



Adsorption Capabilities of Activated Carbon Derived from *Detarium microcarpum* Seeds in Removing Co^{2+} and Pb^{2+} from Wastewater

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Abstract

This study was carried out to evaluate the efficiency of metals (Pb and Co) removal from solution using *Detarium microcarpum* seeds as adsorbent. The effect of initial concentration and adsorbent dosage on the adsorption process of these metals were studied, the percentage removal of these metals increased with increased in weight (0.5 - 2.5g) in 50ml of the solution and the adsorption efficiency increased with increasing initial metal ion concentration (0.01-0.05 moldm⁻³). The percentage removal obtained for Lead and Cobalt were compared. The result of adsorption were fitted to Langmuir models and coefficients indicated favorable adsorption of Pb^{2+} and Co^{2+} ions on the adsorbents. The adsorption of Pb^{2+} and Co^{2+} in aqueous solution was in the following order (1400 μm >420 μm >150 μm). More than 55.4% of studied Lead cations were removed by 1400 μm , 47.2% by 420 μm and 29.8% by 150 μm . While for Cobalt cations only 53.2% by 1400 μm , 38.6% by 420 μm and 24% by 150 μm respectively, from aqueous solution it was concluded that, activated Carbon derived from *Detarium microcarpum* seed is good in removing both lead and cobalt ions, which make it good adsorbent.

Introduction

Vast number of work has been reported on the remediation of different toxic metal

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from the environment. Innocent et al. [8] carried out an experiment on bioadsorption of heavy metal ions from aqueous solution using a biomaterial they reported that an increase in population initiating rapid industrialization was found to consequently increase the effluent and domestic waste water into the aquatic system. Heavy metals are major toxicants found in industrial waste water. They may adversely affect the biological treatment of wastewater. Conventional methods for the removal of heavy metals from waste water are often cost prohibitive hence, there is a need for cheap methods for effluent/treatment. The residual metallic ion concentration were determined using Atomic Absorption Spectrophotometer (AAS). The results obtain after contacting for 120 minute showed that neem leaves achieved the percent of removal of 76.8, 67.5, 58.4 and 41.45 for Cu^{2+} , Ni^{2+} , Pb^{2+} ions respectively. The percent removal of Ni^{2+} ions was 68.75 with an effective dose of 1.0g of neem leaves (bio adsorbent). The ability of neem leaves to adsorb metal ions as shown from the result can be used for the development of an efficient, clean and cheap technology for effluent treatment.

AL-Othman et al. [2] have investigated the removal of hexavalent chromium from aqueous medium by activated carbon prepared from Peanut shell by chemical activation with KOH. Unoxidized activated carbon was prepared in nitrogen atmosphere, which was then heated in air at a desired temperature to get oxidized activated carbon. The prepared carbons were characterized for surface area and pore volume and utilized for the removal of Cr (VI) from aqueous solution. The effects of pH, contact time, initial concentration of adsorbate and temperature on adsorption of Cr (VI) were investigated. Adsorption kinetics of Cr (VI) was analyzed by pseudo first order, pseudo second order and intra particle diffusion kinetic models. Results showed that Cr (VI) adsorption on both oxidized and unoxidized samples followed the first and second order kinetics models most appropriately. Isotherm data were treated according to Langmuir and Freundlich models. The results showed that both Langmuir and Freundlich models fitted the data reasonably but the Langmuir adsorption isotherm model fitted better in the temperature range studied. The adsorption capacity was found to increase with temperature, showed endothermic nature of Cr (VI) adsorption. The thermodynamic parameters, such as Gibb's free energy change, standard enthalpy change, and standard entropy change were evaluated. The value of change in Gibb's free energy was found negative for the adsorption of Cr (VI), which confirmed the feasibility, and spontaneity of the adsorption process.

In this cobalt and lead were chosen because of their environmental important as

related to their toxicity. Exposure to cobalt and lead may cause weight loss, dermatitis, bleeding, vomiting, sterility, hair loss, coma, respiratory hypersensitivity and even death therefore, it is of great relevance to develop a new method of their removal from water, and this is the aim of the present work.

