REMOVAL OF LEAD AND CADMIUM IONS FROM AQUEOUS SOLUTION USING *Vigna subterrenea* SEED SHELLS CARBON

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ABSTRACT

Carbon derived from Vigna subterrenea seed shells (CVSS) was employed for the effective removal of Pb (II) and Cd (II) by adsorption. CVSS was prepared via the chemical activation method using the nitric acid solution as activating agent. The effects of operational parameters such as pH, adsorbent dosage and contact time were studied. Adsorption isotherms and kinetics experiments were performed at 25 °C and 30 °C. The metal ions uptake increases with an increase in solution pH for the carbon for both Pb (II) and Cd (II) ions. Across the temperatures, equilibrium removal efficiencies of CVSS for Pb (II) and Cd (II) were 89.77≤ and≤ 73.81) respectively. Maximum adsorption capacity Q_{max} *of CVSS for Pb (II) and Cd (II) were 9.25 and 8.56mg/g respectively. Langmuir's model provides the best fit for both lead and cadmium. Adsorption kinetics obeyed the pseudo-second-order model.*

Keywords: *Metal ions, Vigna subterrenea seed shells, Adsorption isotherm, Adsorption Kinetics, Effluent remediation.*

INTRODUCTION

Rapid industrialization and urbanization have accelerated the release of industrial effluents and related wastes into the atmosphere, land, and water[1]. The mutual problems associated with unauthorized management and discarding of wastes include infections, disease transmission, and soil and water pollution[2]. Due to industrial expansion, large amounts of industrial wastes are gathering in the environment and cannot be disposed of without prior special treatment[2]. Heavy metal pollution is a serious environmental problem[3]. The principal hazardous metals which are of great concern in the world today in terms of their environmental load and health effects are lead, mercury, chromium, cadmium, copper, and aluminum. Among heavy metals, Cd, as one of the most important persistent inorganic pollutants, can generate severe toxicity to plants, animals, and humans, even at low concentrations [4]. Lead has been classified as a mutagen and a probable carcinogen[5,6] and has been reported to impair reproductive, respiratory, and digestive systems and suppress the immune system; this metal is particularly harmful in children, damaging their intelligence and nervous systems[7]. Various treatment technologies have been employed to remove metal from aqueous solutions[8]. Adsorption has been reported to be the most commonly used water treatment technology used for the removal of organics and heavy metals[9]. The growing interest in the preparation of low-cost adsorbents for wastewater treatment makes the use of natural and abundant materials like *Vigna subterrenea* seed shells important for the cost-cutting of the processes. *Vigna subterrenea* is indigenously used in Northern Nigeria for water purification (mainly turbidity removal)[10]. A lot of agricultural wastes have been used to prepare activated carbon such as coconut tree sawdust[11], coconut shell carbon[12], grape stalk[13], tyre activated carbon[14]. Reports have shown that the activated carbon obtained from these agricultural wastes showed a high degree of removal of both organic and inorganic harmful substances present in wastewater effluents. Activated carbon adsorption in particular is considered to be a predominantly effective process for the removal of heavy metals and due to its ease of operation and insensitivity to toxic substances and efficiency in the removal of pollutants at low concentrations[15,16]. Activated carbons are preferred adsorbents that have unique characteristics owed to their high surface area, surface acid groups, micro, and mesoporous structure, and large sorption capacities[17]. The main purpose of this study is to investigate the adsorption of lead (II) and cadmium (II) from aqueous solutions onto activated carbon prepared from seed shells of *Vigna subterrenea.* Pb (II) and Cd (II) were selected because they are priority toxicants obtained in several industrial wastewater and streams.

MATERIALS AND METHODS

Materials

Nitric acid (HNO_3) Sodium hydroxide (NaOH), Sulphuric acid (H_2SO_4), Hydrochloric acid (HCl) BDH chemicals Limited England, Instruments used include Fourier Transform Infrared spectrophotometer (FTIR-8400S Shimadzu Japan), AAS (Perkin Elmer Analyst 100 Atomic Absorption Spectrophotometer equipped with Perkin Elmer HGA 850 Graphite Furnace, Japan), analytical weighing balance (Adam Equipment Co, Ltd US), muffle furnace (Carbolite, UK), and a Thermostatic mechanical shaker (Heldolp Unimax 2010, Germany).

