International Journal of Biomass & Renewables, 11(1) : 10 - 18, 2022

COMPARATIVE ANALYSIS OF THE FEASIBILITY OF OIL PALM BIOMASS AND FACTORY TEA WASTE AS BIOSORBENT FOR COPPER IONS REMOVAL FROM WASTEWATER

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Received: 23 March 2022, Accepted: 21 April 2022, Published: 11 May 2022, Publisher: UTP Press, Creative Commons: CC BY 4.0

ABSTRACT

Numerous research have been conducted to produce low-cost biosorbents. Because of this, this study aims to analyse the feasibility of Oil Palm Biomass (OPB) and Factory Tea Waste (FTW) as the biosorbent for fixed-bed adsorption column system in removing copper ions from wastewater under two parameters: initial concentration and pH value. Both biosorbents were compared in their surface area, pore volume, width and diameter. They were then analysed regarding their isotherm behaviour. FTW is found to have a larger surface area, pore volume and pore width, while OPB has a larger pore diameter than FTW. Besides, OPB showed higher efficiency of copper ions removal at low initial concentrations (25 and 50 mg/L), but FTW was more effective for high initial concentrations (100, 150 and 200 mg/L). FTW was more favourable than OPB in acidic and alkaline conditions, but the copper ions removal efficiency was over 99% for both biosorbents when operating at pH 7 of solution. Furthermore, it was proven that both biosorbents showed a better fit to Langmuir Isotherm as the R^2 for both showed the highest value. In conclusion, this study suggested that FTW provided better performance in copper ions removal than OPB.

Keywords: *copper ions removal; oil palm biomass; factory tea waste; fixed bed adsorption column*

1 INTRODUCTION

Earth is covered with 71% of water. However, 97% of the total water found in the oceans is saltwater and is unsuitable for human and industrial uses except for cooling [1]. The remaining 3% is freshwater, but 2.5% is unavailable for several reasons (high in pollution, too far from the earth's surface and locked up as glaciers, polar ice caps and atmosphere) [1]. Hence only 0.5% of the freshwater is available [1]. This happened because most industries are discharging wastewater into rivers, lakes, and the sea without proper treatment, which is harmful to the environment. It has been identified that wastewater contains toxic heavy metals such as lead (Pb), zinc (Zn), mercury (Hg), cadmium (Cd), copper (Cu), chromium (Cr) and arsenic (As), which likely to harm human health and aquatic lives [2]-[3]. These include nervous damage function, interrupting blood composition, kidneys, lungs and other significant organs. Hence, it is a must to remove those contaminants from wastewater.

Removing copper ions from wastewater is essential. It is a carcinogenic compound high in toxicity and may also cause headaches, nausea, respiratory issues, abdominal pain, liver and kidney failure when exposed to substantial amounts [4]-[6]. According to Malaysian Environmental Quality (Industrial Effluent) Regulations 2009, the permissible discharge downstream for copper ions must be lower than 1.0 mg/L [7]. It was found that many industrial activities contributed to copper ions sources, such as electroplating, electrolysis, electric appliances and electrical components [5],[8]-[9].

Various conventional methods have been used in the industry, including physical, chemical and biological processes such as reverse osmosis, advanced oxidation, ion exchange, solvent extraction and membrane filtration processes for heavy metals ion removal [10]-[11]. However, these conventional methods have been identified to have some limitations due to excessive energy demand, bulk toxicity, sludge production in flocculation/coagulation methods and fouling through the filtration process caused by short half-life in ozonation [12]. The biosorption method has been introduced as an attractive alternative for the decontamination of water as it is recognised as an effective, economic and eco-friendly process [11],[13]. Biosorption is a process that provides the ability for the biological materials (known as biosorbent) used to accumulate heavy metals through physicochemical from the wastewater and remove them. The most common biosorbent used is activated carbon derived from biomass, but using activated carbon as biosorbent in wastewater treatment [14]-[15]. Numerous researches have

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been conducted to develop low-cost biosorbents for heavy metal removal [11],[14]-[15]. For instance, a coal combustion ash (CCA) has been introduced as an alternative low-cost sorbent to replace commercial activated carbons (GAC) for cadmium and zinc removal from polluted water [14].

Among many alternatives to low-cost biosorbents, Oil Palm Biomass (OPB) has proven to be effective in removing heavy metals from wastewater [16]. The biggest advantage of OPB is that there is abundant OPB available as the palm oil industry has rapidly expanded in recent years [16]. Given this, this study has been carried out to compare the feasibility of Oil Palm Biomass OPB and Factory Tea Waste (FTW) as the biosorbents for fixed-bed adsorption column system in removing copper ions from wastewater. This study aims to compare the performance between OPB and FTW as biosorbent for copper ions removal with two different parameters: initial concentration (25, 50, 100, 150 and 200 mg/L) and pH value (3, 5, 7, 9 and 11). The isotherm behaviour of both biosorbents was also analysed to evaluate whether they fit Langmuir or Freundlich adsorption isotherm. In addition, Barrett, Jayher & Halenda (BJH) and Brunauer-Emmett-Teller (BET) were then used to compare both biosorbents in terms of their surface area, pore depth, pore width and pore diameter.

2 MATERIAL AND METHOD

2.1 Preparation of Adsorbent

2.1.1 Oil palm biomass (OPB)

OPB was prepared from an oil palm trunk, and the new trunks were collected locally from Kilang Sawit Felcra Nasarudin, Perak, Malaysia. The new trunks were washed thoroughly with distilled water and deionised water thrice. Then, the trunks were dried in an oven at 60°C for 5 to 7 days. After that, the dried trunks were sieved to achieve a standard form of 1.0 mm particle size, in accordance to the American Society Testing and Materials (ASTM) method.

