Indonesian Journal of Chemical Science and Technology (IJCST)
State University of Medan, https://jurnal.unimed.ac.id/2012/index.php/aromatika

IJCST-UNIMED 2023, Vol. 07, No. 2 Page; 104 – 111
Received : Apr 12th, 2024 Accepted : July 02th, 2024 Web Published : July 31st, 2024

Adsorption Equilibrium Properties of Zn(II) on Activated Carbon Composite of Derived Empty Palm Oil Fruit Bunches with Metal Organic Frameworks Cu(TAC)

Jasmidi *, Moondra Zubir, Rini Selly, Ahmad Shafwan Pulungan, Putri Faradilla, Siti Rahmah and Amar Lohot Tanjung

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Medan, 20221, Indonesia
**Corresponding author : jasmidi@unimed.ac.id*

ABSTRACT

This study aims to determine the adsorption equilibrium of the activated carbon of empty palm oil fruit bunches and KA-Cu(TAC) on Zn(II). Oil palm empty fruit bunches are used as a bio-sorbent in making carbon at a temperature of 5000 C, the resulting carbon is activated using H_3PO_4 and modified into a composite with metal organic frameworks of Cu metal and terephthalic acid. MOFs and KA-Cu(TAC) composites were produced by reflux method. Activated carbon, MOFS and KA-Cu(TAC) were characterized using XRD. The adsorption process of Zn(II) metal was analyzed using AAS and determined the optimum conditions with various concentrations to determine the adsorption equilibrium. XRD characterization results show that activated carbon has an amorphous structure, while MOFs Cu(TAC) and KA-Cu(TAC) have a crystalline structure. The optimum condition of activated carbon and KA-Cu(TAC) at a concentration of 180 ppm with the appropriate adsorption isotherm model is the Langmuir isotherm.

Keywords: Oil palm empty fruit bunches, activated carbon, KA-Cu(TAC), adsorption isotherm, Zn(II)

1. INTRODUCTION

The rapid industrial development has an impact on environmental problems that must be seriously addressed. The oil palm plantation industry is one that generates the most waste, be it solid, liquid or gas. Indonesia is ranked 1st in the world's palm oil producer with an area of 14,456,611 ha and a total production of 47.1 million tons in 2019.[1] One of the very dangerous components is heavy metals from liquid waste, namely Zn, Pb, Mn, Cd, Fe, and Cu.[2] Heavy metals can be harmful to humans and can spread from one organism to another through the food chain.[3] One of the most common heavy metals found in waters is

e-ISSN : 2622-4968, p-ISSN : 2622-1349

zinc(Zn), and environmental pollution by heavy metals is a problem that needs to be addressed thoroughly. According to data from the Environment Agency (2018), the concentration of Zn metal in water exceeding the set quality standard of 0.06 mg/L is a significant hazard. The presence of heavy metal zinc (Zn) in water that exceeds the limit can cause toxic effects,[4] because it can accumulate in living things and cannot be degraded.[5]

Efforts that can be made to reduce the heavy metal content of palm oil industrial waste is by adsorption method. Activated carbon can be an alternative adsorbent because it has several advantages, namely low cost, simple operation, and long service life.[6] Activated carbon can be made from organic waste, one of which is empty oil palm fruit bunches (EFB). OPEFB includes solid waste from oil palm plantations and is very abundant because it accounts for around 23% of the total fresh fruit bunches.[7] One of the innovative ways to increase the adsorption yield is to synthesize composite materials with a view to achieving new adsorption characteristics such as high pore volume and porosity. Carbon composites based on metal organic frameworks (MOFs) have received attention because of their high surface area and reactivity as well as their extraordinary adsorption capacity and thermal stability.[8] MOFs have a strong and highly porous structure that can accommodate a variety of guest molecules.[9] Various studies have applied MOFs to remove various toxic pollutants from wastewater, including heavy metals, pesticides, volatile and persistent organic pollutants.[10] More than 20,000 types of MOFs have been prepared due to the large number of metal and organic linkage combinations available for synthesis.[9]

