AJChE 2016, Vol. 16, No. 1, 23 – 37

# Packed Bed Biosorption of Lead and Copper Ions Using Sugarcane Bagasse

***Norwin Dale F. Duga*** [1]
***Pauline Edrickke A. Imperial*** [1]
***Allan N. Soriano*** [1]
***Aileen D. Nieva*** *, [1]

[1] *School of Chemical Engineering and Chemistry, Mapúa Institute of Technology, Manila*
**e-mail:* adnieva@mapua.edu.ph

Bagasse, a waste material from sugarcane has been studied as a biosorbent for removing heavy metals, $Pb^{2+}$ and $Cu^{+2}$, in a continuous system using a packed bed column. This study was undertaken to determine the influence of varying the bed height and flow rate on the breakthrough and saturation time. Thomas, Adams-Bohart and Yoon-Nelson models were used to assess the effects of varying parameters and both Thomas and Yoon-Nelson models were found to be satisfactory to describe the column data obtained in the experiment. Moreover, lead ions are adsorbed more efficiently with an adsorption capacity of 4.54 mg/g compared to copper ions with 3.98 mg/g at the most feasible parameters having a flow rate of 100 mL/min and a bed height of 30 cm.

**Keywords:** biosorption; heavy metal; continuous system; packed bed column; sugarcane

## INTRODUCTION

Lead and copper are two of the major heavy metal contaminants affecting the water as a consequence of rapid industrialization. Lead is utilized in the production of ceramic products, paints, metal alloys, batteries, and solder. Toxicological effects of lead in humans include inhibition of hemoglobin formation (anemia), sterility, hypertension, learning disabilities, abortion, kidney damage, and mental retardation (Mudipalli, 2007). Copper is mostly released from mining, steel and semiconductor production. Ingestion of copper can cause irritation of the nose, mouth and eyes and it causes stomachaches, dizziness, vomiting and diarrhea. Biosorption process is one among the new competitive and efficient alternative used for the removal of heavy metals from wastewater. It generated promising results due to its high metal binding capacity, low operational cost, high efficiency in dilute effluents and environmental friendliness (Volesky et al., 2000). Numerous investigators observed that rich-fiber agricultural wastes could serve as biosorbents. These agro-wastes biosorbents are currently receiving wide attention because of their abundant availability and relatively high fixed carbon content and a porous structure.

Furthermore, they also address the issues in solid wastes and have simpler approach in removing heavy metals in wastewater (Blazquez et al., 2011; Khormaei et al., 2007; Ofomaja et al., 2011).

Agricultural wastes are largely composed of cellulose, hemicelluloses, lignin, condensed tannins and structural proteins that have good potential as metal scavengers from solutions and wastewaters since they contain functional groups of carboxylate, aromatic carboxylate, phenolic, and hydroxyl groups (Brown et al., 2000). Sugarcane bagasse, a by-product of cane sugar processing, has been used in previous studies as an agro-based biosorbent. Its compositions such as cellulose, hemicellulose and lignin, which have abundant carboxyl functional groups, can strongly bind metal cations in aqueous solution enabling sugarcane bagasse to become a suitable biosorbent (Aksu & Isoglu, 2005). However, batch process biosorption is not applicable in industrial operations of wastewater treatment and treating the material can be costly for a large scale purpose to increase its adsorptive capacity. A continuous fixed bed column can be used in order to evaluate more the applicability of sugarcane bagasse in industrial wastewater biosorption operation. The fixed bed adsorption processes utilize a solid mass separating agent packed inside a column to separate one or more components from a fluid stream as it flows through the packed bed. It is conducted to evaluate the column performance in terms of the adsorptive characteristics which and is usually described using breakthrough curves indicating the specific combination of equilibrium and rate factors that control process performance.

This study intends to assess the performance of sugarcane bagasse as a biosorbent by determining the effects on varying the bed height and flow rate in a continuous system and also to determine the effect of the combination of varying parameters. The continuous process involved a fixed bed column that is packed with the biosorbent.

The results of this study can contribute in the search of less expensive biosorbents which may be useful in modeling and designing an economical, effective and eco-friendly alternative in removing toxic materials from industrial effluent. Moreover, this is to enhance the existing batch studies to large scale biosorption of heavy metals particularly using sugarcane bagasse as a biosorbent. Current understanding and perspectives pertaining to applications of this study on laboratory and on industrial scale as well as environmental protection can be supported and enhanced as well.

The system of the study involved two heavy metal contaminants, lead and copper and sugarcane bagasse as the biosorbent. It focused only on continuous adsorption process using the existing batch process experiments as reference. The models used for describing the breakthrough curves are Adams-Bohart, Thomas, and Yoon-Nelson models only. Optimization of the data was based on two factors, namely, bed height and volumetric flow rate.

## METHODS

### Preparation of the Adsorbate

Stock solutions of of $Pb^{+2}$ and $Cu^{+2}$ were prepared separately from $Cu(NO_3)_2$ and $Pb(NO_3)_2$ in distilled water. The pH of the solution was then adjusted to the desired pH of 5.0 and 6.0 for copper and lead, respectively, by addition of 0.1 M NaOH or 0.1 M HCl solution in order to prevent co-precipitation at higher pH. The pH of the sorbate solution is also based on the optimum pH required to achieve maximum adsorption.

### Preparation of Adsorbent

Raw sugarcane bagasses were collected from Central Azucarera de Tarlac in Tarlac City. The adsorbent was washed several times to remove unnecessary substances and dried in oven at 70°C for 24hrs. Dried materials were ground and sieved into a particle size of 30 mesh screen.

