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Surface interaction of sweet potato peels (*Ipomoea batata*) with Cd(II) and Pb(II) ions in aqueous medium

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A R T I C L E   I N F O

Article type:
Research article
Article history:
Received June 2018
Accepted September 2018
October 2018 Issue
Keywords:
Potato peels
Adsorption
Heavy metal
FT-IR
Modeling

A B S T R A C T

The removal of Cd(II) and Pb(II) ions from aqueous medium was studied using potato peels biomass. The adsorption process was evaluated using Atomic Absorption Spectrophotometer (AAS). The Vibrational band of the potato peels was studied using Fourier Transform Infrared Spectroscopy (FTIR). The adsorption process was carried out with respect to concentration, time, pH, particle size and the thermodynamic evaluation of the process was carried at temperatures of 30, 40, 50 and 60(^{0}C), respectively. The FTIR studies revealed that the potato peels was composed of –OH, -NH, –C=N, –C=C and –C-O-C functional groups. The optimum removal was obtained at pH 8 and contact time of 20 min. The adsorption process followed Freundlich adsorption and pseudo second-order kinetic models with correlation coefficients (R^2) greater than 0.900. The equilibrium adsorption capacity showed that Pb(II) ion was more adsorbed on the surface of the potato peels biomass versus Cd (II) ion (200.91 mg/g > 125.00 mg/g). The thermodynamic studies indicated endothermic, dissociative mechanism and spontaneous adsorption process. This study shows that sweet potato peels is useful as a low-cost adsorbent for the removal of Cd(II) and Pb(II) ions from aqueous medium.

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Capsule Summary: The removal of Cd(II) and Pb(II) ions from aqueous medium was studied using potato peels biomass, which was found highly efficient for the adsorption Cd(II) and Pb(II) ions and could possibly be extended for the other removal of divalent metal ions.

Cite This Article As: O. Chidi and R. Kelvin. Surface interaction of sweet potato peels (*Ipomoea batata*) with Cd(II) and Pb(II) ions in aqueous medium. Chemistry International 4(4) (2018) 221-229.

INTRODUCTION

The extent of heavy metal pollution in our environment has undergone dramatic increase with increasing population and sophistication in human activities, especially since the beginning of industrial revolution (Nriagu, 1979). Its presence in the environment is of major concern because of their toxicity to many life forms. Various industries produce and discharge wastes containing different heavy metal concentrations into the environment; such noxious environment is as a result of intense mining, smelting, metal finishing, leather tanning, dyeing, radioactive material processing, pesticide and fertilizer application, etc (Agouborde and Navia, 2009).

