

Factory Tea Waste Biosorbent for Cu(II) and Zn(II) Removal from Wastewater

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Abstract. Recent studies have shown great interest toward heavy metal removal due to its hazardous and non-biodegradable properties. Many approaches have been used for this purpose and one of them is adsorption. In this study, several experiments were carried out to investigate the feasibility of factory tea waste as a biosorbent in a fixed-bed adsorption column for heavy metal removal (zinc and copper) in wastewater. The results highlighted that zinc has better performance compared to copper in terms of the effect of initial ion concentration, pH value, and the mixed ions with respect to the removal efficiency. Zinc showed higher removal efficiency and adsorption capacity at the initial metal ion concentration of 200 mg/L, which are 99.21% and 39.68 mg/mg compared to copper. Meanwhile, for the effect of pH values and mixed ion concentration, zinc also showed slightly higher removal efficiency which are 99.91% and 98.47%, respectively compared to copper. However, both zinc and copper showed a better fit to the Langmuir isotherm. The factory tea waste was characterized using Micromeritics ASAP 2020 instrument and results showed that the factory tea waste biosorbent consists of mesopores with the diameter and width of 4.85205 and 2.546985 nm, respectively.

1 Introduction

Rapid urbanization and industrialization in Malaysia have increased the amount of solid waste being discharged to the environment throughout the decades [1–3]. These solid wastes are produced from various industries such as mining, chemical manufacturing, metal plating, and textile, which contain a huge amount of heavy metals. Most of the common heavy metal ions found in polluted water streams are copper (Cu), zinc (Zn), chromium (Cr), cadmium (Cd), iron (Fe), manganese (Mn), and lead (Pb), which are classified as hazardous pollutants [2–4]. Heavy metals are known as non-biodegradable compounds that cannot be degraded or destroyed naturally [5,6]. These heavy metals have caused contamination toward the environment. Heavy metals may result in the reduction or damage of mental and central nervous function, damage to lungs, kidneys, and other major organs, and lower the body energy levels. The

presence of heavy metals in marine water will be a threat to living things in the water [7]. Hence, many countries in the world have introduced regulations to restrict discharge of polluted wastewater. In Malaysia, wastewater containing heavy metals should undergo stringent wastewater treatment to meet the requirement in Standard A and B stated in the Environmental Quality Act 1974 before discharge to any water source.

Various wastewater treatment processes are designed for heavy metal removal, which include adsorption, precipitation, ultrafiltration, electro dialysis, liquid extraction, and oxidation [8]. These methods have proven their ability in removing heavy metals from wastewater; however, several factors need to be considered when choosing the appropriate method. Adsorption has been proven to have better performance compared to other methods as mentioned in several studies [9]. The most employed adsorbent for adsorption process is activated carbon due to its large surface area and also high

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adsorption capacity [10–12]. However, there are some limitations in using activated carbon as an adsorbent, such as expensive and complicated process [13,14]. These limitations have led to extensive research for a cheaper and more sustainable alternative process. One of the alternatives is using waste biomass as adsorbents, such as kenaf fiber, cotton wool, coconut coir fiber, *Luffa cylindrical* fiber, jute fiber, sugarcane bagasse, factory tea waste, and palm oil mill effluent [15–23]. There are various degrees of heavy metal adsorption due to different adsorbent properties and operating conditions [24]. Waste biomass has gained a lot of interest as the biomass is environmentally friendly and has high availability. Furthermore, the cost of using waste biomass for adsorption process is much lower compared to activated carbon.

In view of this, this study was carried out to understand the feasibility of using factory tea waste as a biosorbent to remove heavy metal ions from wastewater [25]. Copper and zinc are the targeted heavy metals to be removed from the wastewater using factory tea waste as the biosorbent. The permissible discharge for copper and zinc must be lower than 1.0 and 2.0 mg/L, respectively, according to the Malaysian Environmental Quality (Industrial Effluent) Regulations 2009 [26]. The experiment was carried out with a fixed-bed column to test the applicability of factory tea waste as the biosorbent. Throughout the test, granular activated carbon was set as the benchmark to compare the adsorption characteristics of factory tea waste. Besides, heavy metals in wastewater are normally mixed with various types of metal ions; hence, adsorption of zinc and copper from a mixed metal ion solution was also studied to further understand the potential of factory tea waste for the removal of zinc and copper [25].