### Characterization of adsorbent

The surface properties of sugarcane bagasse was analyzed using zeta potential (ZP) analyzer (ZEN3600, MALVERN Nano-ZS) to determine surface charges, and elemental analysis (HORIBA 7021H) was used to determine elemental composition.

### Continuous system studies

Sugarcane bagasse was packed up to the desired bed height in water filled column and was kept submerged throughout the runs to avoid air entrapment in the bed. The synthetic wastewater was pumped by a centrifugal pump from the storage tank of lead and copper contaminated water (separate system). Room temperature will be at ambient temperature. The samples are collected every 10 minutes until there are no more changes in concentration. The final metal ion concentrations will be determined using Atomic Absorption Spectrometry (AAS). Shown in Table 1 are the bed heights and flow rates varied in the experiment.

**Table 1. Parameters to be varied for SB-Pb and SB-Cu systems**

| Bed Height (cm) | Flow Rate (mL/min) |
|---|---|
| 10 | 100 |
| | 150 |
| | 200 |
| 20 | 100 |
| | 150 |
| | 200 |
| 30 | 100 |
| | 150 |
| | 200 |

Figure 1 below shows the Biosorption Equipment Set-up.

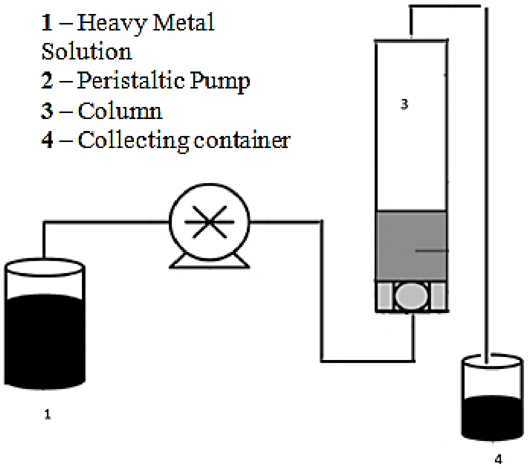

**Fig. 1: Biosorption Equipment Set-Up**

**Table 2. Summary of Optimum Parameters Used in Column Study**

| Parameter | Value | Source/s |
|---|---|---|
| Adsorbate Concentration (mg/L) | | |
| Lead | 20 | Nieva, unpublished |
| Copper | 18 | Nieva, unpublished |
| pH | | |
| Lead | 6.0 | Han et al. (2006); Tasar et al. (2014); Momčilović et al. (2011) |
| Copper | 5.0 | Han et al. (2006); Blazquez et al. (2012); Khormaei et al. (2007) |

The flow rates were based from the minimum flow rate requirement for the ion exchanger set-up used. Only an increment of 50 mL each was applied since large amount of water would be needed and large amount of wastewater would be generated for long periods of time. The bed heights used were based from the minimum required column diameter-to-height ratio of ½. Since the column has a diameter of 5 cm, the minimum bed height starts from 10 cm with an increment of 10 cm until half of the column capacity is reached. Table 2 shows the optimum parameters utilized in this column study.

## RESULTS AND DISCUSSION

### Composition of sugarcane bagasse

The nature of the counterion/s present in their elemental composition on the surface of the biosorbent plays an important role to its adsorptive performance. The transition-metal ion present in the aqueous sorbate solution can undergo ion-exchange with the counterion/s available on the surface of the biosorbent during the adsorption process. The nature and properties of the available counterions on the surface of the sugarcane bagasse would dictate whether it is suitable for the sequestration of lead and copper ions. Some of the properties considered are the ionic radius, hydrated radius and electronegativity of the counterion present on the surface of the adsorbent. Table 3 shows the zeta-potential elemental analysis of the biosorbent (SB) identifying the possible counterions that may undergo ion-exchange mechanism with lead and copper ions.

**Table 3. Elemental Composition of Sugarcane Bagasse in (%) (Nieva, unpublished)**

| Biosorbent | C | O | K |
|---|---|---|---|
| **SB** | 59.08 | 40.06 | 0.86 |

Based from the elemental composition, $K^+$ is the counterion present on the surface of SB. The properties of $K^+$ is now compared with the properties of $Pb^{2+}$ and $Cu^{2+}$ to determine whether ion-exchange can occur during the biosorption process.

**Table 4. Summary of Optimum Parameters Used in Column Study**

| Composition | Ionic Radius , Å | Pauling's Electronegativity | Hydrated Ionic radius, Å |
|---|---|---|---|
| $K^+$ | 1.38 | 0.82 | 3.31 |
| $Pb^{2+}$ | 1.19 | 2.33 | 4.01 |
| $Cu^{2+}$ | 0.73 | 1.9 | 4.19 |

This comparison is summarized on Table 4.

$K^+$ has a larger ionic radius of 1.38 Å compared to that of $Pb^{2+}$ and $Cu^{2+}$ with 1.19 Å and 0.73 Å, respectively. Both ions are able to fit readily through the pores of SB as ion exchange process occurs. Metal ions with larger radii than the counterion tend to saturate the adsorbent faster than ions with smaller ones making the adsorbent ineffective for its purpose. Ions with smaller radii have high electrostatic bond strength, and therefore are likely to attach strongly to an oppositely charged solid surface, whereas ions of low charges and larger radii form relatively weaker electrostatic bonds. However, electronegativity also plays an important role in making $Pb^{2+}$ adsorbed more effectively than $Cu^{2+}$. The law of electronegativity states that as the difference between the electronegativity of the ions increases, the power of an atom in a molecule to attract electrons to itself increases. The difference between the electronegativity of $K^+$ and $Pb^{2+}$ is 1.51 which is higher compared to that of the $Cu^{2+}$ which is 1.08.