2.1.2 Factory Tea Waste (FTW)

FTW was prepared from rejected tea leaves grown in BOH Tea Plantation in Cameron Highlands, Malaysia. They were rejected due to the factory's specification and kept in the freezer before further use. The leaves were washed thoroughly with distilled water and hot water (80°C) thrice. Then, the leaves were dried in an oven at 80°C for 6 hours. After that, the leaves were sieved to achieve a standard form of 1.0 mm particle size, in accordance with the ASTM method.

2.2 Preparation of Stock Solutions

The stock solutions were prepared by mixing 1000 mg of the copper (II) sulphate powder with 1000 ml of deionised water in a volumetric flask. The first manipulated variable is the initial ion concentration. The stock solution was divided into different concentrations (25, 50, 100, 150 and 200 mg/L) by using a measuring cylinder. The measured solutions were then transferred into another volumetric flask and then again mixed with 1000 ml of deionised water. On the other hand, another manipulated variable is the pH value. The stock solutions were prepared with 100 mg/L of copper solution. The stock solution was diluted with hydrochloric acid (0.1N) or sodium hydroxide (99%) by using a pH meter as an indicator in order to prepare the solution with different pH values (3, 5, 7, 9 and 11).

2.3 Adsorption Studies

The experiment consisted of a fixed-bed adsorption column (3 cm × 10 cm) filled with 4 cm of glass wool (2 cm on top, another 2 cm at the bottom), 4 cm of glass beads (2 cm on top, another 2 cm at the bottom) and 2 cm of biosorbent (OPB or FTW), as shown in Figure 1. The function of glass wool was to serve as a filter aid, while glass beads provided proper distribution of the inlet stream entering the column. Before starting the experiment, distilled water was fed to the column as a step to ensure that all

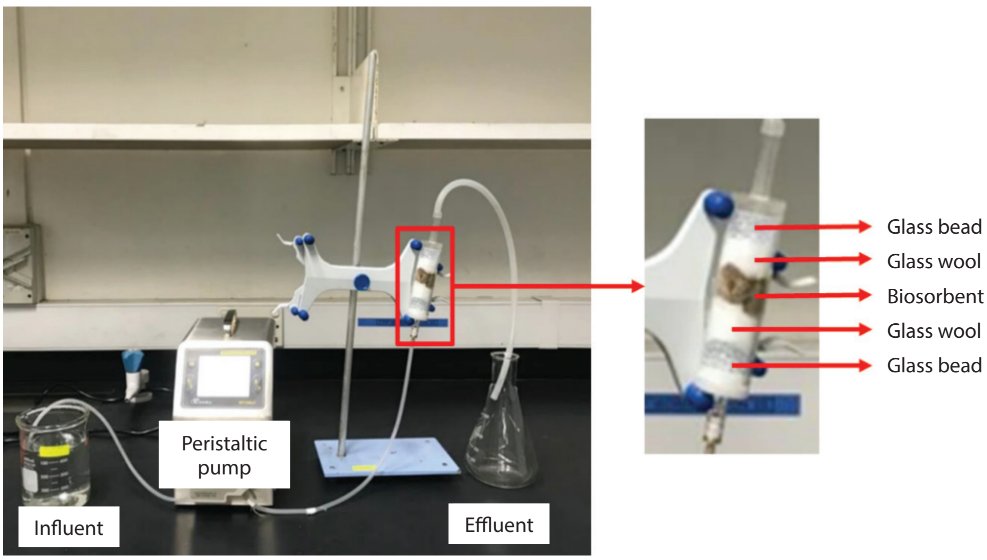


Figure 1 Fixed-bed adsorption column for biosorption process

adsorbent impurities were removed. During the investigation, the influent (copper solution) entered the column via the bottom part of the column using a peristaltic pump at a constant flow rate of 20 ml/min. In contrast, the effluent (treated solution) was obtained and collected in a conical flask. Each experiment was run for 20 minutes. The adsorption process was conducted at different initial copper ions concentrations (25, 50, 100, 150 and 200 mg/L) and pH values (3, 5, 7, 9 and 11).

2.4 Removal Efficiency

The final concentration of each sample (effluent) obtained was measured by using Atomic absorption spectrometry (AAS). The removal efficiency of biosorbent was calculated using the equation shown in Equation 1.

$$\% \, Removal\text{:} \; \frac{(C_o - C_e)}{C_o} \times 100\% \qquad (1)$$

where % Removal is the percentage of removal efficiency of biosorbent, C_o is the initial concentration of copper ions (mg/L), and C_e is the final concentration of copper ions (mg/L).

2.5 Biosorbent Characterisation

The effluents obtained were analysed using Barrett, Jayher & Halenda (BJH) and Brunauer-Emmett-Teller (BET) to examine the surface area, pore- volume, and pore width pore diameter of both biosorbents.

3 RESULTS AND DISCUSSIONS

3.1 Biosorbent Characterisation

The properties of biosorbent from OPB are evaluated by Barrett, Jayher & Halenda (BJH), while Brunauer-Emmett-Teller (BET) was used for biosorbent from FTW. The biosorbents were assessed in surface area, pore-volume, pore width and pore diameter. The results of both biosorbents were summarised in Table 1. FTW showed a larger surface area than OPB, which are 1.2451 and 0.043 m^2/g, respectively. In terms of pore width, FTW also showed a larger width compared to OPB. The pore width for FTW is 2.546985 nm. Meanwhile, the pore width for OPB is 1.700 nm.

