

Continuous Biosorption of Pb²⁺ with Bamboo Shoots (*Bambusa spp.*) using Aspen Adsorption Process Simulation Software

Mc Lein Roger M. Lubiano II¹

Cris Vincent L. Manacup¹

Allan N. Soriano^{*,2}

Rugi Vicente C. Rubi³

¹School of Chemical, Biological, and Materials Engineering and Sciences, Mapúa University, Intramuros, Manila, Philippines

²Department of Chemical Engineering, Gokongwei College of Engineering, De La Salle University, 2401 Taft Avenue, Manila, Philippines

³Chemical Engineering Department, College of Engineering, Adamson University, 900 San Marcelino St. Ermita Manila, Philippines

*e-mail: allan.soriano@dlsu.edu.ph

Submitted 26 August 2022

Revised 10 March 2023

Accepted 13 July 2023

Abstract. The health risks impact of heavy metal contamination in the environment has prompted researchers to study its mitigation in an efficient and cost-friendly approach. Recently, simulated continuous biosorption using agricultural wastes is gaining popularity because it offers cheaper and faster alternative study methods using efficient large-scale removal of lead, which is known to cause adverse effects even at low concentrations. Bamboo shoots (*Bambusa spp.*), a delicacy known in Southeast Asia, are recognized worldwide, but the inedible sheath husks are thrown. This study evaluated the continuous Pb²⁺ biosorption performance of *Bambusa spp.* using Aspen Adsorption V8.4 by varying bed height, influent concentration, and volumetric flow rate. Linear driving force model was used to simplify, according to a separate batch biosorption study, ion exchange mechanism and Langmuir isotherm for equilibrium conditions. The backward differencing method was used to solve the resulting differential equation. Results showed that increasing the volumetric flowrate from 4.00x10⁻⁵ to 8.00x10⁻⁵ m³/s, the bed height from 0.2 to 1.0 m, and influent concentration from 80 to 120 ppm resulted in changes in the breakthrough time by a factor of 0.5, 4.0, and 0.67 respectively. Analysis of the breakthrough curves showed that increasing volumetric flow rate shortens breakthrough time due to reduced contact time, and increasing Pb²⁺ concentration facilitated ion exchange by increasing concentration difference. Bed height provides more binding sites available hence, higher Pb²⁺ removal.

Keywords: Aspen Adsorption, Bamboo Shoots, Biosorption, Breakthrough Curve, Lead

INTRODUCTION

Lead (II) is widely recognized as a potent neurotoxicant (*i.e.*, brain damage and nervous and renal breakdown), exhibiting

adverse effects on the human body even at concentrations as low as 0.01-5 ppm, and also affects the bones, kidneys, and the cardiovascular, immune, and reproductive systems (White et al., 2007; Cecil et al., 2008;

Mehdipour, 2015). Lead (II) unavoidably transfers to humans through the food chain from aquatic life, exposed to effluents from anthropogenic activities (*e.g.*, battery, metal plating, oil refining, and pigment and paint industries), due to bioaccumulation and biomagnification (De Luna, et al., 2023). The risks involved cause major industrial and environmental concerns for the removal of lead; the Department of Environment and National Resources (DENR) Administrative Order No. 35 Series of 1990 set the effluent standard for lead (II) for protected waters for old and existing industries that the maximum limit is 0.2 ppm (mg/L) and DENR Administrative Order No. 26-A Series 1994 states that the maximum lead content for drinking water is 0.01 ppm. Biosorption is suggested as an alternative potential for conventional lead removal techniques (*e.g.*, chemical precipitation, solvent extraction, reverse osmosis, and membrane filtration) because it is simpler, cheaper due to its utilization of locally available biomass such as agricultural wastes, high selectivity, and effectiveness even at low concentrations, and involves less usage of chemicals and absence of hazardous sludge by-product (Hasan et al., 2009).

Recently, biosorption has been proven as one of the most effective physicochemical methods for heavy metals removal like lead and involves passive transportation of lead (sorbate) in the liquid phase onto the solid phase (biosorbent) where it depends on the system's entropy rather than providing chemical energy that can be operated in either batch or continuous process (Papirio, et al., 2017). Batch studies are usually conducted to determine the biosorbent's effectiveness (Yildez, 2017), the mechanism involved (*e.g.*, ion-exchange), and its kinetics under certain conditions (*i.e.*, pH,

temperature, selectivity for multi-metal system, *etc.*), and the biosorbent's physical and chemical characteristics (*e.g.*, intra and inter-particle porosity, particle diameter, and density, functional groups present) (Diniz et al., 2007; Hasan et al., 2009). However, the data obtained in batch systems do not apply to the industrial scale due to insufficient contact time to attain equilibrium, limiting biosorption to a small amount of wastewater. This problem can be solved by continuous biosorption study using a packed bed column which provides a practical approach due to its simple operation and making better use of a concentration gradient that utilizes more of the biosorbent's capacity, using the data gathered from the batch study as a basis to the continuous biosorption study and on the observed column performance. The fundamental part of continuous biosorption studies is the breakthrough curve, which is the plot of effluent concentration versus time because it provides information for the design of the column adsorption system and can be determined by direct experimentation or simulation. Direct experimentation provides a concise breakthrough curve of a given system, but is time-consuming due to long residence time and economically undesirable process. Hence simulating process parameters in the industrial context is utmost importance to ensure the reliability of data gathering. Using simulation softwares such as Aspen Adsorption provides faster and cheaper continuous biosorption studies and a new area for biosorption studies (Xu et al., 2013).

