

Full Length Research Paper

Evaluation of kinetics and equilibrium studies of biosorption potentials of bamboo stem biomass for removal of Lead (II) and Cadmium (II) ions from aqueous solution

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The discharged of lead and cadmium above maximum permissible limits into surface water and environment without any pre-treatment methods has caused severe health challenges to humanity. In order to minimize the reoccurrence, this research aim to ascertain biosorption capacity of bamboo stem biomass to remove lead and cadmium from aqueous solution. Batch experiment and data evaluation under optimum removal conditions (such as pH, contact time, temperature, biosorbent dosage, initial heavy metal concentration) were determined. Maximum optimum removal was observed for both metal ions at pH 5, 90 min contact time, 298K temperature with 50 ppm of initial concentration for 95.92 and 80.98% removal for lead and cadmium. Lead revealed better results at all concentrations for bamboo stem biomass with increase in percentage removal as concentration of heavy metal increases. Kinetics and isotherms models were applied and this shows that kinetic models are described and fitted well with pseudo-second order reaction while adsorption isotherm model supported Freundlich model with high R^2 values. Thermodynamically, biosorption of lead and cadmium was exothermic and lead was greater than cadmium in the order of spontaneity and entropy. From these results, it can be concluded that bamboo stem biomass has been shown to be productive in removal of heavy metals from aqueous solution.

Key words: Biosorption, bamboo stem biomass, heavy metals, kinetics, isotherms, thermodynamics.

INTRODUCTION

The world we live in today is being threatened by extinction due to the activities of mankind in their desire

to recondition the environment for their conduct. Such activities include agricultural practices, mining, military,

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Table 1. European standards (EU) standards for heavy metals in soil, food and drinking water.

Heavy metal	Soil ($\mu\text{g}/\text{kg}$)	Food (mg/kg)	Water (mg/L)	EU standard soils ($\mu\text{g}/\text{g}$)
Cd	3-6	1.5	0.01	3
Cr	-	20	0.05	150
Cu	135-270	30	0.05	140
Fe	-	-	0.03	-
Ni	75-150	1.5	-	75
Pb	250-500	2.5	0.1	300
Zn	300-600	50.0	5.0	300
As	-	1.1	0.05	-
Mn	-	-	0.1	-

Source: Tóth et al. (2016).

and wastes from research activities, construction works and industrial activities. Prominent amongst the effects of these activities is pollution of air, water, and land. Environmental pollution has posed a serious concern and challenging problem due to rapid population and diverse progress in societies, sciences, technologies, and industries. The industrial effluent containing both inorganic and organic toxic compounds which are discharged into surface water majorly stream and river without any pre-treatment techniques have seriously affected biodiversity, ecosystem functioning and natural activities of aquatic system (Martín-González et al., 2014; Mohammed et al., 2014).

According to Comprehensive Environmental Response Compensation and Liability Act, USA, the maximum permissible limit of heavy metals concentrations in aqueous medium is as follows, Cr-0.01 mg/L, Ar-0.01 mg/L, Cd-0.05 mg/L, Hg-0.002 mg/L, Pb-0.015 mg/L, and Ag-0.05 mg/L, respectively (Jaishankar et al., 2014). If the heavy metal concentration exceeds those recommended permissible limits, it can be major contribution to many life threatening diseases. In human, Pb may cause severe damage to kidney, brain, liver, reproductive and nervous systems (Babarinde et al., 2016; WHO 2016), as well as oxidative stress and impaired respiratory infections (Roy et al., 2015; Jurdzia et al., 2015) whereas Cd in human and other aquatic animal cause behavioral alterations (Pan et al., 2017), immunity disruption (Wang et al., 2019), genotoxicity (Pereira et al., 2016) reproductive impairment, mortality, among other toxic effects (Hani et al., 2019; Krzykwa et al., 2019). Therefore, in order to protect the environment and human health, the removal of heavy metal ions from water is very important (Saad et al., 2016). This has led many researchers to develop various technological processes to remove contaminations levels caused by these heavy metals and bring them within permissible limits in the environment in terms of soil, food and water (Tóth et al., 2016) (Table1). Most of the industrial scale remediation techniques involving physical, chemical, and biological methods as conventional method such as

chemical precipitation, ion exchange, reverse osmosis, adsorption, membrane separation, electro kinetics, coagulation, biosorption etc (Gautam et al., 2015) have been used as single techniques for heavy metal removal from soil, water and sediments and despite the huge contribution by the processes they still have some high level of disadvantages in terms of low efficiency, high operational cost, sludge production and failure at large scale implementation (Selvi et al., 2015), therefore in order to overcome these disadvantages, associate with these conventional methods and provide feasible alternatives that can help to increase the efficiency of heavy metals remediation as reported by many researchers in recent years (Mao et al., 2016; Selvi and Aruliah, 2018) which must have various advantages, there is need for effectiveness, eco-friendly, versatile, short duration, on-site adaptability, and large scale option, easy to set up etc (Mao et al., 2016). Owing to these outcomes, biological methods such as biosorption processes are gaining much popularity due to metal binding capacity of various biological materials and have been considered as novel, economic, efficient, and eco-friendly technology (He and Chen, 2014) treatment alternative for the removal of heavy metals from various environmental matrices generated from various industries. Biosorption can be defined as a simple metabolically passive physicochemical process involved in the binding of metals ions (biosorbate) to the surface of the biosorbent which is of biological origin (Mrvčić et al., 2012). This biological removal method include the use of microorganisms, plant derived materials, agriculture or industrial wastes, biopolymers, and so on. The biosorption process involves a solid phase (sorbed or biosorbent) and liquid phase (solvent, usually water containing a dissolved species to be sorbed). Because of higher affinity capacity of the sorbent materials for the sorbate species, the latter gets attracted and bounded through different mechanisms. The use of different low cost biosorbent materials have been employed in the treatment of wastewater to remove different types of heavy metals concentrations in many industries like food,

mining, fertilizer, paper, pharmaceuticals, etc, and these biosorbent materials include industrial by-products (such as tea waste, sugar waste, antibiotic waste, paper mill waste, cement waste, etc), agricultural waste materials (such as rice husk, sugar cane bagasse, green coconut shell, peanut hull, barley straw, neem bark, cassava peeling, bamboo etc) and microbial biosorbent (algae biomass, bacteria biomass and fungi biomass). Algae biomass includes; *Spirogyra* sp, *Enterobacter* sp, *Palmaria palmate*, *Oedogonium hatei* etc; Bacteria biomass includes; *Bacillus cereus*, *E. coli*, *Pseudomonas putida*, *Arthrobacter* sp, *Rhizobium* spp etc; Fungi biomass includes; *Penicillium canescens*, *Aspergillus niger*, *Pleurotus oestreatus*, *Saccharomyces cerevisiae* etc and also inorganic precursors (such as chitosan, red mud, clay, zeolites, blast furnace slag etc) (Bilal et al., 2013; Grassi et al., 2012) to mention a few. The literatures from past researchers have shown that basic and applied aspects of heavy metal biosorption by varieties of agricultural waste biomass have gained much popularity. Among all these agricultural waste biomass, bamboo still remain notable adsorbent for the removal of pollutants from polluted gaseous and liquid streams and is readily available in large quantities, is a cheap material, can be disposed without expensive regeneration process and highly effective capacity in removing heavy metals pollutants from any wastewater. Bamboo is a perennial woody grass, which belongs to the family Gramineae and subfamily Bambuseae (He et al., 2014). It is an evergreen, monocotyledonous (or non-woody) plant, which produces primary shoot without any later secondary growth (Kleinhenz et al., 2001). It is flexible, elastic and has a higher compressive and tensile strength due to ability to resist forces. According to their morphology, bamboos are broadly divided into monopodial (or running) bamboos with 'leptomorph' rhizome system and sympodial (clumping) bamboos with 'pachymorph' rhizome system. These differences in rhizome systems can be because of their adaptations to climate conditions to which the bamboos belong.

Cellulose, hemicelluloses and lignin are the three major chemical compositions of bamboo, and they are closely bonded together and associated in a complex structure (Li et al., 2014). They contribute to about 90% of the total bamboo mass. The minor components are pigments, tannins, protein, fat, pectin, ash and aqueous extracts. Others include resins, waxes and inorganic salts. These constituents play a vital important role in physiological activity of bamboo, and they are found in cell cavity or special organelles (Khalil et al., 2012). The chemical composition of bamboo is known to be similar to that of wood, but bamboo has a higher content of minor components compared with wood (Nurul et al., 2016), and all other agricultural waste materials make bamboo biomass to have high sorption capacity for removal of heavy metals pollutants when compared to other agricultural biosorbent materials. From other studies, it

has been reported that the chemical composition of bamboo fibre was 73% cellulose, 12.49% hemi cellulose, 10.15% lignin, 3.16% aqueous extract, and 0.37% pectin which was very high when compared to all other agricultural fibers (Li et al., 2010). From different previous researches using other agricultural waste, the biosorption capacities of bamboo have been used for the removal of heavy metals. This study assesses the capabilities of two common plants in tropical wetlands; *Raffia bambusa* and *Bambusa vulgaris* to remove Cu^{2+} , Pb^{2+} , Ni^{2+} and Cd^{2+} from wastewater. The *R. bambusa* appeared to have more pronounced groups than *B. vulgaris* in terms of removal capacity by showing maximum sorption of 95% Cu and Pb but have lower maximum sorption capacity of about 40% for Cd and Ni by biomass derived from roots of these plants (Ofori-Sarpong et al., 2016).