It is worthy of mentioning that the *D. microcarpum* grows in dry savanna. The seeds of *D. microcarpum* can be stored at ambient temperature (26°C) for 5 years (Mariod et al. [1]). *D. microcarpum* occurs naturally in the drier regions of West and Central Africa. It is capable of vegetative propagation by coppice regeneration and suckering from stumps or roots, as well as propagation by rooted cuttings and grafting using scions from mature trees (Mariod et al. [1]) until the present work these waste have not been put into any important use and no information's available on metal removal by this agricultural waste. In this study, the capabilities of *D. microcarpum* waste for cobalt and lead ions adsorption were tested at several experimental conditions such as pH, dosage and concentration. The equilibrium data is described by Freundlich and Langmuir adsorption isotherm.

Material and Method

Materials and reagents

Conical flask, measuring cylinder, mechanical shaker, beakers, water bath, electric oven, sieve mesh 150µm, 425µm, muffle furnace, mortar and pestle, whatmanns filter papers, pH meter. Electric weighing balance, lead nitrate (Pb(NO₃)₂), cobalt chloride (COCl₂).6H₂O, solution of KOH and HCl, reagent bottles and spatula

Methodology

Sample collection

Sample of *Detarium microcarpum* seeds was collected from Rimi market Kano, were identified by Dr. Auwal Ibrahim Magashi (Department of Crop Science), Kano University of Science and Technology Wudil.

Adsorbent preparation

Carbonization and activation of sample

D. microcarpum seed was washed with hot tap water then with distilled water and allowed to dry in an oven at 105°C for five hours. The dried samples were burned in a

muffle furnace at 400°C for one and half hour. However, activation was carried out by soaking the carbonized samples in potassium hydroxide (KOH) overnight. The activated carbon were then filtered, washed with standard solution of HCl and finally with distilled water and dried it in an oven for 30 minutes. After drying the sample were then ground and passed sieve series in which two different samples of activated carbon were obtained in powdered and one granular size respectively.

Preparation of synthetic wastewater

Synthetic wastewater samples were prepared by using analytical grade cobalt chloride and lead nitrate (99 % Labosi, India) by using double distilled water. The stock solution was prepared by dissolving the salt in double distilled water, which contains 1000 mg/L. Working solutions of 5, 10, 20, 50, 60 and 100 mg/L were prepared by dilution

Batch adsorption experiment

The adsorption isotherm for heavy metals solutions were determined by using Batch adsorption experiment: (50 ml) of heavy metal solution (lead and cobalt) of a known concentration ranged from (0.01M) to (0.05M) were added separately to reagent bottle containing 5g of different size of each adsorbents. At a certain temperature 30°C and optimum pH, the flasks were shaken in a mechanical shaker at a constant speed for 15 minutes. The sample was filtered by using (No. 42) Whatman filter paper. The metal Equilibrium concentrations were measured by using Atomic Absorption Spectrometer (AAS) and comparing the experimental data with the calibration curve. The amount of heavy metals adsorbed was calculated from the initial and final concentrations and the volume of solution according to the following equation,

$$Q_e = \frac{V(C_e - C_o)}{m},$$

where V = Volume of solution (dm^3), C_o = initial concentration (mol dm^{-3}), C_e = equilibrium concentration (mol dm^{-3}), m = weight of adsorbent (g).

Result and Discussion

The adsorption of cobalt and lead ions is observed to increase linearly as the amount of adsorbent is increased gradually from 0.5 g to 2.5 g (Figures 1, 2, 3). The maximum adsorption is obtained at the adsorbent dose of 2.5 g of 1400 μm size of the adsorbent.

Therefore, the study indicated that as the size of the activated carbon increased the site for the ions to attach themselves also increased. The study further alluded that the removal efficiency is associated with the adsorbent dose increases which is due to the availability of more adsorbing sites at higher doses as illustrated in the figures below.

