Biosorption of Copper (II) from Aqueous Solution using a Combination of Orange Peels and Tea Waste

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Abstract. The ability of biosorbents, which are a combination of orange peels and tea waste to treat copper (II) using the biosorption method was examined. The experiment was performed under batch biosorption studies with various operating parameters. The pH, biosorbent dosage, contact time, and initial copper (II) concentration were optimized from pH 3 - 8, 0.25 - 1.0 g, 2 - 20 minutes and 10 - 100 mg/L, respectively. The findings found that a pH of 5.5, a biosorbent dosage of 0.75 g, a contact period of 5 minutes, and an initial copper (II) concentration of 10 mg/L were shown to be the best operating parameters for copper (II) biosorption. For isotherm models, the experimental data for copper (II) biosorption was fitted to the Langmuir isotherm with R² value of 0.7775 compared to the Freundlich isotherm model with R² value of 0.1073. The value for R² was 0.4, indicating that copper (II) biosorption using the combination of orange peels and tea waste is favourable. For kinetic models, the experimental data for copper (II) biosorption was well fitted to the pseudo-second-order kinetic model with R² value of 0.9865 compared to the pseudo-first-order kinetic model with R² value of 0.1006. In conclusion, the combination of orange peels and tea waste functions very well for biosorption of copper (II).

1. Introduction

Heavy metals can be found in a wide range of wastewater, especially wastewater from industrial activities. Heavy metals are persistent, non-biodegradable and toxic [1]. Heavy metals can contaminate aquatics life in streams, lakes, and seas. Besides, human health has also become at risk because heavy metals can be bioaccumulated via the food chain. Long-term exposure to heavy metals can cause degenerative muscle, physical and neurological processes that are like Parkinson's and Alzheimer's disease. Nickel, zinc, copper, chromium, and lead are the most common heavy metals in industrial wastewater [2]. Copper is a heavy metal that could damage the human body if it is excessively present in water. For both humans and animals, copper is a required trace element, however, too much copper intake can negatively affect health.

Many conventional methods have been used to treat heavy metals in industrial wastewaters over the last few decades. The commonly used methods include ultrafiltration, ion exchange, reverse osmosis, and chemical precipitation. However, all conventional methods have limitations such as inadequate metal removal, increases toxic sludge production, high reagent and energy demands, metal precipitate
aggregation, expensive and sensitive to pH solution [3][4][5]. Therefore, when conventional methods are not feasible to treat heavy metals, another option is the biosorption method. Biosorption is a biological-chemical treatment processes that quite familiar nowadays. Biosorption may be simply defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physio-chemical pathways of uptake [6]. It has been regarded as an innovative, cost-effective, efficient, and environmentally friendly technology to treat heavy metals from industrial wastewaters [7].

Several researchers have used banana peels, waste tea leaves, maize corn cobs, apple peels, wheat husk, coconut husks, mango peels, bean hulls, cotton stalks, and other food waste and agriculture waste materials to remove heavy metals [8]. The biosorption capability of agriculture waste products, typically containing cellulose, is high. Metal complexation is accelerated by their components, which include starch, hemicellulose, lignin, proteins, lipids, hydrocarbons, and other functional groups, which help for heavy metals removal [9]. Due to numerous benefits connected with agricultural waste, as previously stated, it is suitable to be a right choice for heavy metal removal. As a result, using food wastes and agriculture waste as biosorbent for removal heavy metals is a developing and potentially alternative technique that has received a lot of attention in recent years. The aims of the study are 1) to optimize parameters of operating condition for copper (II) removal using combination of orange peels and tea waste, and 2) To analyse copper (II) biosorption using existing sorption isotherms models (Langmuir and Freundlich) and kinetic models (pseudo-first-order and pseudo-second-order), and 3) to compare the copper (II) removal performance between commercial activated carbon and a combination of orange peels and tea waste.

2. Materials and methods

2.1. Preparation of copper (II) stock solution
3.93 g of analytical grade copper sulphate pentahydrate (CuSO₄·5H₂O) was dissolved in 1000 mL of distilled water to make a 1000 mg/L copper (II) stock solution. Then, the stock solution will be further diluted to achieve the desired concentration.

