EPJ Web of Conferences **162**, 01082 (2017) DOI: 10.1051/epjconf/201716201082
*InCAPE2017*

# Biosorption of $Pb^{2+}$ and $Cu^{2+}$ in aqueous solutions using agricultural wastes

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**Abstract.** This study aimed to determine and compare the adsorptive capacity of $Pb^{2+}$ and $Cu^{2+}$ in simulated wastewater onto three agricultural wastes The adsorption capacities of $Pb^{2+}$ onto the agricultural wastes can be arranged as *Litchi chinensis* (4.30 mg of sorbate per g of sorbent (mg $g^{-1}$), 85.68% adsorption) > *Bambusa vulgaris* (3.83 mg $g^{-1}$, 76.19% adsorption) > *Annona squamosa* (2.70 mg $g^{-1}$, 53.66% adsorption) while the adsorption capacities of $Cu^{2+}$ onto the same agricultural wastes can be arranged in the order: *Bambusa vulgaris* (3.86 mg $g^{-1}$, 77.17% adsorption) > *Annona squamosal* (3.58 mg $g^{-1}$, 71.58% adsorption) > *Litchi chinensis* (3.42 mg $g^{-1}$, 68.32% adsorption). The biosorbents had relatively higher adsorptive capacities with $Cu^{2+}$ as compared to that of $Pb^{2+}$ except for *Litchi chinensis*. Although the results show lower adsorptive capacity as compared to a number of treated agricultural wastes showing 80% up to almost 100% adsorption of $Pb^{2+}$ and $Cu^{2+}$, the results show that *Annona squamosa*, *Bamubusa vulgaris*, and *Litchi chinensis* are potential biosorbents and promote sustainable treatment process.

## 1 Introduction

Industrial effluents from different industries contain various contaminants such as heavy metals i.e. $Pb^{2+}$ and $Cu^{2+}$ come from semiconductor industries, paint and battery productions, manufacture of ballast keel of sailboats and polyvinyl chloride (PVC) and coal-based power generation and mining industries. Due to the significant adverse impacts on humans and to the environment of these contaminants, there is a need for more stringent effluent regulatory standards which the different industries need to comply by employing sustainable treatment methodology. Adsorption has been found to be a sustainable treatment as compared to conventional treatments in terms of cost, minimal sludge produced, higher efficiency, no additional nutrient requirements and possible regeneration and recovery of biosorbents and the heavy metal contaminants. Among the adsorbents, agricultural wastes are currently being utilized due to cost and effectivity while helping in minimizing the solid wastes generation problem. A number of agricultural wastes showing the high % removal ranging from 80% up to almost 100% by adsorption were conducted with treated agricultural wastes with chemicals like HCl and $HNO_3$ [1]; with NaOH [2]; or using other treatments like burned until the wastes turned activated carbon [3,4,5]. This study aimed to determine and compare the adsorptive capacity of $Pb^{2+}$ and $Cu^{2+}$ in simulated wastewater onto three agricultural wastes, namely, peels of *Annona squamosa* (custard apple) and *Litchi chinensis* (lychees), and shoot of *Bambusa vulgaris* (bamboo) without any utilization of pre-treatments of the biosorbents to promote sustainability of the process.

## 2 Methodology

### 2.1 Preparation of Biosorbents

Peels of *Annona squamosa* and *Litchi* chinensis, and shoot of *Bambusa vulgaris* were obtained individually in Chungli, Taiwan, washed several times with distilled water to ensure that all adhering dirt was removed, air-dried under room temperature until water was evaporated and oven-dried at 50°C for 24 to 48 hours. Dried materials were ground and sieved to obtain a particle size of 30 mesh screen. The properties of the biosorbents were analyzed using the following laboratory analyses: (1) surface properties using scanning electron microscopy (SEM, Hitachi S-300N), (2) particle size distribution by a laser diffraction particle size analyzer (LS™ 13 320, Beckman, USA), (3) Fourier transform infrared (FTIR, Perkin Elmer Model 1600) spectroscopy, (4) zeta potential analyzer (ZEN3600, MALVERN Nano-ZS) to determine the surface charges and (5) an elemental analyzer (HORIBA 7021H) to determine the composition in terms of the major elements, (6) Cationic Exchange Capacity (CEC) (Bio-Rex 70) analyzer.

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### 2.2 Preparation of Sorbate Solutions.

