Simulated biosorption of Cu$^{2+}$ in aqueous solutions using *Cucumis melo* VAR. *cantalupensis*

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Abstract. This study showed the high adsorptive capacity of the peel of *Cucumis melo* var. *cantalupensis* when used to remove Cu$^{2+}$ adsorbent in a simulated column study using Aspen Adsorption$^\text{®}8.4$. The results confirmed that the bed height, inlet Cu$^{2+}$ concentration and flowrate had significant influence on Cu$^{2+}$ adsorption using *Cucumis melo* var. *cantalupensis*. There was an increased in the breakthrough time with increasing bed height. The breakthrough time remained the same even when the inlet concentration was increased, as long as the bed height and flowrate were maintained constant at any inlet concentration. A steeper slope of the breakthrough curve was attained when the flowrate was increased and the breakthrough time decreased.

1. Introduction

One of the heavy metals that concern the environment, as well as the human health is Cu$^{2+}$ in aqueous solution. Cu$^{2+}$ is generated from wastewater of industries producing metal cleaning, plating baths, paint and pigment, fertilizer, etc. Cu$^{2+}$ is crucial to some living organisms even at lower concentration and may cause potential damage when the concentration is increased. High concentration of this heavy metal causes stark corrosion, extensive capillary damage, and health problems i.e. mucosal irritation and gastrointestinal problems [1]. Philippine government regulates the release of Cu$^{2+}$ from industries through effluent standards of 0.5 mg/L [2] while World Health Organization sets a limit of 0.2 mg/L [3]. Conventional treatments in removing Cu$^{2+}$ i.e. chemical precipitation, filtration, ion exchange, membrane process and reverse osmosis presently used are costly and sometimes generate more sludge [4-7]. With this, biosorption has taken interests of many researchers and small and medium industries. Among the most popular biosorbers used, agricultural wastes serve as a sustainable approach. Using agricultural wastes as biosorbents can address the problem on solid wastes while having a low-cost adsorbent of heavy metal contaminant i.e. Cu$^{2+}$. A number of agricultural wastes such as rice husk, rice hulls, peanut shells, sago processing waste, Nile rose (*Eichhornia speciosa*) plant powder [8]; sugar cane bagasse [9]; banana peels and water melon [10]; yellow passion fruit (*Passiflora edulis*) and *Citrus maxima* peel [11]; orange juice residues [12]; ponkan mandarin peels [13]; pecan wall nuts [14]; and barley straw [15] were utilized in removing Cu$^{2+}$ from aqueous solution via adsorption. None of these studies though deal with simulation experiments, which can save time and operational costs should we want to determine the adsorptive performance of numerous agricultural wastes. The objective of the study was to determine the performance of a simulated continuous column in adsorbing Cu$^{2+}$ present in aqueous solution with *Cucumis melo* var. *cantalupensis* peel as biosorbent.
using Aspen Adsorption® version 8.4 while varying adsorption parameters i.e. initial sorbate concentration, adsorption column height, adsorbate concentration.

2. Methodology

2.1. Column study
Continuous adsorption of Cu\(^{2+}\) onto *Cucumis melo* var. *cantalupensis* was simulated using Aspen Adsorption® 8.4. For the continuous adsorption simulation, the batch adsorption was conducted first by preparing stock solution of Cu\(^{2+}\) with initial concentration of 200 mg/L. The heavy metal salt of Cu(NO\(_3\))\(_2\) was dissolved in 1000 ml of double distilled water. From each stock solution, appropriate dilutions of 50 ml volumes of solutions with initial concentrations (C\(_0\)) of 20, 40, 60, 80, 100, 120, 180, and 200 mg/L. One of the Aspen Properties® assumptions is that there were no formation of any metal–anion complexes from the anion of these salts (NO\(_3\)) and no hydrolysis occurred as well, thus, there was no observable effect on the ion exchange process.

