



## Biosorption of Pb(II) and Ag(I) from Pulp and Paper Mill Effluent using Corn Cob (*Zea mays*) and Plantain Bunch Stalk (*Musa paradisiaca*)

C.O. Nwoko<sup>1,\*</sup>, I. Okwara<sup>1</sup>, C.E. Ihejirika<sup>1</sup>, O.U. Nwosu<sup>2</sup>

<sup>1</sup>Department of Environmental Technology, Federal University of Technology, Owerri, PMB 1526, Nigeria.

<sup>2</sup>Department of Agricultural / Bioenvironmental Engineering, Imo State Polytechnic, Nigeria.

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### ABSTRACT

Biosorption is the removal of substances from solution using biological materials. The use of agro-based agricultural waste as biosorptive materials is an innovative approach towards sustainable environmental management. The suitability of locally obtained corn cob and plantain stalk in the adsorption of Pb and Ag from pulp and paper mill effluent using continuous batch technique was investigated. The results obtained showed that temperature increase affected the movement of solute and encouraged biosorption. Pb (II) and Ag(I) adsorption significantly increased as pH varies from 3 to 6. Also varying the adsorbent dose to 2.0 g/L increased adsorption of Pb (II) and Ag (I), further increase did not affect Pb and Ag adsorption. The contact time also directly affected rate of adsorption, which steadily increased reaching optimum at 40 minutes. Langmuir adsorption isotherm fitted best with the data and showed correlation coefficients ( $R^2$ ) of 0.72, 0.990, 0.966 and 0.955 across the data. It is observed that out of the four variables only Ag on *Musa paradisiaca* adsorbent posed a non-linear form, while others showed linear relationship that intra-particle diffusion took place and may not have only accounted for the rate of the entire reaction process.

### 1. Introduction

Heavy metal pollution is one of the most serious environmental threats as a result of various industrial discharges [1]. Many industrial processes such as leather tanning / chrome plating have contributed to the increase in heavy metal pollution [1] others like the mining companies, pulp and paper, paint factories have also immensely contributed to heavy metal pollution [2]. Heavy metals such as lead, Cadmium, Zinc, Mercury, Chromium are toxic to living organisms' e.g., animals and plants at certain concentration levels [3].

A number of treatment techniques have been applied in the removal of these heavy metal ions from waste water streams (effluents); methods such as ion exchange, solvent extraction, chemical precipitation, oxidation and reduction, fixation or cementation etc., are the most conventional treatment techniques [4]. However, application of these techniques is often limited due to operational costs [2].

Adsorption technique has shown to be an economically feasible and more efficient alternative method for removing heavy metals from wastewater [5, 6]. Biosorption is the removal of substances from solution using biological materials [7]. The use of agro-based waste resources as biosorptive materials is an innovative approach towards sustainable environmental management. Some examples of agro-waste materials used are banana peels, sugar cane bagasse, maize starch, rice husk, and neem leaves, etc., [8, 9].

The presence of heavy metals in our environment both on the soil and water bodies have posed severe danger to plants, animals and humans [10]. One problem of pulp and paper mills is the high cost of immobilization of heavy metals present in the effluents and high cost of equipment maintenance.

The aim of this study was to assess the effectiveness of corn cobs and plantain bunch stalk in the absorption of Pb(II) and Ag(I) ions from pulp and paper mill effluents.

### 2. Experimental Methods

#### 2.1 Effluent Collection and Biomass Preparation

Effluent water samples were collected from pulp and paper mill factory in Abia State Nigeria and taken to the laboratory for characterization. Corn cob (*Zea mays*) and plantain Stalk (*Musa paradisiaca*) waste were collected from local farmers in Owerri, Nigeria. The cobs and plantain stalks were Oven dried for 24 hrs at 60 °C and later ground to powder and sieved to 50 mesh sizes. These powders were soaked separately in 0.1 M HNO<sub>3</sub> for 24 hrs (50 g powder was soaked per litre). They were filtered and washed with distilled water to remove acid contents. The washing was continued till the pH of the filtrate became near neutral. It was first dried at room temperature and then in an oven at 105 °C to remove moisture. These biomass were labeled properly and stored in an air tight glass bottles to protect it from humidity.