In terms of pore diameter and volume, OPB has a larger diameter (129.8511 nm) and volume (0.001385 m^3/g) than FTW (4.85205 nm, 0.000565 m^3/g). According to the International Union of Pure and Applied Chemistry (IUPAC), FTW has mesopore size since the pore diameter is between 2 nm to 50 nm. OPB has macropores size since the pore diameter is more significant than 50 nm. Based on the findings, it is expected that FTW has a better adsorption rate as it has a larger surface area and pore width even with a smaller pore diameter and volume than OPB. For a clear comparison, it is essential to note that pore width and pore diameter are very different by definition. Pore width and pore diameter were measured on two opposite walls (surface) of biosorbent pores, but the difference was pore width measured in the slit-shaped pores. In contrast, the pore diameter is measured by the cylindrical pores [17].

Particle size is a dominant factor, especially for adsorption [18]-[19]. This is because the adsorption rate constant would increased as the particle size decreases which causes the adsorption activation energy to be reduced [20]. JoséJ. Pis et al. [21] stated that the adsorption rate of activated carbon depends on the adsorbent properties such as shape, internal surface area and pore size distribution. Other researchers have proven that the particle size is inversely proportional to the adsorption rate using activated carbon [22] and zeolites [18]-[19] as adsorbents. Besides, Erto et al. [14] claimed that a coal combustion ash (CCA) provided higher adsorption efficiency than Commercial Activated Carbons (GAC) for cadmium and zinc removal from polluted water. Another study compared the performances of wood-based adsorbent, and they found out that smaller particle size (semi-hardwood) has higher efficiency compared to larger particle size (hardwood) [23]. Also, numerous studies mentioned that it is a must to measure the adsorbent properties such as surface area, pore-volume, pore width and pore diameter to assess the adsorption capacity and efficiency of the materials used to remove heavy metals (zinc, copper, cadmium) [24]-[28].

Table 1 Properties of OPB and FTW

Biosorbent Properties	Oil palm biomass, OPB (BJH)	Factory tea waste, FTW (BET)
Surface area (m^2/g)	0.043	1.2451
Pore volume (m^2/g)	0.001385	0.000565
Pore width (nm)	1.700	2.546985
Pore diameter (nm)	129.8511	4.85205

3.2 Effect of initial concentration towards copper ions removal efficiency by using oil palm biomass (OPB) and factory tea waste (FTW)

The removal efficiency of biosorbents is strongly affected by the initial copper ions concentration [29]-[30]. The effect of initial concentration on the removal efficiency of both biosorbents was observed at the initial concentration of 25, 50, 100, 150, and 200 mg/L. The result of both biosorbents is illustrated in Figure 2. The removal efficiency of both biosorbents indicates contrary outcomes. The relationship between removal efficiency and initial copper ions concentration shown inversely proportional for OPB while it is linearly proportional to FTW.

In this study, the highest copper ions removal efficiency when OPB was used as biosorbent was 96.70% which was at the lowest initial ion concentration (25 mg/L). The removal efficiency of OPB at an initial ion concentration of 200 mg/L was found to be the second highest (87.2%) in terms of OPB. However, the highest copper ions removal efficiency when FTW was used as biosorbent was 94.62% which was at the highest initial ion concentration (200 mg/L). Similar findings were reported in another study usinghenna leaves biosorbent for copper ions removal via

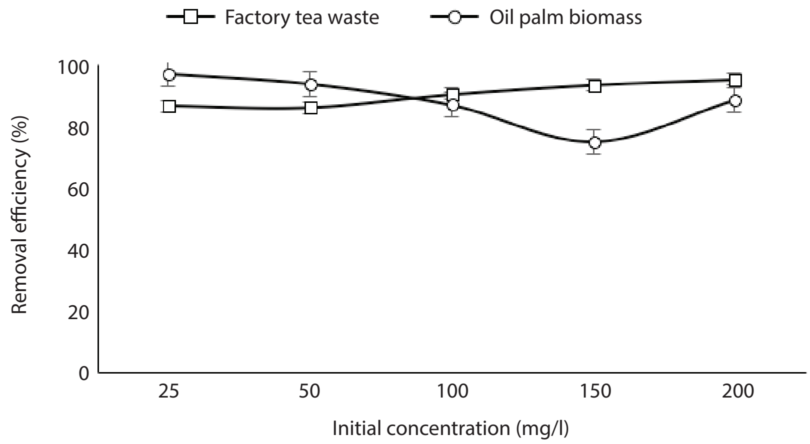


Figure 2 Effect of initial concentration towards removal efficiency by OPB and FTW as biosorbent

conventional filtration method [31]. It was found that the copper ions removal efficiency observed in that study was 93%, 95% and 97% at 70, 90 and 100 mg/L, respectively. Hence, the findings in our study were acceptable since it was in a similar range to the reported literature. Al Moharbi et al. [32] reported that the highest copper ions removal efficiency was achieved by using *Azadirachta indica (A. indica)* powder (produced from neem leaves) biosorbent via centrifugation method was up to 73% at an initial ion concentration of 120 mg/L. They claimed that no further copper ions removal happened at initial ion concentration >120 mg/L due to the blockage of adsorbent surface area.

More vital driving forces established the increase of copper ions removal capacity with the increase of initial copper ions concentration for mass transfer [33], resulting in faster kinetics. Hence, OPB is more suitable for using as biosorbent when applying low initial ion concentrations (25 and 50 mg/L). Still, FTW is more effective for applying high initial ion concentrations (100, 150 and 200 mg/L). As the surface area of FTW is higher than OPB, the ability of FTW to remove a high amount of copper ions from wastewater is higher than OPB. This is due to the driving forces of the copper ions transfer from the bulk solution to the active sites of the biosorbent increasing as the initial concentration increase. Hence, this vigorous competition between copper ions would decrease copper ions' adsorption, especially for biosorbent with low surface area. As conclusion,there are a limited number of active sites for the copper ions adsorption [34]. Besides, this phenomenon would also lead to active sites for the biosorbent becoming saturated, which affected the capacities of the biosorbent to adsorb copper ions [35].