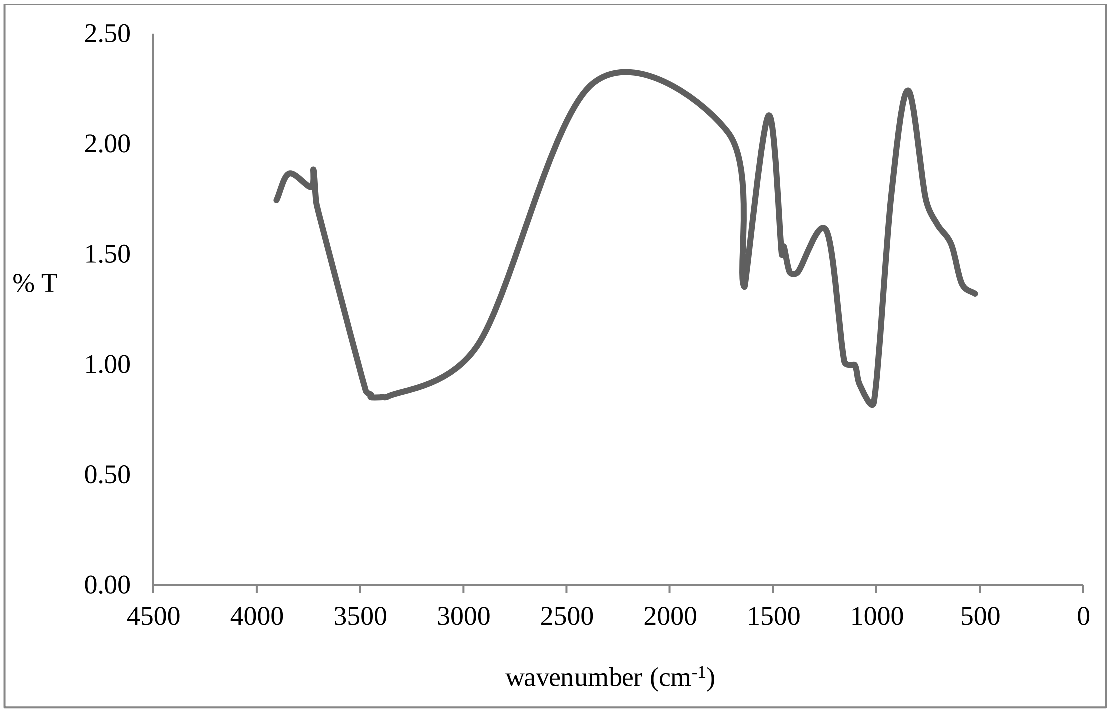

Fig.1: FTIR spectrum of Sweet potato peels

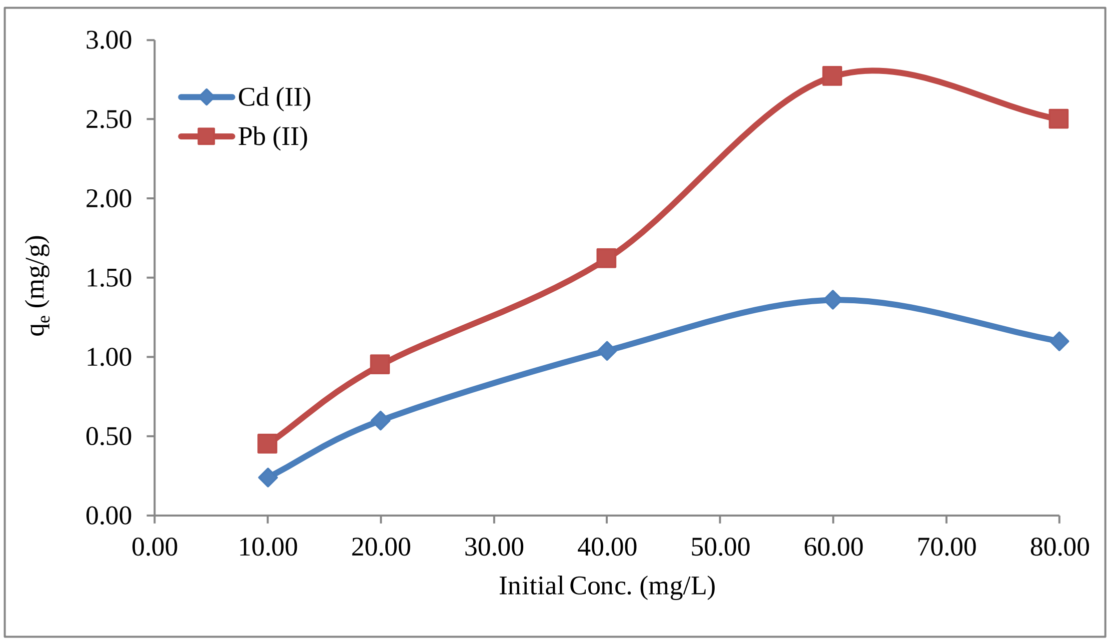

Fig. 2: Uptake capacities for Cd (II) and Pb (II) ions on potato peels at 298 K

With the rising awareness of the occurrences of industrial activities, which has increased deteriorations on the ecosystem and poses numerous health risks, the enforcement of necessary rules and regulations concerning the emission of contaminants from industrial waste streams by various regulatory agencies have been made public. Simultaneously, researchers have applied a wide range of decontamination techniques such as precipitation, sedimentation, flotation, filtration, membrane processes, electrochemical techniques, biological process, chemical reactions, adsorption, ion exchange, photo-catalytic degradation, micellar enhanced ultra-filtration, cation exchange membranes, etc., and these have brought varying degrees of successes in the scientific community (Saha and Chowdhury, 2011). Owing to its economic viability, feasibility and simplicity, adsorption technique is of major interest in this study.