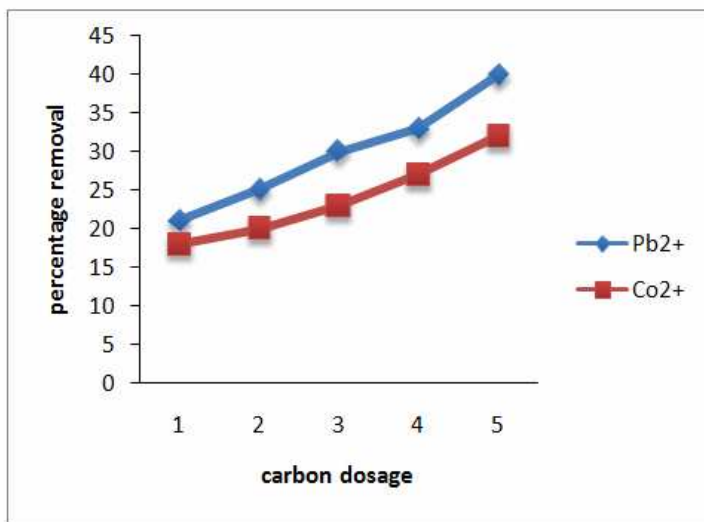


Figure 1. Effect of dosage *D. microcarpum* (150µm size) on the rate of adsorption at constant concentration (0.01M) of Pb²⁺ and Co²⁺.

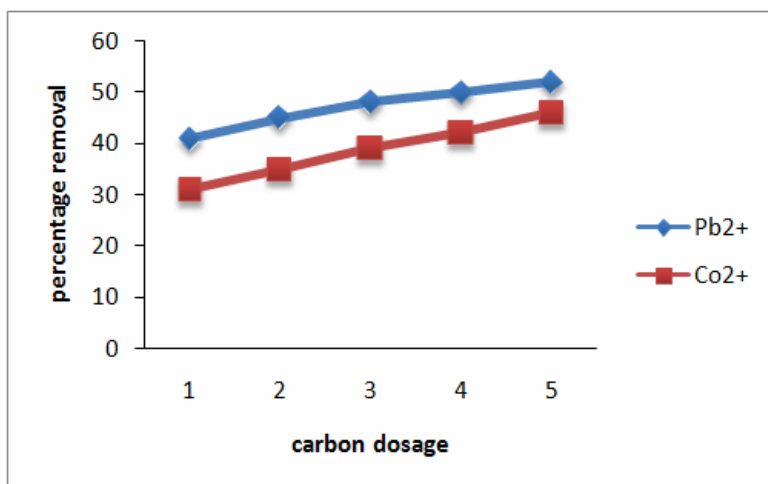


Figure 2. Effect of dosage *D. microcarpum* (420µm size) on the rate of adsorption at constant concentration (0.01M) of Pb²⁺ and Co²⁺.