Hydration of an ion depends on the electrostatic attraction of water molecules to the ion. Hydrated radius is the size of the water molecule in comparison to normally stabilizing cations that leads to physical expansions of the biosorbent which causes reduction in the permeability. The $Pb^{2+}$ has a hydrated radius of 4.01 Å which is lower than that of $Cu^{2+}$ which is 4.19 Å but both are higher than the hydrated radius of the counterion, $K^+$ (3.31 Å) which could explain why sugarcane bagasse could easily be saturated for only a short period of time. Data consistently show that $Pb^{2+}$ was adsorbed more efficiently than $Cu^{2+}$ due to its lower hydrated radius. When the ion's hydration is smaller than the counterion, ion exchange is easier and adsorption is greater. The smaller ions hold the water molecules more strongly which is true with the given data. $Cu^{2+}$ has a smaller radius than $Pb^{2+}$ but $Cu^{2+}$ holds more water molecules which increase its hydrated radius but ions with strong hydration bonds may not be able to detach from the hydration layers and may be too large to pass through the adsorbent's openings. However, the ions with weak hydration bonds can lose some or all the water of hydration and can fit through.

The potential ion exchange mechanism of the counterion $K^+$ with sorbate ions $Pb^{2+}$ but $Cu^{2+}$ is shown in Figure 2.

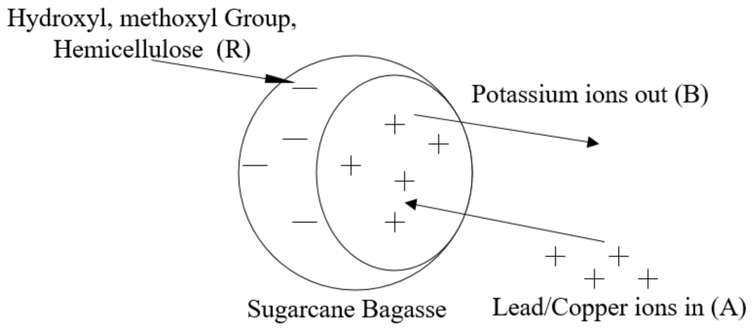

**Fig. 2: Ion Exchange Mechanism in $Cu^{2+}$ and $Pb^{2+}$ Adsorption to SB**

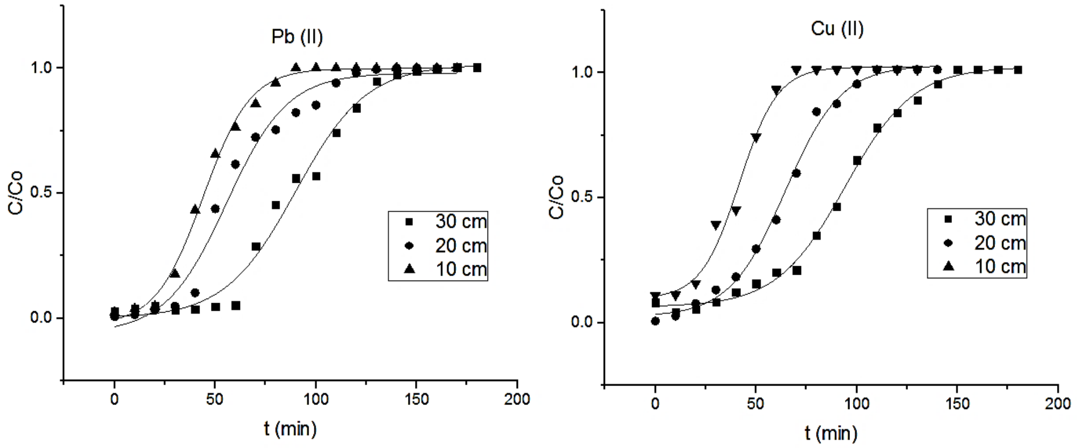

**Fig. 3: Constant Flow Rate (100mL/min), Constant Co, Varying Bed Height**

Equation 1 describes the reaction that takes place during adsorption process.

$$A + mBR \leftrightarrow Arm + mB \qquad (1)$$

where $A$ is the heavy metal ion in the solution ($Cu^{2+}$ and $Pb^{2+}$), m is the stoichiometric coefficient, R is the functional group present in the adsorbent and B is the counterion having the same charge with the metal ions in the sorbate solution.

## Column Studies

### *Effect of varying bed height*

Based on Figure 3, the breakthrough times for the bed heights of 10, 20 and 30 cm for $Pb^{2+}$ adsorption are 70, 100 and 130 minutes, respectively while for $Cu^{2+}$ adsorption are 50, 61 and 89 minutes, respectively. The increase in breakthrough time is observed as the bed height increases from 10 cm to 30 cm for both systems. The increase of breakthrough time is due to higher amount of adsorbent dose in column with higher bed height, which provides greater functional sites and broadened mass transfer zone for lead and copper adsorption.

