

Adsorption Isotherms and Kinetics of Pb (II) and Cd (II) Ions onto Carbonised Sugarcane Bagasse

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To cite this article:

Oklo Ahola David, Enenche Elaigwu Daniel, Adie Agorye Peter, Enyi Ogor Simeon. Adsorption Isotherms and Kinetics of Pb (II) and Cd (II) Ions onto Carbonised Sugarcane Bagasse. *Advances in Biochemistry*. Vol. 9, No. 3, 2021, pp. 44-49. doi: 10.11648/j.ab.20210903.12

Received: May 8, 2021; **Accepted:** June 2, 2021; **Published:** August 18, 2021

Abstract: In the present study, the adsorption of Pb (II) and Cd (II) ions from aqueous solution of lead (II) nitrate and cadmium chloride onto carbonized sugarcane bagasse was investigated. The physicochemical attributes of the adsorbent were: bulk density =0.58 g/mL, Ash content =21%, Attrition =31.33% and moisture =0.79%. The effects of adsorption dosage, effect of concentration, effect of ion concentration, effect of adsorbent contact time and effect of pH was discussed and detailed. Batch adsorption experiments revealed that the amount of ion adsorbed decreased with increase in adsorbent dosage; the effect of concentration on ion uptake increased with increase in concentration; there was a rapid increase in amount adsorbed as contact time increased with maximum adsorption reached at 80 minutes before subsequent reduction. The effect of pH showed that there was effective removal of ions at acidic pH than in alkaline pH level. The linearized form of Langmuir model revealed isotherm parameters that confirmed the sorptive capacity of the sugarcane bagasse and thus fit for heavy metal remediation from aqueous solution. Besides, the adsorption isotherm indicated that the adsorption occurred at homogeneous sites and form a monolayer. The Langmuir model was also able to explain the sorption equilibrium with maximum biosorption capacity.

Keywords: Sugarcane Bagasse, Adsorption, Activated Carbon, Heavy Metals

1. Introduction

Industrialization and increasing urbanization have led to amplified levels of industrial pollutions which result to significant ecosystem destruction with high pollutant concentrations of organic compounds and heavy metals in water resources [1]. Consequently, there is growing concern globally on the problems created by industrial activities on the environment [2] with various environmentalists highlighting the release of waste products into the environment is a global problem [3].

Industrial activities produce a large percentage of the pollutants that affect our environment and especially for water [4]. This is so because these industrial processes employ significant chemical inputs coupled with the inefficient in the use of the resource components. This leads to proliferated creation of waste sources that will require disposal into the

environment [5]. The poor efficiency of the treatment techniques employed for effluent treatment in these industries mean that pollutants are significantly present in treated discharged effluents. These pollutants include organic and inorganic pollutants amongst which are heavy metal ions, phosphates, sulphates, organic and hydrocarbon compounds [6]. Among the many industrial pollutants, heavy metals remain prominent due to its diverse routes of entry into the ecosystem, as well as its toxic implications across trophic levels [1]. Heavy metals do not biodegrade, implying that their toxic impacts will remain over extended periods of time [7].

Lead and cadmium are important toxic heavy metals that are increasingly present in the environment to which man is exposed to due to their wide applications in materials science and recent technologies [5]. Their effects also impact flora and

fauna. Lead is reported to cause cognitive impairment, encephalopathy, kidney and liver damage [8]. They may also cause anaemia and are toxic to the reproductive system [8, 9], while exposure to cadmium causes brain damage, malfunctioning of the central nervous system (CNS) abnormal growth and impaired development of plants and animals [10]. Also, lead which is a large cation, is particularly prone to reactions with protein functional groups such as sulfhydryl (-SH) groups in a reaction similar to cadmium ions [1].

