore volume, pore size, and crystalline structure. Because porous polymer composites have the advantages of high surface area, high micropore volume, uniform pore size, crystal structure. This is because the porous polymer composite is a synthetic material so that its structure is easy to adjust. During the immersion process, TAC forms a framework in the activated carbon, so that when refluxed the mixed Cu metal will bind to the COOH- group present in the activated carbon after immersion using TAC.

3.1. Adsorption Measurement

a. Optimum Adsorbent Mass

The absorption capacity of an adsorbent is affected by the concentration of the absorbed adsorbate multiplied by the volume of the adsorbate and is inversely proportional to the mass of the adsorbent. This graph shows the effect of carbon mass on Cu(II) metal uptake. It can be seen that as the mass of the adsorbent increases, the adsorption capacity decreases. This happens because the surface of activated carbon has reached a saturation point so that the adsorption ability of activated carbon decreases. The highest adsorption capacity for activated carbon and modified activated carbon was found in the mass variation of 1 gram of adsorbent. Mass variation of 1 gram of activated carbon can absorb 11.90 ppm of Cu (II) metal with an absorption capacity of 1.1883 mg/g while modified activated carbon can absorb 7.91 ppm of Cu (II) metal with an absorption capacity of 0.7874 mg/g .

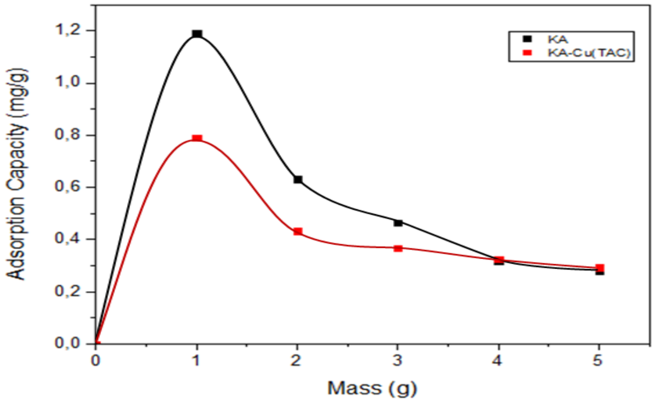

Figure 1. Absorption Capacity of Mass Variation

Based on the data and graphs, it can be seen that the optimum adsorption mass of Cu(II) metal on activated carbon and modified activated carbon is 1 gram. In addition, the data and graphs above also show that at the same optimal mass variation, activated carbon has a better adsorption ability in adsorbing Cu(II) metal. This is indicated by the higher absorption value of activated carbon compared to modified activated carbon, this is because the modified activated carbon in this study still has instability. However, the variations of 4 grams and 5 grams of modified activated carbon are higher. This is because modified activated carbon has a different adsorption mechanism than activated carbon. Where the modified activated carbon mechanism relies on active groups, namely cellulose and pores, while activated carbon only relies on pores.

b. Optimum Concentration

Figure 2 shows the effect of variations in carbon concentration on the absorption efficiency of Cu(II) metal. It can be seen that the adsorption efficiency of activated carbon increases with increasing concentration until the optimum concentration variation is obtained. The increase in adsorption efficiency was caused by an increase in the concentration of Cu(II) metal, causing the amount adsorbed to increase so that the absorption efficiency increased. Optimal efficiency of activated carbon and modified activated carbon is found at a concentration of 100 ppm which is 96.76% and capable of absorbing Cu(II) metal of 96.76 ppm. Meanwhile, modified activated carbon has optimal efficiency with an efficiency of 98.65% and is able to absorb 98.65 ppm of Cu(II) metal. This is indicated by the absorption value of activated carbon which is lower than modified activated carbon. However, there are several variations of modified activated carbon lower than activated carbon. This is because the modified activated carbon has the same instability as the mass variation.