#### 2.2 Surface Morphology

Scanning Electron Microscope (SEM) was used to observe the pore structure of the activated biosorbents. Pores present in them act as the active sites where adsorption takes place. The Scanning Electron Microscope images of activated carbon produced from corn cobs and plantain bunch stalk were activated using hydrochloric acid (HCl) Fig. 1 and Fig. 2. SEM photograph showed that wide varieties of pores are present in the two activated biosorbents which are more visible at 200 magnifications.

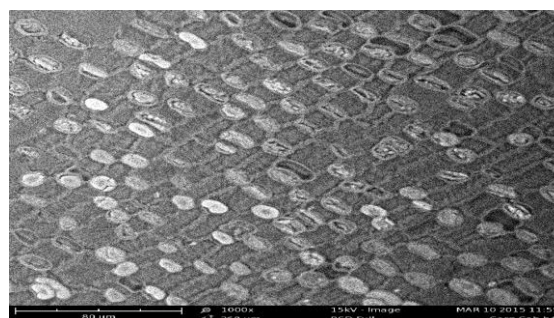


Fig. 1 Activated Corn Cobs before Adsorption; mag. 500x, H536 μm

\*Corresponding Author

Email Address: [conwoko2002@yahoo.com](mailto:conwoko2002@yahoo.com) (C.O. Nwoko)

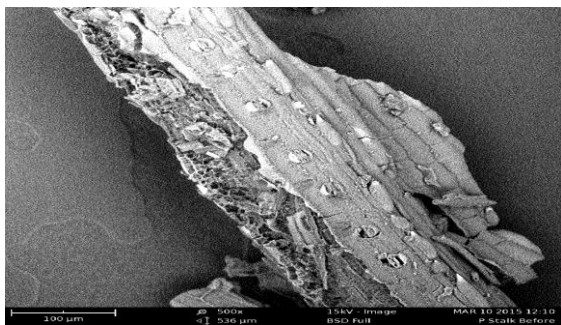


Fig. 2 Activated plantain stalk before adsorption; magnification 500x, H536  $\mu\text{m}$

### 2.3 Sorbate Preparation/ Waste Water Digestion

About 50 mL of the effluent was digested in a 250 mL conical flask by adding 10 mL of Aqua Regia composed of (2:1) hydrochloric acid and nitric acid and then heated on a hot plate until volume remains about 7-12 mL. The digest was filtered using Whatman no 42 filter paper and volume made up to 50 mL volumetric flask and was then stored for Atomic Absorption Spectrophotometer (AAS) analysis.

### 2.4 Biosorption Experiment

Batch experiments were carried out to find the equilibrium time for sorption of Pb and Ag on corn cob and plantain stalk. All experiments were performed in triplicates and mean values were used in all calculations. 1.0 g corn cob powder of 50 mesh sizes was mixed in 100 mL of the effluent. It was mechanically shaken at speed of 200 rpm and samples were collected at different time intervals (10mins, 20mins, 30mins, 40mins and 50mins). This procedure was also carried out with plantain stalk powder. The pH for the experiment was taken as original pH of solutions which was 5.2 for Ag and 5.8 for lead. After completion of each batch of experiments the solution was filtered using vacuum filter assembly (0.002 mm). Filtrate was analyzed using atomic absorption spectrophotometer to determine the amount of metallic element left after sorption. The amount of metal sorbed was calculated by material balance. Sorption capacity  $Q_e$  (mg/g) was determined using the formula:

$$Q_e = (C_t - C_e)V/M \quad (1)$$

Where,

$Q_e$  = mass of metal adsorbed at equilibrium (mg/g)

$C_e$  = is the final concentration of metal ion in the liquid phase at equilibrium (mg/L)

$C_t$  = is the initial concentration of metal ion in the liquid phase at equilibrium (mg/L)

$M$  = is the corn cob/plantain stalk mass (g)

$V$  = volume of the solution

#### 2.4.1 Effect of Adsorbent Dose on Metal Ion Adsorption

To investigate the effect of varying adsorbent dose on metal adsorption, the quantity of the adsorbents were varied from 1.0 to 3.0 g/L for corn cob and plantain stalk while keeping other experimental variables constant.