3.3 Effect of pH on copper ions removal efficiency by using oil palm biomass (OPB) and factory tea waste (FTW)

Another important factor that affected the removal efficiency of biosorbent is the pH value. Many studies claimed that the pH value of copper ions solution would affected the biosorbent surface charge, solubility of copper ions, and the degree of ionisation of biosorbent species [36]-[37]. The effect of pH on thecopper ions removal efficiency of both biosorbents was evaluated at pH values of 3, 5, 7, 9, and 11. The result of both biosorbents is shown in Figure 3. The trend for both biosorbents was observed to be similar. As the pH increased from 3 to 5, the copper ions removal

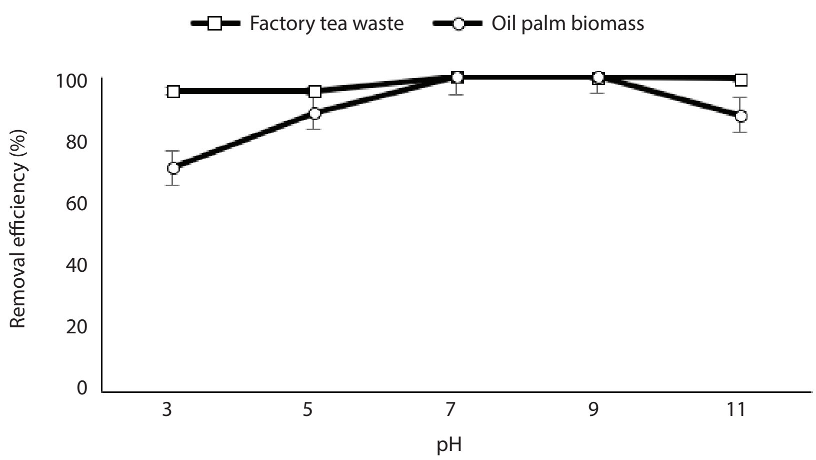


Figure 3 Effect of pH towards removal efficiency by OPB and FTW as biosorbent

efficiency for FTW biosorbent showed only a slight decrement from 95.19% to 95.09% but for OPB biosorbent showed an abrupt increment from 71% to 88.67%, respectively. However, both biosorbents showed an increment in removal efficiency as the pH increased to 7. They reached their maximum removal efficiency at pH 7 with 99.86% and 99.69% efficiency.

Other studies found that copper ions removal via henna leaves biosorbent was 80% [31] copper ions removal using (A. indica) powder (produced from neem leaves) biosorbent was 58.8% [32]. According to Chang et al. [38], there is limited active sites for copper ions adsorption under low pH (<7) solution due to high competition between the copper ions and hydronium ions. Also, Xu et al. [39] also stated that electrostatic interaction played a significant role in the adsorption process. The electrostatic interaction between the biosorbent active sites and copper ions are restricted under low pH (<7) solution hence, reduce the adsorption capacity as well as the copper ions removal efficiency [38].

A high concentration of hydrogen ions is found at a low pH level due to its acidic state; hence the copper ions need to compete with hydrogen ions to bind with the active sites of the biosorbent. Therefore, it would result in low removal efficiency. Moreover, the surface of biosorbents bounded by hydronium ions (H+) prevents the copper ions from approaching the binding sites of the biosorbents, which leads to minimum adsorption at low pH. On the other hand, the solution's alkaline state (high pH) contains a low concentration of hydrogen ions, hence lesser competition between copper ions and hydrogen ions, increasing the copper ions removal efficiency. As the biosorbent surfaces become less positively charged, more excellent copper ions removal is achieved. Biosorbent surfaces with high negative charges attract copper cations in the solutions through electrostatic action [38]. Precipitation of copper ions to form $Cu(OH)_2$ at the biosorbent surfaces starts at a pH of 7 [40], leading to the high removal of copper ions from wastewater at a high pH value. Based on the observation of both biosorbents under various pH values, it is found that FTW is more favourable than OPB under both acidic and alkaline states as it gives higher copper ions removal efficiency than OPB. The result suggested that the FTW biosorbent has a high adsorption capability and affinity toward copper ions. Thus, it can be deduced that FTW biosorbent is more effective for copper ions removal in wastewater.

3.4 Adsorption Isotherm

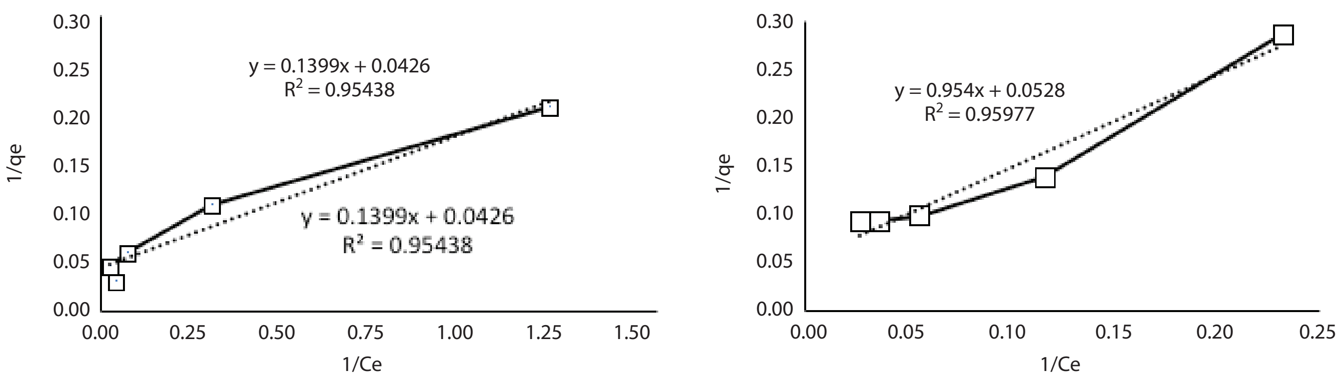
3.4.1 Langmuir Adsorption

The Langmuir Isotherm model assumes that the heavy metal ions removal occurs on a homogenous adsorption surface monolayer without interaction between adsorbed ions. According to Fogler [41], the Langmuir Isotherm is based on four main hypotheses, which are 1) adsorption sites are equal, and the surface is uniform, 2) adsorbed molecules on the adsorbent do not interact with each other, 3) adsorption processes happen in the exact mechanism and 4) all molecules are adsorbed onto the surface of adsorbent only (adsorbate molecules do not deposit or react with other molecules that the adsorbent has adsorbed during maximum adsorption). The Langmuir Isotherm can be expressed as in Equation 2.