2 Procedure

2.1 Preparation of Biosorbent

Rejected tea leaves grown in Cameron Highlands, Malaysia were collected from BOH Tea Plantation and kept in a freezer before further use. All the rejected tea leaves are collected after the production process. They are rejected mainly due to out of specification provided by the factory. The tea leaves were washed thoroughly using distilled water and hot water at 80 °C to remove soluble and colored components. The step was repeated for at least three times until a colorless solution of tea waste was virtually observed at room temperature. Then, the leaves were dried in a hot oven at 80 °C for 6 h. After that, the dried tea leaves were sieved and stored in sealed polythene bags at room temperature for experimental use. 2 g of rejected tea leaves were used for each test run.

2.2 Preparation of Synthetic Wastewater

2.2.1 Pure copper and zinc synthetic wastewater

Copper synthetic wastewater with the concentration of 25 mg of metal/L solutions of was prepared by dissolving 25 mg of copper (II) nitrate trihydrate pure salts in 1 L of deionized water using a magnetic stirrer at 600 rpm for 10 min. Then, the step was repeated by dissolving 50, 100, 150, and 200 mg of copper (II) nitrate trihydrate pure salts with deionized water. The procedure was repeated to prepare zinc solutions using zinc sulfate heptahydrate salts for similar concentrations.

2.2.2 Mixed copper and zinc synthetic wastewater

A mixed copper-zinc synthetic wastewater was prepared by dissolving 12.5 mg of copper (II) nitrate trihydrate pure salts and 12.5 mg of zinc sulfate heptahydrate salts in deionized water using a magnetic stirrer at 600 rpm for 10 min. Next, the procedure was repeated by dissolving 25, 50, 75, and 100 mg of each copper (II) nitrate trihydrate pure salts and zinc sulfate heptahydrate salts with deionized water for the preparation of mixed synthetic wastewater.

2.3 Adsorption Studies

A fixed-bed adsorption column (3 cm × 10 cm) was filled with glass beads, glass wool, and the factory tea waste, as shown in **Figure 1**. Glass wool was used to act as a filter aid and meanwhile the function of glass beads is to ensure proper distribution of inlet stream. 400 ml of copper synthetic wastewater containing 25 mg/L of metal ion solution was prepared and poured into a beaker. The metal ion solution was fed into the bottom of the adsorption column using a peristaltic pump at a constant flow rate of 20 ml/min in 20 min. The effluent (i.e., pure water) was collected in a conical flask during the adsorption process. After the process, the effluent in the conical flask was analyzed using atomic absorption spectrometry (AAS) to determine the remaining concentration of heavy metals in the pure water. The experiment was repeated with different metal ion concentrations of 50, 100, 150, and 200 mg/l. In addition, the experiment was also repeated for the adsorption of zinc.

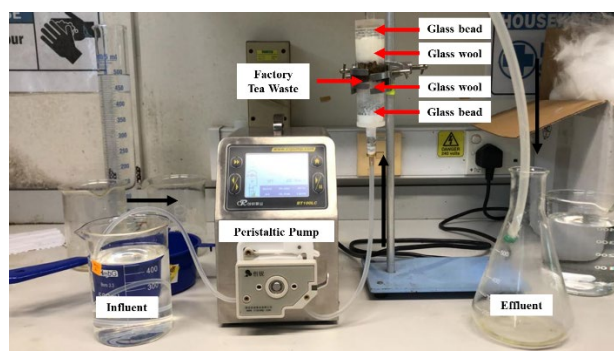


Fig. 1. Fixed-bed adsorption column for adsorption process.

The adsorption study was conducted at various pH values (3, 5, 7, 9, and 11). The concentration of metal ion

was fixed at 200 mg/l. 0.5 M of hydrochloric acid (HCl) and 0.5 M of sodium hydroxide (NaOH) were added to the metal ion solution to obtain the desired pH values. The pH was measured using a Mettler Toledo pH meter. Then, the effluent in the conical flask was analyzed using AAS to determine the optimum adsorption rate of heavy metals at different pH levels. Meanwhile, the effect of mixed metal ion concentration was also studied in which the copper and zinc ions were set at a ratio of 1:1.

2.3.4 Removal Efficiency

The total percentage of heavy metal removal can be calculated by the following equation:

$$\% \text{ Removal} = \frac{(C_o - C_e)}{C_o} \times 100\% \quad (1)$$

Where % Removal is the percentage of removal efficiency of metal ion, C_o is the initial concentration of metal ion (mg/L), and C_e is the final concentration of metal ion (mg/L).