There is not yet a biosorption study using the agricultural waste bamboo shoot husks even though, according to Philippine Council for Agriculture, Aquatic and Natural Resources Research and Development (PCAARD), it has increasing popularity in the

global market, previously known only to Asian countries particularly to the Philippines as a traditional food where its sheaths are usually discarded. Additionally, simulated continuous biosorption studies are still gaining popularity. Simulated continuous biosorption study using bamboo shoots will solve the issues presented.

The simulation study performed the column biosorption of lead (II) ions in bamboo shoot husks (*Bambusa spp.*) using biosorption parameters from a separate batch study based on the column breakthrough using Aspen Adsorption. The simulation study also determined the varying effects of influent flow rate and bed height on the column breakthrough at different influent concentrations. The results provided information on the column performance of bamboo shoot husks and provided insights on how simulated continuous biosorption using Aspen Adsorption works.

This study used the experimental batch mode biosorption performance of husks or sheath leaves of *Bambusa spp.* bamboo shoots from a batch study for user-defined data in simulation using Aspen Adsorption under the assumptions suggested and set by Aspen Adsorption Version 8.4. The assumptions, in addition to those set by Aspen Adsorption, are: isothermal process, overall and component material balances apply for the liquid phase, constant liquid stream pressure, volumetric flow rate, total

exchange capacity of bed and velocity, ideal mixing occurs in the aqueous phase, linear solid lumped film resistance is present, and liquid stream contains only water and the heavy metal ion/s.

METHODOLOGY

The biosorption study involved two major steps- Batch Biosorption Analysis and Continuous Biosorption Simulation Study, using the conceptual framework shown in Figure 1. The batch biosorption analysis part of this work provided data needed for the column biosorption simulation study.

Batch Biosorption Analysis

This section of the work discussed the analysis of batch biosorption of lead (II) ions using bamboo shoots which consists of determining isotherm parameters and characterizing systems involved. The details are discussed in the succeeding sub-sections.

Determination of Isotherm Parameters

Using the batch biosorption results of Nieva (2015) for a similar system, the adsorption characteristic behavior of the adsorbent (bamboo shoots) was determined. Important parameters, including the maximum adsorption capacity (q_{max}) and the equilibrium constant (b) were evaluated from

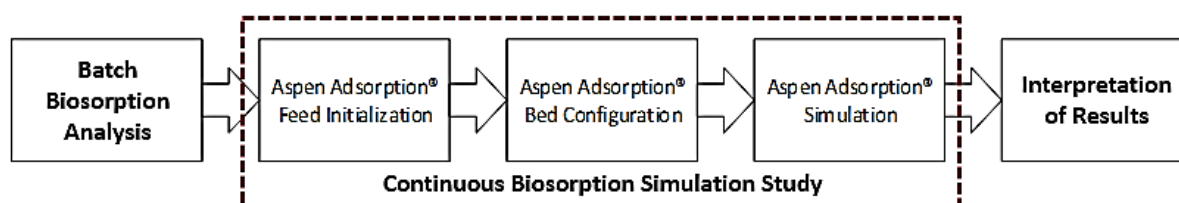


Fig. 1: Conceptual framework for the present work.

the obtained experimental data of Nieva (2015). The most suitable model to represent the data of Nieva (2015) is the Langmuir model, which was given in Eqn. (1), with values of $q_{max} = 5.0356$ mg/g and $b = 1.6237$ L/mg.

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_{max}} C_{eq} + \frac{1}{bq_{max}} \quad (1)$$

Characterization of systems involved

Data needed for the simulation section of this study for all the systems involved were obtained from various available literature whenever possible. These data are those parameters that Aspen Adsorption was not able to provide. The summary of the required parameters is shown in Table 1. The interparticle voidage (Ei), the particle porosity (Ep), and the total resin capacity (Q) were determined using Eqns. (2) to (4).

$$Ei = (\rho_b)(V_{pore}) \quad (2)$$

$$Ep = (\rho_{part})(V_{pore}) \quad (3)$$

$$Q = (\rho_b)(q_{max})(1 - Ep)(C_{Pb}) \quad (4)$$

Where ρ_b , V_{pore} , and ρ_{part} is the bulk density, the pore volume, and the particle density of the biosorbent, respectively, and C_{Pb} is the concentration of Pb(NO₃)₂ in equivalence per mole.

The bamboo shoots elemental analysis (Nieva, 2015) shown in Table 2 was also taken to analyze the biosorption process of lead (II) ions, considering that it has two counter-ions.

Continuous Biosorption Simulation Study

The continuous study involved the column biosorption of lead (II) ions using Aspen Adsorption Version 8.4 and breakthrough modeling. The column simulation required three general steps: (1) feed initialization; (2)

bed configuration; and (3) running the simulation.

Table 1. Summary of data obtained from literature needed for column simulation study

Parameter	Value
Lead (II) ions and Water Properties (CRC Handbook of Chemistry and Physics, 2009)	
D _{AB} (m ² /s) of Lead (II) ions in Biosorbent	1.4422x10 ⁻⁹
Water Viscosity (kg/m/s) at 25 °C	8.9642x10 ⁻⁴
Water Density (kg/m ³) at 25 °C	996.08625
Biosorbent (Bamboo shoots) Properties (Nieva, 2015)	
Bulk Density (g/m ³)	4.53x10 ⁶
Pore Volume (m ³)	1.97x10 ⁻⁹
Interparticle Voidage (m ³ /m ³)	8.9241x10 ³
Particle Density (g/m ³)	1.27x10 ⁷
Particle Porosity (m ³ /m ³)	2.5019x10 ⁻²
Particle Radius (m)	1.535x10 ⁻⁸
Surface Area (cm ² /g)	2.57x10 ⁴
Total Resin Capacity (eq/m ³)	1.3430x10 ²

Table 2. Elemental analysis of bamboo shoots (Nieva, 2015)