#### 2.4.2 Effect of pH

Keeping the same operating conditions as mentioned previously, pH of solution was varied from 2, 4, 6, 8, 10 by the addition of 0.1 M nitric acid and 0.1 M ammonia solution.

#### 2.4.3 Effect of Temperature

Keeping all other parameters constant temperature was varied from 20 °C to 70 °C and to the required time of 40 minutes.

## 3. Results and Discussion

Initial effluent stream characterization showed Pb (II) and Ag(I) metal ions to have highest (33.2 mg/L and 24.4 mg/L concentration, respectively) out of 15 metals screened and were then selected as metal of choice for the biosorption experiment.

### 3.1 Equilibrium Sorption Studies

#### 3.1.1 Effect of Contact Time

The effect of contact time on the removal of Pb(II) and Ag(I) from the effluent is presented in Figs. 3 and 4. Ag(I) removal was rapid within the first 30 minutes and became almost constant thereafter. Similar trend was observed for the two adsorbent materials (Fig. 3).

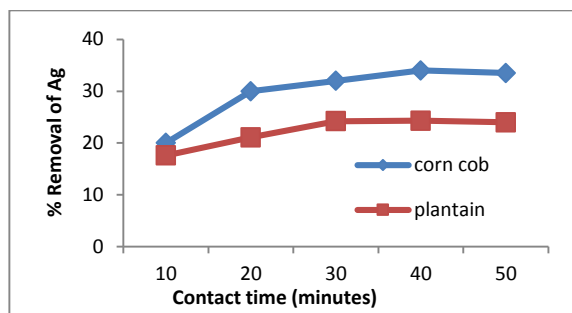


Fig. 3 Effect of contact time on the removal Ag by the adsorbents

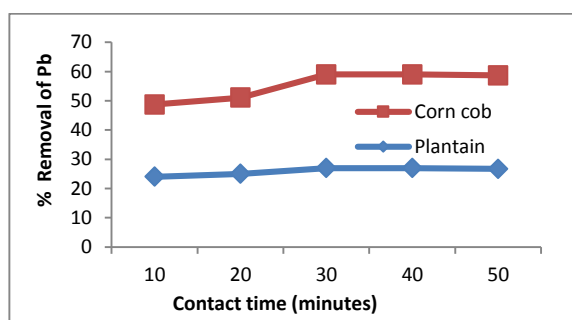


Fig. 4 Effect of contact time on the removal Pb(II) by the adsorbents

As shown in Fig. 4, 60% of Pb(II) adsorption was achieved after the first 32 mins and thereafter Pb(II) concentration almost became constant. The fast initial uptake was due to the accumulation of metal ions on surface of adsorbent which is a rapid step. More time was consumed on diffusion of ions to binding sites. It was concluded that 50 min was sufficient for sorption to attain equilibrium. The equilibrium capacity obtained after 30 min of sorption of Ag(I) was  $0.06 \pm 0.43 \text{ mgg}^{-1}$  and  $0.03 \pm 0.75 \text{ mgg}^{-1}$  for corn cob and plantain adsorbents, respectively.

Similarly, the equilibrium capacity obtained after 30 min of sorption of Pb(II) was  $0.24 \pm 0.04 \text{ mgg}^{-1}$  and  $0.16 \pm 0.03 \text{ mgg}^{-1}$  for corn cob and plantain adsorbents, respectively.

#### 3.1.2 Effect of Adsorbent Dose

The effect of different doses of *Musa paradisiaca* stalk and Corn cobs on Ag(I) and Pb(II) metal removal is presented in Figs. 5 and 6. On increasing the quantity of adsorbents from 1.0 to 2.5 g/L, the percentage removal of Ag (I) increased from and 42 to 44.6 % for plantain stalk and 44-46.5% for corn cob (Fig. 5). The same trend was observed in the adsorption of Pb (II). Metal adsorption increased as the adsorbent material increased from 1.0 to 2.0 g/L (Fig. 6). Increasing the dose further did not affect metal adsorption.