2.4 Characterization Studies

The surface morphology of factory tea waste biosorbent was studied with a surface area analyzer and porosimetry system (Micromeritics ASAP 2020). The surface area, pore volume, width, and diameter were determined through nitrogen adsorption-desorption isotherms.

3 Results and Discussion

3.1 Batch Adsorption Studies

3.1.1 Effect of initial heavy metal ion concentration toward heavy metal ion removal efficiency

The initial heavy metal concentration highly influenced the adsorption of heavy metals by the factory tea waste biosorbent. According to Jnr and Spiff [27], heavy metal ions are adsorbed by specific active sites at low metal concentration solution; however, the binding sites of the biosorbent become saturated faster when the metal ion concentration increased and the mass of biosorbent remained constant. **Figure 2** compares the heavy metal removal efficiency of copper and zinc at different initial concentrations (i.e., 25, 50, 100, 150, and 200 mg/L) when flowing through the biosorbent at 20 ml/min for 20 min. The graph shows that when the initial concentration of heavy metal ions increases, the heavy metal removal efficiency increases gradually.

The heavy metal removal efficiency for zinc and copper increased from 94.30% to 99.21% and 86.04% to 94.62%, respectively, when the initial concentration increased from 25 to 200 mg/L. It is observed from **Figure**

2 that zinc has a higher removal efficiency compared to copper for all initial concentrations of heavy metals for adsorption by the factory tea waste biosorbent. Zinc has a larger atomic radius (i.e., 133.2 pm) compared to copper (i.e., 128 pm) [28]. By referring to the periodic table, the atomic size of an element decreases from left to right, which supported the statement that copper has a smaller atomic radius than zinc. Copper has more atoms in the element and the nucleus will attract atoms toward itself, which may reduce the size of copper. Zinc has larger adsorption rate due to it has larger atomic weight compared to copper. Also, the hydration energy for zinc is lower than copper hence it has higher adsorption rate. The hydration ionic radius for zinc is smaller than copper hence it is easier to be adsorbed. And, the amount energy released by zinc is smaller hence it easier to bind up with the adsorbate.

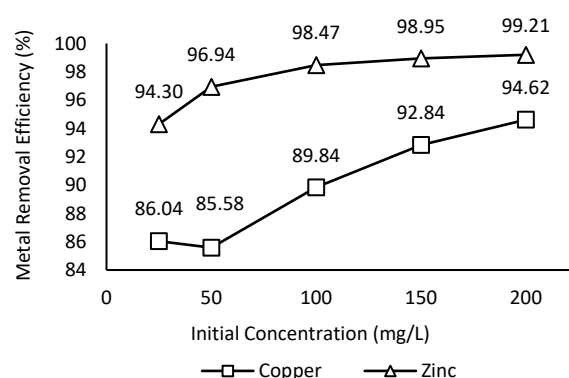


Fig. 2. Effect of initial heavy metal concentration on the percentage of heavy metal removed by factory tea waste biosorbent

3.1.2 Effect of pH toward heavy metal ion removal efficiency

The pH of a heavy metal ion solution is an important parameter for metal adsorption by factory tea waste biosorbent as the parameter affects the solubility of the metal ions, concentration of the ions, surface charge of the biosorbent, and also the degree of ionization and species of the adsorbate. In a low-pH solution, heavy metal ions compete with H^+ ions to bind onto active sites, resulting in lower adsorption. Meanwhile, when the pH increases, the concentration of H^+ ions decrease gradually and the negative charge on the biosorbent increases, leading to higher attraction of cations. This will enhance the adsorption rate of the metal ions by factory tea waste biosorbent to obtain an optimum value.

In order to study the effect of pH level on the metal ion removal, the pH was varied (i.e., pH 3, 5, 7, 9, and 11) for both copper and zinc. According to **Figure 3**, the adsorption of heavy metal ions highly depends on the pH of the metal solution. When the pH increases, the heavy metal ion removal efficiency decreases gradually. The lower the pH of the metal solution, the lower the removal efficiency of heavy metal ions [29]. The results from the experiment showed that pH 7 has the optimal heavy metal

ion removal efficiency for both copper and zinc. The removal efficiency values for both copper and zinc are shown in **Figure 3**. The heavy metal removal efficiency rose gradually from pH 3 to 7 due to the interruption of the charge at the binding sites of factory tea waste biosorbent that was affected by the pH of the solution. Hence, the adsorption of heavy metals onto the biosorbent decreased due to the electrostatic repulsive force between positive charges.

