



Original Research Article

Removal of Aqueous Lead and Cadmium using *Persea americana* Seed Coat: Single and Binary Studies

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ABSTRACT

The presence of heavy metals in water sources is worrisome because heavy-metal pollutants are associated with severe health problems. The resultant health challenges as a result of heavy metal pollution have necessitated the removal of these pollutants from wastewater before being discharged into the environment. This research was carried out to investigate the potentials of avocado pear (*Persea americana*) seed coat as biosorbent of lead(II) and cadmium(II), in single and binary metal systems, from aqueous solutions. Biosorbent particle sizes and dosage were varied in the study. Desorption of biosorbed metal ions was studied using sodium salt of ethylene diaminetetraacetic acid (EDTA) and hydrochloric acid (HCl). Biosorbent of 106 μm particle size gave the best uptake of lead and cadmium from aqueous solutions than those of 850, 1180, 1400 and 2000 μm particle sizes. Biosorption of lead(II) and cadmium(II) increased with an increase in biosorbent dosage (up to threshold dosage). The uptakes of lead(II) and cadmium(II) in single systems are higher than those of binary systems. Biosorption capacities of lead(II) were higher than those of cadmium(II) for both single and binary systems. The observation could be linked to low hydration energy of lead(II) compared with that of cadmium(II). Biosorbed lead(II) and cadmium(II) were desorbed using 1.0 mol/L EDTA (for single system) and 1.0 mol/L HCl (binary system). Lead and cadmium ions were easily desorbed from single metal system unlike binary system. In overall, the avocado pear biosorbent could be used for treatment of wastewater contaminated with lead(II) and cadmium(II).

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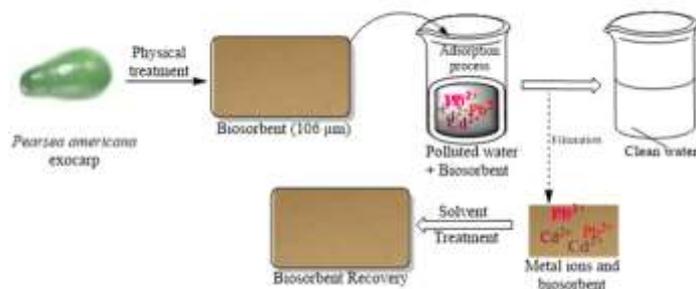
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GRAPHICAL ABSTRACT

Introduction

Uncontaminated and clean water is a necessity for longevity of human life. Water pollution is a worldwide problem that causes about 80% of diseases and the menace needs urgent attention [1–3]. Thousands of hazardous chemicals are discharged daily, either directly or indirectly, from industries into the water body. The presence of heavy metals in industrial and urban wastewater is one of the main causes of water and soil pollution [4]. A number of processes such as mining and burning of fossil fuel as well as other anthropogenic activities are responsible for the release of heavy metal ions into the environment at an unprecedented rate. Some of the effluents from industries are not treated, for elimination of hazardous compounds, before being discharged into environment [5,6]. The contamination of the environment with heavy metals is a serious concern and industrial activities have largely contributed to the wide spread of heavy metal in the terrestrial environment [7].

Lead is extensively used in many industrial applications such as storage battery, printing, pigments, fuels, photographic materials, and explosive production [8] through which the environment can be impacted. Lead is popular for its toxicity for a long time and it is one of the most toxic heavy metals that are associated with health problems such as behavioural anomaly, brain damage, disruption of nervous systems and learning disability, hallucination, seizures,

anaemia, cardiovascular disease, liver dysfunction, miscarriages and subtle abortions, birth defects, decline fertility in men through sperm damage, menstrual problems, deafness, epilepsy, tooth decay, blindness, abdominal pains and poor brain development in children [9,10].

Cadmium is a toxic heavy metal of significant environmental and occupational concerns [11]. Cadmium is released into environment through metal production, combustion of fossil fuels, application of phosphate fertilisers, electroplating, manufacturing of batteries and pigments [12]. Cadmium is known as human carcinogen and teratogen and its presence in the human system can lead to malfunctioning of lungs, kidneys, liver, and reproductive organs. It also affects ion regulation in human body, calcium metabolism and can cause stomach upset, severe vomiting, bone fractures, and psychological disorder [11].