Methods

Preparation of the Adsorbent

A portion of air-dried *Vigna subterrenea* seed shell (VSS) shells was steeped into nitric acid solution overnight for chemical activation. The slurry was filtered and the residue was washed repeatedly with distilled water, and oven-dried to give the activated *Vigna subterrenea* seed shell (AVSS). A portion of AVSS was pyrolyzed in a muffle furnace at 350 ^oC for 90 mins, pulverized, and sieved to 2 mm particle size using standard sieves to give carbonized *Vigna subterrenea* shell adsorbent (CVSS).

FTIR Characterization of the adsorbent

The functional group characteristics of the adsorbent, CVSS was determined using Fourier Transform Infrared spectrophotometer (FTIR-8400S Shimadzu Japan) between 4000 - 630cm^{-1}.

Batch adsorption experiments

The effect of solution pH and adsorbent dosage on Pb (II) and Cd (II) uptake was studied by treatment of 50 mL aliquots of

Pb (II) and Cd (II) solutions adjusted to different pH (3, 5, 7, 9, and 11) and adsorbent masses (0.5, 1.0, 1.5, 2.0 and 2.5 g) for 4 hours at pH 6. Adsorption isotherms were developed at 25°C and 30 °C by dispersing separate 0.5 g portions of the adsorbents in 50-mL aliquots of each standard (0 – 100 mg/L) Pb (II) and Cd (II) solution with the aid of a mechanical shaker for 4 hours. Adsorption kinetic experiments were performed by shaking 0.5 g portions of the adsorbents dispersed in separate 50 mL aliquots of 100 mg/L Pb (II) and Cd (II) solution for 10, 30, 60, 120, 180, and 240 min on a mechanical shaker at temperatures (25 – 30 °C). At the lapse of each specified time interval, the mixtures were filtered and the residual metal concentrations in the filtrate were measured using Atomic Absorption Spectrophotometer (AAS). In all batch adsorption experiments, the amount of metal ions adsorbed per gram of adsorbent, Q (mg/g), and the removal RE (%) efficiency were calculated using Equations (1) and (2) respectively.

$$Q(\text{mg/g}) = \frac{(C_\text{o} - C\ )V}{m_\text{a}} \qquad (1)$$

$$\text{RE}\ (\%) = \left(\frac{C_o - C}{C_o} \right) x100 \qquad (2)$$

where C_o and C are the initial and residual metal lead and mercury concentrations (mg/L), respectively, V is the volume of Pb (II) and Cd (II) solution used (L); and m_a is the mass of adsorbent (g) used for a particular batch treatment.

RESULTS AND DISCUSSION

FTIR Spectra

The FTIR spectroscopy serves as a direct means of identification of the surface functional groups. Fig 1 shows the FTIR spectra of the carbonized *vigna subterrenea* seed shells. This permitted spectrophotometric observation of the CVSS surfaces in the range of 4000 - 630 cm^{-1}. The broad adsorption bands at 3276.3 cm^{-1} may be assigned to the -OH stretching vibrations of hydroxyl groups [5]. The vibrations at a band of 2899.9 cm^{-1} is likely due to a C-H stretching for an alkane. A strong O=C=O stretching and a N=C=S stretching occurs at a vibration of 2370.6 cm^{-1} and 2113.4 cm^{-1} for carbon dioxide and isothiocyanate respectively. The vibrations of band between 1982.2 and 1945.7 may be due to C-H bending for an aromatic compound. An O-H bending for alcohol was observed at a vibration between 1423.8 and 1315.8 cm^{-1}. Adsorption due to C=O vibrations occur between 1699.7 and 1606.5 cm^{-1}, this may be for a conjugated acid or a conjugated aldehyde. The band at 1200.2 cm^{-1} may be due to esters and the strong one at 1028 cm^{-1} to C–O vibration in C–OH[5]. Only bands attributed to C=C vibrations absorbing at a band of 670.9 cm^{-1} due to a disubstituted cis alkene[5].