$$\frac{1}{qe} = \frac{1}{K_L q_{max}} \frac{1}{C_e} + \frac{1}{q_{max}} \tag{2}$$

Where q_e is the adsorption capacity of biosorbent (mg/g), K_L is the adsorption energy (L/mg), q_{max} is the maximum adsorption capacity of biosorbent (mg/g), and C_e is the final concentration of heavy metal ions (mg/L).

The graphs of 1/qe against 1/Ce for both biosorbents are plotted and shown in Figure 4. The gradient from each graph was used to determine the adsorption energy (KL) of each biosorbent. High adsorption energy indicated that biosorbent has a high affinity towards the heavy metals ion [42]. Affinity can be related to biosorption capacity in which high affinity specifies that the biosorption occurred in high capacity [13].This study shows FTW has higher adsorption energy towards copper ions than OPB due to the gradient of the FTW graph being more elevated than OPB, which are 0.954 and 0.1399.



(A) (B)

Figure 4 Langmuir Isotherm plot for adsorption of copper ions by OPB (A) and FTW (B)

On the other hand, the slope value intercept from both graphs is to identify the maximum adsorption capacity (q_{max}) of each biosorbent. From the result obtained, FTW has a higher maximum adsorption capacity compared to OPB, with values of 0.0528 and 0.0426\. Hence, under the Langmuir Iisotherm condition; that FTW is more effective for copper ions removal than OPB as it has high adsorption energy and capacity. Meanwhile, the R^2 value was used to measure the suitability of each biosorbent with Langmuir Isotherm, which was compared with Freundlich Isotherm in the following subsection (3.4.2 Freundlich Isotherm).

3.4.2 Freundlich Adsorption

The isotherm for Freundlich is reported to have similar behaviour to Langmuir Isotherm. However, it assumes that different adsorbate types have a distinct affinity with each site [43]. It is also considered more realistic than Langmuir Isotherm due to the assumption of independence and equivalence of adsorption sites, hence ignoring the possibility of an initial layer that acts as a substrate for the adsorption. The Freundlich Isotherm can be expressed as shown in Equation 3.

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \tag{3}$$

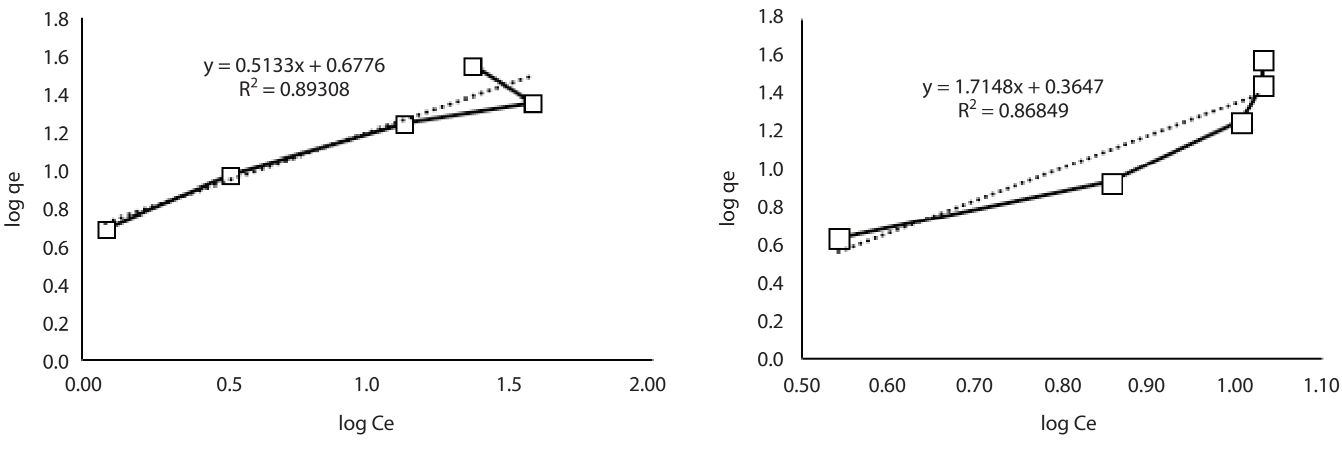
where q_e is the adsorption capacity of biosorbent (mg/g), K_F is the adsorption energy (L/mg), n is the adsorption intensity, and C_e is the final concentration of heavy metal ions (mg/L).

The graphs of log q_e against C_e for both biosorbents are plotted and shown in Figure 5. The gradient from both graphs was used to determine the adsorption intensity (n) of each biosorbent. In this study, it is found that OPB has higher adsorption intensity $\left(n = \frac{1}{gradient} = \frac{1}{0.471} = 2.398\right)$ compared to FTW $\left(n = \frac{1}{gradient} = \frac{1}{1.7148} = 2.398\right)$. On the other hand, the adsorption energy (K_F) was identified from the slope's intercept obtained from the graph. It is revealed that OPB has higher adsorption energy ($K_F = \log^{-1} 0.7328 = 5.405$) compared to FTW ($K_F = \log^{-1}(-0.3647) = 0.432$). Hence, it is concluded that under the Freundlich Isotherm condition, the OPB is more effective for copper ions removal compared to FTW as it has high adsorption intensity and energy.