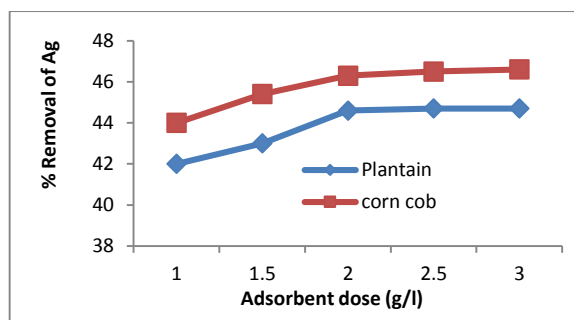


Fig. 5 Effect of adsorbent dose on the adsorption capacity of Ag (I) by Corn cob and Plantain

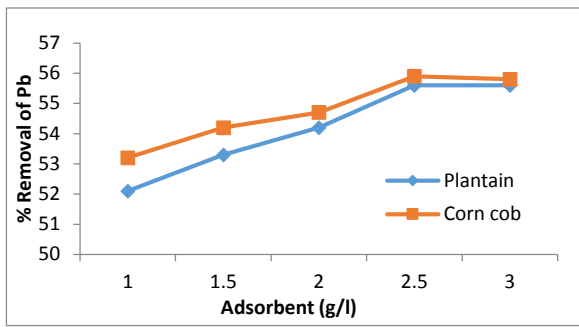


Fig. 6 Effect of Adsorbent dose on the adsorption capacity of Pb(II) by Corn cob and Plantain

It is observed that 2.0 g/L dose was sufficient for optimal removal of Pb(II) and Ag(I) ions. The removal capacity was low at high dose rate and vice versa. This was due to metal concentration shortage in solution at high dose rates. The decrease in the sorption efficiency with the increasing adsorbent dose may be as a consequence of partial overlapping or aggregation of adsorbent surface area available to ion and an increase in diffusion path length, which occurs at high biomass concentration given rise to decrease of active sites [11, 12]. Also differential adsorption capacities of the adsorbents depend on the extent of surface modification [13].

### 3.1.3 Effect of pH

The adsorption of Pb and Ag by the two adsorbent materials increased as the initial pH increased from 2 to 6 (Fig. 7). The trend observed collaborates the work of [14] who obtained similar result for adsorption of Pb using agricultural waste.

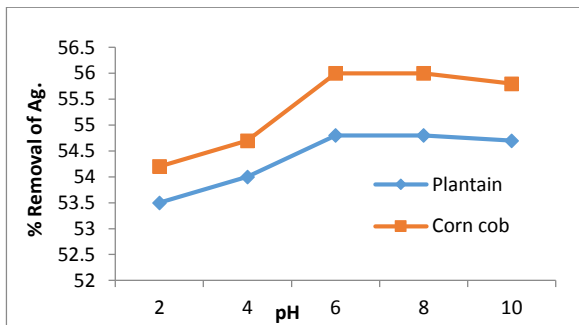


Fig. 7 Effect of pH on the Adsorption Capacity of Ag(I) by activated corn cob and plantain

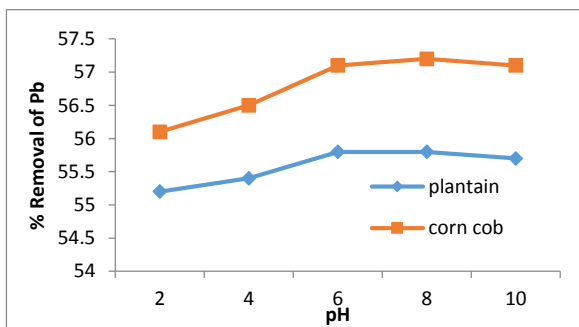


Fig. 8 Dye decolorisation and protein content of the soil consortia at different time intervals

From this study, the adsorbent materials used had maximum metal ion adsorption at pH 6 and further increase in pH did not affect metal ion adsorption. The removal of metals from solution is dependent on pH of solution, which affects the surface charge of adsorbents, the degree of ionization and species of adsorbate [14, 15]. The increase in metal removal as pH increased can be attributed to the decrease in competition between H<sup>+</sup> ions and positively charged metal ions at the surface sites of the adsorbent materials. Also, the binding of metal ions to the adsorbent changes from positive to negative as a result of formation of OH<sup>-</sup> ion. At pH above 6, both metals begin to form precipitates due to formation of OH ions and removal due to sorption was very low.