In this study, activated carbon of empty palm oil fruit bunches was used with metal organic frameworks of Cu metal and terephthalic acid (TAC) organic ligands. The choice of Cu as the central metal in MOFs is due to its high selectivity and high adsorption capacity.[11] In this study adsorption equilibrium was used to describe the adsorption isotherm characteristics of Zn(II) metal on activated carbon and KA-Cu(TAC). The Langmuir isotherm describes the adsorption of a monolayer of adsorbate onto an adsorbent surface that has a limited number of adsorption sites, while the Freundlich isotherm describes that adsorption occurs on a heterogeneous surface of the adsorbent. Based on this explanation, the researcher aims to modify the activated carbon composite of empty oil palm fruit bunches with metal organic frameworks Cu(TAC) to adsorb Zn(II) with the name KA-Cu(TAC) composite to increase adsorption power, to determine the characterization of the material and to determine the adsorption isotherm characteristics of the adsorbent.

2. EXPERIMENTAL

2.1. Chemicals, Equipment and Instrumentation

The materials used in this study were empty oil palm fruit bunches (EFB), metal Zn(II), H_3PO_4, TAC(terephthalic acid), HF(fluoric acid), HNO_3(nitric acid), $Cu(NO_3)_2$(copper(II) nitrate), distilled water, filter paper, universal Ph. The equipment used in this study included: glassware, reflux, grinder, 200 mesh sieve, vacuum pump, analytical balance, oven, furnace, desiccator, hot plate, XRD and AAS.

2.2. Empty Oil Palm Bunches Preparation

The empty oil palm bunches (EFB) used were obtained from PTPN II Pagar merbau's OPEFB waste. OPEFB is first washed to reduce its oil content and then dried in the sun for several days. The dried OPEFB

e-ISSN : 2622-4968, p-ISSN : 2622-1349

were then ground to a fine powder and sieved using a 200 mesh sieve and obtained bio-sorbent of empty palm oil bunches.[12]

2.3. Activation and carbonization

Bio-sorbent empty palm oil bunches that have been dried were heated in a furnace with a temperature of 500^0 C for approximately 2 minutes. After carbonization, Carbon was prepared and weighed total of 10 grams of activated carbon was immersed in 100 mL of 10% H3PO4 for 24 hours. The activated carbon is filtered using filter paper and washed with distilled water until the pH is neutral.[13]

2.4. Synthesis of MOFs Cu(TAC)

MOFs Cu(TAC) was synthesized by mixing 277.5 mg of $Cu(NO_3)_2$, 687.5 mg of terephthalic acid, 200 mL of 35% hydrofluoric acid, and 190 ml of 65 % nitric acid evenly with 20 ml of distilled water under reflux and heated to 105° C for 8 hours. After cooling to room temperature, the solution was vacuum filtered and washed to a neutral Ph.[14]

2.5. Synthesis of Activated Carbon Composites – Cu(TAC)

The synthesis is carried out in two stages. In beaker 1 consists of dispersion of terephthalic acid onto activated carbon. Terephthalic acid ethanol solutions (approx 1 g terephthalic acid per 10 g ethanol) were prepared and then dispersed onto activated carbon (approx. 10 g solution per 0,6 g activated carbon). The terephthalic acid/activated carbon mixture is then soaked for 24 hours to evaporate the ethanol. In beaker 2, copper nitrate, hydrofluoric acid, nitric acid and distilled water are mixed. then the two beakers mixed were refluxed for 8 hours to remove excess acid and evaporate the ethanol.[10]

2.6. XRD characterization

MOFs Cu(TAC) and KA-Cu(TAC) obtained were characterized using XRD to determine the structure of the material.

2.7. Adsorption Equilibrium

Adsorption isotherms for Zn(II) on activated carbon and KA-Cu(TAC) of empty palm oil bunches were determined by varying the Zn(II) concentrations from 60 ppm, 100 ppm, 140 ppm, 180 ppm and 220 ppm. Equilibrium data was determined using Langmuir and Freundlich isotherms.