Stock solutions of $Pb(NO_3)_2$ and $Cu(NO_3)_2$ were prepared to have concentration of 200 mg $L^{-1}$ stock solution by dissolving the solutes in 1000 ml of double distilled water. Appropriate dilutions of 50 ml volumes containing initial concentrations (Co) of 2, 4, 6, 8, 10, 12, 18, and 20 mg $L^{-1}$ were made from the stock solution.

### 2.3 Equilibrium Studiess.

All batch adsorption experiments were conducted in 50-mL plastic bottles with stoppers shaken in the dark on an orbital shaking incubator at 180 rpm until equilibrium was reached. The temperature was controlled at room temperature and the equilibrium time of 24 h was chosen. Adsorption measurement was determined by batch experiments of 0.2 g adsorbent with 50 ml of aqueous sorbate solutions of known concentration in a series of 50 ml conical plastic containers at pH adjusted to 4.0, 5.0, and $6.0 \pm 0.1$ using 0.1N HCl or 0.1N NaOH aqueous solution. The samples were withdrawn from the shaker and the solutions were separated from adsorbent by settling for few minutes followed by filtration using 0.45µm Whatmann filter. At time t = 0 and at equilibrium, sorbate concentrations in the supernatant solution were estimated using atomic absorption spectrophotometer at suitable maximum wavelength to represent the amount of contaminants adsorbed on the biosorbents and concentration was computed from the calibration curve. For each series of measurements, the adsorption calibration curve was constructed composed of a blank and three or more standards from Merck (Germany). Accuracy and precision of the sorbate measurement were confirmed using external standard reference material for trace elements in water.

### 2.4 Isotherm Models

The equilibrium concentration results for the adsorption system were plotted against adsorption uptake in mol $kg^{-1}$. The amount of sorbate adsorbed onto the adsorbent biomass at time t, $q_E$ (mg/g), is calculated by the following mass balance relationship.

$$q_e = \left(C_0 - C_e\right)\frac{V}{W} \qquad (1)$$

where $C_0$ and $C_e$ were the initial and equilibrium liquid phase concentrations of sorbate, respectively (mg $L^{-1}$), V the volume of the solution (L), and W the weight of the biosorbent used (g). The equilibrium data obtained were fit into different isotherms i.e. Langmuir, Freundlich and Temkin linearized isotherm sorption models for comparison to predict which among the models would have the best fit and would give the maximum adsorption capacity among the three biosorbents.

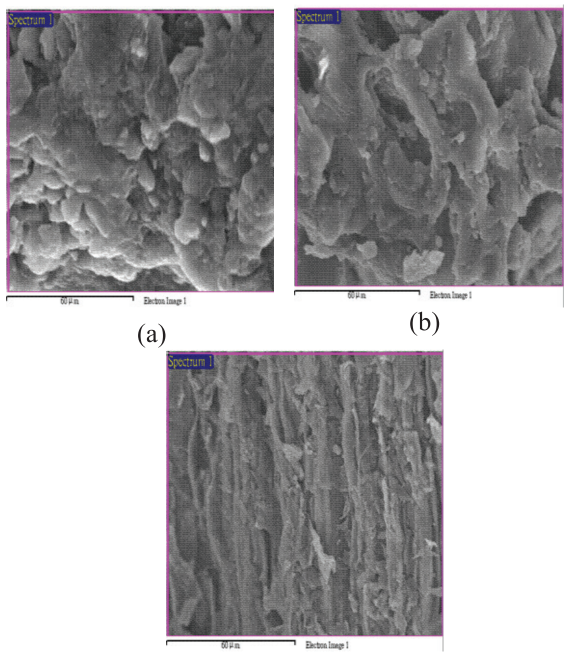
## 3 Results and Discussion

### 3.1 Preparation of Biosorbents.

The preparation method of drying ensured that the cellulose, hemicelluloses, xylose and lignin present on the surface of the agricultural wastes were protonated by drying at 50°C for 24 to 48 hours to produce basic components of functional groups i.e. acetamido groups, carbonyl, phenolic, structural polysaccharides, amide, amino, sulphydryl carboxyl groups alcohols and esters [6] that may serve as the binding sites to the contaminant with strong affinity to the contaminant with positive charges in aqueous solution. The preparation did not involve any chemical nor higher energy requirement to turn the wastes into char like previous studies.