### 3.1.4 Effect of Temperature

Keeping all other parameters constant temperature was varied from 20 °C to 70 °C. The sorption of Ag increased slightly with the increase in temperature up to 40 °C and then decreased. Also removal of lead (Pb) increased considerably on the average with increase in temperature from 20 to 40 °C, further temperature increase decreased metal sorption (Figs. 9 and 10).

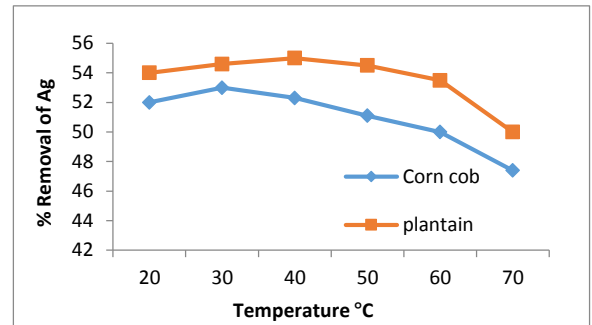


Fig. 9 Effect of Temperature on adsorption capacity of Ag by activated Corn Cob and activated Plantain Stalk

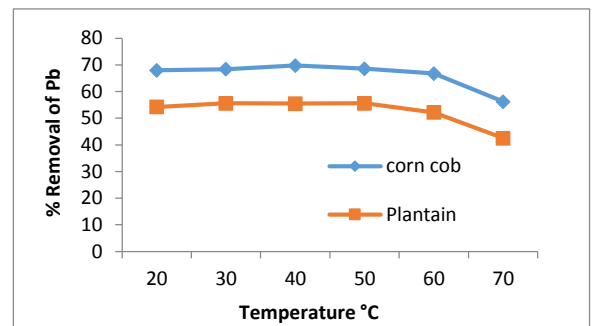


Fig. 10 Effect of Temperature on adsorption capacity of Pb (II) by Corn and plantain stalk

The temperature above 40 °C may have caused deformation in the texture of the biomass and thus the observed reduction in the sorption capacity.

Biomass contains more than one type of sites for metal binding. The effect of temperature on each site is different and contributes to overall metal uptake [16]. The effect of temperature on biosorption also depends on the heat of sorption. Usually for physical sorption heat of sorption is negative; sorption reaction is exothermic and preferred at lower temperature. For chemisorption the overall heat of sorption is combination of heat of various reactions taking place at sorption sites. It depends on type of metal and adsorbent.

### 3.2 Sorption Isotherm Studies

The adsorption characteristics of lead (Pb (II) and silver (Ag (I) were determined by fitting the adsorption data into Langmuir equation. Langmuir Adsorption Isotherm suggests that uptake occurs on homogenous surface by mono-layer sorption without interaction between sorbed molecules.

Langmuir Isotherm Equation:

$$q_e = q_{max} \frac{b C_e}{1 + b C_e} \quad \text{in linear form} \quad \frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \quad (2)$$