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

$$R_L = \frac{1}{1 + K_L C_0}$$

RL = separation factor, KL = Langmuir constant (L/mg), and Co = initial adsorbate concentration (mg/L).[15]

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

$$Log\ q_e = \log K_f + \frac{1}{n} \log$$

qe = amount of adsorbate in the adsorbent at equilibrium (mg/g), KF = Freundlich isotherm constant (mg/g) $(dm^3/g)n$, n = adsorption intensity, and Ce = equilibrium concentration (mg/L).[15]

e-ISSN : 2622-4968, p-ISSN : 2622-1349

3. RESULTS AND DISCUSSION

In this study, carbon was activated using the H_3PO_4 activator because it can form new pores and bind impurity carbon compounds out of the carbon pores so that the diameter of the carbon pores increases and also has low toxicity.[16] KA-Cu(TAC) was also successfully synthesized which visually formed a black powder in the presence of a white mixture. The black color in KA – Cu(TAC) comes from activated carbon, while the white color comes from MOFs Cu(TAC). In this synthesis, a reflux process is carried out with the aim of removing excess acid and evaporating the ethanol.[10]

3.1. XRD Characterization

Characterization by XRD was carried out to analyze the crystal structure, crystallinity and composition of activated carbon, MOFs Cu(TAC) and KA-Cu(TAC). Based on the EXPO 2015 analysis table, it shows differences in crystal systems in Cu(TAC) and KA-Cu(TAC) samples. Cu(TAC) has two crystal systems, namely triclinic and monoclinic which indicates that Cu(TAC) is not homogeneous. Based on the above lattice parameters, the triclinic and monoclinic Cu(TAC) crystal systems are in accordance with the lattice parameters. KA-Cu(TAC) has only one crystal system, namely triclinic, which shows that KA-Cu(TAC) is homogeneous. The unit cell volume of KA-Cu(TAC) also appears to be lower than that of Cu(TAC), this causes the intensity of KA-Cu(TAC) to also be lower.[17] The triclinic lattice parameters show that KA-Cu(TAC) meets the lattice parameters as a triclinic crystal system.

Table 1. Crystal Structure Analysis by EXPO 2015

Biosorbent	a(Å)	b(Å)	c(Å)	α (º)	β(º)	ϒ(º)	Cell Volume (Å³)	Crystal System
Cu(TAC)	6.98	10.15	5.77	92.73	101.56	96.94	396.71	Triclinic
	11.47	19.55	8.16	90.00	100.78	90.00	1797.86	Monoclinic
KA-Cu(TAC)	7.49	7.83	5.73	104.62	98.74	95.84	318.15	Triclinic

3.2. Adsorption Isotherm Properties

The adsorption isotherm is the equilibrium bond that occurs between the concentration of the adsorbate in the solid phase and the concentration in the liquid phase.[18] The Langmuir and Freundlich model was used to describe the adsorption isotherm characteristics of Zn(II) on activated carbon and KA-Cu(TAC). The Langmuir isotherm describes the adsorption of a monolayer of adsorbate onto an adsorbent surface that has a limited number of adsorption sites, while the Freundlich isotherm describes that adsorption occurs on a heterogeneous surface of the adsorbent.[19] Adsorption isotherms were calculated using concentration variation data, in this study the concentration variations were 60, 100, 140, 180, and 220 ppm. Then proven by a good linearization graph and has a coefficient of determination $R^2 \geq 0.9$ (close to 1).