Remediation solutions that enhance the removal of heavy metals from effluents and the general environment has become research priority in the last two decades with many technologies including ion exchange, chemical precipitation, oxidation, coagulation, electro dialysis, membrane separation, solvent extraction and photo-catalytic reduction already explored [3, 11]. The use of adsorbents is also one of such techniques. Commercial activated carbon has mostly been the preferred adsorbent of use for the removal of pollutants because of their versatility in removing a large group of compounds and metals. Nevertheless, the associated cost has somewhat restricted its usage, thus forcing researchers to use cheaper activated carbon sources such as waste materials of agricultural origin as alternatives [12].

Modern agricultural industries produce tons of by-products and wastes every year that have useful potential in adsorption [13]. Waste materials from agricultural sources help to minimize costs coupled with being eco-friendly as a result of their unique chemical composition, availability, abundance, renewability and low cost. One of such residues is sugarcane bagasse which has been reported to remove many target adsorbates from aqueous solution, including toxic heavy metals [14]. Unique functional groups including -OH, -COOH, -NH₂, -CONH₂, -SH₂, and -OCH₃ groups [15] found in the fibrous residue of sugarcane bagasse can bind pollutant ions onto the adsorbent surface [16]. The past decade has thus seen sugarcane bagasse including its derivatives enjoy extensive study as a potential adsorbent in both their raw and modified forms [17].

This work was aimed to evaluate the adsorption of Cd (II) and Pb (II) unto carbonized sugarcane bagasse from aqueous solution.

2. Methodology

2.1. Sample Collection and Preparation of Carbonized Sugarcane Bagasse

Sugarcane bagasse was obtained from Wadata market in Makurdi, Benue State, Nigeria between Jan to Mar 2019. After being washed properly with distilled water to remove sand particles and dirt, they were sundried and then oven dried for 24 hrs in each case. They were pulverized using a porcelain mortar and pestle, then sieved through a 2 mm mesh sieve. The sugarcane bagasse powder was carbonized at 350°C in a muffle furnace for 15 mins. The carbonised sugarcane bagasse was washed with distilled water and later with 0.1 M HCl at pH of 6.5 before being dried and kept for further analysis.

2.2. Preparation of Simulated Wastewater

The aqueous solutions containing Cd and Pb ions was prepared from analytical grade CdCl₂·2H₂O and PbNO₃ respectively. The 1000 ppm stock solutions of the salts were prepared before other concentrations of 5 ppm, 10 ppm, 25 ppm, 50 ppm, 75 ppm, 100 ppm and 150 ppm were prepared by serial dilution of stock solution.

2.3. Measurement of Physical Properties of Adsorbent

2.3.1. Bulk Density Determination

A 10 mL measuring cylinder dried and pre-weighed (w₁) was packed with 3 g of the carbonized sugarcane bagasse, leveled and weighed (w₂). The volume (v) of the packed material was then measured and bulk density calculated in g/mL using the following formula:

$$\text{Bulk density} = \frac{w_2 - w_1}{v}$$

2.3.2. Ash Content

An empty but clean crucible was preheated in a furnace at 500°C for 1 hour and later cooled in a desiccator and weighed (w₁). 2 g of the adsorbent was weighed into the preheated crucible (w₂). The crucible and its content placed in a muffle furnace and the temperature was raised to 500°C for 1 hour, it was allowed to cool in a desiccator before weighing w₃. Ash content was expressed using the below relationship:

$$\text{Ash content (\%)} = \frac{w_3 - w_1}{w_2 - w_1} \times 100$$

Where

W₁ = Weight of empty crucible (g)

W₂ = Weight of crucible + sample (g)

W₃ = weight after ashing (g)

2.3.3. Moisture Content

The moisture content was determined using oven drying method. A 2 g sample of carbonized sugarcane bagasse was transferred into an empty crucible and the total weight was noted as m₂. It was heated at 100°C in an oven, cooled in a desiccator and weighed m₁. The sample as heated repeatedly until a constant weight was obtained. The moisture content was calculated using the weight loss formula.

$$\text{Moisture content} = \frac{m_2 - m_1}{m_2} \times 100$$

Where

M₂ = Weight of crucible + sample (g)