On the other hand, the heavy metal removal efficiency for copper and zinc decreased as the value of pH exceeded 8. As the alkalinity of the metal solution increases, the copper and zinc removal efficiency tend to be decreased. This is because at high pH, heavy metal ions might precipitate to form metal hydroxides, which could reduce the adsorption of heavy metals. This occurrence is due to the production of OH⁻ ions that would adsorb active H⁺ ions [30]. This experiment indicates that pH 7–8 is the optimum pH for the adsorption of heavy metals by the factory tea waste biosorbent for both copper and zinc. The heavy metal removal efficiency of zinc (i.e., 99.91%) is slightly higher than copper (i.e., 99.69%). Hence, the result shows that zinc has better adsorption compared to copper at optimum pH condition.

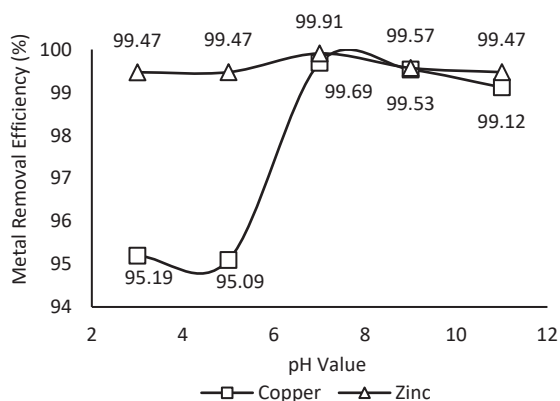


Fig. 3. Effect of pH toward heavy metal removal efficiency by factory tea waste biosorbent

3.1.3 Effect of mixed copper and zinc ions at various initial concentrations toward heavy metal ion removal

Figure 4 shows that the factory tea waste biosorbent exhibited higher selectivity toward zinc for the adsorption of heavy metals from the mixed copper-zinc solution. This study was conducted with different initial concentrations of mixed copper-zinc solutions at equal molar fraction (i.e., 12.5, 25, 50, 75 and 100 mg/L). Based on the results, the reduction of copper adsorption in the presence of zinc was in the range of 85.76%–89.90%. On the other hand, the reduction of zinc adsorption in the presence of copper was in the range of 91.16%–98.47%. The percentage removal of heavy metal ions by the factory tea waste biosorbent for both copper and zinc increased as the initial heavy metal ion concentration

increased. However, zinc has a higher removal efficiency compared to copper. This study indicates that different adsorption mechanisms may be involved in the adsorption of both copper and zinc ions [25]. In short, the factory tea waste biosorbent has a higher selectivity toward zinc compared to copper in metal ion uptake by the binding sites.

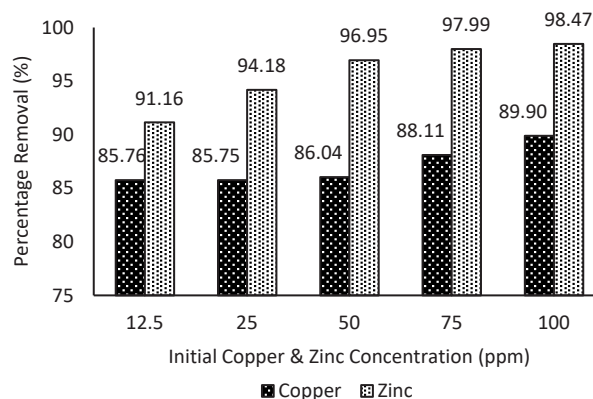


Fig. 4. Effect of percentage removal toward mixed copper and zinc metal ions with various initial mixture concentrations by factory tea waste biosorbent

3.2 Adsorption Isotherms

Adsorption isotherms is a preliminary step in determining the pore textures of the adsorbate. Also, it is able to describe the interaction between adsorbates and adsorbents. Hence, it is important to study the adsorption isotherms as it provides more details on the adsorption process.