### 3.2 Characterization of Biosorbents.

The surface properties of dried and powdered peels of *Annona squamosa* and *Litchi chinensis*, and the shoots of *Bambusa vulgaris* were determined using scanning electron microscopy (SEM, Hitachi S-300N) as shown in Figure 1.




(a) (b) (c)

**Fig. 1.** SEM of the samples of biosorbents (a) Annona squamosal, (b) Litchi chinensis, (c) Banbusa vulgaris.

Sample of *Annona squamosa* has a rough multilayer surface with the compact surfaces lumped together which may provide accessible large surface areas during adsorption. Sample *Litchi chinensis* has rough multi-layer surface formed circular with small amount of pores on the surface which also indicates good adsorbing capacity. Shoot of *Bambusa vulgaris* has compact flat surface with some fissures in its structures mainly on the cross section of the fiber that can initiate contact with the sorbate. The Fourier transform infrared (FTIR) spectroscopy analyses of the biosorbents are shown in Figure 2 indicating the available functional groups on the surface of each biosorbent that provide binding sites and strong affinity to the ions of manganese in aqueous solution of $Pb^{2+}$ and $Cu^{2+}$.

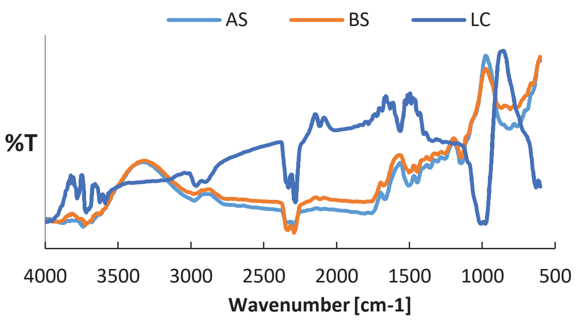
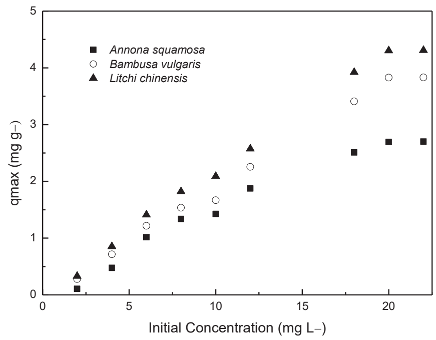



**Fig. 2.** Fourier transform infrared (FTIR) spectroscopy analyses of the biosorbents: *Annona squamosa* (AS), *Bambusa vulgaris* (BS), and *Litchi chinensis* (LC).

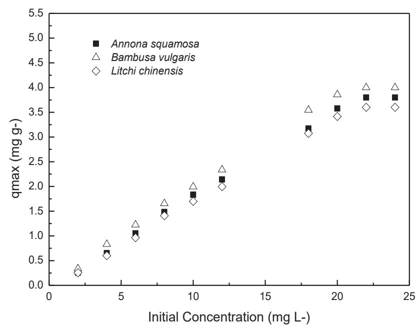
The FTIR spectroscopy analyses indicate that *Annona squamosa* has C–$CH_3$ alkane stretching with wavelength of 2318.02 $cm^{-1}$, C=C aromatic with wavelength 1535.06 $cm^{-1}$, C–H with wavelength 1186.01 $cm^{-1}$, $R_2C$=CHR with wavelength 863.95 $cm^{-1}$ while *Bambusa vulgaris* has the following results: 3781.72 $cm^{-1}$ indicating presence of –OH stretching, 3596.59 $cm^{-1}$ for –OH, 2980.45 $cm^{-1}$ for C–H stretching, 2356.59- 2307.41 $cm^{-1}$for C–H, 1600.00 $cm^{-1}$ for –COO, and 1022.09 $cm^{-1}$ for carboxyl and hydroxyl C–OH. Common functional groups were observed present in both *Annona squamosal* and *Bambusa vulgaris* samples. *Litchi chinensis* shows results having 3726.76 $cm^{-1}$ for –OH, 2900 $cm^{-1}$ for C–H, 1536.99 $cm^{-1}$ for –COO, 1185.04 $cm^{-1}$ for carboxyl and hydroxyl C–OH, and 853.34 $cm^{-1}$ for C–H.