Meanwhile, as mentioned in the previous subsection (3.4.1), the R^2 value was used to measure the suitability of each biosorbent with Freundlich Isotherm, which was compared with the previous Langmuir Isotherm. By comparing both biosorbents under both isotherms, it is proven that both biosorbents showed a better fit for the Langmuir Isotherm than the Freundlich Isotherm. Table 2 summarised the adsorption capacities of both biosorbents in both Langmuir and Freundlich Isotherm to deliver a better comparison. For OPB, the R^2 value for Langmuir and Freundlich Isotherm are 0.9544 and 0.9010, respectively. Meanwhile, for FTW, the R-squared value for Langmuir and Freundlich Isotherm are 0.9598 and 0.8685, respectively. This summarised that the R^2 for both biosorbents showed a higher value for Langmuir Isotherm than Freundlich Isotherm. Hence, both biosorbents have been recognised to have homogeneous binding sites equivalent to monolayer coverage [44]. The copper ions also will not interact with each other. Hence it will not affect the binding of those copper ions to the binding sites on the surface of both biosorbents. This result was found to be aligned with the study made by Darweesh et al.[45]. They mentioned that the adsorption of copper ions follows the Langmuir Isotherm and considers a physically equilibrated mechanism. Hence, it is proven that FTW is more effective for copper ions removal compared to OPB as it has high adsorption energy and capacity under the Langmuir Isotherm condition.

4 CONCLUSIONS

This study provided evidence of the potential benefits of using FTW and OPB to remove copper ions from wastewater. It was suggested that both investigated parameters, initial copper ions concentration and pH value, were observed to significantly



(A) (B)

Figure 5 Freundlich Isotherm plot for adsorption of copper ions by OPB (A) and FTW (B)

Table 2 Adsorption capacities for both biosorbents in Langmuir and Freundlich Isotherm

Type of biosorbent	Oil palm biomass (OPB)	Factory tea waste (FTW)
Langmuir Isotherm		
Adsorption energy (L/mg)	0.1399	0.9540
Maximum adsorption capacity (mg/g)	0.0426	0.0528
Suitability to Langmuir isotherm, R^2	0.9544	0.9598
Freundlich Isotherm		
Adsorption energy (L/mg)	5.4050	0.4320
Adsorption intensity (*dimensionless*)	2.3980	0.5830
Suitability to Freundlich isotherm, R^2	0.9010	0.8685

influence the efficiency of copper ions removal. The highest copper ions removal efficiency when OPB was used as the biosorbent is 96.70% which is at the lowest initial ion concentration (25 mg/L). The highest copper ions removal efficiency when FTW was used as biosorbent is 94.62% which at the highest initial ion concentration (200 mg/L). In terms of pH value, it was found out that FTW is more favourable than OPB under both acidic and alkaline state as it gives higher copper ions removal efficiency than OPB. The biosorption of copper ions on the FTW and OPB fitted the Langmuir Isotherm well. From this study, both FTW and OPB were found to be suitable biosorbents for copper ions removal, depending on the condition of the wastewater solution. However, FTW exhibited better overall performance. This work provided an insight into applying the FTW and OFB as biosorbents of heavy metals in water.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial assistance from PETRONAS via YUTP-FRG (Cost Centre: 015LC0-079) and facilities support from HICoE Centre for Biofuel and Biochemical Research (CBBR) and Chemical Engineering Department. Support from the Ministry of Education Malaysia through the HICoE award to CBBR is duly acknowledged.

REFERENCES

[1] "Water Facts - Worldwide Water Supply | ARWEC| CCAO | Area Offices | California-Great Basin | Bureau of Reclamation", *Bureau of Reclamation*, 2020. https://www.usbr.gov/mp/arwec/water-facts-ww-water-sup.html (accessed Jan. 21, 2021).

[2] M. S. Islam, M. K. Ahmed, M. Raknuzzaman, M. Habibullah -Al- Mamun, & M. K. Islam, "Heavy metal pollution in surface water and sediment: A preliminary assessment of an urban river in a developing country", *Ecological Indicators*, 48, pp. 282–291, 2015. Doi: 10.1016/j.ecolind.2014.08.016.

[3] S. Shanbehzadeh, M. Vahid Dastjerdi, A. Hassanzadeh, & T. Kiyanizadeh, "Heavy Metals in Water and Sediment: A Case Study of Tembi River", *Journal of Environmental and Public Health*, 2014, pp. 1–5, 2014. Doi:10.1155/2014/858720.

[4] X-J. Hu, Y. G. Liu, H. Wang, A-W. Chen, G-M. Zeng, S-M. Liu, Y-M. Guo, X. Hu, T-T. Li, L. Zhou & S-H. Liu, "Removal of Cu(II) ions from aqueous solution using sulfonated magnetic graphene oxide composite", *Separation and Purification Technology*, 108, pp. 189–195, 2013. Doi: 10.1016/j.seppur.2013.02.011.

[5] S. Lan, X. Wu, L. Li, M. Li, F. Guo, & S. Gan, "Synthesis and characterization of hyaluronic acid-supported magnetic microspheres for copper ions removal", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 425, pp. 42–50, 2013. Doi: 10.1016/j.colsurfa.2013.02.059.

[6] Y. Ren, M. Zhang, & D. Zhao, "Synthesis and properties of magnetic Cu(II) ion imprinted composite adsorbent for selective removal of copper", *Desalination*, 228, 1, pp. 135–149, 2008. Doi: 10.1016/j.desal.2007.08.013.

[7] "Indah Water Portal", 2019. https://www.iwk.com.my/do-you-know/effluent-standards (accessed Feb. 22, 2020).