Element	% wt
C	51.68
O	33.84
Cl	0.88
K	6.81
Zr	6.34
S	0.45

Feed Initialization

Lead nitrate was used as the source of lead (II) ions. The properties of lead nitrate and water were taken from Aspen Properties Version 8.6, assuming only a dissociation reaction was present. Only lead (II) ion and its counter-ion were considered in the column adsorption simulation. The flow rate varied from 2x10⁻⁴ to 2x10⁻³ m³/s at influent

concentrations from 20 to 200 ppm. The bed height is a function of biosorbent mass and is solved using the given Equation (5).

$$m_b = \frac{1}{4}\pi D^2 H \rho_b \quad (5)$$

where m_b is the biosorbent mass, D is the bed diameter, H is the bed height, and ρ_b is the bulk density. The bed heights used were 0.2, 0.5, and 1.0 m, corresponding to 0.41, 1.02, and 2.05 kg of biosorbent, respectively.

Bed Configuration

Aspen Adsorption software has four main tabs in bed configuration: General, Material/Momentum Balance, Kinetic Model, and Isotherm tab. The Upwind Differencing Scheme 1 (UDS1) at 20 nodes was used for the General tab; Convection with Estimated Dispersion was used for the Material/Momentum Balance tab; Film Model with Lumped Resistance was used for the Kinetic Model tab, and Langmuir isotherm was used for the Isotherm tab (data were taken from the batch biosorption analysis).

The Internal Diameter of the adsorbent layer was based on the bed diameter used from the batch biosorption study by Nieva (2015). The constant mass transfer coefficients of lead (II) ion was solved using the following equations, taken from Perry and Southard (2019) and CRC Handbook of Chemistry and Physics (2009).

$$Sh = \frac{1.09}{\varepsilon} Re^{0.33} Sc^{0.33}; 0.0015 < Re < 55 \quad (6)$$

$$Sh = \frac{0.25}{\varepsilon} Re^{0.69} Sc^{0.33}; 55 < Re < 10 \quad (7)$$

$$Re = \frac{d_p u \rho \varepsilon}{\mu} \quad (8)$$

$$Sc = \frac{\nu}{D_{AB}} \quad (9)$$

$$Sh = \frac{k_f d_p}{D_{AB}} \quad (10)$$

$$D_{AB} = \frac{(z_+ + |z_-|)D_+D_-}{z_+D_+ + |z_-|D_-} \quad (11)$$

where Sh is the Sherwood number, Re is the Reynolds number, Sc is the Schimdt number, u is the fluid velocity, ρ is the fluid density, μ is the fluid viscosity, ε is the bed voidage, ν is the fluid kinematic viscosity, k_f is the external mass transfer coefficient, d_p is the particle diameter, D_{AB} is the ionic diffusion in water, z_+ and z_- is the cation's and anion's charge respectively, and D_+ and D_- is the cation's and anion's diffusion in water.

Running the Simulation

The flowsheet diagram was created upon completing the data needed for the simulation. This work used the ion-exchange adsorption bed to simulate the continuous adsorption of lead (II) ions using bamboo shoots as biosorbent. Figure 2 shows the flowsheet diagram used in this work. The data necessary for the simulation were then input into the flowsheet, and the continuous biosorption study was performed.

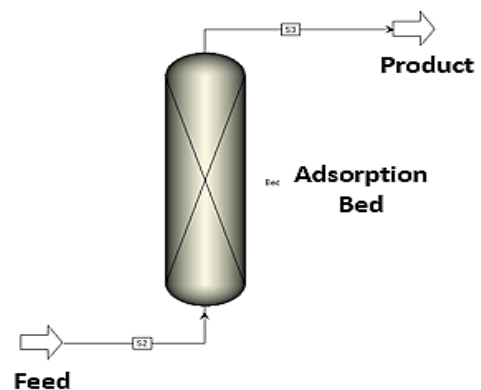


Fig. 2: Flowsheet diagram of the ion-exchange adsorption bed used in this work.

RESULTS AND DISCUSSION

Effect of Flowrate

To illustrate the effect of flowrate on the systems performance, the breakthrough curves at different influent flow rates are representatively shown in Figure 3, and its calculated breakthrough parameters are shown in Table 3, where H is the bed height, Q is the volumetric flow rate, t_b is the breakthrough time, C_o is the initial concentration, and C_b is the breakpoint concentration. Based on the results, the time to achieve the breakthrough time of lead (II) ions in bamboo shoots would be faster as the influent flow rate increases. The maximum biosorption capacity of the biosorbent achieved faster when the volumetric flow rate also increases. Based also on the result, the curve's steepness increases as the influent flow rate increases.

Table 3. Calculated parameters of breakthrough curves at $H = 0.5$ m and $C_o = 100$ ppm/0.9653 eq/m³

Q (m ³ /s)	t_b (s)	C_b (eq/m ³)
4.00×10^{-5}	781	0.484
6.00×10^{-5}	521	0.483
8.00×10^{-5}	391	0.484

The influent flow rates used ranged from 2.00×10^{-5} to 1.00×10^{-3} m³/s. It is noteworthy to mention that values above 1.00×10^{-3} m³/s resulted in calculation errors due to very small breakthrough time, and values below 2.00×10^{-5} m³/s would not be practical due to the much longer time that it needs to achieve the maximum adsorption of the metal ions.

Lower flow rate provides more time for a mass transfer process, allowing the metal ions to access more binding sites of the biosorbent (Cruz-Olivares *et al.*, 2013). It is also impossible to achieve the maximum

adsorption of metal ions at a lesser time by continuously increasing the influent flow rate of the system. Increasing the value of the influent flow rate also reduces the required contact time for biosorption equilibrium to reach the metal ions. The metal solution already left the column before equilibrium is achieved, reducing the metal uptake (Simate & Ndlovu, 2014).