Conventional methods that have been used for removal of toxic metals, such as lead and cadmium ions, from aqueous environment include membrane filtration, ion exchange, reverse osmosis, chemical precipitation, solvent extraction, electrodialysis, supercritical fluid extraction, electro-flotation and adsorption using activated carbons [13]. However, some of these methods are expensive and inefficient when the concentration of the heavy metals in the effluent is low. Biosorption of hazardous metals from

solutions has recently gained attention due to its merits of being a green process, technically feasible, eco-friendly, economical due to availability of biomass, reusability, short operation time, non-production of secondary pollutants, and cost-effective [14–16]. Biosorption is being used as an alternative process for the removal of toxic metal ions from dilute aqueous solutions and industrial effluents [17,18]. A wide range of biosorbents have been utilised for removal of heavy metals from aqueous solutions and some of the promising biosorbents include *Delonix regia* Pods [18], Seaweed [19], passion-fruit shell [20], algae [21], maize leaf [22], sand paper leaf [23,24], lignin [25], and Onion skins [26,27].

In our previous report [28], thermodynamic, kinetic and equilibrium studies of removal of lead(II) and cadmium(II) from solution using avocado pear seed coat powder were discussed. In the present study, other factors (biosorbent dosage and particle size) affecting biosorption of lead(II) and cadmium(II) using avocado pear biosorbent are reported. The biosorption experiments were conducted in single and binary systems of metal ions. Recovery of bound metal ions from the spent biosorbent was also investigated and reported in the present study. Lead and cadmium were chosen for biosorption studies because the metals are widely used in various industries and they have high pollution impact in the environment.

Materials and Methods

Avocado pear (*Persea americana*) seed coat was used as biomass or biosorbent. Lead trioxonitrate (V) and cadmium trioxonitrate (V) pentahydrate were used for the preparation of Pb(II) and Cd(II) solutions, respectively. Sodium salt of ethylene diaminetetraacetic acid (EDTA) and hydrochloric acid (HCl) were used as eluants for desorption study. Adjustment of pH was done using hydrochloric acid and sodium hydroxide solutions when necessary. All reagents used were of

analytical grade and were obtained from the Chemical Store of the Department of Chemistry, The Federal University of Technology, Akure, Nigeria.

Preparation of Biosorbent

The avocado pear was obtained from Irono market, Ado Ekiti, Nigeria. The seed coat was removed, washed, sun-dried for 72 h, oven-dried at 105 °C for 7 h, ground, sieved through different mesh sizes of (106, 850, 1180, 1400, 2000 µm) and kept for use. Samples of different sizes were later washed with 0.1 mol/L HCl and then with deionised water until neutrality. The washed biomass was oven-dried at 105 °C for 7 h, cooled down and kept properly for further experimental work.

Preparation of Stock Solution

Stock solutions (1.0 g/L) of lead and cadmium ions were prepared by dissolving required amounts of $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, respectively, in double distilled water at room temperature. The experimental working solutions were obtained by diluting the stock solutions to desired concentrations using distilled water. Different concentrations (0.1, 0.5, 0.75 and 1.0 mol/L) of HCl and EDTA were prepared for desorption experiments.

Batch Biosorption Studies

Biosorption experiments for single- and two-component systems of lead and cadmium ions were performed using batch methods by adding 0.5 g of the avocado pear biosorbent into 50 mL (100 mg/L solution of metal) under stirring at room temperature (28 °C). All experiments were conducted in triplicates and the mean values were used in data analysis.

From the different particle sizes of the biomass prepared (106, 850, 1180, 1400, and 2000 µm), 0.5 g of each sample was weighed into sample tubes after which 50 mL of 100 mg/L solution of adjusted pH was poured into each beaker and the mixtures were stirred continuously for optimum contact time of 30 min for lead and 60 min for

cadmium [28]. The mixture was later filtered after agitation, and transferred into clean sample tubes for residual metal analysis using Atomic Absorption Spectrophotometer (AAS). For the binary metal system, the same procedure was used, however, 25 mL of lead and 25 mL of cadmium solution were added.

For experiments on biosorbent dosage, metal solution was adjusted to the optimum pH of 4 and 5 for lead and cadmium [28] and different doses of the biosorbent (0.5, 1.0, 1.5, 2.0 and 2.5 g) were used. The biosorbent was added to 50 ml of the metal solution (100 mg/L) of desired pH and stirred for a specific period (30 min for Pb(II) and 60 min for Cd(II)), after which the mixtures were filtered and the filtrates were collected in clean sample tubes for analysis of metal content. The same procedure was used for the experiments performed on binary metal system.