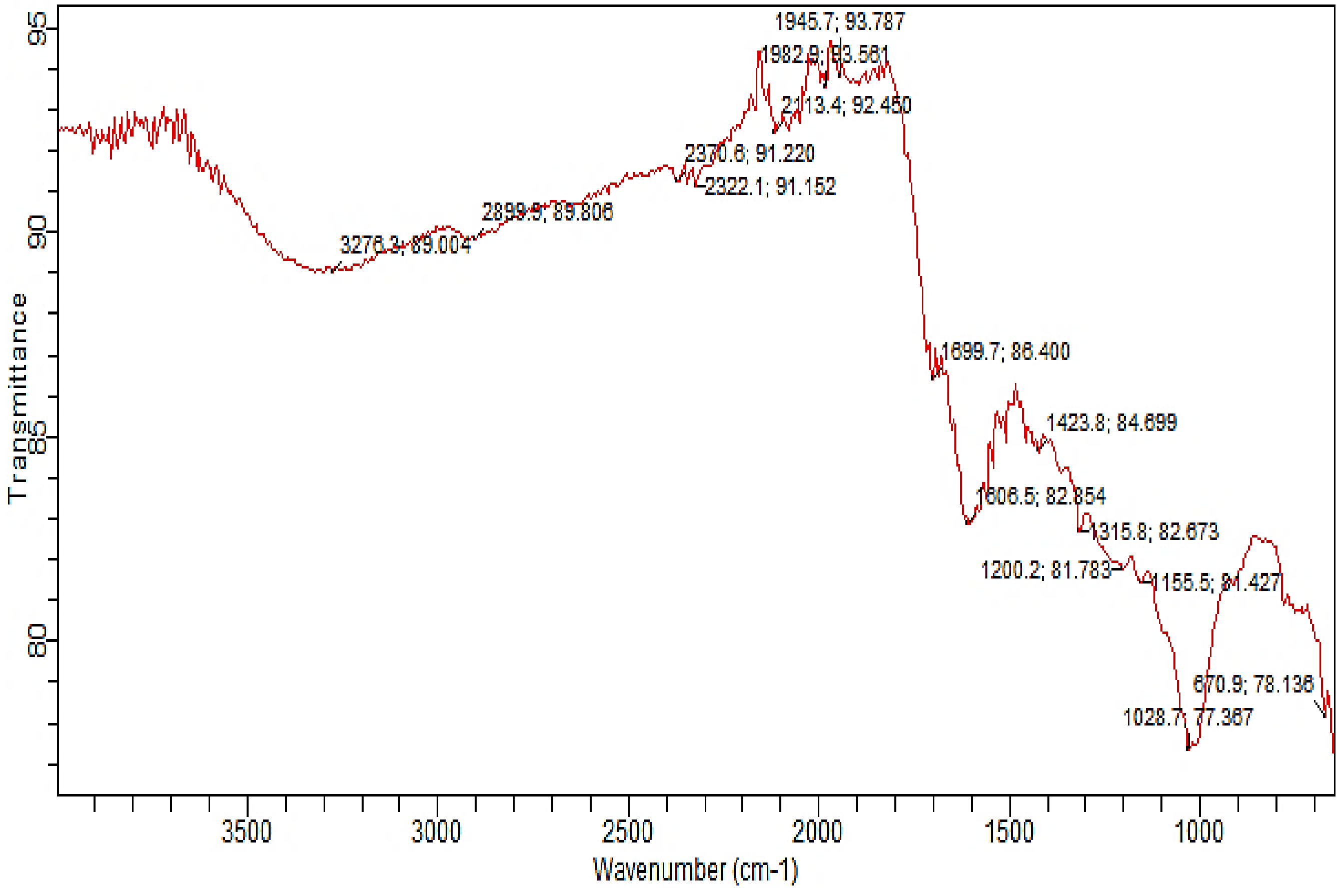


Fig. 1 FTIR Spectrum for Carbonised *Vigna subterrenea* seed shells

Adsorption Experiments

The pH of the solution primarily affects the surface charge of the adsorbents, degree of ionization, and speciation of Pb (II) and Cd (II) solutions which may lead to change in equilibrium and kinetics removal. The effect of initial solution pH (Fig. 2) was investigated over the pH ranges of 3 – 11, at a fixed initial concentration of lead (II)

Effect of Adsorbent pH

and cadmium (II) solutions (100 mg/L). The amount adsorbed increased with an increase in pH for the adsorbent. The highest uptakes: CVSS (9.2 and 8.6 mg/g) for Pb (II) and Cd (II) is recorded at pH 9 for both metals. These results showed the suitability of the adsorbent for the treatment of basic wastewater [18,19].