3.2.1 Langmuir Isotherm

The Langmuir isotherm model assumes that the uptake of metal ions occurs on a homogenous adsorption surface monolayer without interaction between adsorbed ions. The Langmuir isotherm is based on four main hypotheses [31]:

- The adsorption sites are equal and the surface is uniform.
- The adsorbed molecules on the adsorbent do not interact with each other.
- All adsorption processes happen in a same mechanism.
- The adsorbate molecules do not deposit or react with other molecules that have been adsorbed by the adsorbent during maximum adsorption. It is assumed that all molecules are adsorbed onto the surface of adsorbent only.

The Langmuir isotherm can be expressed in the form of the linearized Langmuir equation:

$$\frac{1}{q_e} = \frac{(1)}{K_L q_{max}} \frac{1}{C_e} + \frac{1}{q_{max}} \quad (2)$$

Where q_e is the adsorption capacity of factory tea waste biosorbent (mg/g), K_L is the adsorption energy (L/mg),

q_{max} is the maximum adsorption capacity of factory tea waste biosorbent (mg/g), and C_e is the final concentration of heavy metal ions (mg/L).

The graphs of $1/q_e$ against $1/C_e$ for both copper and zinc are plotted and shown in **Figure 5** and **Figure 6**, respectively. The intercept of the slope was used to identify the value of q_{max} whereas the gradient was obtained from the graph to determine the value of K_L . The R-squared values were close to 1, indicating that the experimental data were suitable with the Langmuir isotherm. Besides, the calculated q_{max} values of the adsorbents for copper adsorption were higher compared to zinc adsorption. According to Sing & Yu [32], the constant value of K_L resulted in high affinity of the factory tea waste biosorbent toward certain heavy metals in high adsorption energy. Hence, this will increase the R-squared and Q_{max} values.

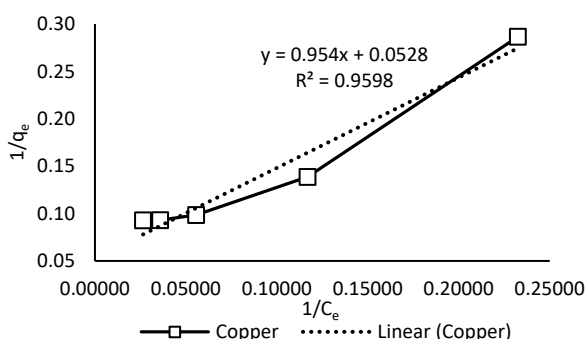


Fig. 5. Langmuir isotherm plot for adsorption of copper metal ion by factory tea waste biosorbent

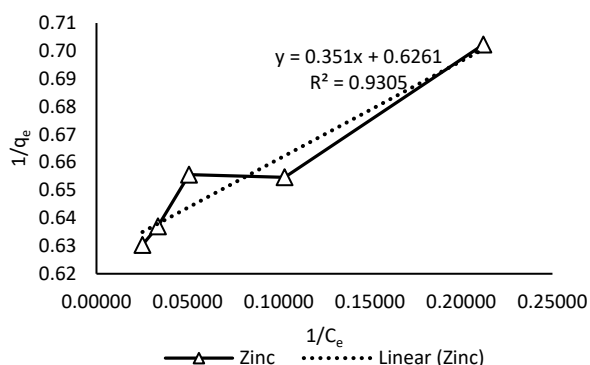


Fig. 6. Langmuir isotherm plot for adsorption of zinc metal ion by factory tea waste biosorbent

3.2.2 Freundlich Isotherm

According to Mengistic, Siva Rao, Prasada Rao, and Singanan [33], the Freundlich isotherm assumes that different adsorbates have different affinities with each site but the isotherm still behaves as the Langmuir isotherm. The Freundlich isotherm is considered to be more realistic compared to the Langmuir isotherm. The latter was developed based on the assumption of independence and equivalence of adsorption sites by ignoring the possibility of an initial layer that may act as a substrate for the

adsorption. The Freundlich isotherm can be expressed in the form of the linearized Freundlich equation:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad (3)$$

Where q_e is the adsorption capacity of factory tea waste 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 ion (mg/L).

The graphs of $\log q_e$ against C_e for both copper and zinc are plotted and shown in **Figure 7** and **Figure 8**, respectively. The intercept of the slope was used to identify the value of K_F whereas the gradient was obtained from the graph to determine the value of n . The calculated R-squared values from the Freundlich isotherm for both copper and zinc were high and near to 1. This shows that the adsorption experimental data followed the isotherm well.