The amount of metal biosorbed at equilibrium (q_{equ}) in mg/L and the percentage of biosorption ($\%R$) were evaluated using Equations 1 and 2, respectively.

$$q_{equ} = \frac{V}{m} \cdot C_o - C_e \quad (1)$$

$$\%R = \frac{C_o - C_e}{C_o} \cdot 100 \quad (2)$$

Where C_o = initial metal concentration (mg/L), C_e = metal concentration at equilibrium (mg/L), m = mass of avocado pear biosorbent (g), and V = volume of lead(II) or cadmium(II) solution (L) in contact with avocado pear biosorbent.

Desorption Studies

Recovery of lead and cadmium ions from spent biosorbent was done using different concentrations (0.1, 0.5, 0.75 and 1.0 mol/L) of HCl and EDTA. Adsorption experiments were first performed under optimum conditions before desorption study was investigated. For these experiments, 50 mL of 100 mg/L metal solution of adjusted pH was poured into designated sample tubes and 0.5 g of avocado pear biosorbent was

added to the solutions. The mixtures were stirred for a period and filtered; the amounts of metal ions in filtrates were read spectroscopically using AAS. The spent biosorbent was contacted with the appropriate concentrations of desorbing agents (eluants) for the optimum contact time, after which the mixture was allowed to settle down, the filtrate was decanted and analysed for metal content. The adsorption-desorption process was carried out for single metal and binary metal systems and percentage of desorption was evaluated using Eq. 3.

$$\% \text{ Desorption} = \frac{\text{Amount of adsorbate released into solution (mg/L)}}{\text{Amount of adsorbate adsorbed (mg/L)}} \cdot 100 \quad (3)$$

Results and Discussion

Avocado pear (seed coat) powder was prepared and used as alternative biosorbent for removal of lead and cadmium ions from aqueous solutions using batch adsorption procedure. The experiments were conducted using single metal and binary metals systems. Previous report had shown that the seed's coat of avocado pear is a potential biosorbent for heavy metal remediation [28]. The report made us to probe further, the other influencing factors that could affect binding and sequestration of lead and cadmium ions from aqueous solutions. Desorption study was also investigated in detail to understand desorption characteristics of the biosorbent-metal ion interaction.

Influence of Particle Size on Biosorption Capacity

To investigate the influence of biosorbent's particle size on removal of Pb(II) and Cd(II) by avocado pear powder, various experiments were carried out using different sizes (106, 850, 1180, 1400 and 2000 μm) of the biosorbent. From the results in **Fig. 1**, it is evident that avocado biosorbent of 106 μm is the most efficient and suitable for biosorption of lead and cadmium ions. This assertion is valid for both single- and binary-metal systems. The amount of metal ions

biosorbed decreased as the particle size of the biosorbent increased. The high percentage removal observed with adsorbent of small particle size is attributed to the availability of large surface area and increasing internal surface area for biosorption of metal ions [25]. As the particle size of biosorbent materials decreases, the number of small pores increases and the surface area also increases, this gives rise to high adsorption rate because it will only take the adsorbate a relatively short distance and time to migrate into the active pores of biosorbent. In the report of Surisetty et al. [29], biosorption of lead(II) onto *Ficus benghalensis L.* decreased with an increase in particle size.

It was stated that a decrease in the average particle size of the biosorbent resulted in an increase in the surface area, which led to an increase in the number of sites available for metal uptake and subsequently resulted in an increase in adsorption. Similarly, Cheraghi et al. [30] investigated the effect of particle size on the removal of Cd(II) using 0.15 – 2 mm particle sizes of Sesame powder.

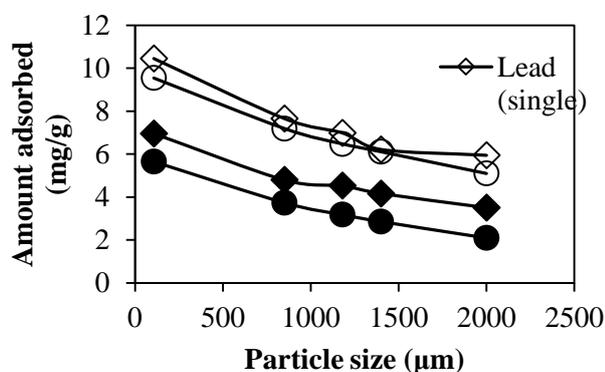


Fig. 1. variation of particle size on biosorption of Pb(II) and Cd(II) in single and binary systems; conditions: pH = 4 (Pb) and 5 (Cd); mass of biosorbent = 0.5 g; contact time = 30 min (Pb) and 60 min (Cd), initial metal ion concentration = 100 mg/L; and temperature = 28 °C (room temperature).

It was found that the removal of Cd(II) onto Sesame powder increased as the particle sizes

reduced. This observation was due to a large total mass transfer surface area available in particle of low sizes.