2.2. Process flow
An ion-exchange process was assumed in this study and the bed model assumptions for this process were: (1) the material balances (both overall and component) were applied for the liquid phase; (2) constant temperature; (3) reaction was either plug flow or plug flow with axial dispersion; (4) constant liquid stream pressure (no frictional pressure drop); (5) constant superficial velocity and volumetric flow rate with dilute ion components; negligible effect of adsorption on the overall mass balance; (6) ideal mixing occurs in the aqueous phase; constant overall molar volume; (7) allowable changes in molar volume between fed fluids; (8) constant Q, total exchange capacity of the bed; (9) applied lumped mass-transfer rate, with a liquid- or solid-film resistance, either linear, quadratic, or user-defined; and (10) mass-action equilibrium can be used as an alternative model for ion-exchange behaviour.

2.3. Physical and chemical properties of sorbate solution
The physical properties of these electrolytes in combination with water were provided by Aspen Properties®. The property method used is ELECNRTL (Electrolyte Non-random Two-Liquid).

2.4. Bed configuration
The following parameters were based from the batch adsorption data of the same adsorption system: (1) inter and intraparticle diameter and particle size of the biosorbent; (2) adsorption capacity recovery of contaminant (Q); (3) amount of biosorbent dosage related to column bed depth or height (H\(_b\)); and, (4) influent flow rate (F). The average particle size diameter was based from the surface area of the biosorbent. Total pore of the biosorbent (ε\(_p\)) was computed from the interparticle size (cm\(^3\)/g) and bulk density (cm\(^3\)/g) while the micro pore (ε\(_m\)) was computed from the intraparticle size (cm\(^3\)/g). The set of equations within the layer of the bed were specified in the “Configure Block/Stream” window (General tab, Material/Momentum balance tab, Kinetic Model tab, and Isotherm tab). Upwind Differencing Scheme (UDS) 1 was chosen as the discretization method.

2.5. Adsorption parameters
The bed height, flowrate, and initial concentration were varied for different systems of the adsorption of Cu\(^{2+}\) using *Cucumis melo* var. *cantalupensis* as biosorbent. Breakthrough curves at varying flow rates from 20 mg L\(^{-1}\), 40 mg L\(^{-1}\), 180 mg L\(^{-1}\), and 200 mg L\(^{-1}\) inlet concentrations were determined with varying flowrates from 0.1 L s\(^{-1}\), 0.82 L s\(^{-1}\), 0.01 L s\(^{-1}\), and 0.0055 L s\(^{-1}\) and bed heights from 0.5 m, 0.75 m, 1 m, and 1.25 m. To determine the effect of flowrate on the adsorption of Cu\(^{2+}\) onto *Cucumis melo* var. *cantalupensis*, flow rate of the influent solution was varied while maintaining the initial concentration and bed height constant. The breakthrough curves for flowrate variation were generated by utilizing extreme values, lowest and highest values, of the bed height of 0.5 m and 1.25
m, and initial concentrations of 20 mg L\(^{-1}\) and 200 mg L\(^{-1}\). The influence of the initial concentration of Cu\(^{2+}\) onto *Cucumis melo* var. *cantalupensis* was probed by varying the initial concentration while maintaining the bed height and flowrate constant. The values used for the bed heights, 0.5 m and 1.25 m, and flowrates, 0.1 L s\(^{-1}\) and 0.0055 L s\(^{-1}\) were taken at the extreme values, lowest and highest values.

### 3. Results and discussion

#### 3.1. Results

The adsorption breakthrough curves of Cu\(^{2+}\) onto *Cucumis melo* var. *cantalupensis* at different bed heights of 0.5 m, 0.75 m, 1 m, and 1.25 m are presented in figures 1-4 indicating that the breakthrough time increases with increasing bed height. Increased breakthrough time also corresponds to the increased contact time Cu\(^{2+}\) onto *Cucumis melo* var. *cantalupensis* resulting to the increase in the adsorbate volume uptake [16]. The increase in height also aided to the increase in surface area of the adsorbent since more adsorbent were present in the column; therefore, providing more binding sites available for sorption which led to higher bed capacity [17].

![Figure 1](image1.png)

**Figure 1.** Breakthrough curves at 20 mg L\(^{-1}\) inlet concentration with varying flowrates (a) 0.1 L s\(^{-1}\), (b) 0.082 L s\(^{-1}\), (c) 0.01 L s\(^{-1}\), and (d) 0.0055 L s\(^{-1}\) and bed heights 0.5 m, 0.75 m, 1 m, and 1.25 m.
Figure 2. Breakthrough curves at 40 mg L$^{-1}$ inlet concentration with varying flowrates (a) 0.1 L s$^{-1}$, (b) 0.082 L s$^{-1}$, (c) 0.01 L s$^{-1}$, and (d) 0.0055 L s$^{-1}$ and bed heights 0.5 m, 0.75 m, 1 m, and 1.25 m.