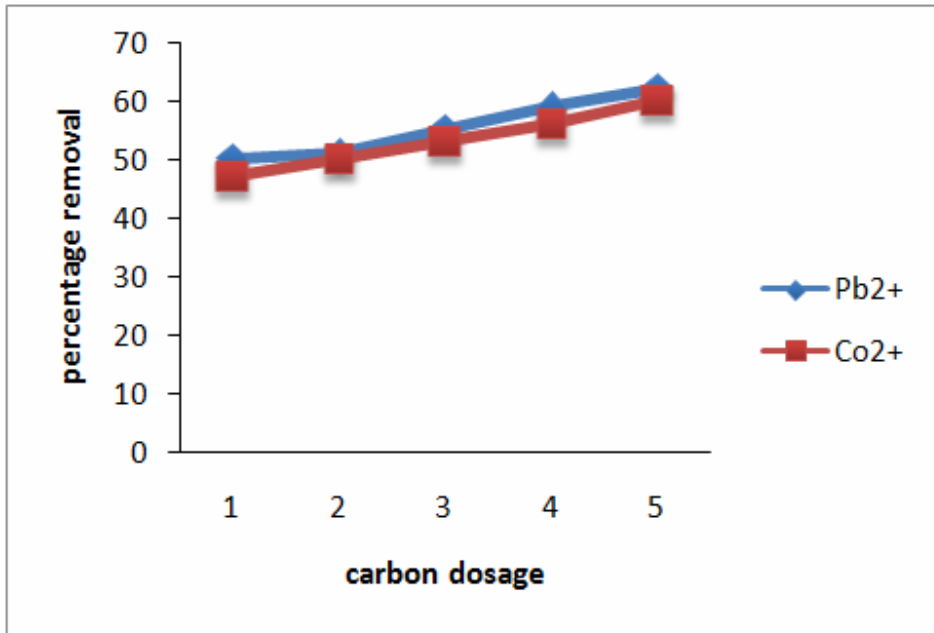


Figure 3. Effect of *D. microcarpum* dosage (1400µm size) on the rate of adsorption at constant concentration (0.01M) of Pb²⁺ and Co²⁺.

Figures 1, 2 and 3 above shows that the removal efficiency is generally increased as the dose concentration increases. This can be explained by the fact that more mass available, more the contact surface offered to the adsorption. These results are qualitatively in a good agreement with those found in the literature. Our results showed that the best removal efficiency was obtained at Figure 3 of Pb²⁺ and Co²⁺ of 1400µm size *D. microcarpum*.

Effect of initial concentration of cobalt and lead ion.

Removal of Co(II) and Pb(II) from wastewater was studied for concentrations ranging from 0.01 to 0.05 Mol/dm³. The percentage adsorption of Co (II) and Pb (II) at different concentrations from 50 mL solution of different initial concentration (equilibrated with 5.0 g of adsorbent) is shown in Tables 1 and 2. As observed from the tables the removal of metal ion is found to increase with decrease in initial concentration. At the experimental condition of 5.0 g dose of adsorbent, maximum adsorption is obtained for the concentrations of 0.01 and 0.02 Mol/dm³.

Table 1. Effect of concentration cobalt ion on the rate of adsorption at constant dosage (5g of 1400 μ m) and contact time (15 minutes).

Co (Moldm ⁻³)	Ce (moldm ⁻³)	X=(Co - Ce)	X/m	1/Co	1/x/m	Log X/m	Log Ce	Percentage removal
0.01	0.0011	0.0089	0.00178	100	563.11	-2.750	-2.959	89
0.02	0.0100	0.0100	0.00200	50	500.98	-2.699	-1.999	50
0.03	0.0192	0.0108	0.00215	33.3	465.23	-2.668	-1.717	36
0.04	0.0286	0.0114	0.00228	25	438.03	-2.642	-1.544	28.5
0.05	0.0381	0.0119	0.00238	20	421	-2.623	-1.419	23.8

Table 2. Effect of concentration of lead ion on the rate of adsorption at constant dosage (5g of 1400 μ m) and contact time (15 minutes)

Co (Moldm ⁻³)	Ce (moldm ⁻³)	X=(Co - Ce)	X/m	1/Co	1/x/m	Log X/m	Log Ce	Percentage removal
0.01	0.0009	0.0091	0.00182	100	594.45	-2.740	-3.048	91
0.02	0.0096	0.0104	0.00208	50	480.77	-2.682	-2.018	52
0.03	0.0192	0.0108	0.00216	33.3	462.96	-2.666	-1.717	36
0.04	0.0290	0.0110	0.00220	25	454.55	-2.658	-1.538	27.5
0.05	0.0386	0.0114	0.00228	20	438.60	-2.642	-1.413	22.80

Adsorption isotherms

To conduct the isotherm studies, Isotherm data of the one of the three different sizes were treated according to Langmuir and Freundlich models. The results showed that both Langmuir and Freundlich models fitted the data reasonably but the Langmuir adsorption isotherm model fitted better.

Freundlich isotherm

Freundlich isotherm model interprets the adsorption on heterogeneous surfaces with interaction occurring between the adsorbed molecules and is not restricted to the formation of a monolayer. This model proposes heterogeneous energetic distribution of active site. The Freundlich linear form is given by the following equation

$$\log \frac{X}{m} = \log K + \frac{1}{n} \log Ce,$$

where X/m is the amount adsorbed per gram of the adsorbent, Ce is the equilibrium

concentration, while K and $1/n$ are constants. K is the function of energy of adsorption and temperature and is the measure of adsorption capacity; $1/n$ determined the intensity of adsorption (Uddin et al. [25], Khan et al. [15]).