Effect of Biosorbent Dosage

Another important factor that affects biosorption of heavy metals onto biosorbents is biosorbent dosage. The effect of biosorbent dosage on Pb(II) and Cd(II) biosorption by *Persea americana* biomass was investigated in the range 0.5 – 2.5 g and the results are presented in **Fig. 2**. The results show that the percentage of lead and cadmium ions removed from solution increased with increase in the dose of biosorbent for single and binary systems.

When the dosage of the biosorbent was increased from 0.5 to 2.5 g, the percentage removal increased from 97% to 100% and 83% to 100% for lead(II) and cadmium(II), respectively, for a single system. The corresponding percentage uptakes increased from 48 to 100% and 42 to 93% for lead(II) and cadmium(II) in a binary system.

An increase in the percentage removal for lead and cadmium ions as the biosorbent dosage increases up to threshold value of adsorbent dosage is attributed to the presence of high surface area of biosorbent, which increases the number of adsorption sites available for adsorption [31].

The greater the surface area, the higher the number of adsorption sites and then the better the adsorption process. When the biosorbent dosages are greater than the threshold value of biosorbent dosage, the percentage of adsorbate removal remained almost constant. As shown in **Fig. 2**, the threshold dosage is 1.5 g for lead (II) removal in both single and binary systems. This value is also 1.5 g for cadmium (II) removal in a single system but the value seems to be high for cadmium (II) in a binary system because the threshold biosorbent value was not attained within the experimental dosages used in this study.

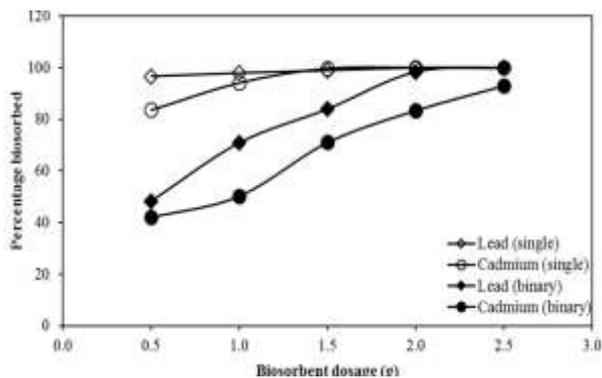


Fig. 2: influence of biosorbent dosage on biosorption of Pb(II) and Cd(II) in single and binary systems; conditions: pH = 4 (Pb) and 5 (Cd); mass of biosorbent = 0.5 – 2.5 g; particle size of biosorbent = 106 μm; contact time = 30 min (Pb) and 60 min (Cd), initial metal ion concentration = 100 mg/L; and temperature = 28 °C (room temperature)

Desorption Studies

It is necessary to regenerate the spent biosorbent to make adsorption process more economical. Both HCl and EDTA were used as eluants. Hydrochloric acid most times does not aid precipitation of metal ions while EDTA usually forms stable complexes with metal ions. The desorption studies of Pb(II) and Cd(II) were investigated using different concentrations of EDTA and HCl. Data obtained are presented in **Fig. 3** and **4** for single-metal and binary-metal systems, respectively. For the single metal system (**Fig. 3**), the highest percentages of lead and cadmium ions recovered are 82% (Pb) and 78% (Cd) and were achieved with 1.0 mol/L EDTA as eluant. The desorption efficiencies are satisfactory with EDTA (especially 1.0 mol/L of EDTA), however, desorption efficiencies are not promising with HCl. The results agreed with the report of Deng *et al.* [32, 33].

For the binary metal system, however, the result shows that 1.0 mol/L HCl gave the best percentage recoveries of lead (44%) and cadmium (38%). This result is in agreement with the work of Bulut and Basal [9], where wheat bran was used for the removal of Pb(II) from wastewater. Desorption of metal ions from binary systems are somehow difficult.

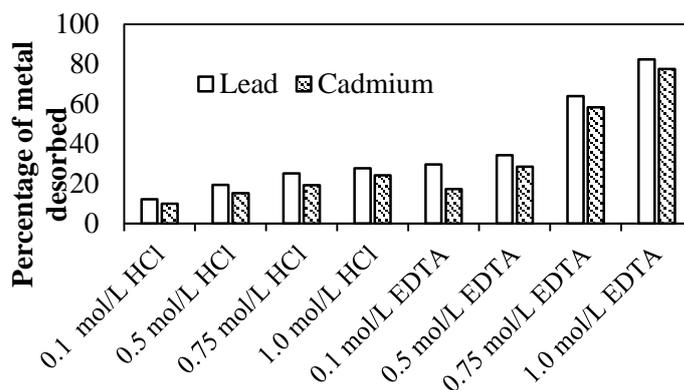


Fig. 3: Desorption of lead and cadmium ions from *Persea americana* biosorbent in a single system