M₁ = Constant weight obtained (g)

2.3.4. Attrition

A 1 g sample of carbonized sugarcane bagasse was steeped in 50 mL distilled water and stirred for 2 hrs using a magnetic stirrer. The solution was filtered and the residue was dried off for the weight of the residue to be determined using a weighing balance. The attrition was calculated based on the weight loss by the following expression.

$$\text{Attrition (\%)} = \frac{\text{Initialweight (g)} - \text{Finalweight (g)}}{\text{Initialweight (g)}} \times 100$$

2.4. Batch Adsorption Studies

Batch adsorption studies were carried out to obtain the rate of adsorption and equilibrium data. It was performed at different concentrations, adsorption dosage, contact time and varying pH.

2.4.1. Contact Time

The effect of contact time was studied at time intervals of 20, 40, 60, 80, 100, and 120 mins at room temperature using 0.2 g of the adsorbent in 20 mL of 15 mg/L of lead (II) nitrate solution in a container placed on a mechanical shaker at 130 rotation per minutes (rpm). The same process was carried out for cadmium chloride solution using 20 mL of 40 mg/L. They were later filtered and analyzed using atomic absorption spectrophotometer.

2.4.2. Adsorbent Dosage

Sample of carbonized sugarcane bagasse of masses 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 were added to 20 mL of 15 mg/L of lead (II) nitrate solution. The same process was carried out for hydrated cadmium chloride solution using 20 mL of 40 mg/L. They were stirred by a mechanical shaker for 1 hr then filtered and analyzed using atomic absorption spectrophotometer.

2.4.3. PH Variation

Adsorption was done at various pH; 2, 4, 6, 7, 9, and 12. The acidic and alkaline pH of the medium was adjusted using hydrochloric acid and sodium hydroxide solution. It was placed in a mechanical shaker for 1 hour and then filtered and the filtrate was taken for analysis using atomic absorption spectrophotometer.

2.4.4. Effect of Concentration

Exactly 0.2 g of the adsorbent was contacted with 20 mL of lead (II) nitrate solution of concentration 2.5, 5, 7.5, 10, 12.5, 15 mg/L and with 20 mL of hydrated cadmium chloride solution of concentration 20, 25, 30, 35, 40 mg/L respectively. They were placed in a mechanical shaker for 1 hour before they were filtered. The filtrates were taken for analysis using atomic absorption spectrophotometer.

2.5. Data Analysis

The adsorptive capacity of metal ions per unit adsorbent (mg/g) was determined using the expression:

$$Q_e = \frac{C_i - C_e}{M} \times V$$

Where Q_e = amount of metal removed per unit of the adsorbent (mg/g),

V = volume of metal solution (litres)

C_i = initial concentration of metal ions in the solution (mg/L)

C_e = final concentration of metal ions in the solution

M = dry weight of adsorbent.

Percentage removal of heavy metal ions from initial solution concentration was calculated from the following Equation:

$$\text{Percentage adsorption} = \frac{C_i - C_e}{C_i} \times 100$$

2.6. Kinetics Modeling

Equilibrium data for the adsorption of Pb (II) and Cd (II) ions from aqueous solution were fitted into the linearized form of the Langmuir model at constant temperature of 293K. Langmuir adsorption is used to quantify and contrast the adsorptive capacity of adsorbent. It accounts for the surface coverage by balancing the relative rates of adsorption and desorption.

3. Results and Discussion

3.1. Physicochemical Attributes of the Adsorbent

Bulk density gives an estimate of packing volume, and it is of great importance in the adsorbate uptake by the adsorbent. Table 1 has the bulk density of carbonised sugarcane bagasse to be 0.58 g/mL, when compared with date palm seed activated carbon with bulk density 0.69 g/mL, it can be observed that they result are in close agreement which suggests it would be a good adsorbent.