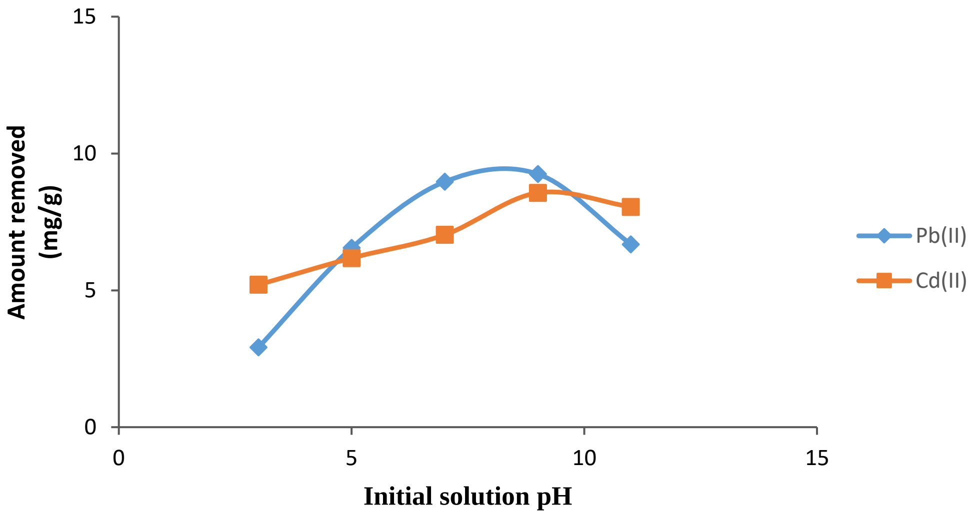


Fig 2. Effect of pH on Pb (II) and Cd (II) removal

Effect of Adsorbent Dosage

The adsorbent load determines the capacity of CVSS for a given Pb (II) and Cd (II) concentration, which furnishes the adsorbate/adsorbent equilibrium relations. Adsorption capacity decreased with the increase in adsorbent loading (Fig. 3), at increasingly higher sorbent dosages (0.5 – 2.5 g), fixed initial concentration (100 mg/L), fixed aliquot volume (50 mL) and a fixed pH (pH = 6). At higher adsorbent doses, an aggregration of adsorbent particles may have occurred leading to less availability of exchangeable adsorption sites which consequently lead to a decreased uptake at higher dosages[20,21].

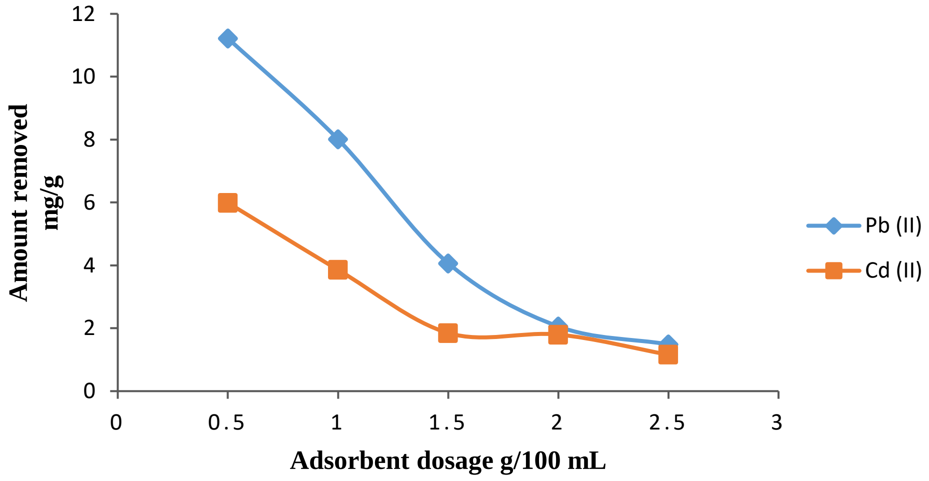


Fig 3. Effect of adsorbent dose on Pb (II) and Cd (II) removal

3.4 Equilibrium Adsorption Capacities and Isotherm Profiles

Equilibrium data from adsorption experiments are usually presented in the form of an isotherm, which graphically displays the ratio of sorbed to non-sorbed solute per unit mass of the adsorbent at constant temperature (Figs 4 – 13). At operating initial metal ions concentration ($20 \leq C_e \leq 100$ mg L^{-1}), removal efficiencies *RE* (%) for Pb (II) and Cd (II) were (89.77≤ (*RE%*) ≤73.81) which were calculated from the equilibrium adsorption data as the percent of metal ion removed. The isotherms for the CVSS is somewhat L-shaped for both metals indicating that the intermolecular forces of the metals are comparatively weaker than the sorptive forces, which implies that the activation energy of adsorption is independent of surface coverage [22].