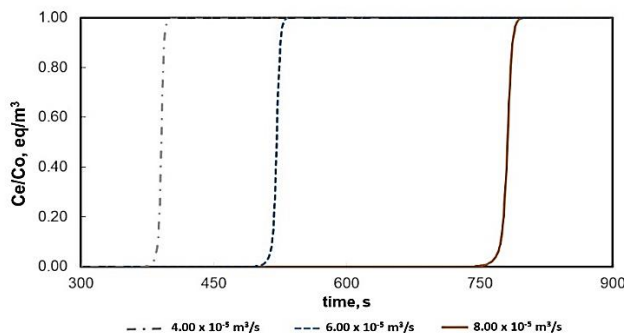


Fig. 3: Plot of the effect of flow rate on breakthrough curve ($H = 0.5$ m, $C_o = 100$ ppm/0.9653 eq/m³).

From one of the governing equations used in the simulation as in Eqn. (12), the axial dispersion coefficient for convection with estimated dispersion is directly affected by the volumetric flow rate of the system. One of the essential parameters of Eqn. (12) is the Reynolds number (Re) which is dependent on the volumetric flow rate of the system. The higher value of Re indicates that the volumetric flow rate is also high and would have a turbulent flow regime, while the lower Re value indicates lower volumetric flow rate (Geankoplis, 2004). As shown in the relation, as the volumetric flowrate increases, the Reynolds number increases but the axial dispersion coefficient decreases and vice versa. This shows that as the volumetric flow rate increases, the metal uptake of the biosorbent decreases due to less dispersion of the metal ions to the binding sites of the biosorbent.

$$\frac{v_i d_p}{E_z} = 0.20 + 0.11 \left(\frac{Re}{\varepsilon_i} \right)^{0.48} \quad (12)$$

Effect of Bed Height

The effect of bed height was representatively shown by plotting the breakthrough curves at different bed heights, as shown in Figure 4, and its calculated breakthrough parameters are shown in Table 4. From the results, as the bed height increases, the time to achieve the maximum biosorption capacity of lead (II) ions in bamboo shoots also increases. Increasing the bed height also increases the time to achieve the breakthrough time. The steepness of the curve also increases as the bed height decreases. It can be observed from Figure 4 that the high steep curve indicates that the breakthrough time is achieved for only a short period time and the biosorbent would be easily saturated. In contrast, less steep curve indicates that the breakthrough time is achieved gradually or takes a period time before the biosorbent in the column would be saturated.

Table 4. Calculated parameters of breakthrough curves at $Q = 6.00 \times 10^{-5} \text{ m}^3/\text{s}$ and $C_o = 100 \text{ ppm}/0.9653 \text{ eq}/\text{m}^3$

$H \text{ (m)}$	$t_b \text{ (s)}$	$C_b \text{ (eq}/\text{m}^3)$
0.2	209	0.484
0.5	521	0.483
1.0	1040	0.484

The maximum biosorption capacity would increase as the bed height increases due to the longer contact time of the Pb (II) ions to the surface of the biosorbent. The increase in breakthrough time means that there would be more volume treated. Decreasing the bed height would have an axial dispersion phenomenon that predominates the mass

transfer and reduce the diffusion of metallic ions, resulting in insufficient time to diffuse into the whole biosorbent (Taty-Costodes et al., 2005). As mentioned in that study, the breakthrough time is the determining parameter of column adsorption; the larger the bed height of the column, the better the intra-particulate phenomena and bed biosorption capacity, which can be observed in the present simulation result.

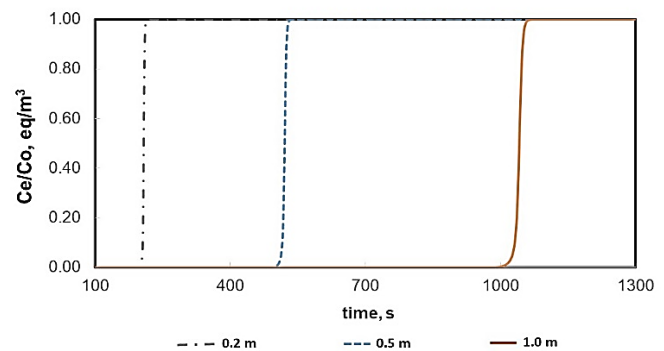


Fig. 4: Plot of the effect of bed height on breakthrough curve ($Q = 6.00 \times 10^{-5} \text{ m}^3/\text{s}$, $C_o = 100 \text{ ppm}/0.9653 \text{ eq}/\text{m}^3$).

From the relation presented in Eqn. (12), the column bed height is directly proportional to the mass of the biosorbent, i.e., as the column bed height increases, the biosorbent mass also increases and vice versa. This could be accounted to the fact that increasing the column height also increases the metal uptake of the biosorbent due to longer contact time between the metal ions to the binding sites of the biosorbent.

Effect of Influent Concentration

The effect of influent concentration was representatively shown using the plot of the breakthrough curves at different influent concentrations, as shown in Figure 5, and its breakthrough parameters are presented in Table 5. Based on the result, as the influent concentration increases, the time to achieve the maximum biosorption capacity or the

breakthrough time of the lead (II) ions in bamboo shoots would be faster. The steepness of the curve increases as the influent concentration increases.