[8] M. Bilal, J. A. Shah, T. Ashfaq, S. M. H. Gardazi, A. A. Tahir, A. Pervez, H. Haroon & Q.Mahmood, "Waste biomass adsorbents for copper removal from industrial wastewater—A review", *Journal of Hazardous Materials*, 263, pp. 322–333, 2013. Doi: 10.1016/j.jhazmat.2013.07.071.

[9] D. Yin, X. Du, H. Liu, Q. Zhang, & L. Ma, "Facile one-step fabrication of polymer microspheres with high magnetism and armored inorganic particles by Pickering emulsion polymerization", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 414, pp. 289–295, 2012. Doi: 10.1016/j.colsurfa.2012.08.038.

[10] F. Fu & Q. Wang, "Removal of heavy metal ions from wastewaters: A review," *Journal of Environmental Management*, 92, 3, pp. 407–418, 2011. Doi: 10.1016/j.jenvman.2010.11.011.

[11] A. Tripathi & M. Ranjan, "Heavy Metal Removal from Wastewater Using Low Cost Adsorbents", *Journal of Bioremediation & Biodegradation*, 06, 2015. Doi: 10.4172/2155-6199.1000315.

[12] Renu, M. Agarwal, & K. Singh, "Heavy metal removal from wastewater using various adsorbents: a review", *Journal of Water Reuse and Desalination*, 7, 4, pp. 387–419, 2016. Doi: 10.2166/wrd.2016.104.

[13] S. L. R. K. Kanamarlapudi, V. KumarChintalpudi, & S. Muddada, "Application of Biosorption for Removal of Heavy Metals from Wastewater", *Biosorption*, 2018. Doi: 10.5772/intechopen.77315.

[14] A. Erto, L. Giraldo, A. Lancia, & J. Moreno-Piraján, "A Comparison Between a Low-Cost Sorbent and an Activated Carbon for the Adsorption of Heavy Metals from Water," *Water, Air, & Soil Pollution*, 224, 2013. Doi: 10.1007/s11270-013-1531-3.

[15] J. Ndi Nsami & J. Ketcha Mbadcam, "The Adsorption Efficiency of Chemically Prepared Activated Carbon from Cola Nut Shells by on Methylene Blue", *Journal of Chemistry*, 2013. https://www.hindawi.com/journals/jchem/2013/469170/ (accessed Jan. 21, 2021).

[16] M. Vakili, M. Rafatullah, M. H. Ibrahim, A. Z. Abdullah, B. Salamatinia, & Z. Gholami, "Oil Palm Biomass as an Adsorbent for Heavy Metals", in *Reviews of Environmental Contamination and Toxicology*, 232, D. M. Whitacre, Ed. Cham: Springer International Publishing, pp. 61–88, 2014. Doi: 10.1007/978-3-319-06746-9_3.

[17] F. Rouquerol, J. Rouquerol, & K. S. W. Sing, "Adsorption by Powders and Porous Solids", *Elsevier*, 2014. Doi: 10.1016/C2010-0-66232-8.

[18] B. R. Müller & G. Calzaferri, "Sorption properties of Mo(CO)6 on thin Y-zeolite layers", *Microporous and Mesoporous Materials*, 21, 1, pp. 59–66, 1998. Doi: 10.1016/S1387-1811(97)00048-6.

[19] B. R. Müller G. Calzaferri, "Thin Mo(CO)6–Y-zeolite layers: preparation and in situ transmission FTIR spectroscopy", *Journalof the Chemical Society, Faraday Transactions*, 92, 9, pp. 1633–1637, 1996. Doi: 10.1039/FT9969201633.

[20] H. Wang & F. Shadman, "Effect of particle size on the adsorption and desorption properties of oxide nanoparticles", *AIChE J*, 59, 5, pp. 1502–1510, 2013. Doi: 10.1002/aic.13936.

[21] J. Pis, T. A. Centero, M. Mahamud, A. B. Fuertes, J. B. Parram, J. A. Pajares & R. C. Bansal, "Preparation of active carbons from coal Part I. Oxidation of coal," *Fuel Processing Technology*, 47, 2, pp. 119–138, 1996. Doi: 10.1016/0378-3820(96)01003-X.

[22] H. Marsh & F. Rodríguez-Reinoso, "Activated carbon", 1st ed. Amsterdam; Boston: *Elsevier*, 2006.

[23] I. Pn & U. Cp, "Overview on the Effect of Particle Size on the Performance of Wood Based Adsorbent", *Journal Chemical Engineering & Process Technology*, 07, 05, 2016. Doi: 10.4172/2157-7048.1000315.

[24] I. Ali, Mohd. Asim, & T. A. Khan, "Low-cost adsorbents for the removal of organic pollutants from wastewater", *Journal of Environmental Management*, 113, pp. 170–183, 2012. Doi: 10.1016/j.jenvman.2012.08.028.

[25] A. Alihosseini, V. Taghikhani, A. A. Safekordi, & D. Bastani, "Equilibrium sorption of crude oil by expanded perlite using different adsorption isotherms at 298.15 k", *International Journal of Environmental Science & Technology*, 7, 3, pp. 591–598, 2010. Doi: 10.1007/BF03326168.

[26] B. H. Hameed, L. H. Chin, & S. Rengaraj, "Adsorption of 4-chlorophenol onto activated carbon prepared from rattan sawdust", *Desalination*, 225, 1, pp. 185–198, 2008. Doi: 10.1016/j.desal.2007.04.095.

[27] A. S. Jadhav, M. Y. Naniwadekar, N. H. Shinde, & S. V. Anekar, "STUDY OF ADSORBTION OF OIL FROM OILY WATER USING HUMAN HAIR," pp. 15, 2011.