Langmuir isotherm

Langmuir isotherm: This model is based on Langmuir adsorption theory, molecule are adsorbed at a fixed number of well-defined active site which are homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for adsorption of a mono molecules layer and there is no interaction between the adsorbed molecules. Langmuir isotherm in linear forms gives.

$$\frac{1}{X} = \frac{1}{Xm.K} + \frac{1}{Xm}$$

where Xm is the monolayer capacity and K indicate binding constant which relate to the heat of adsorption. All constant are specific to test condition and the adsorbent type (Uddin et al. [25]).

The plot of $1/Xm$ versus $1/Co$ and $\text{Log } 1/Xm$ and $\text{Log } Ce$ were made to test the Langmuir and Freundlich adsorption isotherm models respectively.

Langmuir and Freundlich isotherm model are frequently used for describing the short term and mono-component adsorption of metal ions by different materials (Aksu and Kabasakal [3], Yu et al. [27]).

From the values obtained for these parameters the theoretical Langmuir and Freundlich curves were calculated and plotted in Figure 4. The Langmuir and Freundlich parameters as well as the correlation coefficient are also indicated in the figure.

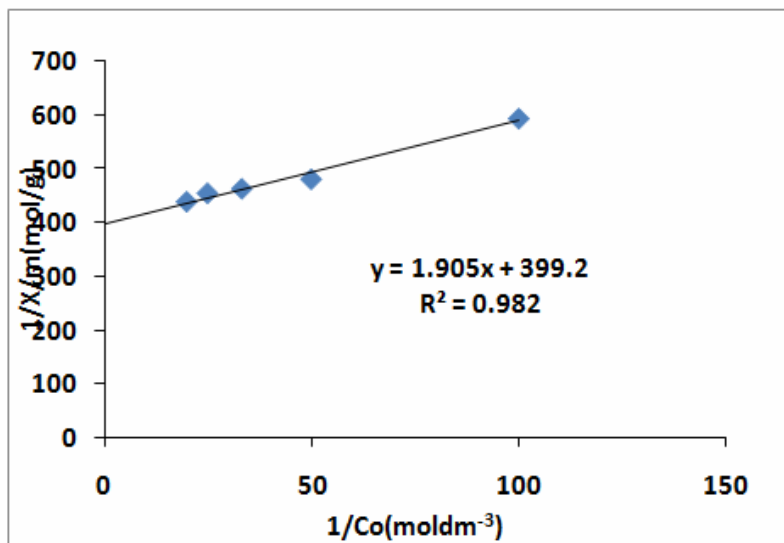


Figure 4. Langmuir adsorption isotherm of lead by (1400µm) activated carbon.

It can be observed that experimental data fit the isotherm adequately. The applicability of the Langmuir model to the experimental data indicates monolayer coverage on heterogeneous adsorbent surface by each of Pb(II) ions. For comparison the Freundlich adsorption isotherm is also given in Figure 5.

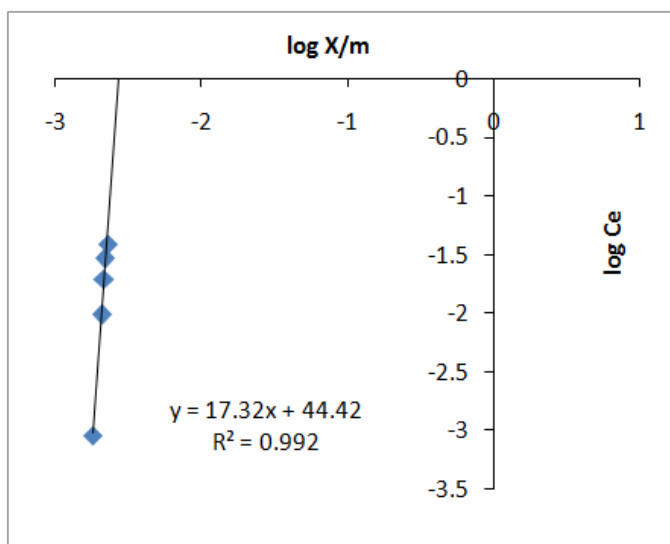


Figure 5. Freundlich adsorption isotherm of lead by (1400µm) activated carbon.