Furthermore, research have shown that biosorption of Lead (II) from aqueous solution and industrial effluent by using leaves of *Araucaria cookie* revealed batch studies under optimum parameters were to evaluate biosorption efficiency to remove Lead (II) from wastewater and reached a maximum sorption removal of 98.52%. Isotherms and kinetic models were applied and this shows that kinetic models are described and fitted well with Pseudo-second order reaction. The model and experimental data was favourable in the removal of Lead (II) in the industrial waste water and leaves of *Araucaria cookie* be used as low cost biosorbent (Deepa et al., 2014). In addition, the potential and feasibility of compost and biogas residues have been used for the biosorption and removal of Pb from contaminated water using a batch experiment to explore at equilibrium state using adsorption isotherm and kinetic model shows a greater sorption capacity and removal of 65-85% of Pb using compost residue compared to 41-69% removal using biogas residues. It concluded that compost residue was more porous and had greater surface area potentials than biogas residue for the removal of heavy metals from aqueous solution (Shah et al., 2018). Also, it has been described that adsorption capacity of bamboo stem activated carbon was used to remove Pb^{2+} from aqueous solution showing the maximum sorption capacity at lower pH, and bamboo activated carbon revealed better results at lower metal concentration and high solution temperature. Isotherm model supported multilayer adsorption of Pb^{2+} on bamboo activated carbon and thermodynamic parameter revealed negative free energy, positive entropy and enthalpy as spontaneous and endothermic nature of adsorption process using activated bamboo stem (Masood et al., 2015). The aim of this study is to evaluate biosorption of Pb^{2+} and Cd^{2+} ions from aqueous phase by bamboo stem biomass. Batch experiment and data evaluation under optimum removal conditions (such as pH, contact time, temperature, biosorbent dosage, initial heavy metal concentration and metal recovery) were determined. Various kinetics and equilibrium model were applied to describe the biosorption

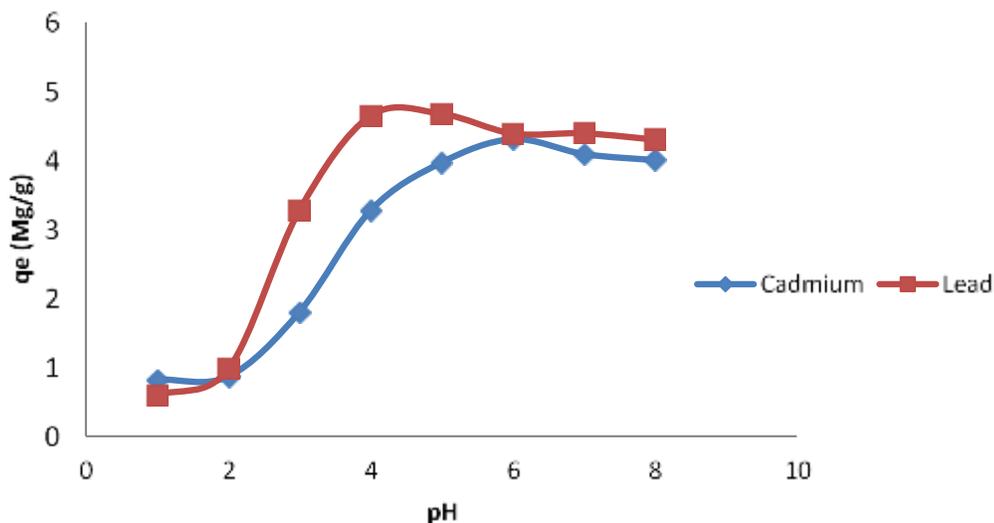


Figure 1. Plot of impact of pH on the adsorption of Cadmium (II) and Lead (II) ions.

behavior of bamboo stem biomass.

MATERIALS AND METHODS

Aqueous solutions of cadmium and lead were prepared from cadmium chloride and lead (II) trioxonitrate (V) respectively. Different experimental solutions were prepared by diluting the stock solution to the required concentration using distilled water. The pH of the systems was kept constant using 0.1 M HNO₃ and 0.1 M NaOH. The concentrations of metals were determined with Atomic Absorption Spectrometer (Bulk 210VGP).

Preparation of bamboo stems biomass

A big bamboo stem (*B. vulgaris*) was collected from the bush at Iloko-ljasha, Oriade Local Government, Osun State; Nigeria. It was allowed to dry by making it spend several days in the sun. It was later cut into bits and pieces by a mechanical cutter and taken to the mechanical grinder for grinding. The powdery substance was sieved using the 75 μ mesh size sieve, therefore the particle size was between 0-74 μ and the sieved sample was kept inside a polythene bag and stored in a dry place.

Batch adsorption studies

The adsorption highlights of the biosorbent bamboo stem biomass were researched as a component of pH, initial heavy metal concentration, biosorbent portion, contact time and temperature. The equilibrium and kinetics were obtained from batch experiments; 1 g of the bamboo stem biomass was weighed into reaction vessels containing 100 ml of 50 ppm each cadmium and lead solution of a particular pH (1–8) mixed together and agitated for six hours. The adsorbents were filtered into clean sample bottles and taken for metal analysis. The final pH of the solution was measured with a pH meter and the metal concentration in each sample was measured using an Atomic Absorption Spectrophotometer (AAS). The effect of sorbent resident time was monitored by allowing 1 g of bamboo

stem biomass to interact with 100 ml each of 50 ppm metal solutions at the optimum pH, room temperature and shaken for different time. The adsorbents were filtered into clean sample bottles and taken for metal analysis. The biomass dosage on the biosorption was studied using different masses of bamboo stem biomass ranging from 0.25, 0.5, 1.0, 1.5 and 2.0 g that were placed in 100 ml of 50 ppm of each Cadmium and Lead solutions at pH 5 and room temperature. The mixture was shaken for 90 min, filtered and filtrate collected for metal analysis using Atomic Absorption Spectrophotometer. On the basis of data obtained from resident time study, applicable sorption kinetics was determined using the Lagergren pseudo first order and pseudo second order kinetic models and Elovich model. Recovery of bound metals unto bamboo stem biomass was carried out using 0.05, 0.1, 0.5 and 1.0 M HCl solution. After each experiment, the mixtures were shaken for 90 min, filtered and filtrates collected for metal analysis.

RESULTS AND DISCUSSION

Impact of pH on the adsorption of Lead (II) and Cadmium (II) ions

Several researchers have reported that biosorption capacity of heavy metals in wastewater depend on pH of the solution (Demirbas, 2008; Johnson et al., 2008; Ioannidou and Zabaniotou, 2007). Therefore, the pH at which the optimum sorption of metal ions by bamboo stems biomass is important at solid- liquid interphase. According to (Ngah et al., 2008; O'Connell et al., 2008), adsorption increases as pH of the solution increases.

Presented in Figure 1 is the plot of pH profile study for cadmium and lead metals. Both metals showed an optimal binding pH of 5. Binding decreased after pH 5 due to the formation of soluble hydroxides. The effect of pH on adsorption capacity of lead and cadmium is shown in Figure 1. As the pH of the lead solution increased from

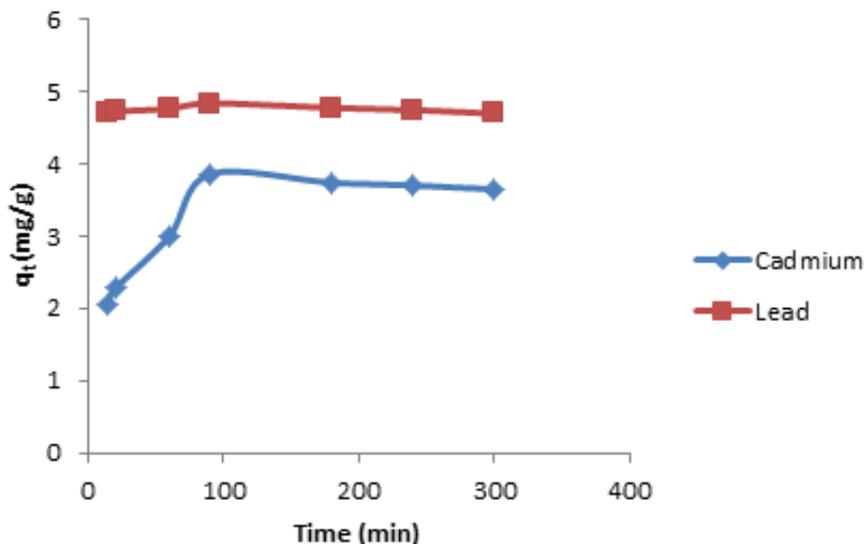


Figure 2. Plot of Effect of contact time on the adsorption of Cadmium (II) and Lead (II) ions.