As shown in Equation 2, breakthrough time is directly proportional to the amount of adsorbent in the column. The active surface of the biosorption column which is where biosorption occurs is the mass transfer zone. Increasing the dosage of SB increases the bed height in the column

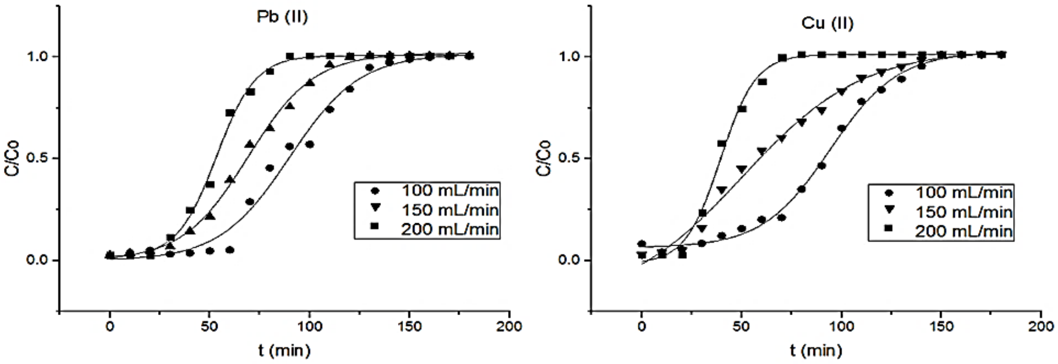

**Fig. 4: Constant Bed Height (30 cm), Constant Co (20 ppm), Varying Flow Rate**

which results to an increase in the number of active sites that promote mass transfer. This principle can be related to the breakthrough capacity of the adsorbent as shown in Equation 2.

$$Breakthrough\ capacity = \frac{metal\ adsorbed\ on\ adsorbent\ (mg)}{mass\ of\ adsorbent\ in\ bed\ (g)} = \frac{(breakthrough\ time)(flowrate)(feed\ concentration)}{(mass\ of\ adsorbent\ in\ bed)} \qquad (2)$$

### *Effect of Varying Volumetric Flow Rate*

Based on Figure 4, the breakthrough for the flow rates of 100, 150 and 200 ml/min for $Pb^{2+}$ adsorption are 170, 130 and 80 minutes, respectively while for $Cu^{2+}$ adsorption are 89, 65 and 33 minutes, respectively. Longer breakthrough curves are observed when running on the minimum flow rate of 100 ml/min while shortest breakthrough curve time on 200 ml/min for all variation of bed heights. The breakthrough time decreases with the increase of flow rate since more $Pb^{2+}$ and $Cu^{2+}$ are only able to exchange with the counterions in a shorter period of time. The property of the counterion in terms of its high electrostatic bond strength is minimized as flow rate increases. This implies that it would take a longer time for the sugarcane bagasse to be completely saturated at slow flow rates since decreasing the movement of the fluid decreases the flow of the ions entering the pores of the adsorbent resulting to a slower clogging of the adsorbent pores.

### *Nonlinear Curve Fitting: Boltzmann Function (Origin 8.1)*

Experimental data are plotted using Origin 8.1 software and Boltzmann function fit the points obtained with a coefficient of determination of 0.997 denoting the statistical measure of how close the data are to fit the graph as shown in Figure 5.

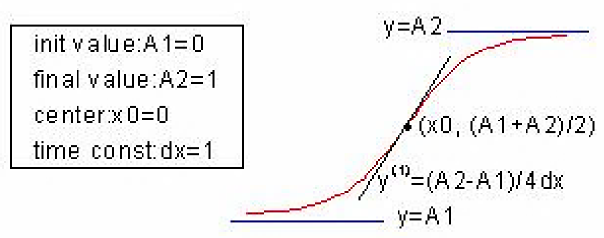

**Fig. 5: Sigmoidal Wave - Boltzmann Function (originlab.com)**

The curve converges at the 7th iteration and a Chi-Sqr tolerance value of 1E-9 was reached for all systems and combination of parameters performed. Shown in Equation 3 is the Boltzmann function used for the curve fitting.

$$y = \frac{A_1 - A_2}{1 + e^{(x - x_0)/dx}} + A_2 \qquad (3)$$

where $A_1$ and $A_2$ are the initial and final values of the fraction of the effluent and influent concentrations, respectively. The x values indicate the independent variable or time consumed as the adsorption process progresses and $x_o$ is the value of time at the center with set time constant (dx) of 1.

## Dynamic Adsorption Models

### *Adams – Bohart Model*

The Adams -Bohart model is based on the surface reaction theory which assumes that equilibrium is not instantaneous. Thus, the rate of the adsorption is proportional to the adsorption capacity which still remains on the sorbent. The Adam's–Bohart model is used for the description of the initial part of the breakthrough curve by estimation of characteristic parameters such as maximum adsorption capacity ($N_0$) and kinetic constant ($k_{AB}$) by using Equation 4:

$$ln(\frac{C_t}{C_o}) = k_{AB} C_o t - k_{AB} N_o (\frac{Z}{U_o}) \qquad (4)$$

where *No* is the saturation concentration (mg/L), *Z* is the bed depth of the fix-bed column (cm) and *Uo* is the superficial velocity (cm/min) defined as the ratio of the volumetric flow rate *Q* (ml/min) to the cross-sectional area of the bed *A* ($cm^2$) and *t* is the service time at breakthrough point.

Shown in Table 5 are the effects on the Adams - Bohart model parameters with respect to the change in flow rate and bed height. Values of determined coefficients ($R^2$) ranged from 0.79 to 0.96 and 0.70 to 0.97 for $Pb^{2+}$ and $Cu^{2+}$, respectively.