Figure 3. Breakthrough curves at 180 mg L$^{-1}$ inlet concentration with varying flowrates (a) 0.1 L s$^{-1}$, (b) 0.082 L s$^{-1}$, (c) 0.01 L s$^{-1}$, and (d) 0.0055 L s$^{-1}$ and bed heights 0.5 m, 0.75 m, 1 m, and 1.25 m.
3.2. Effect of flowrate

The effect of flowrate on the adsorption of Cu$^{2+}$ onto *Cucumis melo* var. *cantalupensis* was explored by varying the flow rate of the influent solution while maintaining the initial concentration and bed height constant. The breakthrough curves for flowrate variation were accomplished by utilizing extreme values, lowest and highest values, of the bed height as 0.5 m and 1.25 m, and initial concentrations as 20 mg L$^{-1}$ and 200 mg L$^{-1}$ shown in figures 5(a) and 5(b). It is evident from the plots that as the flowrate decreases, the breakthrough time increases. It also shows that with varying flowrates and a constant bed height of 0.5 m, the breakthrough time with flowrates of 0.1 L s$^{-1}$, 0.082 L s$^{-1}$, 0.01 L s$^{-1}$, and 0.0055 L s$^{-1}$ were 20.3 s, 26 s, 234 s, and 430 s validating the observation that when the flow rate is low, the contact time between Cu$^{2+}$ and *Cucumis melo* var. *cantalupensis* is greater which results in a higher breakthrough time [18]. On the other hand, when the flowrate is high, the influent solution leaves the column even before achieving equilibrium thus results in the decrease of Cu$^{2+}$ being adsorbed.
Figure 5. Breakthrough curves at (a) 20 mg L\(^{-1}\) and (b) 200mg L\(^{-1}\) inlet concentration both with varying flowrates (0.1 L/s, 0.82 L/s, 0.01 L/s, and 0.0055 L/s) and bed heights (0.5 m, and 1.25 m).

3.3. Effect of initial concentration
The influence of the initial concentration of Cu\(^{2+}\) onto Cucumis melo var. cantalupensis was investigated by varying the initial concentrations while maintaining the bed height and flowrate constant. The values used for the bed heights, 0.5 m and 1.25 m, and flowrates, 0.1 L/s and 0.0055 L/s were the extreme values, lowest and highest values. The breakthrough curves are the same with the same breakthrough time and ratio of instantaneous concentration with initial concentration when the flowrate and bed height remained constant. With varying initial concentrations and a constant bed height of 0.5 m, the breakthrough time with initial concentrations of 20 mg/L, 40 mg/L, 180 mg/L, and 200 mg/L were 20.3 s, 20.8 s, 20.3 s, and 20.3 s, respectively concludes that when the initial concentration is high, the adsorbate volume uptake is also high due to a higher driving force or concentration gradient for the Cu\(^{2+}\) that overcomes the mass transfer resistance in the system [19]. On the other hand, when the initial concentration is low, the adsorption capacity of the bed is also low [20].

4. Conclusion
Cucumis melo var. cantalupensis showed high adsorptive capacity when used to remove Cu\(^{2+}\) in a continuous column as shown in the simulated results from Aspen Adsorption® 8.4. Variations of parameters showed an 80% to almost 100% adsorption of the sorbate with the proposed biosorbent as indicated in the different breakthrough curves. The experimental data confirmed that the bed height, inlet Cu\(^{2+}\) concentration and flowrate had significant influence on Cu\(^{2+}\) adsorption using Cucumis melo var. cantalupensis. The breakthrough time increased with increasing bed height. On the other hand, when the inlet concentration was increased, the breakthrough time remained the same as long as the bed height and flowrate were maintained constant at any inlet concentration. Furthermore, when the flowrate was increased, the slope of the breakthrough curve became steeper and the breakthrough time
decreased.

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