### 3.3 Equilibrium Studies

The preparation method of drying ensured that the cellulose, Figure 3 shows comparison of the equilibrium studies of $Pb^{2+}$ with the three sorbents and $Cu^{2+}$ with the three sorbents. At the highest initial sorbate concentration of $Pb^{2+}$ 20 mg $L^{-1}$, the adsorption capacities of the three sorbents can be arranged as *Litchi chinensis* (4.30 mg of sorbate per g of sorbent (mg $g^{-1}$), 85.68% adsorption) > *Bambusa vulgaris* (3.83 mg $g^{-1}$, 76.19% adsorption) > *Annona squamosal* (2.70 mg $g^{-1}$, 53.66% adsorption). As the initial sorbate concentrations were increased, the amount adsorbed also increased. With regards to $Cu^{2+}$ 20 mg $L^{-1}$, the adsorption capacities of the three sorbents can be arranged as *Bambusa vulgaris* (3.86 mg $g^{-1}$, 77.17% adsorption) > *Annona squamosa* (3.58 mg $g^{-1}$, 71.58% adsorption) > *Litchi chinensis* (3.42 mg $g^{-1}$, 68.32% adsorption). This can be attributed to the available binding sites on the surface of *Litchi chinensis* and *Bambusa vulgaris* due to the presence of counterions as shown in the elemental analysis and selected properties of the metals which are summarized in Table 1.




(a)




(b)

**Fig. 3.** Results of batch adsorption equilibrium studies of $Pb^{2+}$ (a) and $Cu^{2+}$ (b) onto the three biosorbents.

**Table 1.** Selected Properties of Metals in the Sorbates and the Cations Present in Each Biosorbent

| Metal/Cation | Ionic Radius (Å) | Hydrated Ionic Radius (Å) | Pauling's Electronegativity |
|---|---|---|---|
| $Pb^{2+}$ | 1.20 | 2.61 | 2.33 |
| $Cu^{2+}$ | 0.72 | 2.95 | 2.00 |
| $K^{+}$ | 1.49 | 3.31 | 0.82 |
| $Zr^{2+}$ | 0.80 | 5.50 | 1.33 |
| $Mg^{2+}$ | 0.73 | 6.00 | 1.31 |

Based from the elemental analysis of the biosorbents, all biosorbents contain $K^+$ which has higher ionic radius than that of $Pb^{2+}$ which may allow possible cationc exchange [7]. *Annona squamosa* has the lowest percentage composition of $K^+$ (2.54%). Although *Bambusa vulgaris* has the highest percentage composition of $K^+$ (6.81%), it also has 6.34% of $Zr^{2+}$ that may serve as a competing ion during the reaction. $Mg^{2+}$ in *Litchi chinensis* is only 0.53%, thus it is negligible to cause this competition. According to Arshadi, the smaller the ion's hydration than that of the counterion, the greater the adsorption is and the easier the ion exchange occurs [7]. $Pb^{2+}$ and $Cu^{2+}$ have relatively smaller ionic radius and smaller hydrated ionic radius as compared to all the counterions present on the surface of all the three biosorbents allowing possible cationic exchange. The difference in adsorptive capacities can be explained by the amount of counterion present on the

surface of the biosorbents. Although *Litchi chinensis* has higher percentage composition of counterions on its surface as compared to that of *Annona squamosa*, the presence of another counterion, playing as a possible competing site, decreased its adsorptive capacity.
Since the electronegativity of both $Pb^{2+}$ and $Cu^{2+}$ is higher than the counterions on the biosorbent surfaces thus $Pb^{2+}$ was adsorbed readily by the biosorbents [8]. Cationic Exchange Capacity (CEC) in meq per 100g of the biosorbents also explains the probability of having an ion exchange of the sorbate ion with the counterions on the surface of the biosorbents. *Litchi chinensis* has a CEC of 38.3 meq per 100g, *Bambusa vulgaris* has a CEC of 16.9 meq per 100g and *Annona squamosa* has a CEC of 22.6 meq per 100g.

### 3.4 Isotherm Study

The batch equilibrium adsorption data show that for $Pb^{2+}$ adsorbed onto the three different biosorbents, the best fit observed was in the linearized form of Langmuir isotherm.. The isotherm fitting results are summarized in Table 2. The $q_{max}$ refers also to the amount of sorbate adsorbed per unit mass of the adsorbent to complete monolayer coverage and $b_L$ represents the energy of adsorption.