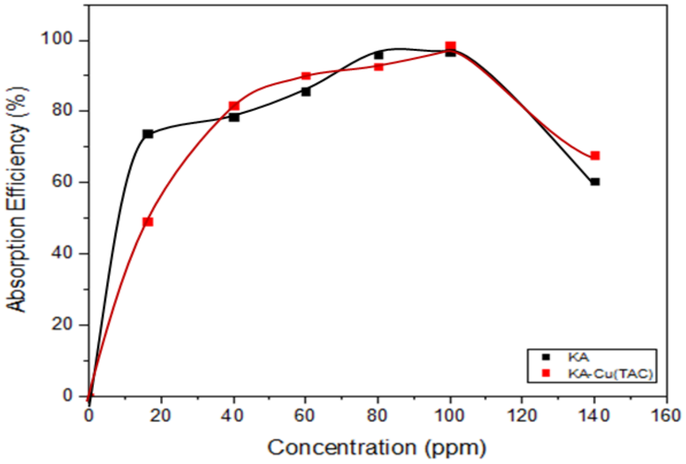

Figure 2. Absorption Efficiency of Concentration Variation

c. Optimum Contact Time

Figure 3 shows the adsorption efficiency value of activated carbon against adsorption time. The adsorption efficiency of activated carbon increases with increasing optimum contact time. The highest efficiency of activated carbon occurs at a contact time of 30 minutes with an absorption efficiency of

96.86%. As for the modified activated carbon, the optimum contact time variation is 90 minutes with an absorption efficiency of 99.38%. This shows that the value of the absorption efficiency of modified activated carbon is greater than that of activated carbon. This is because the modified activated carbon in this study has begun to stabilize. However, it still requires a longer time than activated carbon.

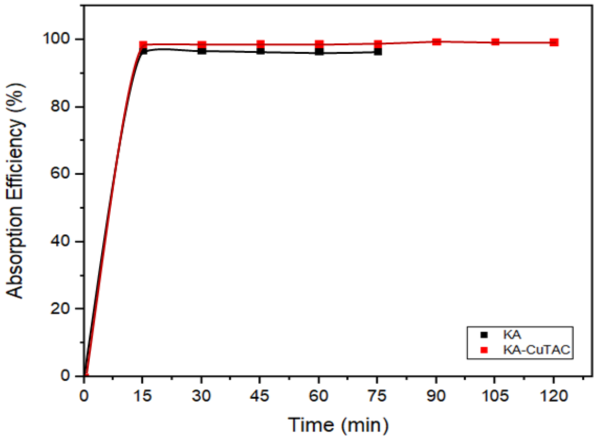

Figure 3. Absorption Efficiency of Time Variation

3.2 Determination of Langmuir and Freundlich Adsorption Isotherms

Langmuir and Freundlich adsorption isotherms were used to describe the characteristics of Cu(II) adsorption isotherms on activated carbon and modified activated carbon. The Langmuir isotherm describes the adsorption of a single layer of adsorbate onto an adsorbent surface that has a limited number of adsorption sites, while the Freundlich isotherm explains that adsorption occurs on a heterogeneous adsorbent surface [22]. The Langmuir adsorption model test (Figure 4) and Freundlich (Figure 5) are proven by good linearization graphs and have a coefficient of determination of R2 ≥ 0.9 (close to 1).