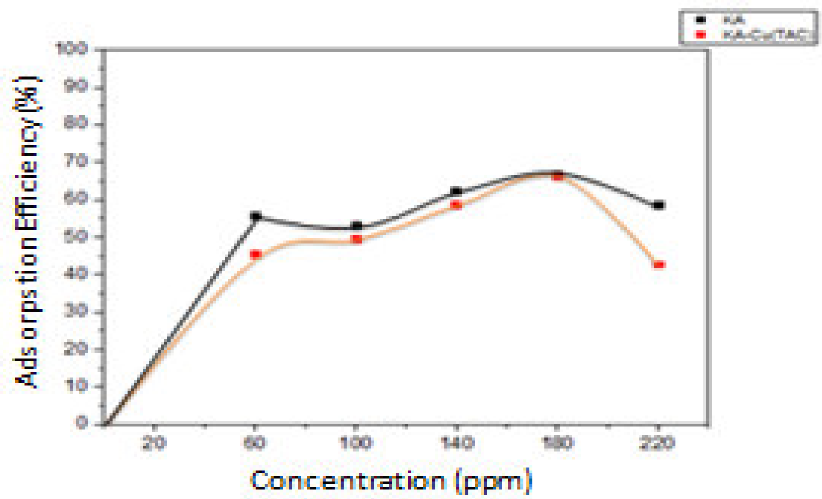

Figure 1. Absorption Efficiency of Variations in Concentration

The graph above shows the effect of varying Zn(II) concentrations on the adsorption efficiency of the adsorbent. The absorption efficiency of activated carbon and KA-Cu(TAC) increased with increasing concentration until the optimum concentration of both adsorbents was obtained at 180 ppm. The increase in adsorption efficiency is due to the increasing concentration of Zn(II) metal causing the amount of adsorbate to be adsorbed to increase so that the efficiency increases.

Based on the data above, it can be determined whether the adsorption isotherm is the Langmuir isotherm or the Freundlich isotherm.

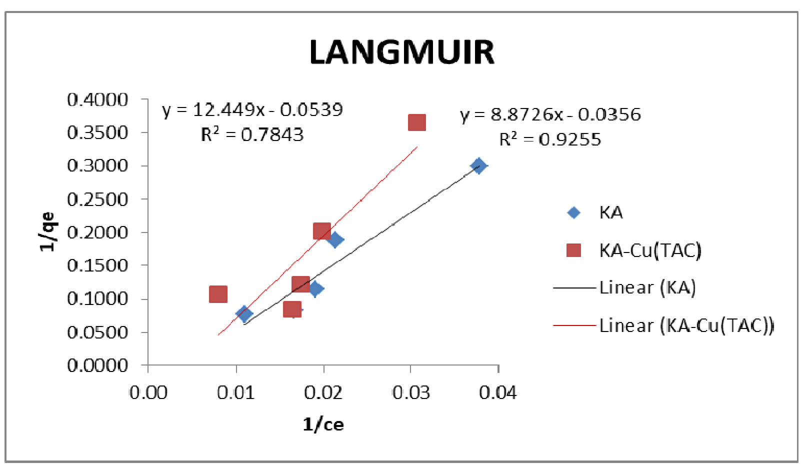

Figure 2. Langmuir Isotherm plot

e-ISSN : 2622-4968, p-ISSN : 2622-1349

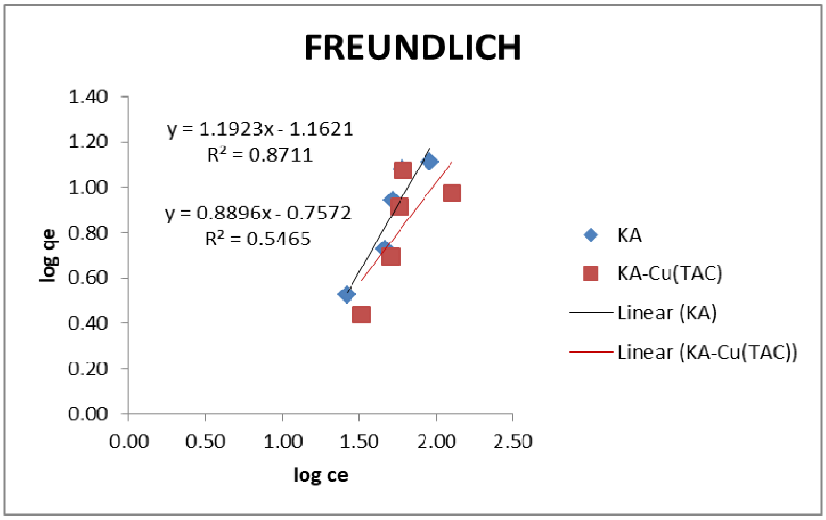

Figure 3. Freundlich Isotherm plot

From the linearization graph above, Langmuir and Freundlich parameters for activated carbon and KA-Cu(TAC) can be obtained which can be seen in the table below.