The increase of flow rate causes the Adams - Bohart constant, $k_{AB}$, to increase while the saturation concentration, *No*, to

**Table 5. Adams - Bohart Model Parameters**

| Bed Height | Flow rate | Lead | | | Copper | | |
|---|---|---|---|---|---|---|---|
| | | $k_{AB}$ | No | R2 | $k_{AB}$ | No | R2 |
| 10 | 100 | 2.29E-03 | 5.95E+05 | 0.90 | 1.21E-03 | 4.14E+05 | 0.70 |
| | 150 | 5.04E-03 | 6.02E+05 | 0.79 | 1.49E-03 | 3.82E+05 | 0.77 |
| | 200 | 7.92E-03 | 4.60E+05 | 0.88 | 1.60E-03 | 3.50E+05 | 0.76 |
| 20 | 100 | 1.01E-03 | 3.18E+05 | 0.87 | 1.02E-03 | 2.61E+05 | 0.92 |
| | 150 | 2.73E-03 | 2.38E+05 | 0.83 | 2.09E-03 | 2.13E+05 | 0.97 |
| | 200 | 4.19E-03 | 2.18E+05 | 0.96 | 4.32E-03 | 2.09E-03 | 0.90 |
| 30 | 100 | 1.30E-03 | 7.94E+04 | 0.90 | 1.21E-03 | 4.14E+05 | 0.94 |
| | 150 | 1.11E-03 | 7.50E+04 | 0.82 | 1.49E-03 | 3.82E+05 | 0.73 |
| | 200 | 2.10E-03 | 6.89E+04 | 0.92 | 1.60E-03 | 3.50E+05 | 0.77 |

decrease for both $Cu^{2+}$ and $Pb^{2+}$. Higher flow rate lowers the saturation concentration since as the ions are adsorbed vastly; it blocks the pathway of adsorption even if metal ions are not fully adsorbed internally. The pathway in the internal part of SB can also affect the adsorption process. This model implies that external mass transfer is governing the mass transfer process. Results also show that the increase in bed height accounts for decrease in $k_{AB}$ and increase in *No*. Higher values of saturation concentration are evident on $Pb^{2+}$. This implies that SB can hold higher concentrations of $Pb^{2+}$ more than $Cu^{2+}$ until it becomes saturated.

### *Thomas Model*

The Thomas model is one of the most widely used model in describing the behavior of the biosorption process in a fixed bed column. The basic assumptions of Thomas or reaction model are: (i) negligible axial and radial dispersion in the fixed bed column; (ii) the adsorption is described by a pseudo second-order reaction rate principle which reduces a Langmuir isotherm at equilibrium; (iii) constant column void fraction; (iv) constant physical properties of the biomass (solid-phase) and the fluid phase; (v) isothermal and isobaric process conditions; (vi) the intra particle diffusion and external resistance during the mass transfer processes are considered to be negligible. The Thomas model is suitable for adsorption process, which indicates that the external and internal diffusions are not the limiting steps as shown in Equation 5:

$$ln(\frac{C_o}{C_t} - 1) = \frac{k_{Th} q_o m}{Q} - k_{Th} C_o t \qquad (5)$$

where *Co* is the influent concentration, *Ct* is the effluent concentration, $k_{th}$ is the Thomas rate constant (mL/min/mg), $q_o$ is the adsorption capacity (mg/g), *Q* is the volumetric flow rate, *m* was the dry weight of adsorbent in the column and *t* stands for total flow time (min).

Evident from Table 6 are the effects on the Thomas model parameters with respect to the change in rate of flow and

**Table 6. Thomas Model Parameters**

| Bed height | Flow rate | Lead | | | Copper | | |
|---|---|---|---|---|---|---|---|
| | | $k_{th}$ | *qo* | $R^2$ | $k_{th}$ | *Qo* | $R^2$ |
| **10** | **100** | 4.50E-03 | 4.27 | 0.98 | 1.06E-03 | 3.64 | 0.92 |
| | **150** | 1.10E-02 | 4.21 | 0.93 | 3.61E-02 | 3.37 | 0.99 |
| | **200** | 1.60E-02 | 4.06 | 0.98 | 5.42E-03 | 2.48 | 0.97 |
| **20** | **100** | 3.36E-03 | 4.46 | 0.97 | 3.75E-03 | 3.93 | 0.98 |
| | **150** | 4.71E-03 | 4.32 | 0.94 | 4.41E-03 | 3.77 | 0.97 |
| | **200** | 7.62E-03 | 4.13 | 0.95 | 9.11E-03 | 3.30 | 0.98 |
| **30** | **100** | 1.76E-03 | 4.54 | 0.91 | 1.95E-03 | 3.98 | 0.94 |
| | **150** | 3.77E-03 | 4.32 | 0.87 | 2.82E-03 | 3.49 | 0.97 |
| | **200** | 4.26E-03 | 4.15 | 0.96 | 5.83E-03 | 3.29 | 0.90 |

**Table 7. Yoon – Nelson Model Parameters**

| Bed height | Flow Rate | Lead | | | Copper | | |
|---|---|---|---|---|---|---|---|
| | | $k_{yn}$ | $\tau$(min) | $R^2$ | $k_{yn}$ | $\tau$(min) | R2 |
| **10** | 100 | 0.086846 | 46.74 | 0.97 | 0.078648 | 50.23 | 0.92 |
| **10** | 150 | 0.149625 | 36.09 | 0.93 | 0.097523 | 23.95 | 0.99 |
| **10** | 200 | 0.283353 | 22.05 | 0.98 | 0.131156 | 19.21 | 0.97 |
| **20** | 100 | 0.065169 | 64.50 | 0.90 | 0.071811 | 60.66 | 0.98 |
| **20** | 150 | 0.086013 | 51.60 | 0.94 | 0.079397 | 43.26 | 0.97 |
| **20** | 200 | 0.133142 | 34.91 | 0.96 | 0.130809 | 36.69 | 0.97 |
| **30** | 100 | 0.062981 | 91.34 | 0.93 | 0.043867 | 89.29 | 0.96 |
| **30** | 150 | 0.075369 | 61.26 | 0.87 | 0.050823 | 65.07 | 0.97 |
| **30** | 200 | 0.085153 | 57.54 | 0.96 | 0.130630 | 33.07 | 0.90 |

bed height. Values of determined coefficients ($R^2$) ranged from 0.87 to 0.98 and 0.90 to 0.99 for $Pb^{2+}$ and $Cu^{2+}$ ions, respectively making this model more fit or suitable for the gathered data compared to the Adams-Bohart model.