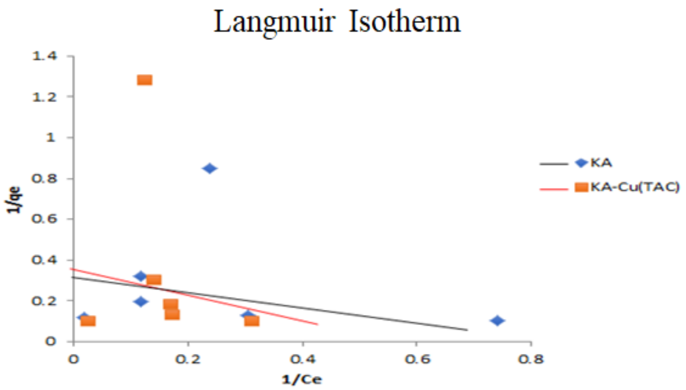

Figure 4. Linearization of Langmuir Adsorption Isotherm

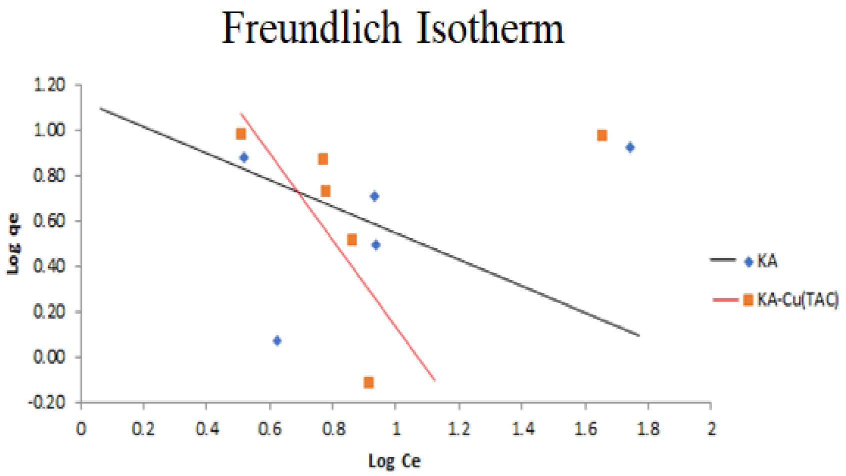

Figure 5. Linearization of Freundlich Adsorption Isotherm

Using the correlation coefficient (R^2) in Table 1. shows that the Langmuir isotherm is the most suitable because the linear regression coefficient values are on KA ($R^2 > 0.9045$) and KA-Cu(TAC) ($R^2 > 0.8912$) where these isotherms have a higher value than the Freundlich isotherm on KA (R2 > 0.8089) and KA-Cu(TAC) ($R^2 > 0.7289$). This indicates the presence of monolayer and homogeneous surface adsorption on KA and KA-Cu(TAC). The highest correlation coefficient (R^2) for KA also shows that the adsorption using the Langmuir isotherm model is better for KA than for KA-Cu(TAC).

Table 1. Langmuir and Freundlich parameters for adsorption of Cu (II) ions on KA and KA-Cu(TAC)

Sample	Langmuir Isotherm				Freundlich Isotherm		
	Qmax	**KL**	**RL**	**R^2**	**1/n**	**KF**	**R^2**
KA	3,12	-1,17	-0,0086	0,9045	-0,502	12,189896	0,77529
KA-Cu(TAC)	4,26	-0,54	-0,0187	0,8912	-1,1522	41,30475	0,2267

It can be seen that lower RL values reflect that adsorption is more favorable. However, if the RL value is negative then it indicates no adsorption or desorption.

Tabel 2. Adsorption of Copper (Cu)

Adsorbent	**Metal Concentration (mg/L)**	**Model**	**Contact Time (min)**	**Adsorbent Mass (g)**	**Adsorption Capacity (mg/g)**	**Absorption Efficiency**
Activated Carbon	100	Langmuir	30	1	9,686	96,86%
Porous Polymer Composite Carbon Cu(TAC) (KA-Cu(TAC)	100	Langmuir	90	1	9,938	99,38%

4. CONCLUSION

Activated carbon and Cu(TAC) porous polymer polymer composites have superior adsorption and regeneration capabilities, with large surfaces and pores that have the potential to adsorb dissolved metals in wastewater, one of which is Cu metal. This is evidenced by the existence of data showing the efficiency of activated carbon and Cu porous polymer composite carbon (TAC) above 90%. In addition, activated carbon and porous polymer composite carbon Cu(TAC) have an adsorption isotherm equation that is suitable for Cu(II) adsorption is the Langmuir isotherm with linear regression values of 0.9045 and 0.8912.

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