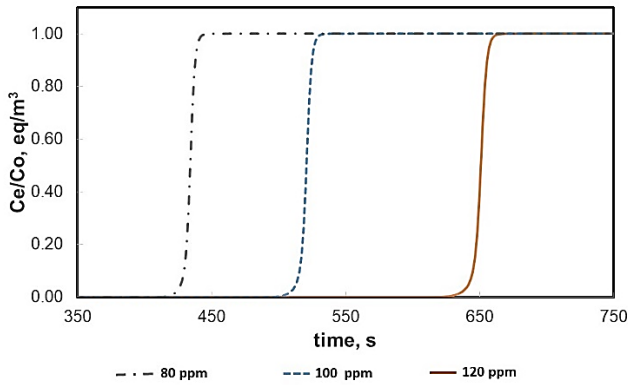


Fig. 5: Plot of the effect of influent concentration on breakthrough curve ($Q = 6.00 \times 10^{-5} \text{ m}^3/\text{s}$ and $H = 0.5 \text{ m}$).

Table 5. Calculated parameters of breakthrough curves at $Q = 6.00 \times 10^{-5} \text{ m}^3/\text{s}$ and $H = 0.5 \text{ m}$

C_o (ppm)	C_o (eq/m ³)	t_b (s)	C_b (eq/m ³)
80	0.7722	651	0.387
100	0.9653	521	0.483
120	1.1583	434	0.579

From the present result, as the influent concentration increases, the breakthrough time would be short which could be due to the early saturation of the adsorbent. As mentioned by Cruz-Olivarez *et al.* (2013), the high steepness of the breakthrough curve indicates that the bed saturates rapidly at a much higher influent concentration which would decrease the volume treated. This low inlet concentration causes slow transport of lead ions from the film layer to the surface due to lower concentration, which implies decreased mass transfer driving force and diffusion coefficient (Cruz-Olivarez *et al.*, 2013).

From one of the governing equations used in the simulation as in Eqn. (13), the influent concentration is an essential factor in the rate of metal uptake of the biosorbent. The difference in the concentration also pertains to the driving force of the solution. As shown in the relation, as the difference between the equilibrium ion concentration in the liquid phase and the ion concentration in the resin increases, the uptake rate of the biosorbent also increases and vice versa. It shows that the biosorbent would be easily saturated and achieve its breakthrough time if the influent concentration is high.

$$\frac{\partial w_k}{\partial t} = MTC_{sk}(w_k^* - w_k) \quad (13)$$

where MTC_{sk} is the solid film mass transfer coefficient, w_k^* is the ion loading in equilibrium with liquid phase ion concentration, and w_k is the ion loading.

Ion-Exchange Mechanism

Based on the description given by Aspen Adsorption software, in an ion exchange process, the aqueous solution containing cations and anions is contacted with an ion-exchange resin which is typically inside a packed bed adsorption column. The bamboo shoots are composed primarily of functional groups, which are carboxylic acid and hydroxyl (Asberry *et al.*, 2014; Wang *et al.*, 2012a and Zhang *et al.*, 2012). The functional groups present carry positive and negative charges accompanied by displaceable ions of opposite charge (counterions) which have the same charge as the ions of interest in the fluid phase, in which the metal ions primarily reside. Since the ions in the fluid phase have a greater affinity to the functional groups present, the counterions present would be displaced (Sheng *et al.*, 2004). The diagram of the ion exchange mechanism can be

observed from Figure 6, as shown below.

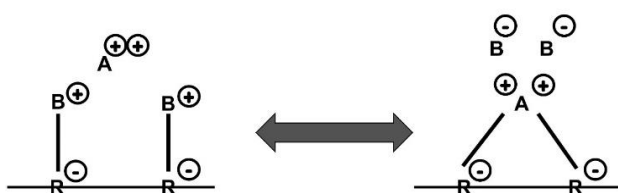


Fig. 6: Schematic diagram of ion exchange mechanism by Aspen Adsorption V8.4.

As shown in Figure 6, R would be represented as the bound group. At the same time, B is the counterion of the ion-exchanger surface, and A refers to the ionic component of the solution, in this case, the metal ion. It can be observed from the diagram that the resin has a fixed total capacity, so one ionic solute is exchanged for another while maintaining charge neutrality. Here, the ion exchange mechanism is reversible in the same way as adsorption. Hence the adsorbent is regenerative (Sheng et al., 2004).

The adsorbent (bamboo shoot) contains two counterions which are K^+ and Zr^{4+} , which indicates that the biosorption mechanism involved in lead (II) removal is an ion-exchange mechanism (Nieva, 2015). The counterions are metal ions that are attached to the sites of the biosorbent and heavy metal ions are replacing them, in this case is the Pb^{2+} ions. Several properties of the counterions and the heavy metal ion were evaluated, such as their ionic radius, hydrated ionic radius, and Pauling's electronegativity to know which of the site between the two counterions the heavy metal ion would likely attach.

As presented in Table 6, the ionic radius of K^+ counterion is larger compared to the Zr^{4+} counterion. Still, the valence electron plays a vital role in adsorption, and the Zr^{4+} counterion has a greater valence electron than K^+ counterion. The greater the valence

electron, the greater also the adsorption of ions. (Arshadi et al., 2014).

Table 6. Properties of selected metal ions (CRC Handbook of Chemistry and Physics, 2009)

Metal Ion	Ionic Radius (Å)	Hydrated Ionic Radius (Å)	Pauling's Electronegativity
Pb^{2+}	1.19	4.01	2.33
Zr^{4+}	0.720	4.79	1.33
K^+	1.38	3.31	0.82

Hydrated radius is the size of the water molecule compared to normally stabilizing cations that causes physical expansions of the biosorbent which causes reduced permeability. The enlargement of the biosorbent can also affect the discharge of other embedded materials to the pore walls, thus, allowing additional linking or blocking in the pore walls (Nieva, 2015). From Table 2.3, the hydrated radius of Zr^{4+} is greater than the hydrated radius of the K^+ . The hydrated radius of Zr^{4+} is also larger than the hydrated radius of the heavy metal ion Pb^{2+} , and it allows the heavy metal ion to easily exchange with the Zr^{4+} counterion. When the ion's hydration is smaller than the counterion, ion exchange is easier, and adsorption is greater (Arshadi et al., 2014).