The increase of flow rate causes the Thomas rate constant, $k_{TH}$, to increase and the adsorption capacity, $q_o$, to decrease for both $Cu^{2+}$ and $Pb^{2+}$. Higher flow rate affects the rate of adsorption by decreasing the contact time between the adsorbent and adsorbate which results to low removal of metals. Results also show that the increase in bed height accounts for decrease in $k_{TH}$ and increase in $q_o$. Bed height affects the driving force of adsorption. Higher bed height would result to increase of adsorption because there will be additional available sites. Higher values of capacity, $q_o$, are evident on $Pb^{2+}$. This implies that SB has higher capacity to adsorb $Pb^{2+}$ than $Cu^{2+}$. The favorability of adsorption of $Pb^{2+}$ is similar from the results of Adams-Bohart model.

### ***Yoon – Nelson Model***

The Yoon - Nelson is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent as shown in Equation 6:

$$ln(\frac{C_t}{C_o - C_t}) = k_{YN}t - \tau k_{YN} \qquad (6)$$

Table 7 shows that the Yoon - Nelson constant, $k_{YN}$, decreases and the time required for 50% adsorbate breakthrough, $\tau$, increases as the bed height increases.

The decrease in the rate constant is due to the increase of needed forces that control the mass transfer in the liquid phase that will cause the decrease in transfer rate of ions from the liquid to the solid phase. Higher bed height will cause more available sites of adsorption, thus, more time needed to be 50% saturated. The increase in flow rate cause the rate constant to increase and the time needed for 50% breakthrough to decrease. The fast transfer rate of ions from the liquid phase to the solid phase causes the sugarcane bagasse to be 50% saturated at a lower amount of time. Higher values of capacity, $q_o$, are evident on $Pb^{2+}$. This implies that SB has higher capacity to adsorb Pb ions than Cu ions. The favorability of adsorption of $Pb^{2+}$ is similar from the results of Adams-Bohart model.

## CONCLUSIONS

Adams-Bohart, Thomas and Yoon-Nelson models were used to analyze the effects of varying bed heights and flow rates to the break-through curve and adsorption parameters of SB for $Pb^{2+}$ and $Cu^{2+}$, and the following conclusions were derived: (1) Breakthrough time increases as the bed height increases from 10 cm to 30 cm for both systems; (2) The increase in flow rate increases the adsorption capacity, $q_o$, since contact time between the fluid and adsorbent decreases; (3) The time required for 50% adsorbate breakthrough, $\tau$, increases as the bed height increases; (4) Sugarcane bagasse possesses carboxylic acid groups, which acts as exchangeable cation sites, that promotes the adsorption capacity for metal ions; (5) $Pb^{2+}$ are adsorbed more effectively with an adsorption capacity of 4.54 mg/g than $Cu^{2+}$ with 3.98 mg/g at the most feasible parameters having a influent flow rate of 100 mL/min and a bed height of 30 cm; (6) In both systems studied, the performed continuous adsorption has higher adsorption capacity than that of the batch adsorption process obtained from literature.

## REFERENCES

1. Acheampong, M.A., Pakshirajan, K., Annachhatre, A.P., Lens, P.N.L. (2012). Removal of Cu(II) by biosorption onto coconut shell in fixed-bed column systems. *Journal of Industrial and Engineering Chemistry APCBEE Procedia*, 3, 255 – 263.
2. Ajmal, M., Rao, R.A.K., Anwar, S., Ahmad, J., Ahmad, R. (2003). Adsorption Studies on Rice Husk: Removal and Recovery of Cd (II) from Wastewater. *Bioresource Tech*., 86: 147-149.
3. Aksu, Z. and F. Gonen (2004). Biosorption of phenol by immobilized activated sludge in a continuous packed bed: Prediction of breakthrough curves. *Process Biochem*., 39: 599-613.
4. Aksu Z. abd Isoglu A.I. (2005). Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp. J. *Process Biochem*, 3031–3044.
5. Annadurai, G., Juang, R.S., Lee, D.J. (2002). Adsorption of heavy metals from water using banana and orange peels. *Water Science and Technology*, 47(1), 185-190.
6. Ayoob, S., A.K. Gupta and P.B. Bhakat (2007). Analysis of breakthrough developments and modeling of fixed bed adsorption system for As(V) removal from water by Modified Calcined Bauxite (MCB). *Sep. Purif. Technol*., 52: 430-438.
7. Bahadur, K. D., Paramatma, M. (2014).

Adsorptive Removal of Cr(VI) from Aqueous Solution by Sugarcane Biomass. *Research Journal of Chemical Sciences*., 4(5), 32-40.