Table 2. Langmuir and Freundlich parameters for Zn(II) adsorption

Langmuir Isotherm		
Sample	**RL**	**R^2**
KA	1.14	0.9255
KA-Cu(TAC)	1.15	0.7843
Freundlich Isotherm		
Sample	**KF**	**R^2**
KA	0.06884937	0.8711
KA-Cu(TAC)	0.1749041	0.5465

By using the correlation coefficient (R^2), it can be seen from the data and linearization graph above that the Langmuir isotherm is the most suitable because the value of the linear regression coefficient on activated carbon ($R^2 > 0.9255$) and KA-Cu(TAC) ($R^2 > 0.7843$), the R^2 value of this Langmuir isotherm is higher than the R^2 value of the Freundlich isotherm where activated carbon ($R^2 > 0.8711$) and KA-Cu(TAC) ($R^2 > 0.5465$). Based on the Langmuir isotherm equation, it can be concluded that adsorption occurs by chemisorption or chemically. Chemisorption occurs when there is a chemical bond between the surface of the adsorbent and the adsorbate molecule.[20] It can also be concluded that monolayer adsorption of Zn(II) occurs on the activated carbon adsorbent and homogeneous KA-Cu(TAC) and the adsorbed molecules of the adsorbate show a single layer on the surface of the adsorbent.[6]

e-ISSN : 2622-4968, p-ISSN : 2622-1349

4. CONCLUSION

Characterization of carbon XRD shows that the active carbon structure of oil palm empty fruit bunches is an amorphous structure. Whereas MOFs Cu(TAC) shows a crystalline structure which is characterized by the appearance of several sharp peaks in the pattern. KA-Cu(TAC) also exhibits a crystalline structure.

The suitable adsorption isotherm is the Langmuir isotherm where the value of the linear regression coefficient on activated carbon (R^2 > 0.9255) and KA-Cu(TAC) (R^2 > 0.7843). Adsorption occurs by chemisorption or chemically. Chemisorption occurs when there is a chemical bond between the surface of the adsorbent and the adsorbate molecule. It can also be concluded that monolayer adsorption of Zn(II) occurs on the activated carbon adsorbent and homogeneous KA-Cu(TAC) and the adsorbed molecules of the adsorbate show a single layer on the surface of the adsorbent.