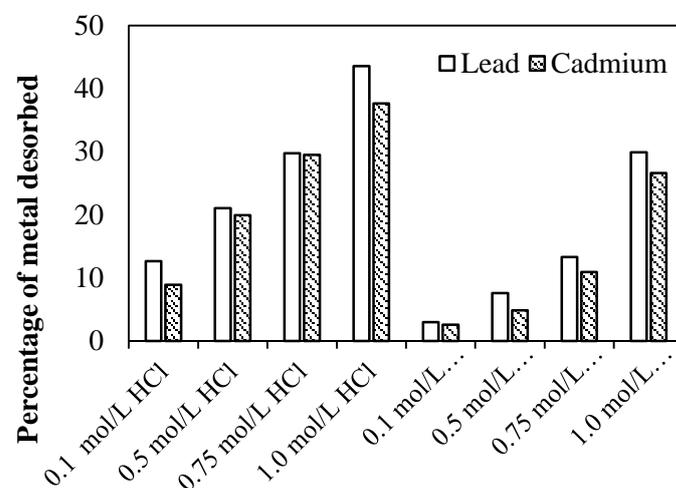


Fig. 4: Desorption of lead and cadmium ions from *Persea americana* biosorbent in binary a system

The desorption data have proven that the lead(II) and cadmium(II) can be effectively recovered from spent avocado biosorbent with EDTA and the recovered biosorbent can be washed and used for further biosorption of heavy metal ions from solutions.

Removal of Heavy Metal Ion in Single and Binary Systems

Industrial wastewater usually contains more than one heavy metal, the metal ions can co-exist in solution and compete for binding of the active sites on the surface of biosorbent. The competition of two bivalent ions, lead(II) and cadmium(II), were explored in this study to know

if their interactions are synergistic or antagonistic. The presence of both lead(II) and cadmium(II) in solution reduced the simultaneous removal of the metal ions from aqueous solution. The removal efficiency in a single-metal system was higher than the corresponding binary-metal system. Hence, the occurrence of both heavy metal ions in wastewater is antagonistic.

From **Fig. 2** and **3**, it is clear that biosorption capacities of lead(II) were higher than those of cadmium(II) for single and binary systems. Different characteristics (electronegativity, ionic radii, electrode potential, softness capacity for hydroxylation, among others) of heavy metals are responsible for preferential binding of metal ions onto adsorbent and hence different adsorption efficiencies are always obtained for different heavy metal ions [34]. The preference of the avocado biomass for lead(II) over cadmium(II) may be connected to lead ion having higher atomic weight and more paramagnetic than cadmium ion [34]. The higher the electrode potential of metal ions, the greater the affinity for biosorbent [34]. The electrode potential of lead(II) (-0.13 V) is higher than that of cadmium ion (-0.40), that was why higher adsorption capacities were obtained for lead than cadmium. In another view, hydration energy and hydrated ionic radius of heavy metals influence adsorption of the metal ions onto adsorbent. The lower hydration energy, the easier and higher the adsorption of such metal ion—the hydration energy of Cd(II) is higher than that of Pb(II) [35, 36].

The combined data from particle size and biosorbent dosage studies for lead(II) and cadmium(II) removal indicate that avocado pear biosorbent has potential to be used for removal of heavy metal ions from solutions.

Conclusion

Avocado pear powder was obtained from the coat of avocado seed and successfully used for removal lead(II) and cadmium(II) from aqueous solutions. Batch biosorption method was used to investigate the variation of particle sizes and dosage on adsorption performance in single-metal and binary-metal systems. Recovery of bound metal ions was carried using different concentrations of ethylene diaminetetraacetic acid (EDTA) and hydrochloric acid (HCl). Promising results were obtained from the study. Biosorption efficiencies of Pb(II) and Cd(II) from solutions are proportional to the avocado biosorbent dosage but inversely proportional to particle size. For the two biosorption systems, moderately high biosorbent dosage and small particle size favoured removal of the lead and cadmium ions from solutions. Removal of lead(II) and cadmium(II) in a single system was higher than that of a binary system. Biosorbed lead(II) and cadmium(II) could be easily desorbed using 1.0 mol/L EDTA in the single system, however, desorption process was not encouraging in the binary system. Avocado pear biomass could serve as alternative low-cost green biosorbent for removal of lead(II) and cadmium(II) from wastewater.

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