1.0 to 8.0, the adsorption capacity of lead was changed, that is, it first increased from pH 1.0 to pH 5.0 and then decreased up to pH 8.0. The removal potency was highest at pH 5 with 93.60% representing the q_e value 4.68 mg/g of the initial metal concentration removed. Lead study shows that 11.8 to 93.60% of the 50 ppm adsorption was attained from pH 1 to 5. The optimum pH value was 5 with 93.60% adsorption corresponding to 4.68 mg/g of metal removal. It is in line with the work reported by (Reddy et al., 2012; Ahmad et al., 2015). The metal sorbed was higher for lead than cadmium even at the alkaline pH of 8. Cadmium ions showed similar trend as lead though the removal potency of the biomass for cadmium was slightly higher at pH 1 with 16.4% of the initial metal concentration, corresponding to 0.82 mg/g removed. Also, slightly higher amount of 0.865 mg/g corresponding to 17.3% was sorbed at pH 2. Subsequently, the removal efficiency was lower at every pH with 79.45%, corresponding to 3.9725 mg/g removed at pH 5 which remained the optimum pH. At low pH values, the adsorption sites are protonated thereby reducing metal ion that can be adsorbed (Henryk et al., 2016).

Effect of contact time on the adsorption of Lead (II) and Cadmium (II) ions

Effect of contact time on adsorption was studied and the results are shown in Figure 2. This result indicated that metal ions removal was increased with an increase in contact time before equilibrium was reached (Zafar et al., 2007; Yin et al., 1999). Other parameters such as dose of adsorbent and pH of solution were kept constant. The

effect of contact time for 100 ml of 50 ppm of cadmium and lead showed that both metals had fairly high adsorption in the first fifteen minutes with 94.00% corresponding to 4.6975 mg/g of lead and 41.2% corresponding to 2.06 mg/g of cadmium sorbed. Thereafter, removal increases and at 90 min, 77.2% corresponding to 3.86 mg/g of cadmium and 97.38% corresponding to 4.8429 mg/g of lead had been sorbed and that was the optimum. Sorption subsequently decreased and at 300 min, sorption was 3.65 mg/g and 4.7005 mg/g respectively for both cadmium and lead. After this equilibrium period, the amount of metal adsorbed did not change significantly with time. The fast adsorption at the initial stage was probably due to availability of sufficient number of vacant sites on the surface of the adsorbent. The underlying increment in metal expulsion was likely because of extra-cell authoritative. The pace of metal evacuation was higher until when harmony was reached because of a bigger surface zone of the adsorbent being accessible for the adsorption of the metals. It is additionally pertinent to bring up that, since dynamic sorption destinations in a framework have a fixed number and every dynamic site can adsorb just one of every monolayer, the metal take-up by the sorbent surface will be quick at first, backing off as the challenge for diminishing accessibility of dynamic locales increases by the metal particles staying in arrangement.

Effect of adsorbent dosage on the adsorption of Lead (II) and Cadmium (II) ions

The effects of variation in bamboo stem biomass dosage

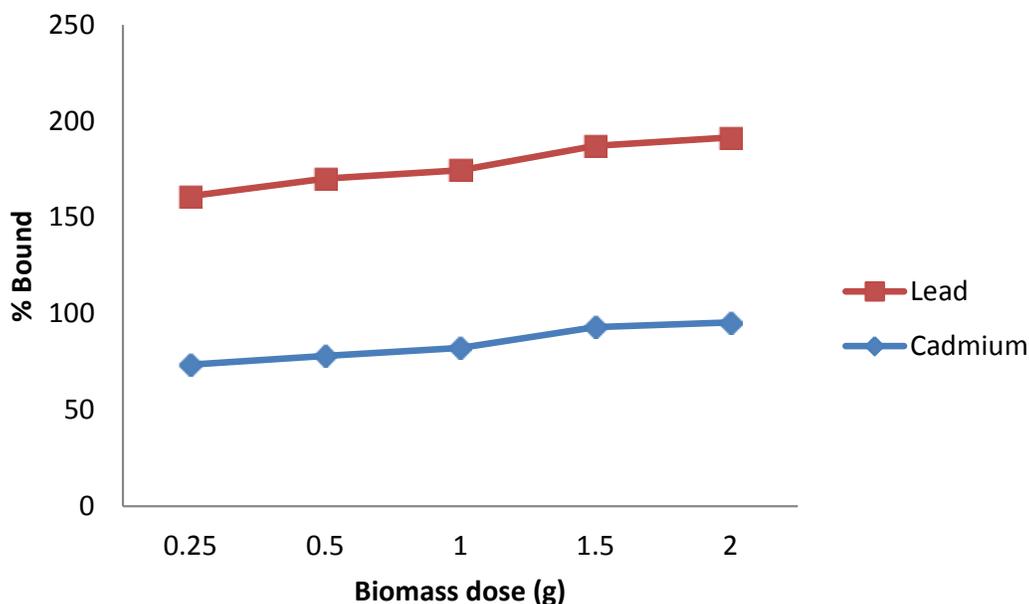


Figure 3. Effect of variation of biomass dose on the adsorption of Cadmium (II) and Lead (II) ions.

on the amount of metals sorbed are shown in Figure 3 for cadmium and lead respectively. The adsorption of metals was studied at various adsorbent dosages of 0.25, 0.5, 1.0, 1.5 and 2.0 g with each dissolved in 100 ml of 50 ppm metal solutions. Adsorbent provides binding sites for the sorption of metal ions, and hence its concentration strongly affects the sorption of metal ions from the solution (Reddy et al., 2012; Stephen and Stilonana, 2004). The amount of adsorbent used for the treatment studies is an important parameter, which determines the potential of adsorbent to remove metal ions at a given initial concentration. Kanamadi et al., (2006) made a similar submission in a technical report on the biosorption of heavy metals by a low cost adsorbent. The percentage lead removed depends on the adsorbent dosage due to adsorption surface area. The percentage metal sorbed increases with increase in biosorbent dose for the heavy metals. Cadmium showed the percentage metal bound at 0.25 g biomass dose was 73.4% and increased to about 95.4% at 2.0 g biomass dose. Lead showed a similar trend with 87.6% at 0.25 g to 96% at 2.0 g. Generally, sorption did not increase significantly with increase in biomass dose beyond 1.5 g which makes the use of biomass dose beyond the amount unnecessary for that concentration. This is consistent with some work which suggested that after a particular dosage level, adsorption is not significant with increase in dosage and may even decrease (Liping et al., 2007). Similar result was reported by (Ghorbani et al., 2012). At low biosorbent dose, all types of sites are entirely exposed and the adsorption on the surface is saturated faster, showing a higher q_e value. But at higher adsorbent dose, the availability of higher energy sites decreases with a larger fraction of lower

energy sites occupied, resulting in a lower q_e value (Aksu 2001). The biosorption capacity of compost per gram reduces as its biomass increases might be due to partial aggregation of biomass, which usually occurs at greater biomass and this phenomenon decreases access of metal ions to active sites for sorption (Ajmal et al., 1998; Gueu et al., 2007).

Temperature effect on the adsorption of Lead (ii) and Cadmium (ii) ions

Temperature is another significant physicochemical parameter as it changes the adsorption limit of the adsorbent. The impact of temperature on the balance take-up of cadmium and lead particles was researched at different temperatures of 298K, 308K, 318K, 328K, and 338K separately and at 50 ppm.

Figure 4 is the temperature plots for both cadmium and lead individually. It has been accounted for that at a high temperature; the thickness of the limit layer diminishes because of the expanded inclination of the metal particle to escape from the biomass surface to the arrangement stage, which brings about abatement in adsorption as the temperature builds (Krishnan, 2002). Increasing temperature may bring down the powers of adsorption between the adsorbate and the adsorption destinations on the biomass surface causing a reduction in adsorption limit (Huang and Blankenship, 1984). This was confirmed in the investigation whereby the adsorption of cadmium and lead by the biomass decreased with increase in temperature. For cadmium at 50 ppm and room temperature (298K), the metal absorbed per gram of the

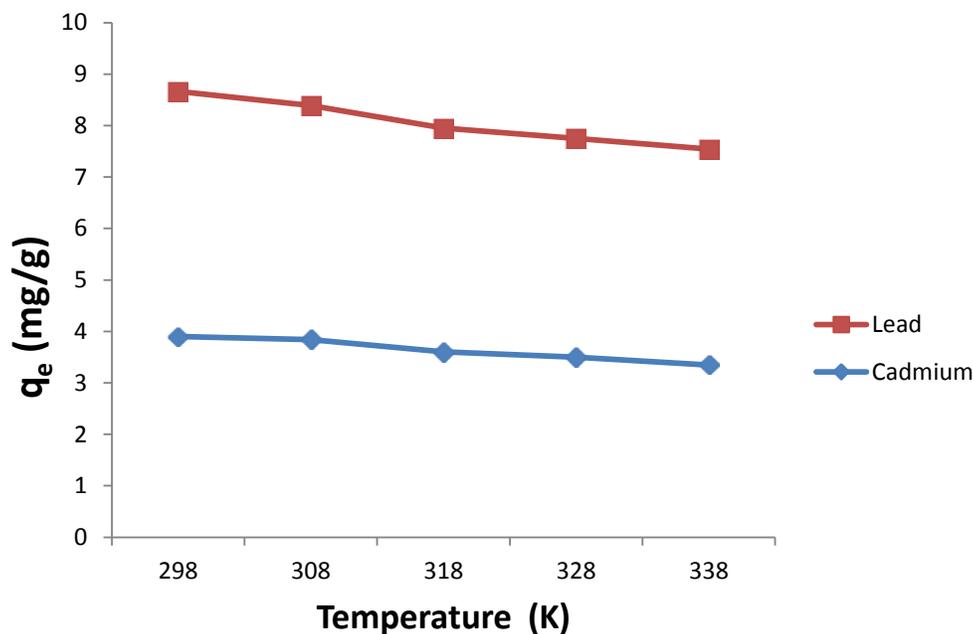


Figure 4. Effect of temperature on the adsorption of Cadmium (II) and Lead (II) ions.

biomass (q_e) was 3.9 mg/g while 3.35 mg/g was sorbed at 338K. For lead, 4.76 mg/g was sorbed at room temperature as against 4.19 mg/g sorbed at 338K. Atef and Manasreh, (2009) presented a comparable report that adsorption limits expanded with diminishing temperature which showed that the adsorption procedure was exothermic.