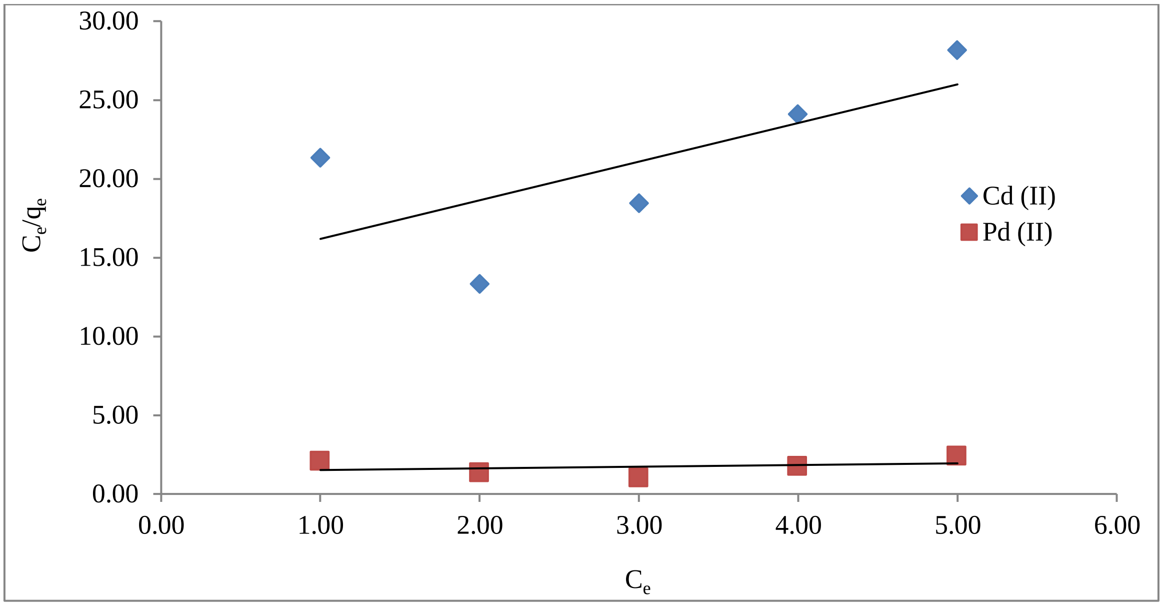

Fig. 3: Langmuir plots for Cd (II) and Pb (II) ions

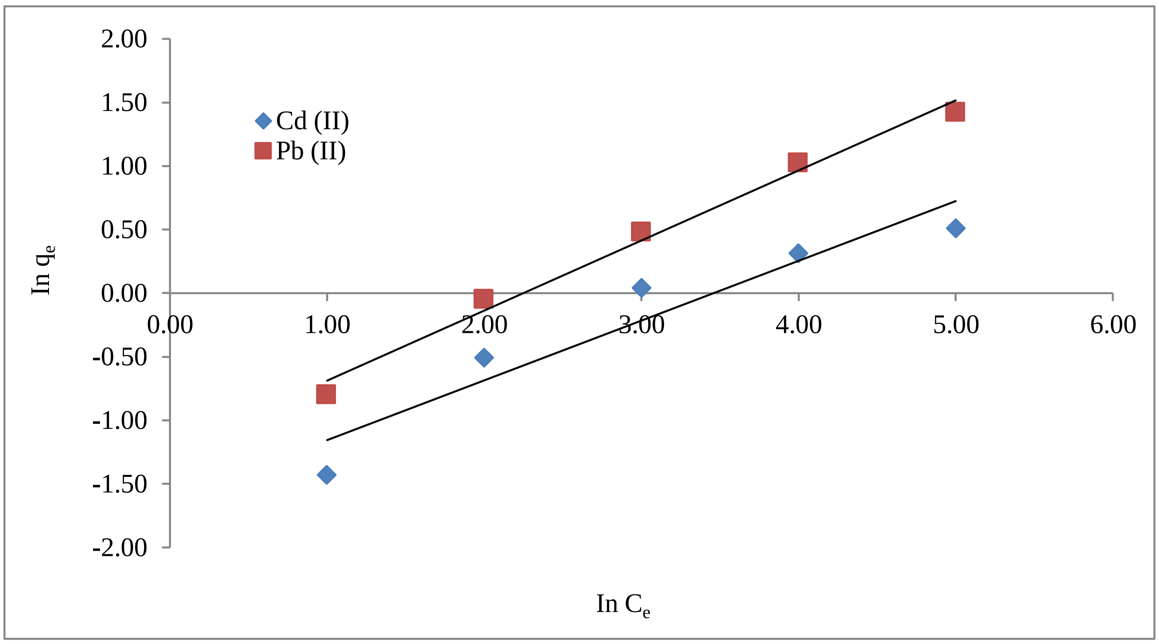

Fig. 4: Freundlich plots for Cd (II) and Pb (II) ions

Cadmium (Cd) is an extremely toxic industrial and environmental pollutant classified as a human carcinogen. It is one of the heavy metals that have been classified by the (WHO) to be of serious health concern (World Health Organisation, 1993). In fact, this metal together with Lead (Pb) and Mercury (Hg) are "the big three" because of their significant negative impact on the environment (Volesky, 1994).

The discharge of untreated industrial effluents from industries such as paints, plating, fertilizers, mining, textile dyeing and processing, automobile manufacturing and metal processing is a major source of heavy metals in the environment (Low and Lee 1991; Habibur et al., 2006).

The increasing awareness of health hazards of toxic heavy metal ions and organic pollutants in the biosphere and the ultimate reach to humans and animals via food chain and the exorbitant cost of removal has accelerated efforts to explore the most economical ways of controlling environmental pollution.

In pursuit to discover a cheaper and readily available adsorbent, this study attempts to investigate the capability of potato peels (*Ipomeabatata*), for Cd (II) and Pb (II) ions