The Ash content of sugarcane bagasse is the residue that remains after all the combustible matter in it has been completely burned off and it is a chemical property relating to quality indexing. The ash content of the adsorbent is 21% which is relatively higher and thus indicates high presence of organic matter when compared with palm kernel shell that has ash content of 14.2%. The attrition value showed 31.33% indicating that resistance to abrasion was high, while the moisture content of the adsorbent (0.79%) validates the efficiency of the adsorbent as suitable for adsorption studies.

Table 1. Physicochemical attributes of the adsorbent.

Attribute	Result	Standard Values
Bulk density	0.58 g/mL	0.69 g/mL
Ash content	21%	14.2%
Attrition	31.33%	20%
Moisture	0.79	0.60%

3.2. Batch Adsorption Studies

3.2.1. Effect of Adsorbent Dosage

The effect of adsorbent dosage on adsorption of Pb (II) and Cd (II) ions from aqueous solution is given in Figures 1 and 2. The uptake of Pb (II) and Cd (II) ions per unit mass of adsorbent decreased with increase in the adsorbent dosage. This may be explained on the basis of mass balance relationship. As adsorbent dosage is increased and the initial solution concentration is fixed as well as volume of solution, the available ions were not enough to cover all the active adsorption sites on the adsorbent, resulting in low adsorbate uptake.

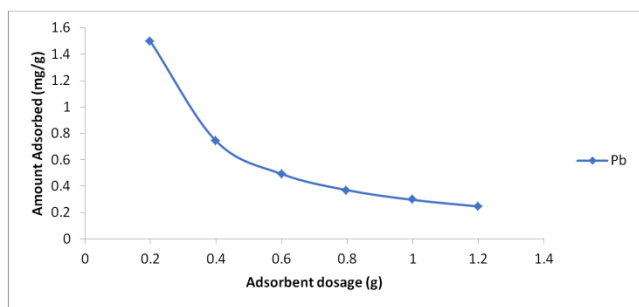


Figure 1. Effect of adsorbent dosage on removal of Pb ion from aqueous solution.

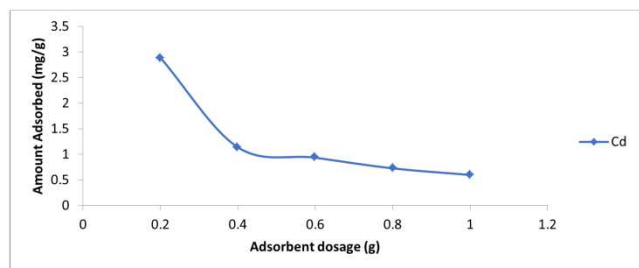


Figure 2. Effect of adsorbent dosage on removal of Cd ion from aqueous solution.

3.2.2. The Effect of Concentration

The Figures 3 and 4 show the effect of concentration on adsorption of Pb (II) and Cd (II) ions. The equilibrium sorption capacities are seen to increase with an increase in concentration. The reason for this may be credited to the fact that higher aqueous concentrations increases the driving force of the concentration gradient at solid-liquid interface which results in an increase in adsorption.

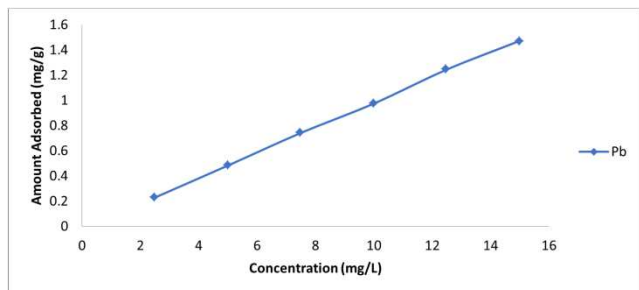


Figure 3. Effect of concentration on removal of Pb ion from aqueous solution.