2.2. Preparation of materials
The orange peels and tea waste were obtained from a nearby market. These food wastes were rinsed twice with distilled water after being cleaned several times with tap water. The orange peels were cut into small pieces. The orange peels and tea waste were then left to dry in the open air for two days and placed in an oven at a temperature of 80°C for 24 hours to ensure that all moisture is eliminated. The dried orange peels and tea waste were grinded and sieved using a 0.5 mm sieve and kept in a storage box for further use [10].

2.3. Batch biosorption experiment
The biosorption studies for copper (II) removal were performed using batch experiments at different parameter such as pH, biosorbent dosage, contact time and initial concentration. The pH range of 3 to 8, biosorbent dosage range of 0.25 to 1.0 g, contact time range of 2 to 20 minutes, and initial copper (II) concentration range of 10 to 100 mg/L were tested and optimized for copper (II) biosorption. The ratio of orange peels to tea waste is 1:1. For the first step, the pH was adjusted using HCl or NaOH and the biosorbents were weighted before added into the copper (II) solution. Next, the copper (II) solution was placed on an orbital shaker with the rotational speed of 120 rpm and temperature 25±1°C. After the completion of biosorption process, the biosorbent was filtered through qualitative filter paper and the filtrate was analysed using an Atomic Absorption Spectrometer (AAS). Table 1 shows the summary of parameters for optimization study.
### Table 1. Summary of parameters for optimization study

| Optimization parameter | Operational conditions |
|------------------------|------------------------|
|                        | pH (pH)                | Biosorbent dosage (g) | Contact time (min) | Initial Conc. (mg/L) |
| pH                     | 3 - 8                  | 1.0                   | 15                 | 50                   |
| Biosorbent dosage      | 5.5                    | 0.25 – 1.0            | 15                 | 50                   |
| Contact time           | 5.5                    | 0.75                  | 2 – 20             | 50                   |
| Initial Conc.          | 5.5                    | 0.75                  | 5                  | 10 - 100             |

3. Results and discussion

3.1. Optimization parameters for copper (II) biosorption

3.1.1. pH. The pH of the solution has a significant impact on copper (II) biosorption as illustrated in Figure 1. The optimum pH value was obtained at pH 5.5 with a copper (II) biosorption of 44.51% and an uptake capacity of 4.25 mg/g. From Figure 1, the copper (II) biosorption improved from 38.13% at pH 3 to 44.51% at pH 5.5. Then, the copper (II) biosorption was significantly reduced at pH 6, pH 7 and pH 8 with percentage removal of 44.38%, 42.6% and 41.49%, respectively. According to Gadd (2009) [11], heavy metal biosorption is generally reduced at low pH due to competition between heavy metal cations and hydronium ions for the biosorbent binding sites. More negatively charges on the biosorbent surface are available as the pH increases, allowing for higher copper removal. It is widely accepted that when the metal ionic species in the solution become less stable, the sorption of metal cations rises with increasing pH [12]. Also, as pH rises, deprotonation causes functional groups like carboxyl, hydroxyl, and phosphate groups on the biosorbent surface to experience negative charges (acid amino and imidazole groups become neutral), enhancing metal cation binding and hence biosorption ability and speed [13][14]. The results obtained agreed with previous work [15]. The study suggested that pH 5.5 is optimal for subsequent experiments in order to prevent Cu (OH)\(^{2+}\) precipitation, as Cu\(^{2+}\) cannot precipitate to form Cu (OH)\(^{2+}\) beyond pH 6.5.

![Figure 1. Copper (II) biosorption versus pH](image-url)
3.1.2. Biosorbent dosage. The amount of biosorbent used has a significant impact on copper (II) biosorption as shown in Figure 2. The optimum biosorbent dosage was obtained at 0.75 g with a copper (II) biosorption of 43.19% and an uptake capacity of 5.49 mg/g. Based on Figure 2, the copper (II) biosorption was improved from 18.91% to 43.19% as the biosorbent dosage was added from 0.25 g to 0.75 g. However, the copper (II) biosorption dropped from 39.58% to 36.88% when the biosorbent dosage was increased from 0.85 g to 1.0 g. The highest copper (II) biosorption was 43.19%, which was obtained at the biosorbent dosage of 0.75 g. Increases in biosorbent dosage can increase the percentage of copper (II) removal. The results obtained almost similar with previous work carried out by Raghuwanshi & Lal (2018) [16]. The biosorption performance increases rapidly as the biosorbent dosage is increased due to more binding sites being available on the surface of biosorbent. However, an excessive amount of biosorbent will reduce the biosorbent’s uptake capacity due to un-saturated binding sites. As a result, a biosorbent dosage of 0.75 g was employed for the following experiments in order to optimize the biosorption performance while minimizing the use of the biosorbent.