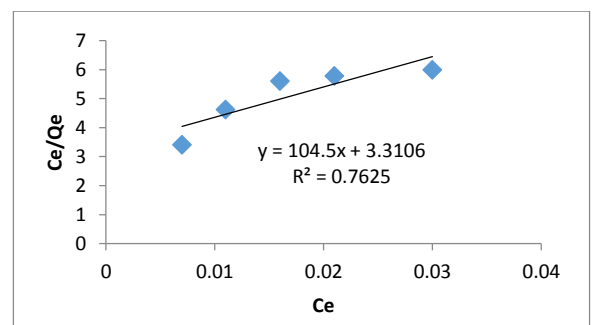


Fig. 11 Langmuir isotherm of adsorption of Ag(I) by activated corn cob

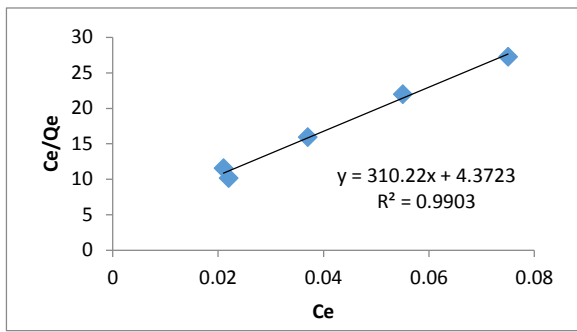


Fig. 12 Langmuir isotherm of adsorption of Ag (I) by activated plantain stalk

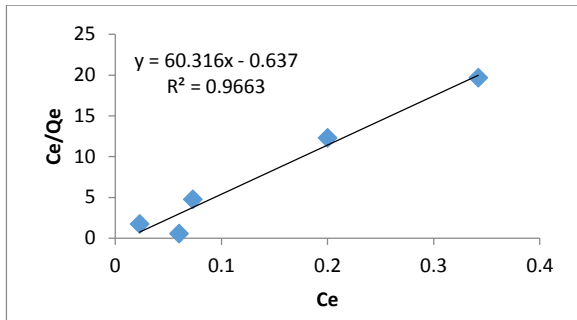


Fig. 13 Langmuir isotherm for the adsorption of Pb(II) by activated corn cob

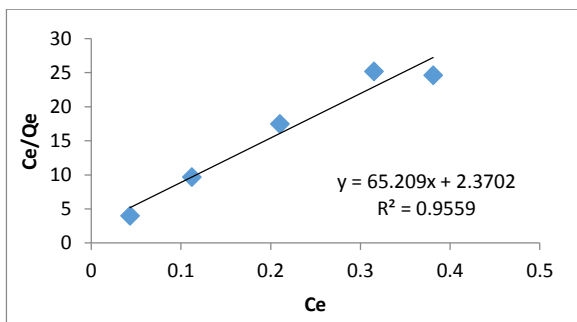


Fig. 14 Langmuir isotherm for the adsorption of Pb(II) by activated plantain stalk

Figs. 11 to 14 show the applicability of Langmuir model to the metals using plantain stalk and corn cobs adsorbents. The model fitted well for the adsorption studies given the high correlation coefficients depicted by the models. The implications of this trend are that adsorption of Pb(II) and Ag(I) are due to specific interactions of the metal ions with groups on the surface of the carbon thus when the monolayer covers these groups, there is no further adsorption of the metals ions.

### 3.3 Adsorption Mechanism

When the effluent sample is shaken, the adsorbate species, i.e. Pb(II) and Ag are transported to the solid phase by the intraparticle transport phenomenon. The intraparticle transport is supposed to be the rate controlling step. The rate of particle transport through this mechanism is slower than adsorption on the exterior surface site of the adsorbent. The amount of adsorbed species, Pb and Ag varies proportionately with a function of retention time. The equation can be expressed as

$$q_e = K_d t^{1/2} + C \quad (3)$$

After [17] where  $q_e$  is the equilibrium metal ion concentration on the adsorbent (mg/g),  $K_d$  is the constant coefficient, the initial rate of intraparticle diffusion (mg/Lmin<sup>1/2</sup>).

The result of Intra particle diffusion studies of Ag (I) and Pb(II) using activated corn cobs and activated plantain stalk is presented in Table 1. Probably, the transport of the effluent sample through the particle-sample interface into the pores of the particles, as well as the adsorption on the available surface of the adsorbents, is responsible for adsorption. The ions

diffused quickly among the particles at the beginning of the adsorption process, and then intra-particle diffusion slowed down and stabilized.

**Table 1** Intra-particle Diffusion model parameters for adsorption of Ag(I) and Pb(II) onto ACC and APS

Adsorbate	$K_d$ (mg/L) $t^{1/2}$	C (mg/g)	$R^2$
Ag			
ACC	0.001	-0.003	0.948
APS	0	0.004	0.481
Pb			
ACC	0.003	0.006	0.937
APS	0.003	0	0.94

ACC= activated corn cob, APS= Activated plantain stalk

From the result, out of the four variables only one posed a non-linear form, while others showed that intra-particle diffusion (linear) took place but it's not the sole rate determining factor [17].

### 4. Conclusion

The pulp and paper mill effluent bears considerable concentrations of metal species especially Pb and Ag. The significant percentage metal removal recorded in this study while varying the physicochemical conditions of adsorbents point to the fact that the adsorbents: plantain stalk (*Musa paradisiaca*) and corn cobs (*Zea mays*) are good economic alternatives in the treatment of metal bearing effluent materials. Adsorption isotherm study showed a good fit to the metal removal by the adsorbents. The intra-particles diffusion were linear and may not have only accounted for the rate of the entire reaction process.

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