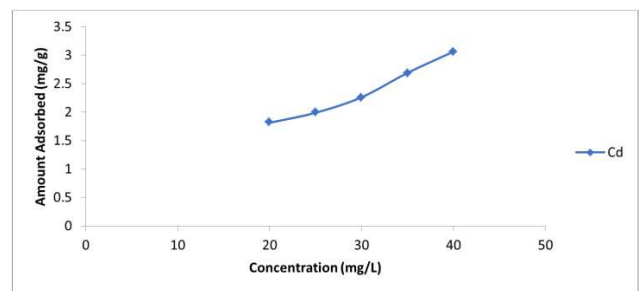


Figure 4. Effect of concentration on removal of Cd ion from aqueous solution.

3.2.3. Effect of Contact Time

Figures 5 and 6 show the effect of contact time on the

adsorption capacity of the carbonized sugarcane bagasse. Metal removal increased rapidly with the increase of contact time from 20 minutes and maximum adsorption capacity is reached at 80 minutes for both metals after which decrease in adsorption occurred. The increase in adsorption can be attributed to the rapid attachment of Pb (II) and Cd (II) ions to the surface of the carbonized sugarcane bagasse by surface mass transfer. And the rapid decrease in adsorption may be due to available external sites already occupied.

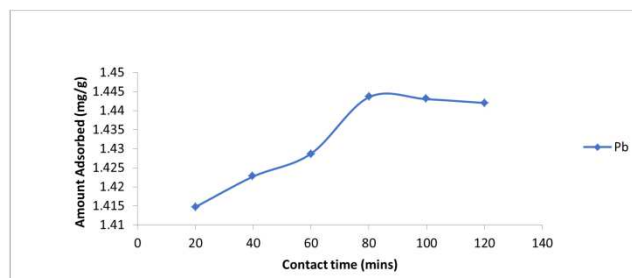


Figure 5. Effect of contact time on removal of Pb ion from aqueous solution.

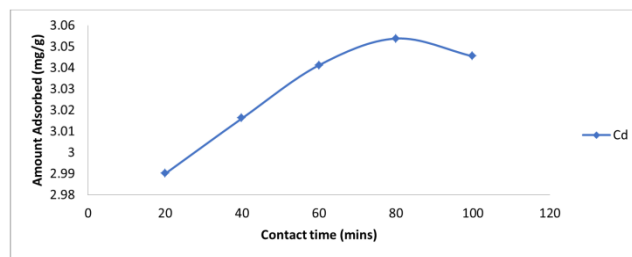


Figure 6. Effect of contact time on removal of Cd ion from aqueous solution.

3.2.4. Effect of PH

The Figures 7 and 8 show the effect of pH on Pb (II) and Cd (II) ions onto carbonized sugarcane bagasse. It can be noticed that Pb (II) and Cd (II) ions uptake increase with increase of pH from pH 2 till it reaches its maximum at pH 6 for Pb (II) and pH 4 for Cd (II) and a decrease in adsorption is observed followed by constant uptake at higher pH from pH 8 to 12 for Pb (II) and pH 6 to 12 for Cd (II) ions respectively. The increase in sorptive removal of ions at acidic pH (2 to 6) is probably due to the absence of excess H^+ ions competing with the Pb (II) and Cd (II) ions for the sorption sites. At higher pH (>7), the presence of OH^- ions concentration compete with the negative active sites on the adsorbent leading to a constant adsorption and hence its uptake [18].

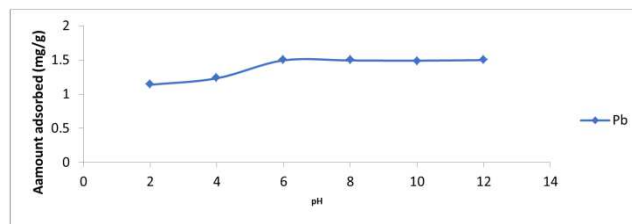


Figure 7. Effect of pH on removal of Pb ion from aqueous solution of lead (II) nitrate.