![Figure 2. Copper (II) biosorption versus biosorbent dosage](image)

3.1.3. Contact time. The time allocated for the biosorption process to occur is commonly referred as contact time. The performance of copper (II) biosorption at different contact time is illustrates in Figure 3. The optimum contact time was obtained at 5 minutes of biosorption process with a copper (II) biosorption of 74.61% and an uptake capacity of 10.4 mg/g. However, after 10 minutes, the copper (II) biosorption decreased to 42.99% and then remained constant after 15 to 20 minutes with 45.23% of percentage removal. The contact time between the biosorbents and the sorbate has no direct effect on biosorption capability, but it can be a limiting factor. According to Hajahmadi et al., (2015) [17], the binding sites are entirely saturated when the biosorbent's maximum biosorption capacity is attained under given conditions and increasing contact time has no further effect. Metal uptake by non-living or inactive biological materials is considered a quick process that takes a few minutes to complete. The study obtained nearly identical results to previous research [18]. Based on this finding, the next experiment was performed with 5 minutes of contact time.
3.1.4. Initial concentration. The initial concentrations of solutes will influence biosorption process. The performance of copper (II) biosorption at different initial concentration is shown in Figure 4. The optimum initial concentration was obtained at 10 mg/L with a percentage removal of copper (II) was 44.68% and an uptake capacity of 1.5 mg/g. From Figure 4, the copper (II) biosorption was gradually reduced from 44.68% to 6.07% when the initial concentration of copper (II) increased from 10 to 100 mg/L. The number of active binding sites for biosorption reduces as the concentration of heavy metal increases in proportion to the number of moles of heavy metal present. Hence, the amount of heavy metal removed is highly influenced by the initial heavy metal concentration [19]. The lack of sufficient active binding sites for heavy metal biosorption could explain the decline in copper (II) biosorption. At lower concentrations, all heavy metal ions in the solution can interact with the active binding sites on the biosorbent surface, the percentage of biosorption is expected to increase. At higher concentrations, the biosorption performance is low because of the saturation of biosorption binding sites [20]. Generally, initial heavy metal concentration provides a driving force between aqueous and solid phases to overcome mass transfer resistance. Increase in initial concentration of metal has led to the reduction of available binding sites on the surface of the biosorbent. This has resulted in a reduction of heavy metal biosorption due to less collision between the biosorbent and heavy metal ions.

![Figure 3. Copper (II) biosorption versus contact time](image1)

![Figure 4. Copper (II) biosorption versus initial concentration](image2)

3.2. Evaluation of isotherm and kinetic models
Results from biosorption of copper (II) were evaluated using existing isotherm and kinetic models, namely Langmuir isotherm, Freundlich isotherm, pseudo-first-order kinetic and pseudo-second-order kinetic model.

3.2.1. Isotherm models. The summary of findings for the Langmuir and Freundlich isotherm models for copper (II) biosorption is shown in Table 2. For the Langmuir isotherm model, the maximum biosorption capacity (q_{max}), the Langmuir constant (K_L) and the coefficient of determination (R^2) values were 1.7419 mg/g, 0.1282 L/mg and 0.7775, respectively. The experimental data for biosorption of copper (II) was fitted to the Langmuir isotherm model. The results indicated that the copper (II) biosorption occurred in a monolayer, involving interaction of heavy metal ions with functional groups on the surface of orange peels and tea waste biosorbents. The separation factor of equilibrium, R_L, was used to predict whether the biosorption system is favourable or unfavourable [21]. The value for R_L in the present investigation was 0.4, indicating that the biosorption of copper (II) onto the combination of orange peels and tea waste is favourable. Based on Ruthven (1984) [22], the range when the isotherm is favourable is when R_L is between 0 and 1. On the other hand, the Freundlich constants 1/n, K_F and coefficient of determination (R^2) values were 0.12142, 1.456129 and 0.1073, respectively. The biosorption of copper (II) using the combination of orange peels and tea waste did not fit into the Freundlich isotherms model.

| Heavy Metal | Langmuir | Freundlich |
|-------------|----------|------------|
| Copper (II) | q_{max} (mg/g)  | K_L (L/mg) | R^2 | 1/n | K_F | R^2 |
|             | 1.7419 | 0.1282 | 0.7775 | 0.1214 | 1.4561 | 0.1073 |