Effect of metal ion concentration on the adsorption of Lead (II) and Cadmium (II) ions

Initial concentration has effect on biomass. Initial concentration of Cd (II) and Pb (II) were varied from 25 - 200 ppm and the quantity of biosorbent was kept constant at 1 g, pH 5 maintained with contact time 90 min. Figure 5 is a plot of q_e (mg/g) against initial metal ion concentrations. Cadmium had maximum adsorption at 25 ppm with 80.98% corresponding to a q_e (mg/g) of 2.0245 mg/g adsorbed, but the percentage metal bound decreases from 77.9 to 51.0% as the concentration progressed from 50 to 200 ppm. Lead biosorption decreases with increase in the initial metal ion concentration. Lead showed that removal was highest and 25 ppm with 95.92%, corresponding to a q_e value of 2.398 mg/g. This is consistent with the reported works of some analysts. Adsorption efficiency reduced as the initial ion concentration increased (Ghorbani et al., 2012). From the result, the amount of Pb^{2+} ions removed was higher than Cd^{2+} ions by the biomass. This may be due to difference in their ionic radii. The size of ionic radius has effect on hydrolysis which lead to sorption removal. The

ionic radius of Pb^{2+} is 1.20 while that of Cd^{2+} is 0.97 (Banat et al., 2007).

Effect of metal recovery on the adsorption of Lead (ii) and Cadmium (ii) ions

Desorption was studied by treating biomass with various initial HCl concentrations of 0.05 M, 0.1 M and 0.5 M and 1.0 M respectively. Mineral acids have been found to be effective desorbents of Pb^{2+} and Cd^{2+} when bound to a biomass (Low, 1960). In acidic solution, the carboxyl, carbonyl or hydroxyl groups inside the biomass are protonated and do not attract metal ions; besides, protons replace the bound metal ions (Langmuir, 1916). The data obtained from this experiment are consistent with this observation. 89.5% of Cd^{2+} was desorbed at 0.05 M, and this increased to 92.3% Cd^{2+} at 0.1 M HCl concentration, which is the optimum, and fell to 81% at 1.00 M. while 88.63% Pb^{2+} was desorbed at 0.5 M HCl concentration and 81.86% at 1.0 M concentration of the acid. Higher concentration of the acid beyond 0.1 M in the case of Cd^{2+} and 0.50 M in Pb^{2+} was therefore unnecessary. The percentage metal ions recovery at various concentrations of HCl was illustrated in the bar charts shown in Figure 6.

Kinetics of Cadmium and Lead adsorption

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and

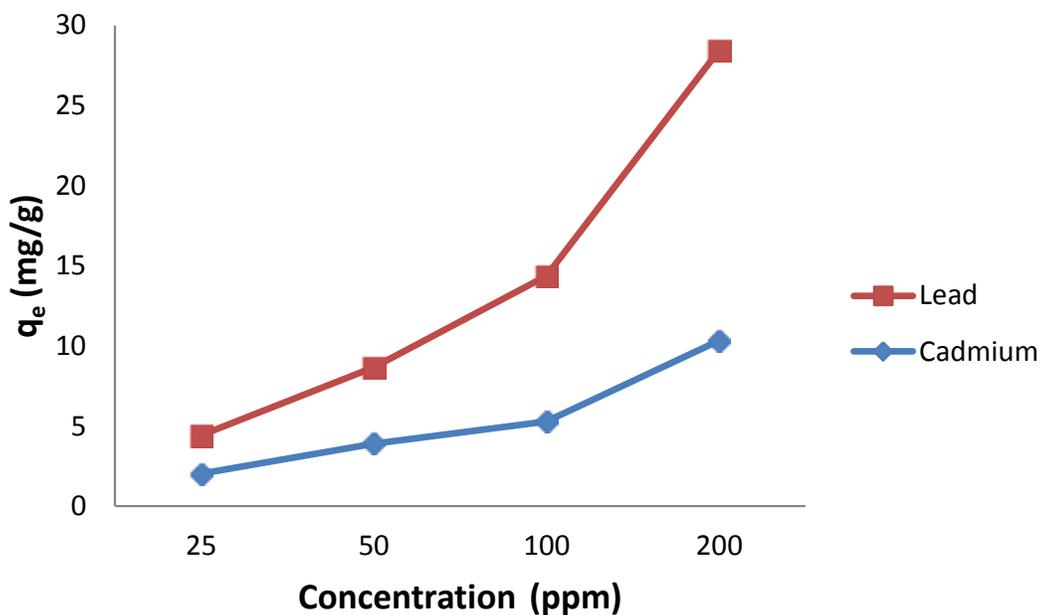


Figure 5. Effect of initial metal ion concentration on the adsorption of Lead (II) and Cadmium (II) ions.

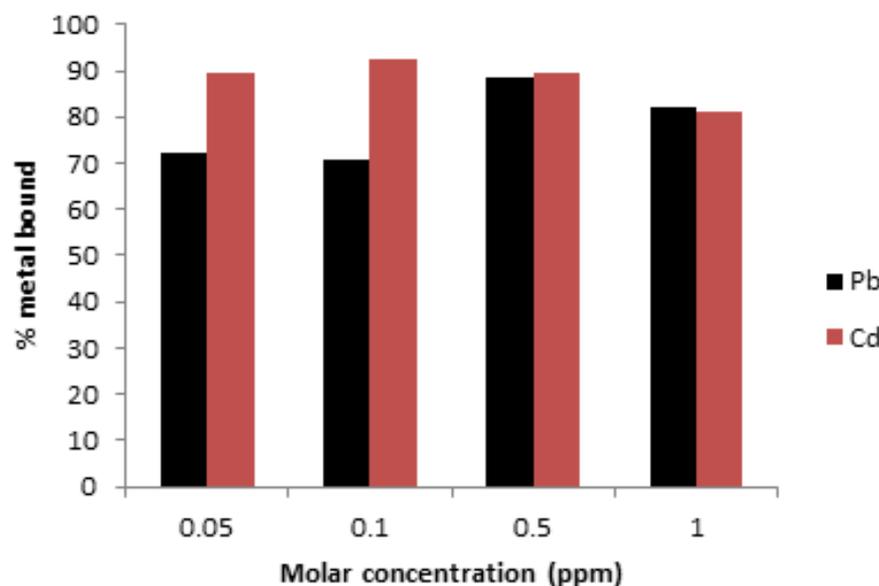


Figure 6. Metal recovery bar-charts for Cadmium and Lead.

chemical reaction, the Lagergren pseudo-first order and pseudo second order equations were applied to model the kinetics of Cadmium and Lead adsorption onto bamboo biomass in metals solution

Pseudo-first-order kinetic model

The pseudo-first-order rate expression, based on solid

capacity, is generally expressed as follows

$$\frac{dq}{dt} = K_{ads}(q_e - q_t) \quad (1)$$

This in logarithm form is

$$\text{Log}(q_e - q_t) = \text{Log}q_e - \frac{K_{ads}t}{2.303} \quad (2)$$

The plot of $\log(q_e - q_t)$ against time was plotted to give a

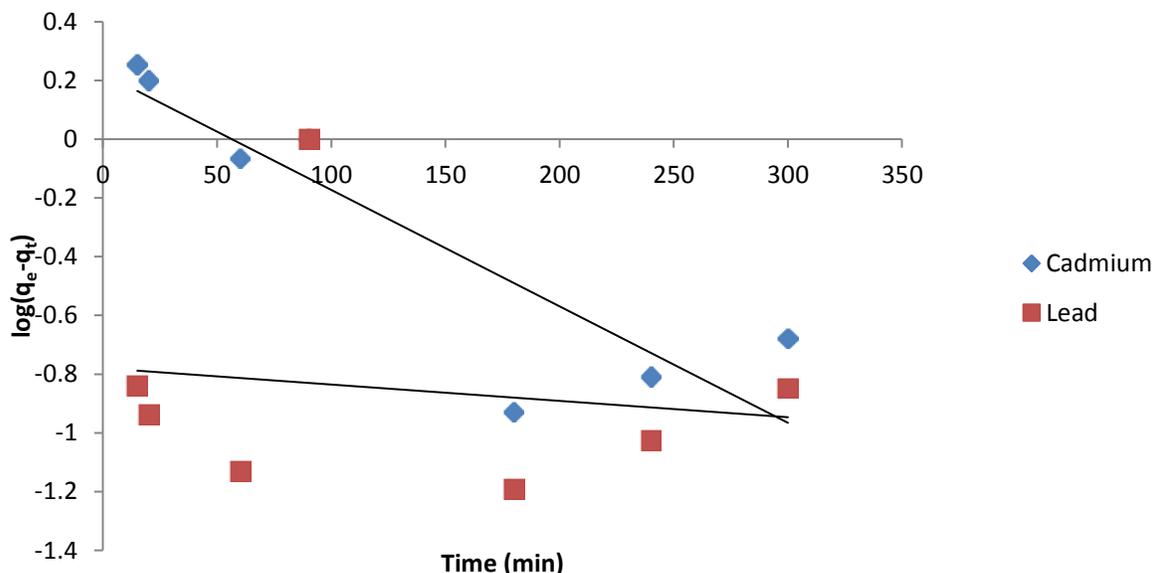


Figure 7. Plot of Lagergren pseudo-first-order kinetic model.