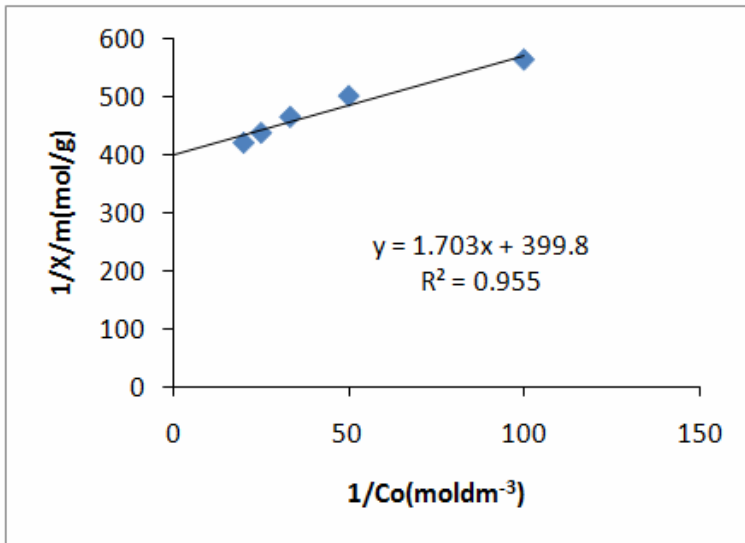


Figure 6. Langmuir adsorption isotherm of cobalt by (1400 μm) activated carbon.

It can be observed that experimental data fit the isotherm adequately. The applicability of the Langmuir model to the experimental data indicates monolayer coverage on heterogeneous adsorbent surface by each of Co(II) ions. For comparison the Freundlich adsorption isotherm is also given in Figure 8.

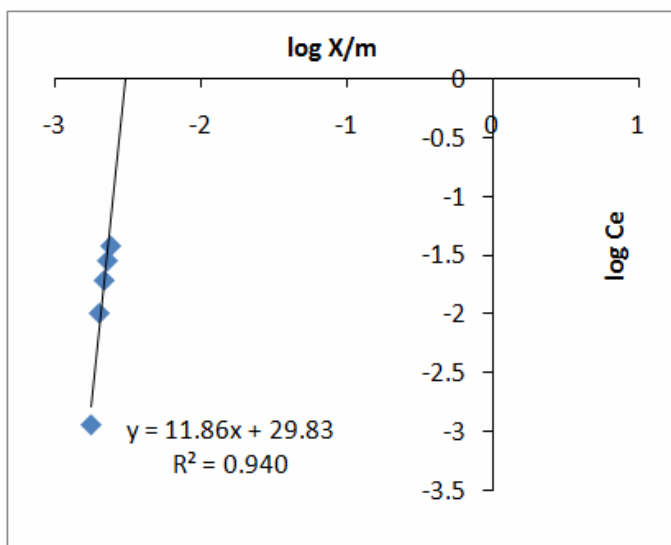


Figure 7. Freundlich adsorption isotherm of cobalt by (1400 μm) activated carbon.

Conclusion

The removal of Pb(II) and Co(II) in waste water by using *Detarium microcarpum* was studied in the batch experimental systems. Based on the results, the following conclusions can be drawn. The prepared activated carbon is an efficient biomaterial for removal of cobalt ion and lead ion from industrial wastewater. The percentage removal increased with increase dosage of *Detarium microcarpum*. Equilibrium metal adsorption decreased with the increase in the initial concentration of Co(II) and Pb(II) ions suggesting the applicability of the biomaterial at lower concentrations. Adsorption Isotherm studies showed that the experimental data are best fitted to Freundlich and Langmuir models. The sieve size of 1400 μ m activated carbon toward the removal of lead and cobalt is higher than 450 μ m and higher than 150 μ m activated carbon. The method was simple, cost effective and environmental friendly.

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