8. Barka N., Abdennouri M., El Makhfouk M., Qourzal S. (2013). Biosorption characteristics of cadmium and lead onto eco-friendly dried cactus (Opuntia ficus indica) cladodes. *Journal of Environmental Chemical Engineering*,1, 144–149.
9. Blázquez G., Calero1 M., Hernáinz F., Tenorio G., Martín-Lara M.A. (2010). Equilibrium biosorption of lead(II) from aqueous solutions by solid waste from olive-oil production. *Chemical Engineering Journal*, 160, 615–622
10. Blázquez G., Martín-Lara M.A., Dionisio-Ruiz E., Tenorio G., Calero M. (2011). Evaluation and comparison of the biosorption process of copper ions onto olive stone and pine bark. *Journal of Industrial and Engineering Chemistry,* 17, 824–833.
11. Brown, P.A., Gill, S.A., Allen, S.J. (2000). Metal removal from wastewater using peat. *Water Research, 34*, 3907–3916.
12. Chuah, T.G., Jumasiah, A., Katayon, S., Thomas Choong, S.Y. (2005). Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview. *Desalination*, 175, 305–316.
13. Dermibas, E., Kobya, M., Senturk, E., Ozkan, T. (2004). Adsorption kinetics for the removal of Cr (VI) from aqueous solutions on the activated carbon prepared from agricultural wastes. *Journal of water*. 30 (4), 533-539.
14. Dwivedi C.P., Sahu, J.N., Mohanty, C.R., Mohan B., Meikap, B.C. (2008). Column performance of granular activated carbon packed bed for Pb(II) removal. *Journal of Hazardous Materials*. 156. 596–603
15. Esfandiar, N., Nasernejad, B., Ebadi, T. (2014). Removal of Mn (II) from groundwater by sugarcane bagasse and activated carbon (a comparative study): Application of response surface methodology (RSM*). Journal of Industrial and Engineering Chemistry*. 20, 3726–3736.
16. Gaballah, I., Goy, D., Allain, E., Kilbertus, G., Thauront, J. (1997). Recovery of copper through decontamination of synthetic solutions using modified barks. *Met. Metall. Trans*. B., 28, 13–23.
17. Goksungur, Y., Uren, S., Guvenc, U. (2005). Biosorption of cadmium and lead ions by ethanol treated waste baker's yeast biomass. *Bioresource Technology*. 96, 103–109.
18. G.L. Guo, W.H. Chen, W.S. Hwang. Journal Bioresource Technology, 99 (2008), p. 6046.
19. Gurisik, E., Arica, M.Y., Bektas, S., Genc¸ O. (2004). Comparison of the heavy metal biosorption capacity of active, heat-inactivated and NaOH-treated phanerochaete chrysosporium biosorbents. *Eng. Life Sci*. 4 (1), 86–89.
20. Hamza I., Martincigh B., Ngila J., Nyamori V. (2013). Adsorption studies of aqueous Pb(II) onto a sugarcane bagasse/multi-walled carbon nanotube composite. *Physics and Chemistry of the Earth*, 66, 157–166.
21. Han, R., Li H., Li, Y., Zhang J., Xiao H., Shi J. (2006). Biosorption of copper and lead ions by waste beer yeast. *Journal of Hazardous Materials*, 137, 1569–

1576.

22. Hanafiah, M.A.K.M., Ngah, W.S.W., Ibrahim, S.C., Zakaria, H., Ilias, W.A.H.W. (2006). Kinetics and thermodynamic study of lead adsorption onto rubber (Hevea brasiliensis) leaf powder. J. Appl. Sci. 6, 2762–2767.
23. Hassani, A., Vafaei, F., Karaca, S., Khataee, A.R. (2013). Adsorption of a cationic dye from aqueous solution using Turkish lignite: Kinetic, isotherm, thermodynamic studies and neural network modeling. *Journal of Industrial and Engineering Chemistry*. 20, 2615–2624.
24. Homagai, P.L., Ghimire, K.N., Inoue, K. (2010). Adsorption behavior of heavy metals onto chemically modified sugarcane bagasse. *Bioresour. Technol*. 101, 2067–2069.
25. Kalavathy, M.H., Karthikeyan, T., Rajgopal, S., Miranda, L.R. (2005). Kinetic and isotherm studies of Cu(II) adsorption onto $H_3PO_4$-activated rubber wood sawdust, J. *Colloid Interface Sci*. 292 354–362.
26. Karnitz, O., Jr., Gurgel, L. V. A., Perin de Melo, J. C., Botaro, V. R., Melo, T. M. S., Gil, R.P. F., & Gil, L. F. (2007). Adsorption of heavy metal ion from aqueous solution single metal solution by chemically modified sugarcane bagasse. *Bioresource Technology*, 98(6), 1291–1297.
27. Karthikeyan, G., Ilango, S.S. (2007). Fluoride sorption using morringa indica-based activated carbon. *Iranian Journal of Environmental Health, science and Engineering* 4, 21-28.
28. Khoramzadeh, E., Nasernejad, B., Halladj, R. (2013). Mercury biosorption from aqueous solutions by Sugarcane Bagasse. *Journal of the Taiwan Institute of Chemical Engineers* 44 266–269.
29. Khormaei M., Nasernejad B., Edrisi M., Eslamzadeh T. (2007). Copper biosorption from aqueous solutions by sour orange residue. *Journal of Hazardous Materials*, 149, 269–274.
30. Kim, Y., Kim, C., Choi, I., Rengraj, S., Yi, J. (2004). Arsenic removal using mesoporous alumina prepared via a templating method, *Environ. Sci. Technol*. 38, 924–931.
31. Lawal O.S., Sanni A.R., Ajayi I.A., Rabiu O.O. (2010). Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II) ions onto the seed husk of Calophyllum inophyllum. *Journal of Hazardous Materials*, 177, 829–835.
32. Liu C., Ngo H.H., Guo W., Tung K. (2012). Optimal conditions for preparation of banana peels, sugarcane bagasse and watermelon rind in removing copper from water. *Bioresource Technology*, 119, 349–354.
33. Momcilovic, M., Purenovic, M., Bojic, A., Zarubica, A., Randelovic, M. (2011). Removal of lead(II) ions from aqueous solutions by adsorption onto pine cone activated carbon, *Desalination* 276, 53–9.
34. Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Holtzapple, M. and M.; Ladisch, M. (2005), Features of promising technologies for pretreatment of lignocellulosic biomass, *Bioresource Technology*, 96, 673–686.
35. Mudipalli, A. (2007). Lead hepatotoxicity & potential health