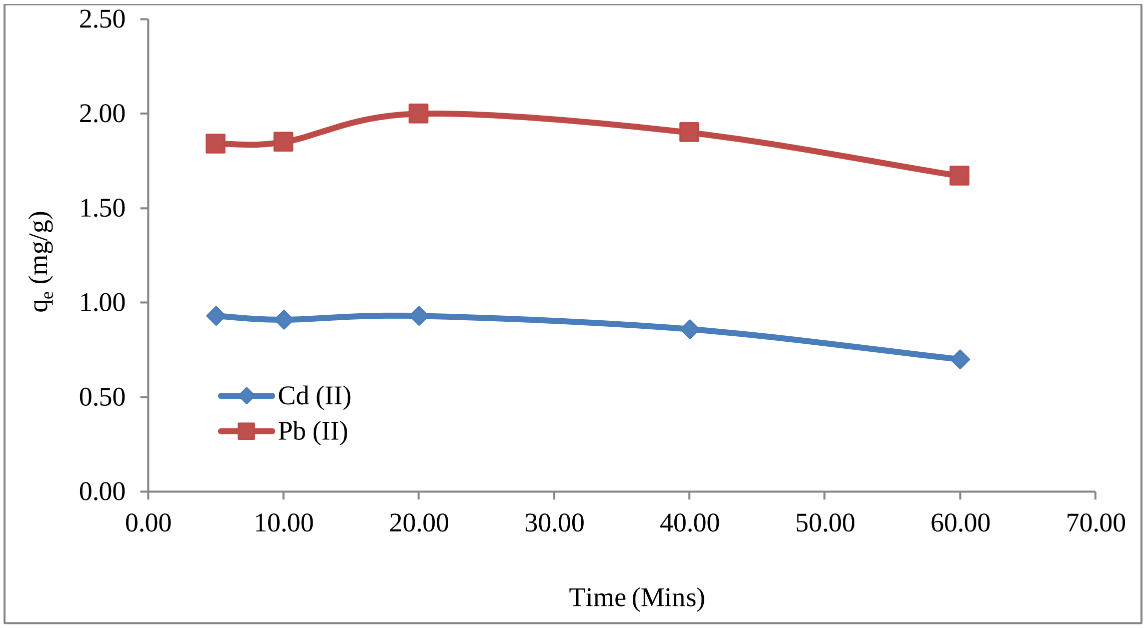

Fig. 5: Effect of time for Cd (II) and Pb (II) ions adsorption on potato peels at 298 K

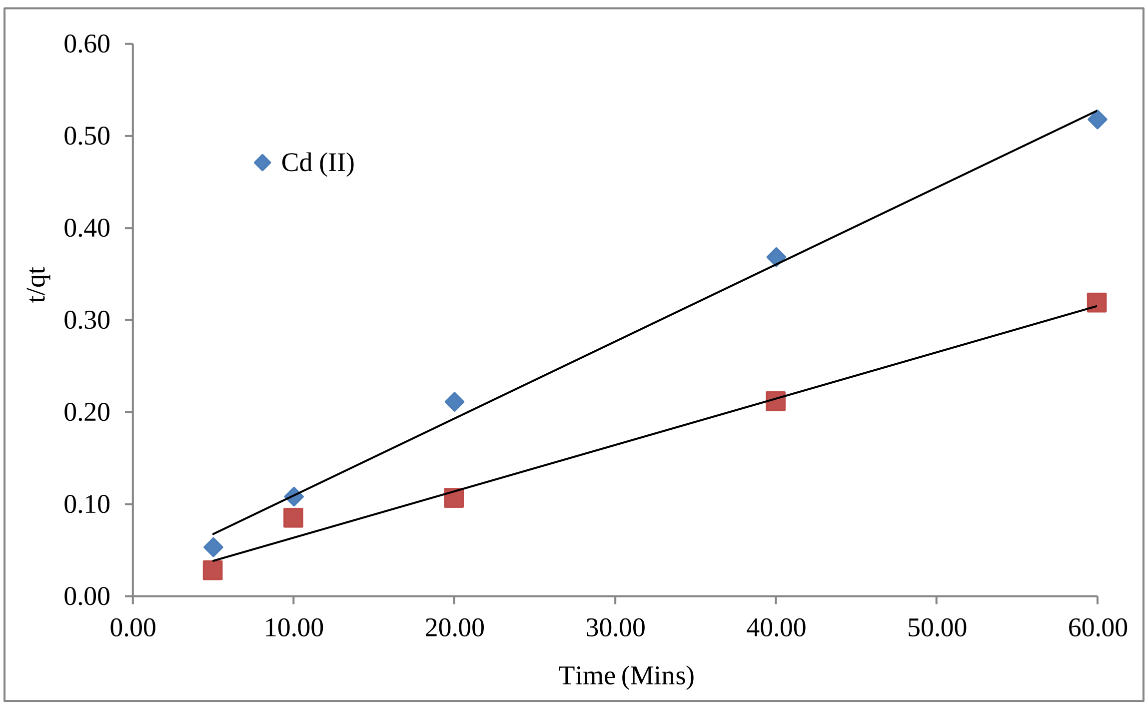

Fig. 6: Pseudo second-order plots for Cd (II) and Pb (II) ions on potato peels biomass

removal from aqueous environment and to establish the conditions for optimum result.

MATERIAL AND METHODS

Biomass collection and preparation

The sweet potatoes were bought from Choba market. The sample (sweet potato peels) was identified from the plant science and Biotechnology department; University of Port Harcourt. It was washed clean, peeled and air-dried for 14 days and oven-dried for 12 hrs. The sample was ground into fine powder using a petroleum-powered milling machine. It was passed through a 2 mm steel sieve and stored in a labeled plastic bottle till its use for the sorption study. The peel was characterized using Fourier Transform Infrared Spectrometer.

Table 1: Langmuir and Freundlich parameters

Model	Parameter	Cd (II) ion	Pb (II) ion
Langmuir	q_m (mg/g)	0.408	9.434
	K_L (L/mg)	0.179	0.075
	R^2	0.473	0.095
Freundlich	K_F (L/mg)	0.486	0.214
	n	2.128	1.815
	R^2	0.909	0.988

Table 2: Pseudo second-order parameters for the adsorption of Cd (II) and Pb (II) ions by potato peels biomass

Metal ion	q_e (mg/g)	k_2 (g/mg/min)	R^2
Cd (II)	125.00	0.00256	0.995
Pb (II)	200.91	0.00192	0.988

Table 3: Thermodynamic parameters for the adsorption process

Parameter	Cd (II) ion	Pb (II) ion
ΔH^o (kJ/mol)	3537	9278
ΔS^o (J/mol)	6.568	14.358
ΔG^o (kJ/mol)	- 1.954	- 4.270