Lastly, the electronegativity of Zr^{4+} counterion is larger compared to that of the electronegativity of K^+ counterion. The greater the value of the electronegativity of an ion, the greater it would attract other ions (Whitten et al., 2010). In this case, the Pb^{2+} ion would most likely attract to the Zr^{4+} counterion because the Zr^{4+} ions have a higher electronegativity than K^+ ions, thus having more electronegative force for the Pb^{2+} ion to be attracted.

CONCLUSION

The adsorption of lead (II) ions using bamboo shoots (*bambusa spp.*) was significantly affected by volumetric flow rate, column bed height, and initial sorbate concentration. A good indication of a good adsorption capacity is the ability to have a longer breakthrough time. This implies that the bamboo shoots can be used for a long period time until the Pb (II) metal ions saturate the biosorbent and are subjected to replacement or regeneration. The breakthrough time depends on several factors such as volumetric flow rate, initial sorbate concentration, bed height, particle size of the biosorbent and sorbate, the pH of the solution, temperature, and the properties of the biosorbent material used.

Based on the results, increasing the volumetric flow rate and the initial sorbate concentration achieve the breakthrough time faster, and the maximum biosorption capacity of the Pb (II) ions on the biosorbent increases. The biosorbent saturates faster due to decreased contact time between the biosorbent and the sorbate. There are also lower removal capacities observed as the volumetric flow rate and the initial sorbate concentration increases, probably due to the insufficient contact times between the metal ions and the biosorbent for the adsorption equilibrium to be fully developed. Increasing the bed height of the column, the longer the time to achieve the maximum adsorption capacity of sorbate on the biosorbent. It is due to more available binding sites for removing the sorbate and having a longer time for the biosorbent to be saturated. The slowest breakthrough time in the study was 3120 s with a volumetric flow rate of $2.00 \times 10^{-5} \text{ m}^3/\text{s}$, initial sorbate concentration of 20 ppm and a column bed height of 1.0 m. The fastest

breakthrough time in the study was 16.1 s with a volumetric flow rate of $2.00 \times 10^{-3} \text{ m}^3/\text{s}$, initial sorbate concentration of 200 ppm, and a column bed height of 0.2 m.

The simulation study presented in this paper, particularly the continuous biosorption of heavy metals like lead, can be an important tool in the actual implementation of wastewater treatment and will open opportunities for enhancing the design parameters of separation process equipment.

NOMENCLATURE

C_{eq}	: equilibrium concentration
q_{eq}	: equilibrium adsorption capacity
q_{max}	: maximum adsorption capacity
b	: equilibrium constant of Eqn. (1)
ρ_b	: bulk density of the biosorbent
V_{pore}	: pore volume of the biosorbent
ρ_{part}	: particle density of the biosorbent
Ei	: interparticle voidage
Ep	: particle porosity
Q	: total resin capacity
C_{pb}	: concentration of Pb(NO ₃) ₂ in equivalence per mole
m_b	: biosorbent mass
D	: bed diameter
H	: bed height
Sh	: Sherwood number
Re	: Reynolds number
Sc	: Schimdt number
u	: fluid velocity
ρ	: fluid density
u	: fluid velocity
μ	: fluid viscosity
ε	: bed voidage
ν	: fluid kinematic viscosity
k_f	: external mass transfer coefficient
d_p	: particle diameter
D_{AB}	: ionic diffusion in water
z_+	: cation's charge
z_-	: anion's charge

- D_+ : cation's individual diffusion in water
- D_- : anion's individual diffusion in water

REFERENCES

- Aftab, K., Akhtarm, K., and Jabbar, A., 2014. "Batch and column study for Pb-II remediation from industrial effluents using glutaraldehyde-alginate-fungi bio composites." *Ecol. Eng.*, 73, 319-325.
- Albadarin, A., Al-Muhtaseb, A.H., and Al-laqtah, N.A., 2011. "Biosorption of toxic chromium from aqueous phase by lignin: mechanism, effect of other metal ions and salts." *Chem. Eng. J.*, 169, 20-30.
- Annadurai, G., Juan, R.S., and Lee, D.J., 2003. "Adsorption of heavy metals from water using banana and orange peels." *Water Sci. Technol.*, 47, 185-190.
- Apiratikul, R., and Pavasant, P., 2008. "Batch and column studies of biosorption of heavy metals by *Caulerpa lentillifera*." *Bioresour. Technol.*, 99, 2766-2777.
- Arshadi, M., Amiri, M.J., and Mousavi, S., 2014. "Kinetic, equilibrium and thermodynamic investigations of Ni(II), Cd(II), Cu(II) and Co(II) adsorption on barley straw ash." *Water Resour. Ind.*, 6, 1-17.
- Asberry, H.B., Kuo, C.Y., Gung, C.H., Conte, E.D., and Suen, S.Y., 2013. "Characterization of water bamboo husk biosorbents and their application in heavy metal ion trapping." *Microchem. J.*, 113, 59-63.
- Asano & Burton, F., 2007. *Water Reuse: Issues, Technologies, and Applications*. McGraw-Hill.
- Bhaumik, M., Choi, H.J., Seopela, M.P., McCrindle, R.I., and Maity, A., 2014. "Highly effective removal of toxic Cr (VI) from wastewater using sulfuric acid-modified avocado seed." *Ind. Eng. Chem. Res.*, 53, 1214-1224.
- Blethen, C., Miles, C., and Alleman, G.P., 2001. Washington State University Cooperative Extension and the American Bamboo Society, WSU Extension Bamboo Research.
- Cecil, K.M., Brubaker, C.J., Adler, C.M., Dietrich, K.N., Altaye, M., Egelhoff, J.C., Wessel, S., Elangovan, I., Hornung, R., Jarvis, K., and Lanphear, B.P., 2008. "Decreased brain volume in adults with childhood lead exposure." *PLOS Med.*, 5, e112.
- Costa, J.F.D., Vilar, V.J.P., Botelho, C.M.S., da Silva, E.A.B., and Boaventura, R.A.R., 2010. "Application of the Nernst-Planck approach to lead ion exchange in Ca-loaded *Pelvetia canaliculate*." *Water Res.*, 44, 3946-3958.
- CRC (2009). *Handbook of Chemistry and Physics*. CRC Press, New York
- Cruz-Olivares, J., Perez-Alonso, C., Barrera-Diaz, C., Urena-Nunez, F., and Chaparro-Mercado, M.C., 2013. "Modeling of lead (II) biosorption by residue of allspice in a fixed-bed column." *Chem. Eng. J.*, 228, 21-27.
- da Rosa, C.A., Ostroski, I.C., and Meneguim, J.G., 2014. "Study of Pb²⁺ adsorption in a packed bed column of bentonite using CFD." *Appl. Clay Sci.*, 104, 48-58.
- De Luna, M.S., Navarrete, I.A., Adornado, A.P., Tayo, L.L., Soriano, A.N., Rubi, R.V.C., 2023. "Influence of nutrient supplement in the single heavy metal (Pb⁺², Cd⁺², Cr⁺³) uptake and mineral nutrients absorption by water kangkong (*Ipomoea aquatica forsk*)."