effects. *Indian J. Med. Res*. 126, 518-527.

36. Munaf E., Zein R. (1997). The Use of Rice Husk for Removal of Toxic Metals from Wastewater. *Environmental Technology*, 18, 359-362.
37. Ofomaja, A.E., Naidoo, E.B. (2011). Biosorption of copper from aqueous solution by chemically activated pine cone: A kinetic study. *Chemical Engineering Journal*, 175, 260–270.
38. Ozer, A., Ozer, D., Ozer, A. (2004). The adsorption of copper(II) ions onto dehydrated wheat bran (DWB): determination of equilibrium and thermodynamic parameters. *Process Biochem*. 39, 2183–2191.
39. Parvathi K., Nagendran R., Nareshkumar R. (2007). Lead biosorption onto waste beer yeast by-product, a means to decontaminate effluent generated from battery manufacturing industry. *Electronic Journal of Biotechnology*, Vol 10 No. 1
40. Pagnanelli F., Esposito L., Veglio F. (2003). Metal speciation and pH effect on Pb, Cu, Zn and Cd biosorption onto Sphaerotilus natans: Langmuir type empirical model. *Water Res*., 37, 627–633.
41. Ronda A., Martín-Lara1 M.A., Dionisiol E., Blazquez G., Calerol M. (2013). Effect of lead in biosorption of copper by almond shell. *Journal of the Taiwan Institute of Chemical Engineers*, 44, 466-473.
42. Sciban, M., Kukic, D., Prodanovic, J. (2013). Potential of agro-based waste materials as adsorbents of heavy metal ions from water. Report. *Sustain.*, 325-329.
43. Srinivasan K., Balasubramaniam N., Ramakrishna T.V. (1998). Studies on Chromium Removal by Rice Husk Carbon. *Indian Journal Environmental Health*, 30 (4), 376-387.
44. Tasar, S., Kaya, F., Ozer, A. (2014). Biosorption of lead (II) ions from aqueous solution by peanut shells: Equilibrium, thermodynamic and kinetic studies. *Journal of Environmental Chemical Engineering,* 2, 1018–1026.
45. Tayeb, E.S., Abdelhafez, A.A., Ali, S.H., Ramadan, E.M. (2012). Effect of acid hydrolysis and fungal biotreatment on agro-industrial wastes for obtainment of free sugars for bioethanol production. *Brazilian Journal of Microbiology*, 1523-1535.
46. Tempkin, M.I., Pyzhev, V. (1940). Kinetics of ammonia synthesis on promoted iron catalyst. *Acta Phys. Chim.* 12, 327–356.
47. Volesky, B., Davis, T.A., Vieira, R.H.S.F. (2000). Sargassum seaweed as biosorbent for heavy metals, *Water Research*, 34 (17), 4270–4278.
48. Volesky B., Holan Z.R. (1995). Accumulation of cadmium, lead, and nickel by fungal and wood biosorbents. *Appl Biochem Biotechnology*, 5, 133–146.
49. Wongjunda J.and Saueprasearsit P. (2010). Biosorption of Chromium (VI) using rice husk ash and modified rice husk ash. *Environmental Research Journal*, vol. 4, no. 3, pp. 244–250.
50. Wood, G.O., Stampfer, J.F. (1993). Adsorption rate coefficients for gases and vapors on activated carbons, Carbon, 31, 195–200.

51. Yan C., Li G., Xue P., Wei Q., Li Q. (2010). Competitive effect of Cu(II) and Zn(II) on the biosorption of lead(II) by Myriophyllum spicatum. *Journal of Hazardous Materials*, 179, 721–728.
52. *Yan* G., Viraraghavan T. (2001). Heavy metal removal in a biosorption column by immobilized M. rouxii biomass, *Bioresour. Technol*. 78 (2001) 243–249.
53. Yang, J., Volesky, B. (1999). Modeling uranium – proton ion exchange in biosorption. *Environ. Sci. Technol.* 33, 4079–4085.
54. Yargıç A.Ş., Yarbay Şahin R.Z., Özbay N., Önal E. (2013). Assessment of toxic copper(II) biosorption from aqueous solution by chemically-treated tomato waste (Solanum lycopersicum). *Journal of Cleaner Production*, 1-8.
55. Yoon, Y.H. and J.H. Nelson (1984). Application of gas adsorption kinetics. I. A theoretical model for respirator CARTRIDGE service life. *Am. Ind. Hyg. Assoc.* J., 45: 509-516.
56. Yu, J. X., Wang, L.Y., Chi, R.A., Zhang, Y.F., Xu, Z.G., Guo, J. (2013). Competitive adsorption of $Pb^{2+}$ and $Cd^{2+}$ on magnetic modified sugarcane bagasse prepared by two simple steps. *Applied Surface Science*, 268, 163–17.