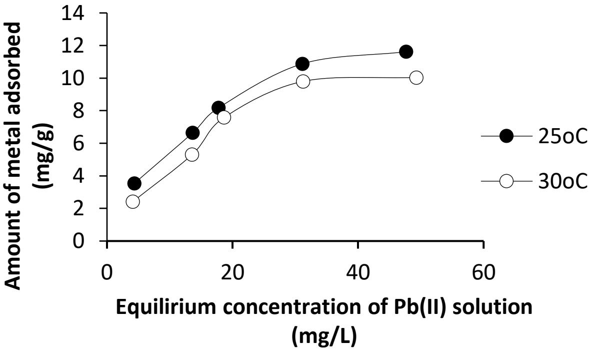


Fig. 4 Isotherm Profiles for Adsorption of Pb (II) onto CVSS at Different Temperatures

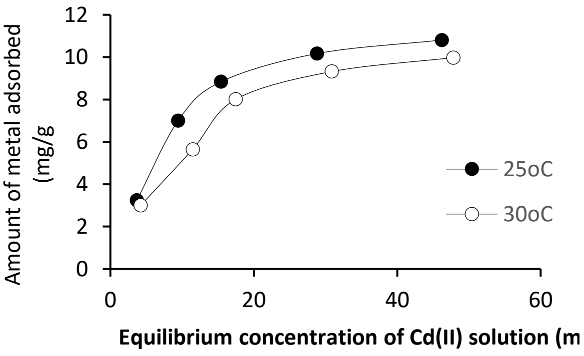


Fig. 5 Isotherm Profiles for Adsorption of Cd(II) onto CVSS at Different Temperatures

Equilibrium data were fitted into the Langmuir and Freundlich isotherms represented by Equations (3) and (4), respectively.

$$\frac{C}{Q} = \frac{C}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \qquad (3)$$

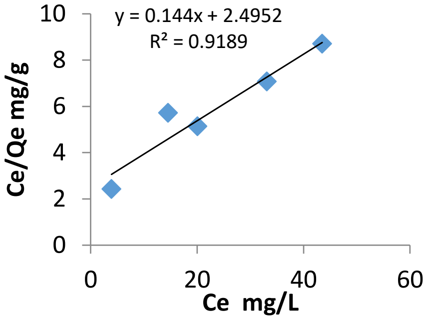
$$\ln Q_e = \frac{1}{n_F} \ln C_e + \ln K_F \qquad (4)$$

where Q is the equilibrium amount of Pb (II) and Cd (II) adsorbed per unit mass of the adsorbent (mg/g), and C is the residual concentration (mg/L). $Qmax$ is the maximum amount of metal ion adsorbed per unit mass of adsorbent (mg/g) corresponding to complete coverage of the adsorptive sites, K_L is the Langmuir constant (L/mg) related to the energy of adsorption. K_f is Freundlich constant, related to the adsorption capacity, and n_f is a dimensionless empirical parameter related to the adsorption intensity which varies with the heterogeneity of the material [23].A linear plot of C/Q versus C gives the inverse of the slope as $Qmax$ and K_L are derived from the intercept; while a linear plot of ln$Q$ versus ln$C$ gives the inverse of the slope as nF and intercept Kf.

The Langmuir and Freundlich isotherm parameters are recorded in Table 1. The higher regression values showed that the equilibrium data for the lead and cadmium fitted well to both the Langmuir and Freundlich isotherms in the studied concentration ranges.

Based on the regression coefficient (R^2), the equilibrium data was slightly better fitted in Langmuir adsorption isotherm. This demonstrates the formation of monolayer coverage of the metal surfaces by *the Carbonized vigna subterrenea*[24].