Batch adsorption study

The adsorption study was determined by batch experiments. The process was conducted to determine the effect of pH, contact time, initial metal ion concentration, particle size and temperature (using thermo-stated water bath). Desorption process was also conducted. The residual metal ion concentrations of the filtrate of each metal solution were analyzed using Buck Scientific Model 210 VGP Atomic Absorption Spectrometer (AAS). All experiments were conducted for a period of 60 min except for the contact time where the time was varied. The amount of the metal ion adsorbed per gram of the biomass is calculated using the expression in equation [1].

$$q_e = \frac{C_i - C_e}{M} \times V \qquad (1)$$

Where, C_i and C_e represent initial and equilibrium concentrations of metal ions in aqueous solution respectively in mg/L, q_e is the amount of metal ion adsorbed per gram of biomass, M is the mass of the biomass in grams and V is volume of the solution in L.

Initial concentration dynamics

A 0.5 g sample of the 105 µm sweet potato peels (SPP) biomass was transferred into five plastic bottles each for Cd (II) and Pb (II) ions. This was followed by addition of 20 ml of 10-80 mg/L of both Cd (II) and Pb (II) ions into separate bottles respectively. The bottles were mechanically shaken at 180 revolutions per minute (rpm) for 1 hr. It was then filtered and the supernatant taken for Atomic Absorption Spectrophotometer (AAS) analysis.

Contact time dynamics

A 0.5 g sample of the 105 um SPP biomass was added into separate bottle containing 20 ml of 10 mg/L Cd (II) and Pb (II) ions and mechanically shaken at 180 rpm for time intervals of 5, 10, 20, 40 and 60 mins. The mixture was filtered and the supernatant taken for AAS analysis.

Temperature dynamics

A solution of 10 ml of 10 mg/L Cd (II) and Pb (II) ions each was mechanically shaken at 180 rpm for 1 hr with 0.5 g samples of 105 um SPP biomass at temperatures of 301 K, 313 K, 333K and 353 K respectively using a thermo-stated water bath. The mixture is then filtered and the supernatant taken for AAS analysis.

pH dynamics

A 0.5 g of 105 um SPP biomass was shaken mechanically at 180 rpm for 1 hr with 20 ml of 10 mg/L each of Cd (II) and Pb (II) ions in separate experimental bottles. The pH was adjusted from 2-12 respectively using 0.1 M NaOH and 0.1 M HCl. The mixture was filtered and the supernatant taken for AAS analysis.

Particle size dynamics

A 0.5 g of the 105 um, 250 um, 500 um and 750 um SPP biomass was added to 20 ml of 10 mg/L each of Cd (II) and Pb (II) ions and was mechanically shaken at 180 rpm for 1 h.

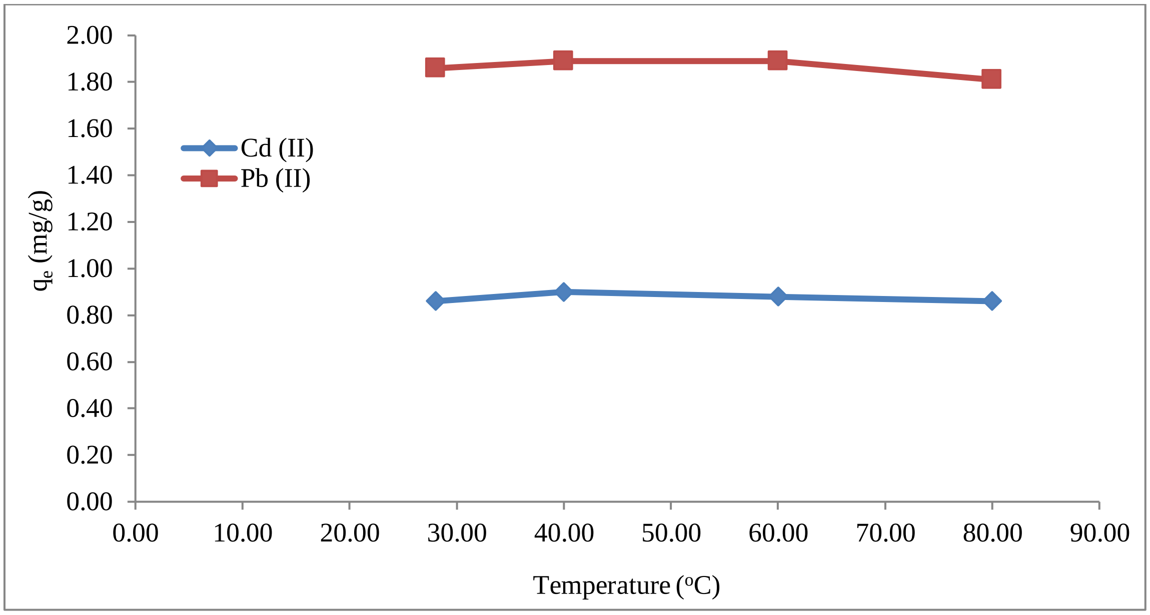

Fig. 7: Effect of Cd (II) and Pb (II) ions adsorption with respect to temperature