- Applied Science and Engineering Progress*, 16(2), 1-20.
- Diniz, V., Weber, M.E., Volesky, B., and Naka, G., 2007. "Column biosorption of lanthanum and europium by *Sargassum*." *Water Res.*, 42, 363-371.
- Duranoglu, D., Trochimczuk, A.W., and Beker, U., 2012. "Kinetics and thermodynamics of hexavalent chromium adsorption onto activated carbon derived from acrylonitrile-divinylbenzene copolymer." *Chem. Eng. J.*, 187, 193-202.
- Foo, K.Y. & Hameed, B.H., 2010. "Insights into the modeling of adsorption isotherm systems." *Chem. Eng. J.*, 156, 2-10.
- Fu, F., & Qi, W., 2011. "Removal of heavy metal ions from wastewaters: A review." *J. Environ. Manage.*, 92, 407-418.
- Gallarte, B., 2014. Cd (II), Cu (II), and Pb (II) Simulated Adsorption by *Sargassum cristaefolium*: Affinity, Competitiveness, and Selectivity. Master's Thesis. School of Chemical Engineering and Chemistry, Mapúa Institute of Technology.
- Geankoplis, C., 2004. Principles of Momentum Transfer and Overall Balances. In C. Geankoplis, Chapter 2 : Principles of Transport Processes and Separation Processes (pp. 34-120)., Pearson Education Inc, New Jersey.
- Goel, J., Kadirvelu, K., Rajgopal, C., and Garg, V.K., 2005. "Removal of lead (II) by adsorption using treated granular activated carbon: Batch and column studies." *J. Hazard. Mater.*, 125, 211-220.
- Gopal, N., Asaithambi, M., Sivakumar, P., and Sivakumar, V., 2014. "Adsorption studies of a direct dye using polyaniline coated activated carbon prepared from *Prosopis juliflora*." *J. Water Process Eng.*, 2, 87-95.
- Gupta V.K., & Ali, I., 2003. "Removal of lead and chromium from wastewater using bagasse fly ash – a sugar industry waste." *J. Colloid Interface Sci.*, 271, 321-328.
- Elizalde-Gonzalez, M.P., Mattusch, J., Pelaez-Cid, A.A., and Wenrich, R., 2006. "Characterization of adsorbent materials prepared from avocado kernel seeds: Natural, activated and carbonized forms." *J. Anal. Appl. Pyrolysis.*, 78, 185-193.
- Hasan, S.H., and Srivastava, T.M., 2009. "Biosorption of lead using immobilized *Aeromonas hydrophila* biomass in up flow column system: Factorial design for process optimization." *J. Hazard. Mater.*, 177, 312-322.
- Hossain, M.A., Ngo, H.H., Guo, W.S., Nghiem, L.D., Hai, F.I., Vigneswaran, S., and Nguyen, T.V., 2014. "Competitive adsorption of metals on cabbage waste from multi-metal solutions." *Bioresource Technol.*, 160, 79-88.
- Issabayeva, G., Aroua, M.K., and Sulaiman, N.M., 2007. "Continuous adsorption of lead ions in a column packed with palm shell activated carbon." *J. Hazard. Mater.*, 155, 109-113.
- Kumari M., Pittman Jr, C.U., and Mohan, D., 2014. "Heavy metals [chromium (VI) and lead (II)] removal from water using mesoporous magnetite (Fe₃O₄) nanospheres." *J. Colloid Interface Sci.*, 442, 120-132.
- LeVan, M., & Carta, G., 2007. Section 16: Adsorption and Ion Exchange. In D. Green, & R. Perry, *Perry's Chemical*
-