Fig. 6: Langmuir isotherm for Pb (II) @ 25^{0}C



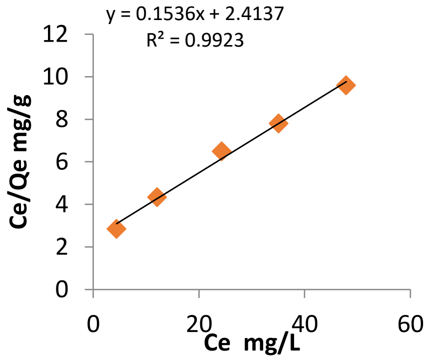


Fig. 7 Langmuir isotherms for Cd (II) @ 25^{0}C

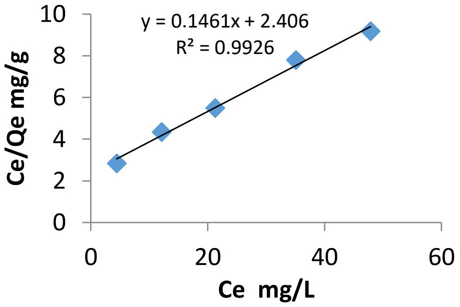


Fig. 8 Langmuir isotherms for Pb (II) @30 ^{0}C

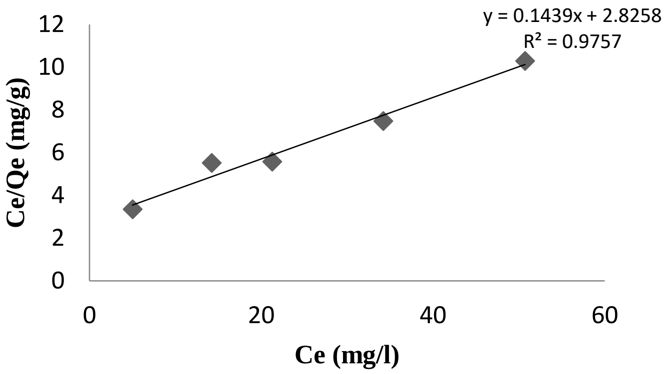
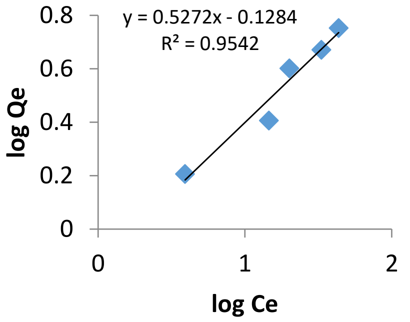


Fig. 9 Langmuir isotherm for Cd (II) @30^{0}C



ig. 10 Freundlich Isotherms for Pb (II) @ 25^{0}C

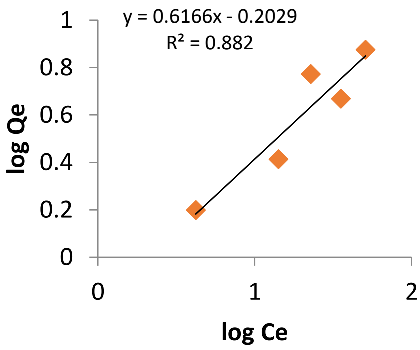


Fig. 11 Freundlich Isotherm for Pb (II) @30 ^{0}C

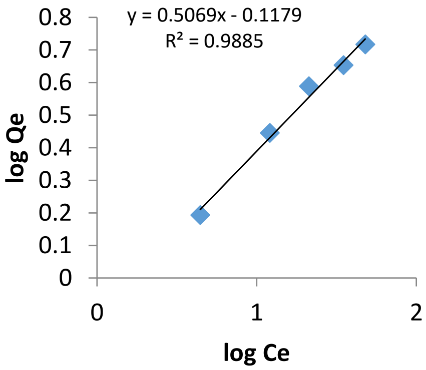


Fig 12 Freundlich Isotherms for Cd (II) @25 ^{O}C

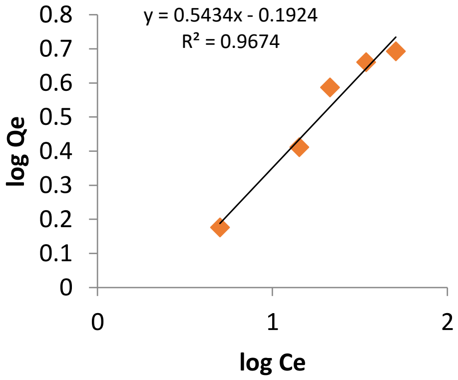


Fig. 13 Freundlich Isotherm for Cd (II) @ 30^{0}C

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Table 1. Isotherm Parameters for Pb (II) and Cd (II) Removal unto *Vigna Subterrenea* Seed Shells Carbon at Different Temperatures