REFERENCES

1. Direktorat Jenderal Perkebunan. (**2021**). Statistik Perkebunan Unggulan Nasional. In Sekretariat Direktorat Jenderal Perkebunan.
2. Barakat, M. A. (**2011**). New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry*, *4*(4), 361–377.
3. Largitte, L., & Pasquier, R. (**2016**). A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon. *Chemical Engineering Research and Design*, *109*, 495–504.
4. Farma, R., & Wahyuni, F. (**2019**). Physical Properties Analysis of Activated Carbon from Oil Palm Empty Fruit Bunch Fiber on Methylene Blue Adsorption. *Journal of Technomaterial Physics *Corresponding Author at: Bina Widya Km*, *1*(1), 28293.
5. Karri, R. R., & Sahu, J. N. (**2018**). Process optimization and adsorption modeling using activated carbon derived from palm oil kernel shell for Zn (II) disposal from the aqueous environment using differential evolution embedded neural network. *Journal of Molecular Liquids*, *265*, 592–602.
6. Wang, Y., Pan, J., Li, Y., Zhang, P., Zhang, X., Li, M., Zheng, H., Sun, Y., Wang, H., & Du, Q. (**2021**). Preparation and Characterization of Activated Carbon from Oil-palm Fiber and Its Evaluation for Methylene Blue Adsorption. *Materiali in Tehnologije*, *55*(3), 449–457.
7. Maslahat, M., Hutagaol, R. P., Lestari, S., Sholeh Iskandar, J. K. H., & Sareal -Bogor, T. (n.d.). *POTENSI BIOSORBEN TANDAN KOSONG KELAPA SAWIT (TKKS) DALAM RECOVERY LIMBAH FENOL*.
8. Indah, D. R. (**2020**). Adsorpsi Logam Tembaga (Cu) Pada Karbon Baggase Teraktivasi Natrium Hidroksida (NaOH). *Jurnal Ilmiah IKIP Mataram*, *7*(1), 12–26.
9. Solis, K. L. B., Kwon, Y. H., Kim, M. H., An, H. R., Jeon, C., & Hong, Y. (**2020**). Metal organic framework UiO-66 and activated carbon composite sorbent for the concurrent adsorption of cationic and anionic metals. *Chemosphere*, *238*.
10. Muñoz-Senmache, J. C., Kim, S., Arrieta-Pérez, R. R., Park, C. M., Yoon, Y., & Hernández-Maldonado, A. J. (**2020**). Activated Carbon–Metal Organic Framework Composite for the Adsorption of Contaminants of Emerging Concern from Water. *ACS Applied Nano Materials*, *3*(3), 2928–2940.
11. Zhang, Y., Chen, Z., Liu, X., Dong, Z., Zhang, P., Wang, J., Deng, Q., Zeng, Z., Zhang, S., & Deng, S. (**2020**). Efficient SO2 Removal Using a Microporous Metal-Organic Framework with Molecular Sieving Effect. *Industrial and Engineering Chemistry Research*, *59*(2), 874–882.
12. Allwar, A. (**2018**). Preparation and characteristics of highly microporous activated carbon derived from empty fruit bunch of palm oil using KOH activation. *Rasayan Journal of Chemistry*, *11*(1), 280–286.
13. Zubir, M., Muchtar, Z., Syahputra, R. A., Sudarma, T. F., Nasution, H. I., Lubis, R. A. F., Fadillah, L., & Sandi, K. (**2021**). Characterization of Modified Fe-Cu Nanoparticle Activated Carbon Derived of Oil Palm Empty Bunches. *Journal of Physics*, 1–6.

e-ISSN : 2622-4968, p-ISSN : 2622-1349

14. Huo, S.-H.; Yan, X.-P. (**2012).** Metal-organic framework MIL-100(Fe) for the adsorption of malachite green from aqueous solution. J. Mater. Chem., 22 (15), 7449−7455.
15. Wang, Y., Pan, J., Li, Y., Zhang, P., Zhang, X., Li, M., Zheng, H., Sun, Y., Wang, H., & Du, Q. (**2021**). Preparation and Characterization of Activated Carbon from Oil-palm Fiber and Its Evaluation for Methylene Blue Adsorption. *Materiali in Tehnologije*, *55*(3), 449–457.
16. Kenneth, A., Casimir, G., Agbaji, B. E., & Steven, A. (**2015)**. Structural and Microstructural Properties of Neem Husk and Seed Carbon Activated with Zinc Chloride and Phosphoric Acid. *Journal of Chemical and Pharmaceutical Research*, *7*(3), 2470–2479.
17. Callister, Jr And WD. Rethwisch, D.G. (**2009**). Material Science And Enginering An Introduction. Jhon Wiley & Sons.
18. Febriani, A., Septika, A., Euis, N., & Mochammad, L. (**2022**). Kapasitas Adsorpsi Zat Warna *Malachite Green* Dan *Violet Dye* Menggunakan *Metal Organic Frameworks (FE-BDC). Hydrogen: Jurnal Kependidikan Kimia,* 10(2), 61-72.
19. Ayub, A., Raza, Z. A., Majeed, M. I., Tariq, M. R., & Irfan, A. (**2020**). Development of sustainable magnetic chitosan biosorbent beads for kinetic remediation of arsenic contaminated water. *International Journal of Biological Macromolecules*, *163*, 603–617.
20. Largitte, L., & Pasquier, R. (**2016**). A review of the kinetics adsorption models and their application to the adsorption of lead by an activated carbon. *Chemical Engineering Research and Design*, *109*, 495–504.

e-ISSN : 2622-4968, p-ISSN : 2622-1349