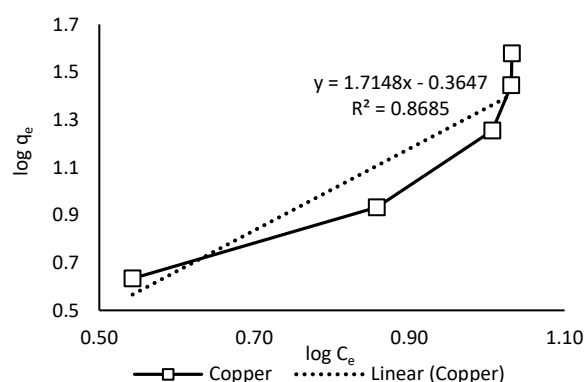


Fig. 7. Freundlich isotherm plot for adsorption of copper metal ion by factory tea waste biosorbent

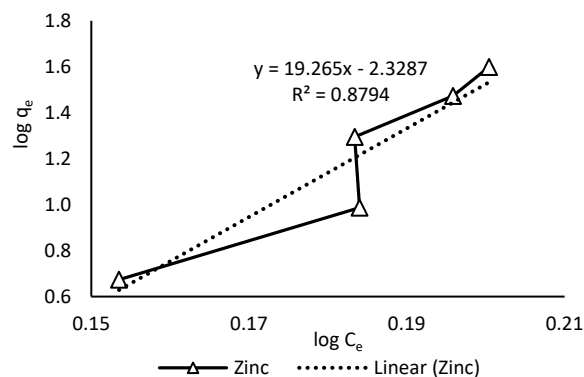


Fig. 8. Freundlich isotherm plot for adsorption of zinc metal ion by factory tea waste biosorbent

By comparison, it can be clearly seen that the Langmuir isotherm is generally better than the Freundlich isotherm. The R-squared values showed a better fit to the Langmuir isotherm. In another word, this means the factory tea waste biosorbent has homogeneous binding sites that are equivalent to monolayer coverage [34]. The heavy metal ions will not interact with each other, hence the binding of heavy metal ions onto the binding sites on the surface of factory tea waste biosorbent surface is not affected. According to Puranik, Chabukswar & Paknikar

[35], the adsorption of copper and zinc that follows the Langmuir isotherm is considered as a physically equilibrated mechanism.

3.3 Characterization Studies

Several characteristics of factory tea waste biosorbent were determined, such as surface area, pore volume, pore width, and pore diameter, as shown in **Table 1**. The Brunauer-Emmett-Teller (BET) surface area and Langmuir surface area were 0.8862 and 1.2451 m²/g, respectively, as determined by nitrogen adsorption method using Micromeritics ASAP 2020 instrument. The total pore volume, width, and diameter of the factory tea waste biosorbent were 0.000565 m²/g, 2.546985 nm, and 4.85205 nm, respectively, according to the stated classification by the International Union of Pure and Applied Chemistry (IUPAC), which stated the size of micropores (diameter $d < 2$ nm), mesopores ($2 \text{ nm} < d < 50$ nm), and macropores ($d > 50$ nm). The average pore width of 2.546985 nm was determined using the BET method. Meanwhile, the average pore diameter was 4.85205 nm as determined using the Barrett-Joyner-Halenda method. The results showed that the tea factory waste biosorbent consists of mesopores as the pore diameter is between 2 and 50 nm.

Table 1. The properties of factory tea waste biosorbent

Adsorbent Properties	Parameters
Sample mass (g)	0.2905
BET surface area (m ² /g)	0.8862
Langmuir surface area (m ² /g)	1.2451
Total pore volume of pores (m ² /g)	0.000565
Average pore width (nm)	2.546985
Average pore diameter (nm)	4.85205

4 Conclusion

The results of this study showed that the factory tea waste biosorbent has higher heavy metal removal efficiency toward zinc based on several parameters, such as the effect of various initial heavy metal ion concentrations, effect of pH, and effect of mixed copper and zinc ions at various initial concentrations. Zinc has better performance in terms of heavy metal removal using the factory tea waste biosorbent compared to copper. However, the biosorbent still showed excellent removal of both zinc and copper from wastewater with the removal efficiency of 91.16%–98.47% for zinc and 85.76%–89.90% for copper. For the adsorption isotherm model, both zinc and copper showed a better fit to the Langmuir isotherm than the Freundlich isotherm ($R \approx 1$). The

characterization studies indicated that the tea factory waste adsorbent consists of mesopores with the diameter of 4.85205 nm and width of 2.546985 nm.

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