3.2.2. Kinetic models. The summary of findings for the pseudo-first-order and pseudo-second-order kinetic models for copper (II) biosorption is shown in Table 3. From the pseudo-first-order kinetics model, the values for q_e, k_1 and R^2 were 1.356 mg/g, 2.885 min^{-1} and 0.1006, respectively. The biosorption experiment data was not fitted with the pseudo-first-order kinetic model. Results inferred that copper (II) biosorption on combination of orange peels and waste is not uni-molecular reaction, thus biosorption does not occur exclusively onto one site per ion. From the pseudo-second-order kinetics model, the values for q_e, k_2 and R^2 were 6.097 mg/g, 783.141 min^{-1} and 0.9865, respectively. The results indicated that the copper (II) biosorption was well fitted to the pseudo-second-order kinetic model, as the coefficient of determination was high. This clearly shows that the rate of biosorption of copper (II) appears to be limited by chemisorption, which is accomplished by the formation of chemical bonds. The findings suggest that the copper (II) biosorption is complicated and includes multiple mechanisms that occur at the same time.

| Heavy Metal | Pseudo-first-order | Pseudo-second-order |
|-------------|--------------------|---------------------|
| Copper (II) | q_e (mg/g) | k_1(min^{-1}) | R^2 | q_e (mg/g) | k_2(min^{-1}) | R^2 |
|             | 1.356 | 2.885 | 0.1006 | 6.097 | 783.141 | 0.9865 |

3.3. Comparison of copper (II) removal between commercial activated carbon and combination of orange peels and tea waste

Activated carbon is without a doubt the most well-known and widely used adsorbent in wastewater treatment around the world. However, activated carbon remains a costly material, since the higher the quality of activated carbon, the greater will be its cost [23]. By using the optimum values, which are pH 5.5, 0.75 g of dosage and a contact time of 5 minutes at 120 rpm, the comparison study was conducted between the commercial activated carbon and the present biosorbent, a combination of orange peels and
CENVIRON 2021
IOP Conf. Series: Earth and Environmental Science 920 (2021) 012039
doi:10.1088/1755-1315/920/1/012039

tea waste. Table 4 shows the comparison of copper (II) removal between the commercial activated carbon and the present study.

| Biosorbent                  | Uptake capacity (mg/g) | Copper (II) Removal (%) |
|-----------------------------|------------------------|-------------------------|
| Tea waste + orange peels    | 2.672                  | 18.11                   |
| Activated carbon           | 3.605                  | 24.36                   |

The result shows the copper (II) removal using commercial activated carbon has obtained a percentage of removal of 24.36% compared to the combination of orange peels and tea waste, which is 18.11%. While the uptake capacity for commercial activated carbon was 3.605 mg/g and for the combination of orange peels and tea waste was 2.672 mg/g. Based on this result, the uptake capacity of copper (II) for commercial activated carbon is only slightly higher than the combination of orange peels and tea waste. The study inferred that the copper (II) removal obtained from the combination of orange peels and tea waste is comparable to that of commercial activated carbon.

4. Conclusion
Copper (II) biosorption using a combination of orange peels and tea waste has been successfully performed in batch experiments. The optimization of operating conditions for the combination of orange peels and tea waste to treat copper (II) from an aqueous solution was studied. The optimum operating conditions for copper (II) biosorption using a combination of orange peels and tea waste were obtained at a pH of 5.5, biosorbent dosage of 0.75 g, 5 minutes of contact time at 120 rpm and an initial concentration of copper (II) at 10 mg/L. In addition, the copper (II) biosorption by a combination of orange peels and tea waste was also successfully analysed using existing sorption isotherm models (Langmuir and Freundlich) and kinetic models (pseudo-first-order and pseudo-second-order). For isotherm models, the experimental data for copper (II) biosorption was fitted to the Langmuir isotherm with $R^2$ value of 0.7775 compared to the Freundlich isotherm model with $R^2$ value of 0.1073. The value for $R_L$ in the present investigation was 0.4, indicating that copper (II) biosorption using the combination of orange peels and tea waste is favourable. For kinetic models, the experimental data for biosorption of copper (II) was well fitted to the pseudo-second-order kinetic model with $R^2$ value of 0.9865 compared to the pseudo-first-order kinetic model with $R^2$ value of 0.1006.

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