Isotherm parameters	Pb(II)		Cd(II)	
	25℃	30℃	25℃	30℃
Langmuir				
Q_o (mg.g^{-1})	9.93	6.85	8.96	6.99
K_L (L.mg^{-1})	0.0577	0.0607	0.0634	0.0506
R_L	0.0189	0.0607	0.0188	0.0180
R^2	0.9189	0.9926	0.9923	0.9757
Freundlich				
(mg$^{1-1/n}$L$^{1/n}$g^{-1})	4.1170	3.0490	4.325	2.8280
n_F	2.4289	0.3279	0.2312	0.3536
R^2	0.9542	0.8820	0.9885	0.9674

Adsorption Kinetics

Contact time is an important parameter to determine the rate of removal time of the adsorption process. The characteristics of *Vigna subterrenea* seed shell and its available sites affected the time needed to reach equilibrium[18,19]. For adsorbent CVSS metal ions uptake as seen (Figs. 14 and 15) increased within the first 50 min but slowed down beyond this point, gradually metal ion uptake was not increased significantly signifying that the process would not offer an additional kinetic advantage when contact times longer than 4 hours were employed [21]. The uptake of metal ions diminished as the equilibrium point was attained. Experimental data for the aqueous phase removal of Pb (II) and Cd (II) on CVSS as a function of contact time were fitted into the Pseudo-first- order (PFO) and pseudo-second-order(PSO) kinetic models in equations (6) and (7), respectively:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \qquad (6)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 {Q_e}^2} + \frac{t}{Q_e} \qquad (7)$$

Where Q_e and Q_t (mg/g), refers to the amounts of Pb (II) and Cd (II) adsorbed on the adsorbent at equilibrium and at a specified time, t (min). k_1 (min^{-1}) and k_2 (g/mg.min) are the pseudo-first and pseudo-second-order and the adsorption rate constant respectively. From the regression values it fitted more to the pseudo-second order. In this condition it means the adsorption rate may be dependent on adsorption capacity and not concentration of the adsorbate. Figures 16 - 19 represent the plots derived by the corresponding models while Table 2 records the kinetic parameters so generated [25, 26].