-
- Engineers' Handbook, 8th Edition* (pp. 1-69). McGraw-Hill, New York.
- Lim, A.P., and Aris, A.Z., 2014. "Continuous fixed-bed column study and adsorption modelling: Removal of cadmium (II) and lead (II) ions in aqueous solution by dead calcareous skeletons." *Biochem. Eng. J.*, 87, 50-61.
- Liu, Y., 2005. "Some consideration on the Langmuir isotherm." *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 274, 34-36.
- Lopez-Garcia, M., P. Lodeiro, J.L., Barriada, R. Herrero, and M.E. Sastre de Vicente, 2010. "Reduction of Cr (VI) levels in solution using bracken fern biomass: Batch and column studies." *Chem. Eng. J.*, 165, 517-523.
- Mehdipour, S., V. Vatanpour, and H.R. Kariminia, 2015. "Influence of ion interaction on lead removal by a polyamide nanofiltration membrane." *Desalination*, 362, 84-92.
- Nieva, A.D., 2015. Biosorption of heavy metals, organic contaminants, and oxyanions in aqueous solution using agricultural residues. Dissertation, Mapúa Institute of Technology.
- Papirio, S., Frunzo, L., Mattei, M.R., Ferraro, A., Race, M., D'Acunto, B., Pirozzi, F., and Esposito, G., 2017. Heavy metal removal from wastewaters by biosorption: mechanism and modeling, In: Rene, E., Sahinkaya, E., Lewis, A., Lens, P. (eds) Sustainable Heavy Metal Remediation. Environmental Chemistry for a Sustainable World, vol 8. Springer, Cham. 58622-9_2
- Perry, D.W. and Southard, M.Z., 2009. Perry's Chemical Engineering Handbook. McGraw Hill Education, New York.
- Prassad, M., H.Y. Xu, and S. Saxena, 2007. "Multi-component sorption of Pb(II), Cu(II) and Zn(II) onto low-cost mineral adsorbent." *J. Hazard. Mater.*, 154, 221-229.
- Ruthven, D.M., 1984. Principles of Adsorption and Adsorptive Processes. John Wiley and Sons, New York.
- Seader, J.D., Henley, E.J., and Roper, D.K., 2010. Separation Process Principles, 3rd Editio. John Wiley and Sons, New York.
- Sheng, P.X., Y.P. Ting, Chen, J.P. and Hong, L., 2004. "Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms." *J. Colloid Interface Sci.*, 275, 131-141.
- Simate, G.S., and Ndlovu, S., 2014. "The removal of heavy metals in a packed bed column using immobilized cassava peel waste biomass." *J. Ind. Eng. Chem.*, 21, 635-643.
- Slater, M.J., 1991. The Principles of Ion Exchange Technology, Butterworth, Heinemann, Boston.
- Srivastava, N.K., and Majumder, C.B., 2008. "Novel biofiltration methods for the treatment of heavy metals from industrial wastewater." *J. Hazards. Mater.*, 151, 1-8.
- Sun, X.F., Imai, T., Sekine, M., Higuchi, T., Yamamoto, K., Kanno, A., and Nakazono, S., 2013. "Adsorption of phosphate using calcined Mg₃-Fe layered double hydroxides in a fixed-bed column study." *J. Ind. Eng. Chem.*, 20, 3623-3630.
- Taty-Costodes, V.C., Fauduet, H., Porte, C., and Ho, Y., 2005. "Removal of lead (II) ions from synthetic and real effluents using immobilized *Pinus sylvestris* sawdust: Adsorption on a fixed-bed
-

- column." *J. Hazard. Mater.*, *123*, 135-144.
- Wang, Y., Wang, X., Wang, X., Liu, M., Yang, L., Wu, Z., Xia, S., and Zhao, J., 2012a. "Adsorption of Pb (II) from aqueous solution to Ni-doped bamboo charcoal." *J. Ind. Eng. Chem.*, *19*, 353-359.
- Wang, Y., Wang, X., Wang, X., Liu, M., Yang, L., Wu, Z., Xia, S., and Zhao, J., 2012b. "Adsorption of Pb (II) in aqueous solutions by bamboo charcoal modified with KMnO₄ via microwave irradiation." *Colloids and Surfaces A; Physicochem. Eng. Aspects*, *414*, 1-8.
- Weber, T.W., and Chakkravorti, R.K., 1974. "Pore and solid diffusion models for fixed bed adsorbers." *Am. Inst. Chem. Eng. J.*, *20*, 228-234.
- White, L.D., Cory-Slechta, D.A., Gilbert, M.E., Tiffany-Castiglioni, E., Zawia, N.H., Virgolini, M., Rossi-George, A., and Lasley, S.M., 2007. "New and evolving concepts in the neurotoxicology of lead." *Toxicol. Appl. Pharmacol.*, *225*, 1-27.
- Whitten, K., Davis, R., Pack, L., & Stanley, G., 2010. Chapter 5 : Chemical Periodicity. In K. Whitten, R. Davis, L. Pack, & G. Stanley, *Chemistry*, 9th Edition (pp. 190-192). Cengage Learning, Belmont, CA
- Xu, Z., Cai, J., and Pan, B., 2013. "Review: Mathematically modeling fixed-bed adsorption in aqueous systems." *Appl. Phys. Eng.*, *14*, 155-176.
- Xuan, Z. Tang, Y., Li, X., Liu, Y., and Luo, F., 2006. "Study on the equilibrium, kinetics and isotherm of biosorption of lead ions onto pretreated chemically modified orange peel." *Biochem. Eng. J.*, *31*, 160-164.
- Yildez, S., 2017. "Artificial neural network (ANN) approach for modelling Zn(II) adsorption in batch process." *Korean J. Chem. Eng.*, *34(9)*, 2423-2434.
- Zhang, Z., Wang, X., Wang, Y., Xia, S., Chen, L., Zhang, Y., and Zhao, J., 2012. "Pb (II) removal from water using Fe-coated bamboo charcoal with the assistance of microwaves." *J. Environ. Sci.*, *25*, 1044-1053.
-