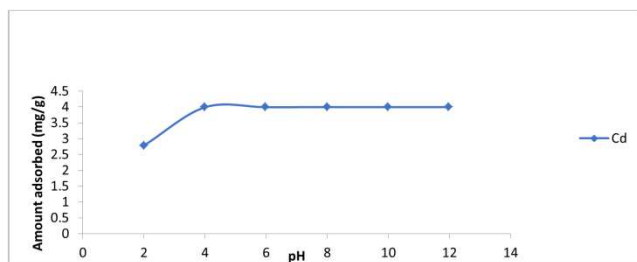


Figure 8. Effect of pH on removal of Cd ion from aqueous solution from Cadmium chloride.

3.2.5. Adsorption Isotherms

Adsorption is proportional to the fraction of the surface of the adsorbent that is open while desorption is proportional to the fraction of the adsorbent surface that is covered [4]. The linearised isotherms in Figures 9 and 10 show that Pb (II) ion has the correlation coefficient ($R^2 = 0.954$) and Cd (II) ion has the correlation coefficient ($R^2 = 0.972$). It can be noticed that the Langmuir isotherm model exhibits satisfactory straight line. It confirms the homogeneous nature of adsorbent surface. The maximum adsorption capacity for Pb (II) ion $Q_m = 7.2993$ (mg. g⁻¹) and the Q_m for Cd (II) ion = 1.1507 (mg. g⁻¹) indicate that the sorptive removal of ion is favourable. The Langmuir constant K_L for Pb (II) ion = -0.6524 (L/mg) and the K_L for Cd (II) ion = 6.6845 (L/mg). The dimensionless equilibrium called separation factor R_L for Pb (II) ion = -0.1284 and K_L for Cd (II) ion = 0.0037. The values of R_L are within $0 < R_L < 1$ range for the adsorbent signifying favourable adsorption.

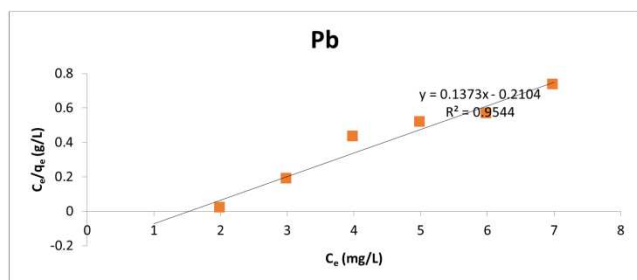


Figure 9. Linearised Langmuir Isotherm for adsorption of Pb (II) and Cd (II) ions at 298K.

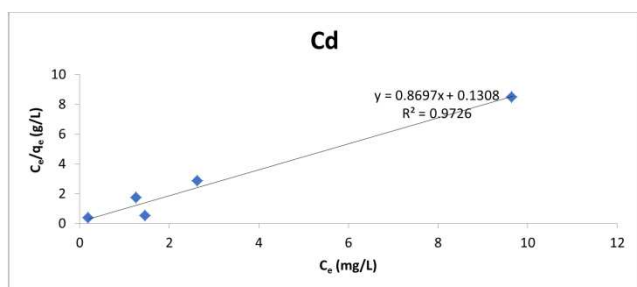


Figure 10. Linearised Langmuir Isotherm for adsorption of Cd (II) ions at 298K.

Table 2. Langmuir Isotherm parameters at 298 K for Pb (II) ion.

Q_m (mg. g ⁻¹)	K_L (L. mg ⁻¹)	R^2	R_L
7.2993	-0.6524	0.954	-0.1284
Langmuir Isotherm parameters at 298 K for Cd (II) ion			
Q_m (mg. g ⁻¹)	K_L (L. mg ⁻¹)	R^2	R_L
1.1507	6.6845	0.972	6.6845

4. Conclusion

The results of this study revealed that carbonized sugarcane bagasse may be a potentially viable adsorbent for application in the removal of Pb (II) and Cd (II) ions from aqueous solutions. The adsorption equilibrium could be well described by the Langmuir adsorption isotherm indicating that the adsorption occurs at homogeneous sites and form a monolayer. The Langmuir model was also able to explain the sorption equilibrium with maximum biosorption capacity.

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