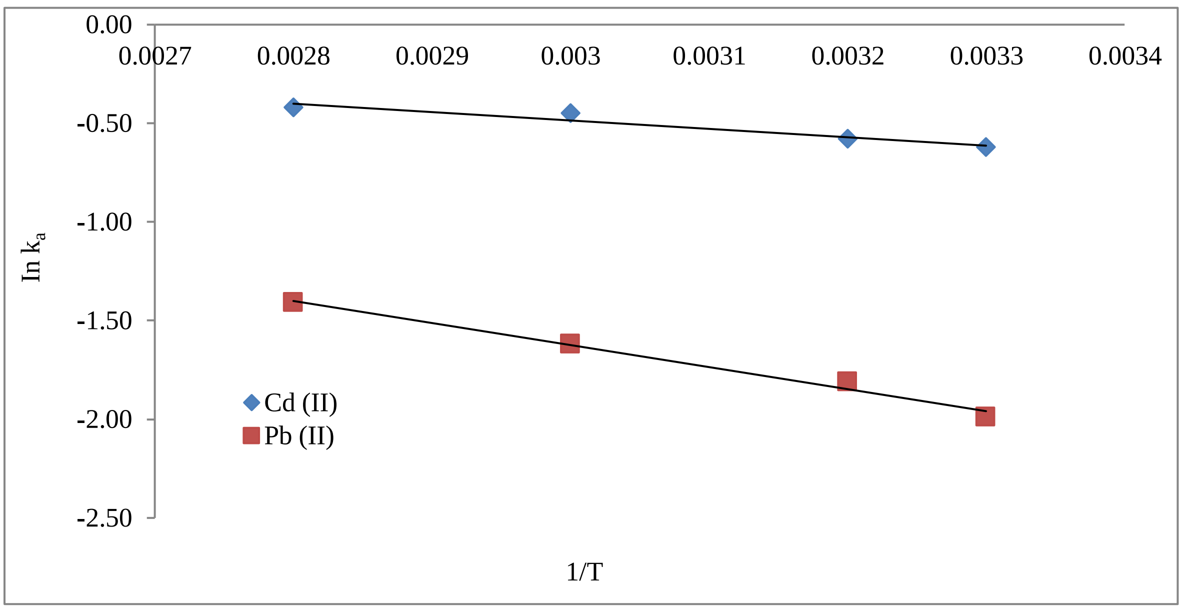

Fig. 8: Plots of In K_a against 1/T for Cd (II) and Pb (II) ions

The mixture was filtered and the supernatant taken for AAS analysis.

Desorption dynamics

A 0.25 g sample of 105 um SPP biomass impregnated with Cd (II) and Pb (II) ions each was weighed and transferred into separate experimental bottles. A solution of 20 ml of 0.1 M HCl, 0.5 M HCl, 0.1 M NaOH and 0.5 M NaOH were added into the separate bottles and shaken mechanically at 180 rpm for 1 hr. The mixture was filtered and the supernatant taken for AAS analysis.

RESULTS AND DISCUSSION

Characterization of Adsorbent

The FTIR analysis was used to determine the functional groups on the surface of the sweet potato peels (SPP) biomass responsible for adsorption and is shown as shown in Figure 1. The spectra indicates broad band at 3446 cm^{-1} representing –OH functional groups, while the presence of –NH, -C=N, -C=C, -C-O-C are indicated by bands at 3367 cm^{-1}, 1647 cm^{-1}, 1637cm^{-1}, 1105 cm^{-1} respectively. The