Table 2. Comparison of pseudo-first order and pseudo second kinetic models

Metal ion	Pseudo-first order				Pseudo-second order		
	K (dm ³ /g)	R ²	Estimate q _t (mg/g)	Experimental q _t (mg/g)	Estimated q _t (mg/g)	R ²	K (dm ³ /g)
Cd	-0.00138	0.0245	0.1660	4.8429	4.7148	0.9991	-0.02445
Pb	-0.009212	0.791	1.673	3.86	3.854	0.9968	0.0242

straight line graph (Figure 7).

Where: q_e is the amount of solute sorbed per mass sorbent at equilibrium. K_{ads} is the pseudo first order rate constant. K_{ads} and q_e can be deduced from the slope and the intercept respectively. The rate constant, K_{ads} and correlation coefficients, as well as r^2 values of the metals removed under different conditions were calculated from the plot of $\log(q_e - q_t)$ against t

The graph of $\log(q_e - q_t)$ against t should give a straight line graph where the following parameters, K_{ads} and q_e can be obtained from the slope and the intercept respectively. So, the result suggests that the sorption of Cd^{2+} and Pb^{2+} by bamboo is not a Lagergren first-order reaction. In Table 2, the R^2 values of 0.791 and 0.0245 for both Cd^{2+} and Pb^{2+} showed that it failed to comply with pseudo-first order kinetic model. The experimental q_e values for both cadmium and lead differ considerably from the calculated values. In applying Lagergren models, experimental equilibrium uptake of Lead and Cadmium should tally with the estimated value (Table 2). In both cases, the estimated values were much smaller than the equilibrium uptake values. This model assumes that rate controlling steps for uptake is due to boundary layer resistance. The major disadvantage is that in most of the cases, pseudo first order Lagergren equation does not fit well for experimental data over the entire range of

contact time.

Pseudo-second order kinetic model

The pseudo-second order equation is also based on the sorption capacity of the solid phase. It predicts the behavior over the whole range of data. The main assumption of pseudo-second-order kinetic model is that rate limiting steps may be chemical sorption involving forces through sharing or exchange of electrons between the metal ions and the biomass (Ghorbani et al., 2012), and is represented as

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \quad (3)$$

Where K_2 is the equilibrium constant of second-order-adsorption (g/mg.min). For the same boundary conditions, the integrated form of the equation becomes

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

The rate constants K_2 and q_e (Cal) of pseudo-second order kinetic model were determined from Figure 8, by the slope and intercept of the linear plot of t/q_t versus t for

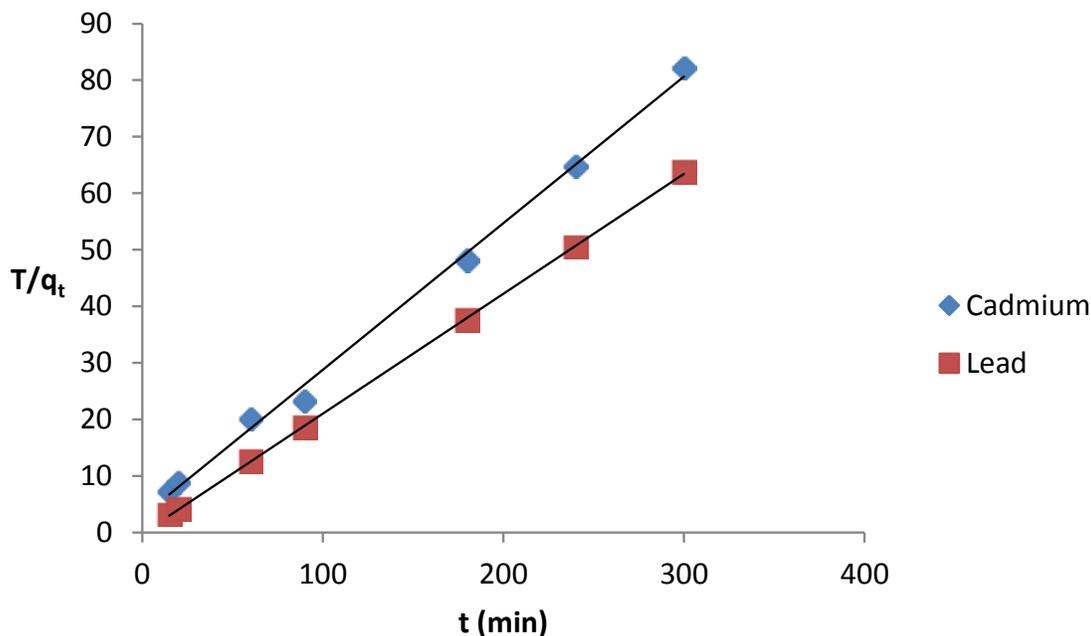


Figure 8. Graph of second order kinetic model.

adsorbent. It can be seen in Table 2 that the linear correlation coefficients for second-order model are good and based on the comparison between experimental and theoretically calculated q_e values; Uptake of Lead and Cadmium by Bamboo stem biomass as exemplified by Figure 8 follows a pseudo – second order pattern. It is evident from this plot with correlation factors (R^2) of 0.99 for Lead and Cadmium respectively that the sorption reactions followed Lagergren second order model. Estimated values of q_t (mg/g), fall well within the range of the experimental data with very high values of coefficient of correlation. This indicates that the rate controlling step of uptake process could be governed by chemisorption process. Sorption kinetics are however controlled by different steps including solute transfer to the sorbent particle surface, transfer from the sorbent particle surface to the intra particle active sites and retention on these sites via sorption, complexation and intra particle precipitation phenomena.

Elovich model of adsorption

Elovich equation is another articulation dependent on the adsorptive capacity of adsorbents and depicts the energy of adsorbate on solids. On the off chance that in adsorption frameworks, equilibrium is portrayed by Temkin empirical equation, then the adsorption energy is communicated well by Elovich model. This was watched usually in adsorption frameworks with solid heterogeneous strong surfaces, for example, the impetus surfaces (Banat et al., 2007). The Elovich equation is given as

follows (Low, 1960).

$$dq_t/dt = \alpha \exp(-\beta q_t) \quad (5)$$

Thus, the constants can be obtained from the slope and the intercept of a straight-line plot of q_t against $\ln(t)$ as can be seen in Figure 9. Considering the low values of R^2 for both Lead and Cadmium at 0.05 and 0.7474 respectively, it can be deduced that the data did not fit well into Elovich model. Equation 5 is used to test the applicability of the Elovich equation to the kinetic of sorption.

Intra-particle diffusion

Intra-particle diffusion model is used to identify the mechanism involved in the adsorption process. Equation of this model can be written as:

$$q_e = K_p t^{1/2} + C \quad (6)$$

Where C is the intercept that describes boundary layer thickness and K_p ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the rate constant of intra-particle diffusion. Figure 10 shows that for both metals, the plots are not linear; more so do not pass through the origin. When extrapolated from origin, the initial steep-sloped portion (from 0-10 min) is attributed to external surface adsorption or instantaneous adsorption and the R^2 value for cadmium and lead metal ions were 0.7137 and 0.0025 respectively. The values of R^2 in the adsorption of cadmium and lead did not show strong

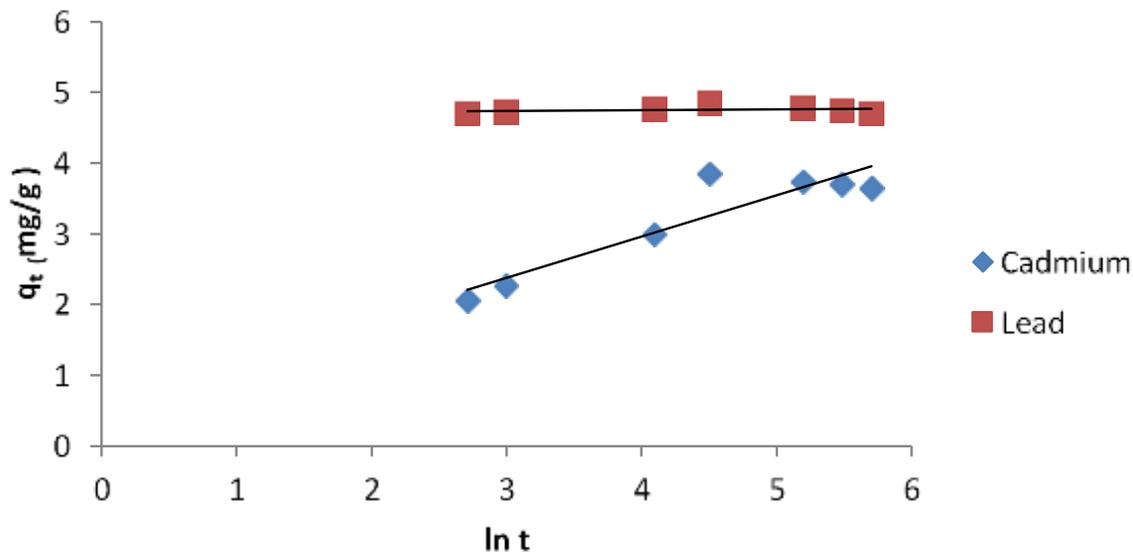


Figure 9. Plot of Elovich model.