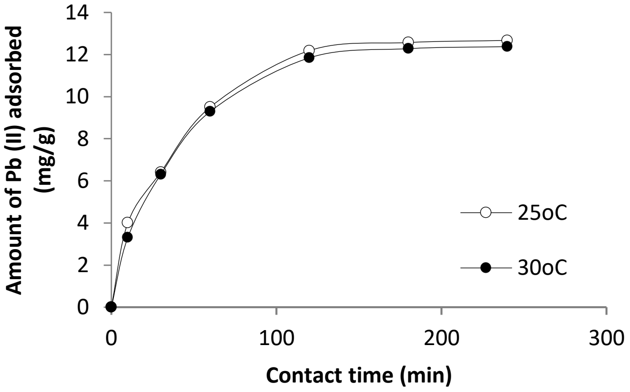

Fig. 14. Rate curves Pb (II) Adsorption onto CVSS at Different Temperatures

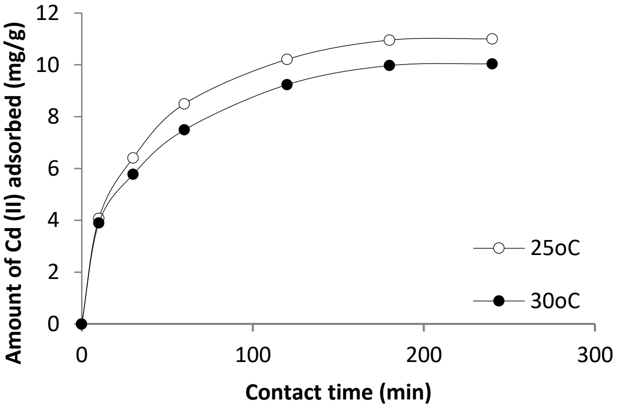

Fig. 15 Rate curves Pb (II) Adsorption onto CVSS at Different Temperatures

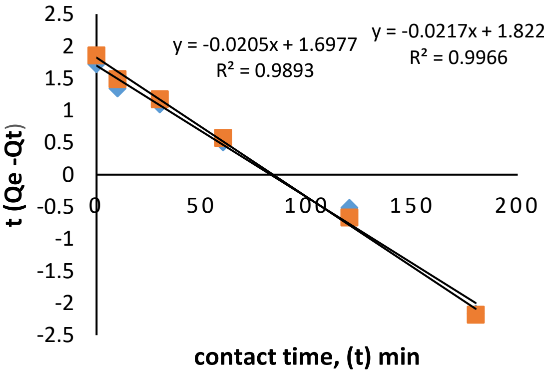

Fig 16 Pseudo-first order kinetic for Pb (II) removal

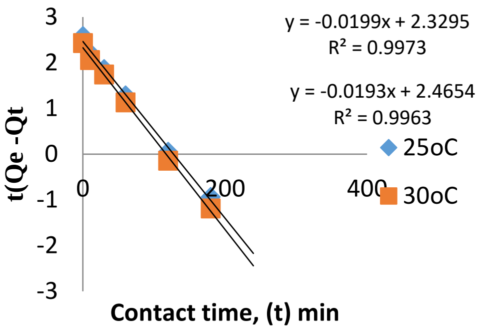

Fig 17 Pseudo-first order kinetic for Cd (II) removal

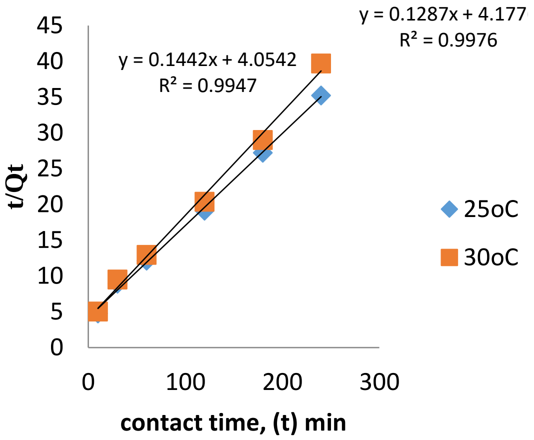

Fig 18. Pseudo- second-order kinetic for Pb (II) removal

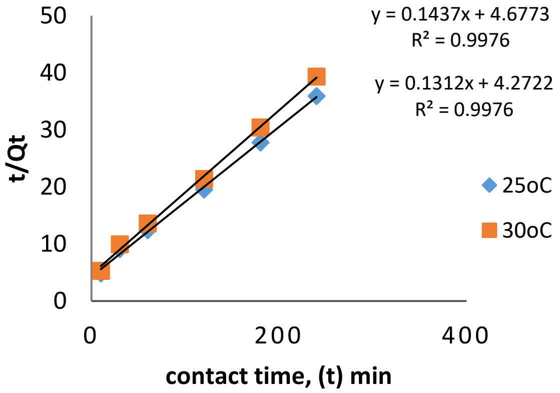

Fig 19 Pseudo- second-order kinetic for Cd(II) removal

Table 2: Kinetic Parameters for Pb(II) and Cd(II) Removal Onto *Vigna Subterrrenea* Seed Shells Carbon At Different Temperatures

Kinetic model parameters	Pb(II)		Cd(II)	
	25°C	30°C	25°C	30°C
PFO				
k_1 (min^{-1})	0.019	0.019	0.019	0.019
R^2	0.998	0.996	0.996	0.995
PSO				
k_2 (g.mg^{-1}min^{-1}	3.92 x 10^{-3}	5.12x10^{-3}	2.37x10^{-3}	2.63x10^{-3}

R^2	0.997	0.994	0.997	0.998

CONCLUSION

The adsorbent showed good adsorptive behavior towards metal ion removal. The equilibrium data fitted very well with the Langmuir isotherm as per Pb (II) and Cd (II) uptake. Adsorption kinetics obeyed the pseudo-second-order kinetic model. From all indications, this adsorbent when used on a large scale may find potential use in lead and cadmium removal from aqueous effluents and industrial wastewater.

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