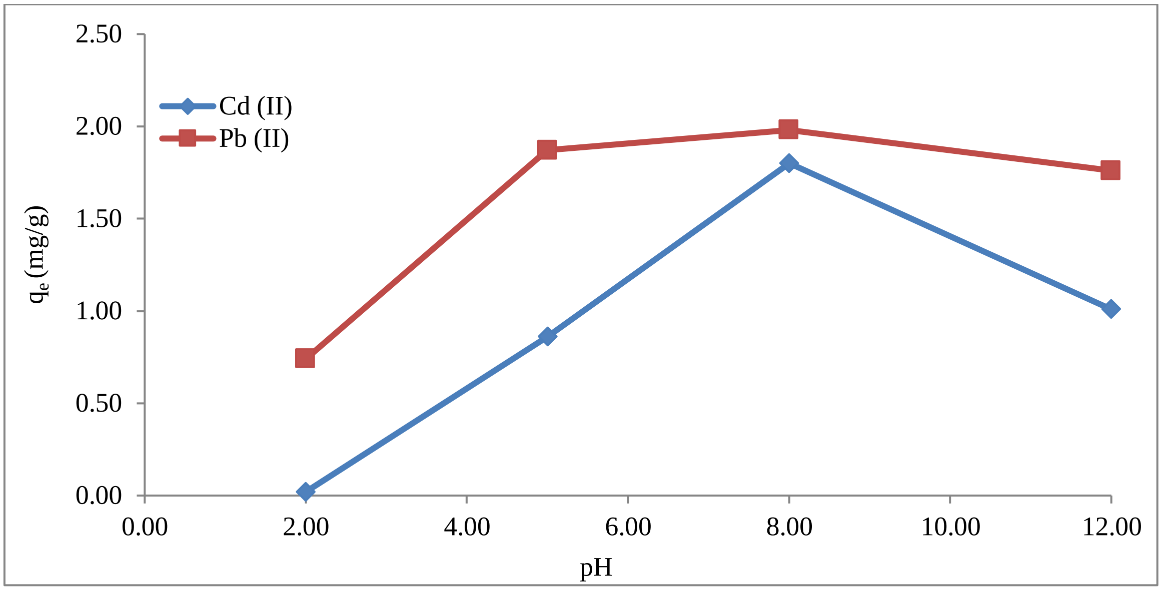

Fig. 9: Effect of metal uptake with respect to pH for Cd (II) and Pb (II) ions

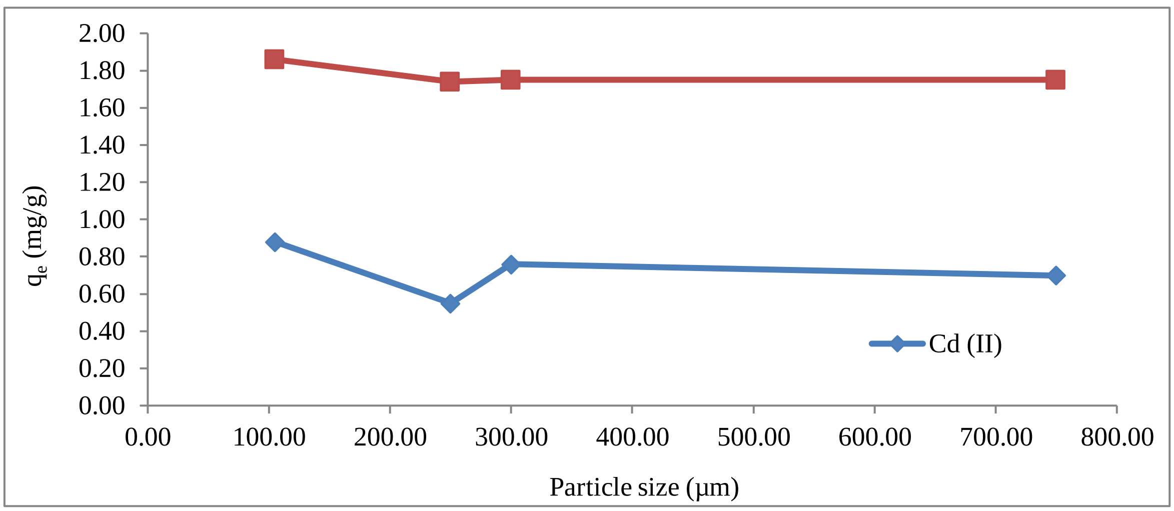

Fig. 10: Effect of particle size on the adsorption of Cd (II) and Pb (II) ions

presence of the –NH, -C=C, C-O-C groups have been studied extensively and are observed to be potential adsorption sites for the metal ions (Giwa et al., 2013).

Concentration dynamics

The effect of concentration in the removal of Cd (II) and Pb (II) ions from aqueous system using potato peels biomass as presented in Figure 2 showed that the uptake was maximum at 60 mg/L. This is an indication that the biomass can remove from systems containing high concentrations of heavy metal ions. The result also revealed that when the active sides on the biomass were saturated, the rate of adsorption began to decrease i.e. indicating a concentration gradient build-up.

However, the equilibrium data obtained was analyzed using Langmuir and Freundlich adsorption isotherm model equations and the plots are presented in Figures 3 and 4. The equations are expressed as follows:

For Langmuir;

$$\frac{C_e}{q_e} = \frac{1}{K_L q_e} + \frac{C_e}{q_e} \quad (2)$$

For Freundlich;

$$\text{In } q_e = \text{In } K_F + \frac{1}{n} \text{In } C_e \quad (3)$$

Where, q_e represents metal uptake capacity in mg/g; C_e represents equilibrium concentration in mg/L; K_L and K_F