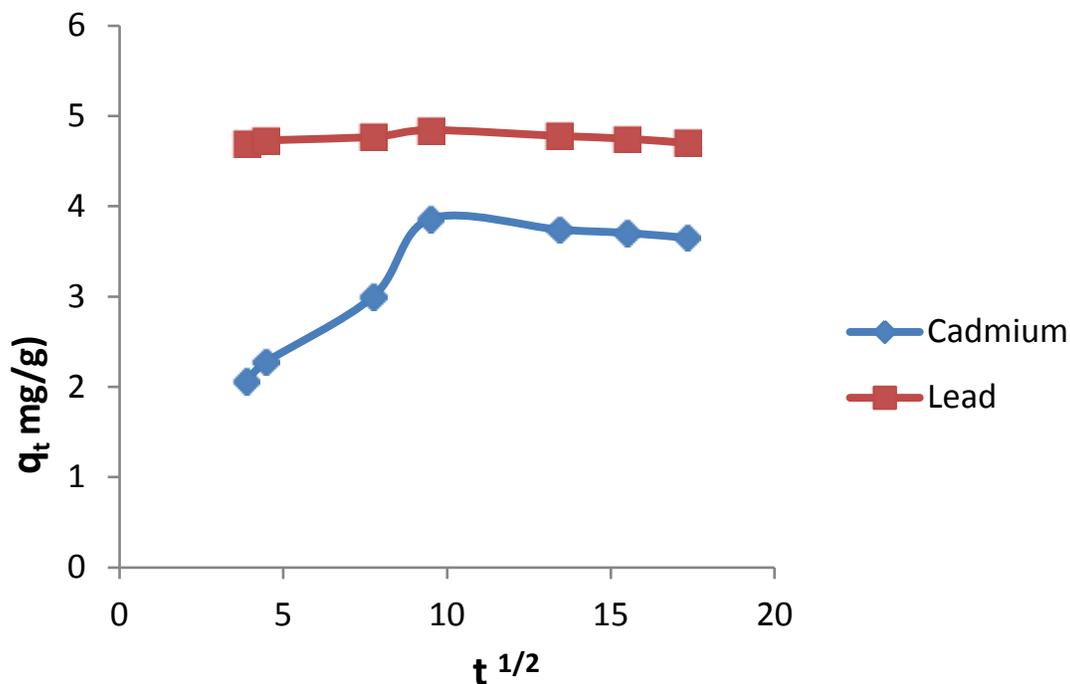


Figure 10. Plot of intra-particle diffusion.

conformity with intra-particle diffusion system due to low R^2 values.

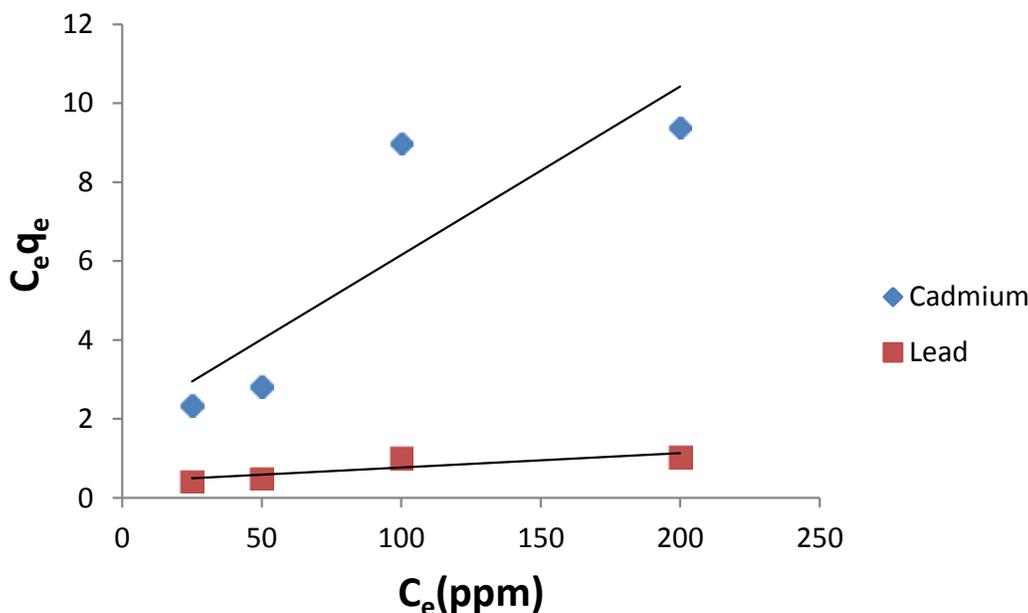
Isotherm studies

The Langmuir isotherm model accept in its definition a

monolayer adsorption at most extreme limit happening through a uniform or identical surface of adsorbent with no cooperation between the adsorbate particles (Langmuir, 1916). Adsorption isotherms are numerical models that portray the appropriation of the adsorbate species among fluid and adsorbent, in light of a lot of suspicions that are basically identified with the

Table 3. Langmuir, Freundlich and Temkin isotherm parameters for Cd(II) and Pb(II) adsorption.

Metal ion	Langmuir parameter			Freundlich parameter			Temkin parameter		
	q_{max} (mg/g)	B	R^2	K_f (dm ³ /g)	n_f	R^2	A (L/g)	B	R^2
Cd(II)	12.34	0.031	0.898099	2.496399	153.19	0.93977	0.4291	2.3898	0.8457
Pb(II)	27.95	0.077	0.891456	2.9653	22.618	0.95471	1.2596	4.9594	0.8821

**Figure 11.** Plot of Langmuir isotherm for Cadmium and Lead.

heterogeneity/homogeneity of adsorbents, the sort of inclusion, and the plausibility of association between the adsorbate species.

The Langmuir isotherm

The Langmuir isotherm is given by:

$$q_0 = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (7)$$

This in linearized form is given by:

$$C_e/q_e = 1/q_{max} K_L + C_e/q_{max} \quad (8)$$

Where: q_{max} and K_L are the Langmuir constants, speaking to the most extreme adsorption limit with regards to the strong stage stacking and adsorption/desorption constants that is identified with the warmth of adsorption individually (Senthil and Kirthikam, 2009). q_e = measure of heavy metal that is adsorbed per unit mass of adsorbent (mg/g) at harmony in ppm. C_e = Concentration of the

heavy metal particles left after adsorption.

The isotherm parameters introduced in Table 3 shows versatility to the Langmuir isotherm. The estimation of R^2 for cadmium is 0.898099 and for lead the R^2 is 0.891456 at the previously mentioned temperatures. It can be found in Figure 11 that the isotherm information genuinely fits into the Langmuir's model.

The Freundlich isotherm

The Freundlich isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption (Freundlich, 1907). The isotherm assumes that adsorption occurs on a heterogeneous adsorbent surface, that is, multilayer adsorption. The Freundlich equation has the general form:

$$q_e = K_f C_e^{1/n} \quad (9)$$

The logarithmic linear form of Freundlich isotherm may be represented as:

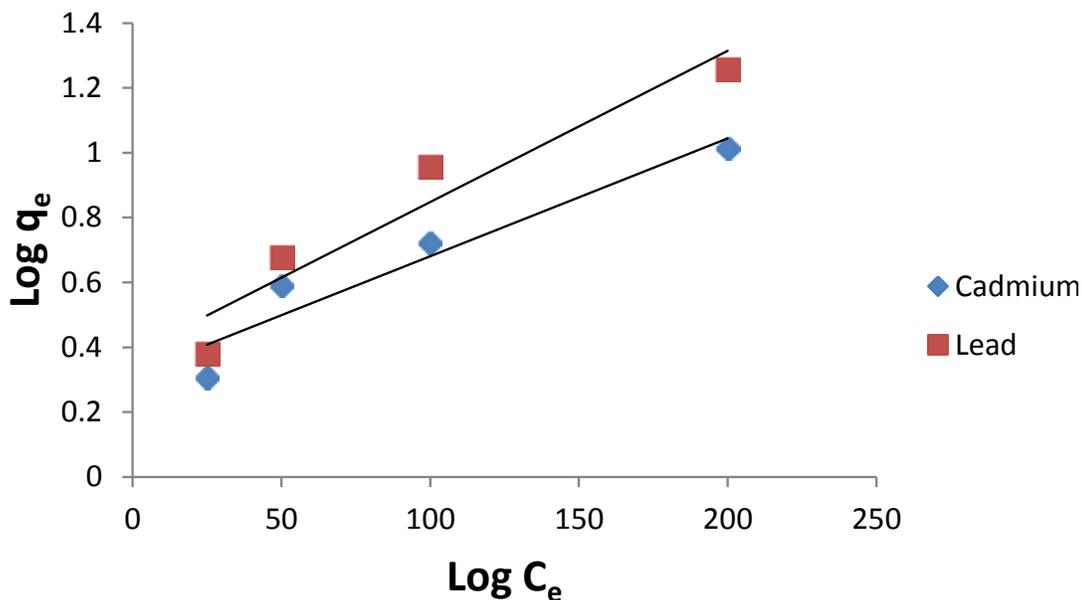


Figure 12. Plot of Freundlich isotherm for Cadmium and Lead.

$$\ln q_e = \ln k_f + (1/n)\ln C_e \dots\dots\dots(10)$$

Where:

q_e = amount of metal adsorbed per unit mass of sorbent (mg/g) at equilibrium

C_e = equilibrium concentration of heavy metal ions (mg/g)

k_f (L/g) and n = Freundlich constants for adsorption capacity and adsorption intensity

Figure 12 had shown the plot of $\log q_e$ against C_e . Table 3 presents the R^2 value of cadmium as 0.93977 and for lead, the R^2 value is 0.95471. This shows that the adsorption process obeys the Freundlich isotherm in both metals. The Freundlich isotherm did not give any information on the monolayer adsorption capacity unlike Langmuir model.

The Temkin isotherm

The Temkin isotherm has generally been applied in the following linear form (Temkin et al., 1940).

$$q_e = B \ln A + B \ln C_e \dots\dots\dots(11)$$

$$B = RT/b \dots\dots\dots(12)$$

Where A is the equilibrium binding constant (L/g), T is the absolute temperature in Kelvin, R is the universal gas constant (J/molK) and b (J/mol) is a constant related to the heat of sorption. q_e is the amount of metal adsorbed

per unit weight of adsorbent (mg/g); a and b are constants, related to adsorption capacity and intensity of adsorption which can be calculated from the plots of q_e against $\ln C_e$. If the value of B is positive, it shows that the reaction is exothermic and vice versa.

Figure 13 is a plot of the Temkin isotherm for cadmium and lead respectively. Table 3 shows the R^2 value is 0.8457 for cadmium and did not fit well into the data while for lead the R^2 value of 0.8821 did not fit well to the Temkin isotherm.

Sorption thermodynamics

Thermodynamic parameters such as change in Gibb's free energy ΔG° , enthalpy change, ΔH° and entropy change, ΔS° were determined using Van't Hoff equation.

$$\ln K_1 = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots(13)$$

The Gibb's free energy, ΔG° is derived from the relationship

$$\Delta G = -RT \ln K_1 \dots\dots\dots(14)$$

Where K_1 is the equilibrium constant obtained from Langmuir's plot; T is temperature (K) and R is gas constant (Jmol⁻¹K⁻¹). Thermodynamic are used to determine if the process is spontaneous or not (Ho and Ofomaja, 2006). The values of thermodynamic parameters ΔG° , ΔH° and ΔS° for Cadmium and Lead respectively are presented in Table 4. The values of ΔG° were negative showing that the sorption reaction is

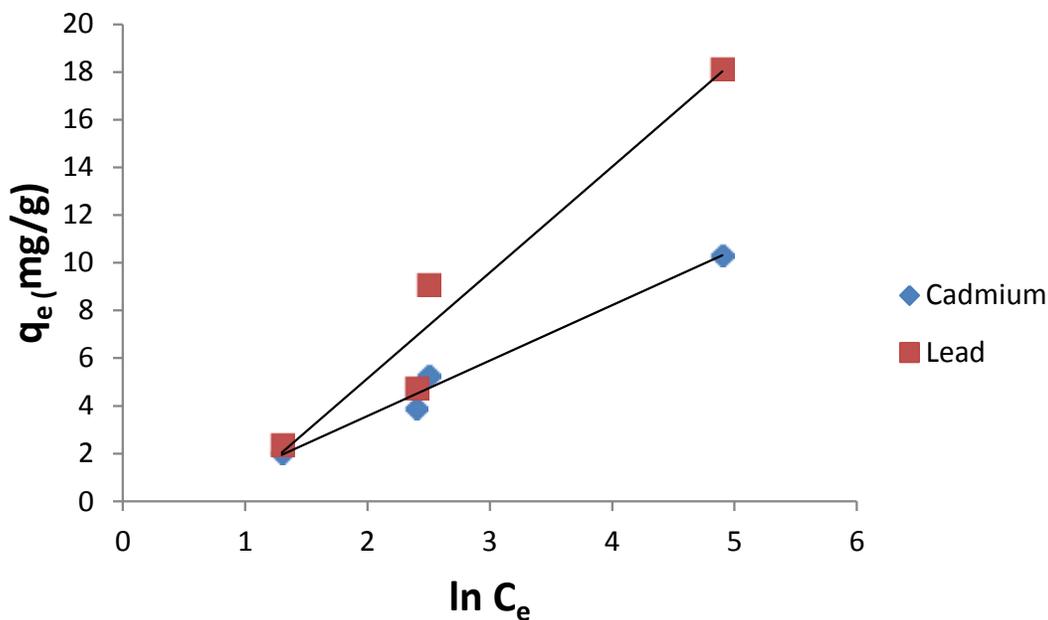


Figure 13. Plot of q_e against $\ln C_e$ for Cadmium and Lead.

Table 4. Thermodynamic parameters of Cadmium and Lead.

Metal ions	$\Delta H^0/\text{KJmol}^{-1}$	$\Delta S^0/\text{KJmol}^{-1}\text{K}^{-1}$	$\frac{\Delta G^0/\text{KJmol}^{-1}}{298\text{K}}$
Cd	-10.95	-0.067	8.61
Pb	-17.12	-0.083	6.35

feasible and the values of ΔH^0 were also negative, suggesting exothermic process.

DISCUSSION OF BAMBOO AS A BIOSORPTION AGENT WITH OTHER ADSORPTION/BIOSORPTION MATERIALS

In comparing biosorption of copper and zinc from aqueous solution by bamboo biomass in batch and column studies by Okoronkwo and Ebisike (2010) to this study using impact of pH, desorption of the heavy metals using metals recovery and kinetics studies. Also, comparing using bamboo stem biomass for removal of Lead (II) and Cadmium (II) ions from aqueous solution and potential use of bamboo biomass for the removal of copper and zinc from contaminated water, revealed that generally pH is an important parameter on biosorption of metal ions from aqueous solution because it affects the solubility of these ions and it was clear that the sorption of heavy metal ions significantly decreased at lower pH values and at higher H^+ concentration, the biosorbent surface becomes more positively charged, thus reducing

the attraction between adsorbent and metal ions. So, both bamboo stem biomass and bamboo biomass shows optimum removal at low pH 5, thereby removing 86% of copper and 92% for Zinc using bamboo biomass while 93.60% removal for Lead and 79.45% removal for Cadmium. In addition, metals bound to the bamboo stem biomass were affected by eluting with 0.5 M HCl after passing different four initial HCl concentrations. Also, 0.5 M HCl showed 88.93% removal for Lead and 0.1 M HCl shows 92.3% removal for Cadmium, thus confirming that higher concentration of the acid beyond 0.1 M in the case of Cd^{2+} and 0.50 M in Pb^{2+} was therefore unnecessary. But for the desorption of Zinc and Copper from effluent using bamboo biomass after passing 10 bed volumes of 0.1 M HCl showed that 99% of bound copper was recovered from the biomass. Zinc recovery was however low. Only about 10% of the bound Zinc was recovered, thus confirming that binding affinity of zinc to this biomass is very high. It is very possible that high concentrations of the acid will have positive effect in desorption of Zinc. Likewise, kinetics studies of biosorption potentials of bamboo stem biomass for removal of Lead (II) and Cadmium (II) ions from aqueous solution biomass gives

95.92 and 80.98% removal for lead and cadmium within the first fifteen minutes of interaction while the biosorption of both metals (Zinc and Copper) on the bamboo biomass was rapid given 90.52% of Zinc and 78.56% of Copper were removed within the first 5 min of interaction but it was found that both bamboo stem biomass and bamboo biomass follow pseudo second order kinetic model. These prove that bamboo stem biomass is an effective biosorbent material to remove heavy metals from aqueous solution.