[28] S. M. Sidik, A. A. Jalil, S. Triwahyono, S. H. Adam, M. A. H. Satar, & B. H. Hameed, "Modified oil palm leaves adsorbent with enhanced hydrophobicity for crude oil removal", *Chemical Engineering Journal*, 203, pp. 9–18, 2012. Doi: 10.1016/j.cej.2012.06.132.

[29] T. A. H. Nguyen, H. H. Ngo, W. S. Guo, J. Zhang, S. Liang, Q. Y. Yue, Q. Li & T.V. Nguyen, "Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater", *Bioresource Technology*, 148, pp. 574–585, 2013. Doi: 10.1016/j.biortech.2013.08.124.

[30] S. Rangabhashiyam, N. Anu, M. S. Giri Nandagopal, & N. Selvaraju, "Relevance of isotherm models in biosorption of pollutants by agricultural byproducts", *Journal of Environmental Chemical Engineering*, 2, 1, pp. 398–414, 2014. Doi: 10.1016/j.jece.2014.01.014.

[31] T. Shanthi & V. M. Selvarajan, "Removal of Cr(VI) and Cu(II) Ions from Aqueous Solution by Carbon Prepared from Henna Leaves", *Journal of Chemistry*, 2013, pp. e304970, 2012. Doi: 10.1155/2013/304970.

[32] S. S. Al Moharbi, M. G. Devi, B. M. Sangeetha, & S. Jahan, "Studies on the removal of copper ions from industrial effluent by Azadirachta indica powder", *Applied Water Science*, 10, 1, pp. 23, 2020. Doi: 10.1007/s13201-019-1100-z.

[33] B. W. Atkinson, F. Bux, & H. C. Kasan, "Bioremediation of metal-contaminated industrial effluents using waste sludges", *Water Science and Technology*, 34, 9, pp. 9–15, 1996. Doi: 10.1016/S0273-1223(96)00781-0.

[34] A. A. Taha, M. A. Shreadah, A. M. Ahmed, & H. F. Heiba, "Multi-component adsorption of Pb(II), Cd(II), and Ni(II) onto Egyptian Na-activated bentonite; equilibrium, kinetics, thermodynamics, and application for seawater desalination",

Journal of Environmental Chemical Engineering, 4, 1, pp. 1166–1180, 2016. Doi: 10.1016/j.jece.2016.01.025.

[35] M. Shirvani, H. Rafiei, S. Bakhtiary, B. Azimzadeh, & S. Amani, “Equilibrium, kinetic and thermodynamic studies on nickel removal from aqueous solutions using Ca-bentonite,” *Desalination and water treatment*, 54, pp. 464–472, 2014. Doi: 10.1080/19443994.2014.887037.

[36] X. Jin *et al.*, “Preparation of novel nano-adsorbent based on organic–inorganic hybrid and their adsorption for heavy metals and organic pollutants presented in water environment”, *Journal of Hazardous Materials*, 186, 2, pp. 1672–1680, 2011. Doi: 10.1016/j.jhazmat.2010.12.057.

[37] X. Liu, H. Chen, C. Ji, M. Yu, & Y. Xuan, “Suspended Emulsion Copolymerisation of Acrylonitrile with Methyl Acrylate: Effects of Reaction Parameters on the Polymerisation”, *Journal of Macromolecular Science, Part A*, 46, 7, pp. 656–662, 2009. Doi: 10.1080/10601320902938814.

[38] Y. S. Chang, P. I. Au, N. M. Mubarak, M. Khalid, P.Jagadish, R. Walvekar & E.C. Abdullah, “Adsorption of Cu(II) and Ni(II) ions from wastewater onto bentonite and bentonite/GO composite”, *Environ Sci Pollut Res*, 27, 26, pp. 33270–33296, 2020. Doi: 10.1007/s11356-020-09423-7.

[39] W. Xu, Y. Chen, W. Zhang, & B. Li, “Fabrication of graphene oxide/bentonite composites with excellent adsorption performances for toluidine blue removal from aqueous solution”, *Advanced Powder Technology*, 30, 3, pp. 493–501, 2019. Doi: 10.1016/j.apt.2018.11.028.

[40] K. J. Powell, P.L. Brown, R. Byrne, T. Gadja, G. Hefter, A-K. Leuz, S. Sjoberg & H. Wanner, “Chemical speciation of environmentally significant metals with inorganic ligands Part 2: The Cu2+-OH-, Cl-, CO32-, SO42-, and PO43- systems (IUPAC Technical Report)”, *Pure and Applied Chemistry*, 79, 5, pp. 895–950, 2007. Doi: 10.1351/pac200779050895.

[41] H. S. Fogler, “Essentials of chemical reaction engineering”, *Upper Saddle River*, , 2011.

[42] C. Sing & J. Yu, “Copper adsorption and removal from water by living mycelium of white-rot fungus Phanerochaete chrysosporium”, *Water Research*, 32, 9, pp. 2746–2752, 1998.

[43] A. A. Mengistie, T. S. Rao, A. V. P. Rao, & M. Singanan, “Removal of lead (II) ions from aqueous solutions using activated carbon from Militia ferruginea plant leaves”, *Bulletin of the Chemical Society of Ethiopia*, 22, 3, 2008.

[44] P. Hadi, J. Barford, & G. McKay, “Synergistic effect in the simultaneous removal of binary cobalt–nickel heavy metals from effluents by a novel e-waste-derived material”, *Chemical engineering journal*, 228, pp. 140–146, 2013.

[45] M. A. Darweesh, M. Y. Elgendy, M. I. Ayad, A. M. Ahmed, N. M. K. Elsayed, & W. A. Hammad, “Adsorption isotherm, kinetic, and optimization studies for copper (II) removal from aqueous solutions by banana leaves and derived activated carbon”, *South African Journal of Chemical Engineering*, 40, pp. 10–20, 2022. Doi: 10.1016/j.sajce.2022.01.002.