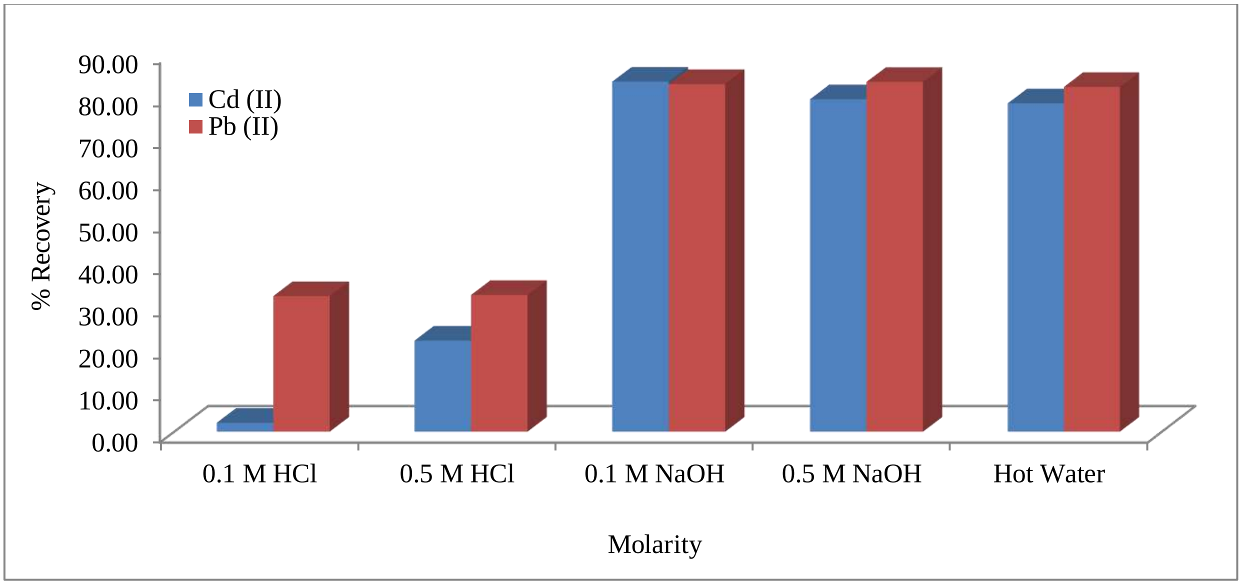

Fig. 11: Desorption studies on Cd (II) and Pb (II) ions using HCl and NaOH solutions

are the constants related to its intensity and n is a measure of feasibility of the adsorbents.

The results obtained from the modeling showed that the removal of Cd (II) and Pb (II) ions using potato peels biomass followed Freundlich adsorption equation with correlation coefficients (R^2) of 0.909 for Cd (II) ion and 0.988 for Pb (II) ion respectively. The implication of this correlation revealed that the Pb (II) ion is better removed than the Cd (II) ion. Generally, the result showed that the interaction between the metal ions and the surface of the potato peels biomass was indicative of a chemical type of adsorption. The parameters for these models are presented in Table 1.

Time dynamics

The effect of time on the adsorption of Cd (II) and Pb (II) ions onto potato peels biomass as presented in Figure 5 showed the amount of time required for maximum to occur. The maximum metal ions uptake was achieved at contact time of 20 mins. This short contact time demonstrates that the process was achieved by chemical adsorption. Equally, the rapid uptake within 20 mins suggests that the binding sites of the potato biomass were controlled by diffusion mechanism.

However, the equilibrium data generated was subjected to pseudo second-order model equation as expressed in equation 4 and the plot presented in Figure 6. The result showed that the process followed pseudo second-order model equation with correlation coefficient (R^2) of 0.988 for Pb (II) ion and 0.995 for Cd (II) ion respectively. This result is similar to the removal of Ni (II) and Pb (II) ions onto grapefruit (Citrus paradisi) Mesocarp Biomass (Obi and Olivia, 2015). This result further revealed the efficiency of potato peels biomass in the removal of Cd (II) and Pb (II) ions from aqueous system. The parameters for the kinetic model equation are presented in Table 2.

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

Temperature dynamics

The effect of temperature on the adsorption process presented in Figure 7 revealed that the metal ions uptake unto potato peels biomass was two-stepped. An initial increase in the metal uptake as the temperature increased followed by a decrease in the metal uptake.

The optimum temperature for the adsorption of Cd (II) and Pb (II) ions onto potato peels biomass was 60°C. The thermodynamic parameters such as entropy, enthalpy and Gibbs free energy were determined following equations 5 and 6 as presented in Figure 8.

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (5)$$

$$\text{In } K_a = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (6)$$

The result obtained in Table 3 showed the adsorption of Cd (II) and Pb (II) ions onto potato peels biomass was endothermic with small degree of disorderliness and spontaneity. This is indicative that the adsorption process was by weak chemical interaction.

pH dynamics

The effect of pH on the metal ion uptake as presented in Figure 9 revealed that at low hydrogen ion concentration, there was no competition between the H^+ and the metal ions and hence the adsorption increased.

However, at high hydrogen ion concentration, there was a serious competition between H^+ and the metal ions whereby the rate of adsorption was decreased. Therefore, the pH of 8.00 was found to be optimum for the adsorption of Cd (II) and Pb (II) ions onto potato peels biomass.

Particle size dynamics

The effect of particle size as presented in Figure 10 showed that the metal ions uptake decreased as the particle size increases.

Desorption studies

The desorption studies as presented in Figure 11 revealed that 83.03 % of Cd (II) and 82.48 % Pb (II) ions was recovered in 0.1 M NaOH and 78.86 % of Cd (II) and 82.97 % Pb (II) ions was recovered in 0.5 M NaOH solutions.

The result also recorded poor recoveries of less than 25 % in 0.1 M HCl and less than 35 % in 0.5 M HCl solutions respectively. However, desorption process using hot water recorded good recoveries of 77.89 – 81.78 %. The result finally revealed that desorption studies can be done without any threat to environment using either sodium hydroxide or hot water.

CONCLUSIONS

Sweet potato peels has been found useful as a low-cost adsorbent for the removal of Cd(II) and Pb (II) ions from aqueous medium. Optimum removal was obtained at pH 8 and contact time of 20 mins. The adsorption process followed Freundlich adsorption and pseudo second-order kinetic models. The equilibrium adsorption capacity showed that Pb (II) ion was more adsorbed on the surface of the potato peels biomass than Cd (II) ion (200.91 mg/g > 125.00 mg/g). The thermodynamic studies indicated endothermic, diffusion mechanism and spontaneous adsorption process.

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