In comparing adsorption of Lead (II) ion from aqueous solution by bamboo activated Carbon by Masood et al. (2015) to this present study using Lead (II) ion with the isotherm, kinetics and thermodynamics of batch adsorption of Pb^{2+} ions from aqueous solution, it was observed that both adsorption and biosorption capacity of adsorbate appeared to decrease with increasing adsorbent dose while the efficiencies removal of $Pb(II)$ ions increased and it can be deduced that 97.33% maximum removal for lead (II) using bamboo activated carbon while 93.6% maximum removal was obtained using bamboo biomass stem. This result can be attributed to the fact that some of the adsorption sites remain unsaturated after the adsorption/biosorption process. It might be because of formation of particle aggregation, resulting in a decrease in the total surface area and an increase in diffusion path length, which contribute to decrease in amount adsorbed per unit mass. In addition, a decrease in efficiency of adsorbent was observed with increasing initial metal ion concentration for both adsorption and biosorption of $Pb(II)$ ions using bamboo activated carbon and bamboo stem biomass. About 99.5% of $Pb(II)$ ions highest removal was observed using bamboo activated carbon while 97.92% highest removal was recorded using bamboo stem biomass. Likewise, both biosorption of bamboo stem biomass and bamboo activated carbon adsorption process follows Langmuir, Freundlich and Temkin isotherms but a better sorption fit of $Pb(II)$ ions using Freundlich isotherm model was obtained. It indicates a multilayer formation over a surface of the material with the correlation coefficient of R^2 of 0.935 for adsorption of $Pb(II)$ ions by bamboo activated carbon and correlation coefficient of R^2 of 0.954 for biosorption of $Pb(II)$ ions by bamboo stem biomass. Furthermore, adsorption kinetics was modeled using pseudo order kinetics and intra-particle diffusion models for both adsorption and biosorption of $Pb(II)$ ions using bamboo activated carbon and bamboo stem biomass. The kinetic data obtained from both study fitted well with the pseudo-second order model. Also, the sorption profiles derived based on the pseudo second order kinetic model showed a good agreement with the experimental curves and the pseudo second order kinetic reaction is the rate controlling step with some intra particle diffusion taking place. The determined negative free energy changes (ΔG) and positive entropy change (ΔS) indicate the

feasibility and spontaneous nature of the adsorption process of $Pb(II)$ ion using bamboo activated carbon while positive free energy changes (ΔG) and negative entropy change (ΔS) indicate the non-feasible and non-spontaneous nature of the biosorption process of $Pb(II)$ ion using bamboo stem biomass. The positive value of enthalpy change (ΔH) suggests that the adsorption process was an endothermic using bamboo activated carbon for the removal of $Pb(II)$ ion while it is exothermic for biosorption process using bamboo stem biomass for removal of $Pb(II)$ ion. Finally, activated carbon produced from bamboo and bamboo stem biomass demonstrated that they are promising adsorbent derived from agricultural waste material used for the removal of heavy metal ions like $Pb(II)$ ion from an aqueous solution. From this, it is shown that biosorption of bamboo stem biomass can be used as low cost biosorbent to remove heavy metals from aqueous solution.

In comparing adsorption of Cadmium (II) ion from aqueous solution by a new low-cost adsorbent—Bamboo charcoal by Fa et al. (2010) to this present study using Cadmium (II) ion with kinetics and batch adsorption of Pb^{2+} ions from aqueous solution, it was shown that adsorption of $Cd(II)$ ion using bamboo charcoal and biosorption capacity of bamboo stem biomass (adsorbate) appeared to decrease with increasing adsorbent dose while the efficiencies removal of $Cd(II)$ ion increased. Also, the adsorption rate of $Cd(II)$ ions using bamboo charcoal was very fast initially, and about 40% of total $Cd(II)$ ion was removed within 5 min while biosorption of $Cd(II)$ ions by bamboo stem biomass had fairly high adsorption in the first fifteen minutes with 41.2%; there is also fast adsorption at the initial stage probably due to availability of sufficient number of vacant sites on the surface of the adsorbent. Thereafter, the adsorption capacity increased slowly with the contact time before reaching a plateau value after the contact time of 6 h, and then remained constant, for biosorption of $Cd(II)$ ions by bamboo stem biomass, removal increases and at 1 h 30 min show the optimum removal of 77.2%, and then sorption subsequently decreased and at 5 h and the amount of metal adsorbed did not change significantly with time. Generally, adsorption capacity of $Cd(II)$ ions by bamboo charcoal increased with an increase in the pH of the adsorbate solution. The optimum pH for $Cd(II)$ removal is 8.0 because Cd^{2+} is the only ionic species present in the solution at $pH < 6.0$ and the dominant $Cd(II)$ species at $pH < 8.0$ is Cd^{2+} and $Cd(OH)^+$ and at $pH > 8.0$ is $Cd(OH)_2$ while optimum pH for biosorption of $Cd(II)$ removal using bamboo stem biomass was 5.0. Obviously, a negatively charged surface site favors the adsorption of cationic $Cd(II)$ ions due to electrostatic attraction. In addition, both biosorption of $Cd(II)$ ions by bamboo stem biomass and adsorption of $Cd(II)$ ions by bamboo charcoal was found to follow the pseudo-second-order model while Langmuir adsorption model was better fitted for the adsorption of $Cd(II)$ ions than Temkin and

Table 5. Correlative effect of all parameters used in batch adsorption of Lead and Cadmium.

Metal ion	Effect of pH		Effect of contact time at 90 min		Effect of metal ion concentration		Effect of adsorbent dosage		Effect of temperature		Effect of metal recovery	
	% Removal	mg/g	% Removal	mg/g	% Removal	mg/g	% Removal	Adsorbent dosage (g)	Temp (K)	mg/g	% Removal	HCl Molar Conc. (M)
Pb (II)	93.6	4.68	97.38	4.84	95.92	2.39	96.0	2.0	298	4.76	88.63	0.5
Cd(II)	79.45	3.97	77.2	3.86	80.98	2.04	95.4	2.0	298	3.90	92.3	0.1

Freundlich isotherms due to the highest monolayer adsorption capacity that gave 12.08 mg/g for the adsorption of Cd (II) ions by bamboo charcoal but biosorption of bamboo stem biomass give a better sorption fit of Cd (II) ions using Freundlich isotherm model and it indicates a multilayer formation over a surface of the material was 12.34 mg/g. Therefore, the present study had chosen bamboo stem which is a self-regenerating agricultural product and application of these bamboo stem biomass biosorbent offers highly effective technological means in dealing with the pollution of heavy metals with the requirement of minimum investment.

From Table 5, the correlating effect of all the optimum parameters shows that biomass dosage gives a major factor that highly affects biosorption of Lead (II) and Cadmium (II) ions from aqueous solution. Lead (II) and Cadmium (II) ions have very similar percentage removal of 96.0% Lead (II) and 95.4% Cadmium (II) ions at the same adsorbent dosages.

Conclusion

Bamboo stem biomass has proven to be an effective heavy metal pollutants arrestor. The biosorption was found to vary with pH, with the optimum adsorption at pH 5. With an increase in

Pb (II) and Cd (II) ions concentration, biosorption capacity of Pb (II) and Cd (II) ions by bamboo stem biomass increased but the removal percentage of Pb (II) and Cd (II) ions decreased. Increase in adsorbent dosage led to increase in Pb (II) and Cd (II) ions removal but decrease in biosorption capacity. The kinetics of the system showed that the pseudo-second order model was more suitable than the pseudo-first order model with the optimal adsorption at ninety minutes. Adsorption diminishes with increment in temperature indicating the procedure was exothermic. The entropy values were negatives for both cadmium and lead indicating a highly disordered state which favors adsorption. The Gibbs' Free energies were positive indicating biosorption of the metals by the bamboo stem biomass was not spontaneous. Freundlich was found to be the most suitable of the three isotherms using the high R^2 (0.99) values for both Cadmium and Lead. The correlating effect of all the optimum parameters shows that biomass dosage gives a major factor that highly affects biosorption of Lead (II) and Cadmium (II) ions from aqueous solution showing that Lead (II) and Cadmium (II) ions have very similar percentage removal of 96.0% Lead (II) and 95.4% Cadmium (II) ions at the same adsorbent dosages of 2 g. Batch adsorption indicates that bamboo stem biomass has efficient biosorption capacity for Pb

(II) and Cd (II) ions and its use may significantly lower the cost of water treatment.

RECOMMENDATIONS FOR FUTURE STUDIES

(1) Further studies need to conduct on spectroscopic characterization of bamboo stem biomass such as (FTIR–Fourier Transmission Infra-Red, SEM - Scanning Electron Microscope, UV-VISIBLE SPECT - Ultraviolet visible spectroscopy, EDX - Electron Disperse X-ray Spectroscopy, TEM– Transmission Electron Microscope, XRD - X-ray Diffraction, TGA– Thermogravimetry Analysis).

(2) Further investigation can be conducted using live bamboo stem biomass, compared to dry bamboo stem biomass and observe their biosorption effect or capacity on the removal of heavy metals under operational conditions and isotherm and kinetics model. Additionally, the mechanism of interaction with the biomass of water, acid base, and metals should be considered. The specific surface area of bamboo biomass, its swelling kinetics in pure water at different pH and sorption efficiency capacity of both metals in dry and moist biomass.

(3) Also, modification of bamboo stems biomass with various materials such as (minerals, reductant,

organic functional group, decorated with nanoparticles, activated by base) to enhance its biosorption ability for removal of heavy metals from aqueous solution should be further investigated.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests regarding the publication of this paper.

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