**Table 2.** Isotherm Fitting for Sorbate Adsorbed onto the three biosorbents.

| Langmuir Fitting for $Pb^{2+}$ Adsorbed onto the three biosorbents. | | | | | |
|---|---|---|---|---|---|
| Biosorbent | Slope | Intercept | RSS | $q_{max}$ mg $g^{-1}$ | $b_L$ L $mg^{-1}$ |
| *Annona squamosa* | 1.563 | 0.703 | 0.999 | 2.695 | 2.222 |
| *Bambusa vulgaris* | 1.207 | 0.193 | 0.964 | 3.827 | 6.258 |
| *Litchi chinensis* | 1.612 | -0.178 | 0.970 | 4.304 | -9.064 |
| | | | | | |
| Langmuir Fitting for $Cu^{2+}$ Adsorbed onto the three biosorbents. | | | | | |
| Biosorbent | Slope | Intercept | RSS | $q_{max}$ mg $g^{-1}$ | $b_L$ L $mg^{-1}$ |
| *Annona squamosa* | 23.397 | 0.440 | 0.981 | 2.272 | 0.019 |
| *Bambusa vulgaris* | 11.789 | 0.510 | 0.941 | 1.668 | 0.051 |
| *Litchi chinensis* | 34.910 | 0.273 | 0.903 | 3.664 | 0.008 |

*Annona squamosa* and *Bambusa vulgaris* have relatively higher adsorptive capacities with $Cu^{2+}$ as compared to that of $Pb^{2+}$. The ionic radius of $Cu^{2+}$ is 0.72 Å while that of $Pb^{2+}$ is 1.20Å as compared to 1.49 Å of $K^{+}$. Theoretically, the smaller the ionic radius, the greater is the adsorption. However, the valence electron also plays a role in the adsorption process. The greater the valence electron, the greater is the adsorption [7]. The valence electron of copper is at $3d^9$ while that of lead is at $6p^2$. Although the valence electron of copper is greater than that of lead, its valence electrons are not as accessible as those of $Pb^{2+}$. This can explain the better binding capacity of $Pb^{2+}$ over $Cu^{2+}$ onto the surface sites of *Annona squamosa* and *Bambusa vulgaris*. However, if the adsorption of $Pb^{2+}$ and $Cu^{2+}$ onto *Litchi chinensis*, $Pb^{2+}$ has higher percentage of adsorption since $Pb^{2+}$ has a shorter hydrated radius (2.61 Å) compared to that of $Cu^{2+}$ (2.95 Å). When the ion's hydration is smaller than the counterion, ion exchange is easier and adsorption is greater [7]. This allows $Pb^{2+}$ easier exchange with counterions present onto *Litchi chinensis* which have relatively higher hydrated radii than that of $Pb^{2+}$. Hydrated radius is the size of the water molecule in comparison to normally stabilizing cations that causes the physical expansion or swelling of the biosorbent which further causes reduction in permeability. In certain situations, the expansion of biosorbent can also cause other embedded materials to be discharged from the pore walls that may allow additional bridging or blocking [8]

## 4 Conclusion

At 20 mg $L^{-1}$ of $Pb^{2+}$, the adsorption capacities of the three sorbents can be arranged as *Litchi chinensis* (4.30 mg of sorbate per g of sorbent (mg $g^{-1}$), 85.68% adsorption) > *Bambusa vulgaris* (3.83 mg $g^{-1}$, 76.19% adsorption) > *Annona squamosa* (2.70 mg $g^{-1}$, 53.66% adsorption). As the initial sorbate concentrations were increased, the amount adsorbed also increased. With regards to 20 mg $L^{-1}$ of $Cu^{2+}$, the adsorption capacities of the three sorbents can be arranged as *Bambusa vulgaris* (3.86 mg $g^{-1}$, 77.17% adsorption) > *Annona squamosal* (3.58 mg $g^{-1}$, 71.58% adsorption) > *Litchi chinensis* (3.42 mg $g^{-1}$, 68.32% adsorption). The biosorbents had relatively higher adsorptive capacities with $Cu^{2+}$ as compared to that of $Pb^{2+}$ except for *Litchi chinensis*. Although the results show lower adsorptive capacity as compared to a number of treated agricultural wastes showing 80% up to almost 100% adsorption of $Pb^{2+}$ and $Cu^{2+}$, the results show that *Annona squamosa*, *Bamubusa vulgaris*, and *Litchi chinensis* are potential biosorbents and promote sustainable treatment process.

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