economically viable and environmentally sound adsorbent for removal of heavy metals from contaminated waters [19].

The present study aims at assessing: (1) to evaluate the potential use of unripe banana (*Musa sapientum*) peel biomass as an adsorbent for the sorption of Cd (II) and Cr(VI) ions from aqueous solutions; (2) to evaluate the interactive effect of contact time, metal ion concentration, pH, adsorbent mass dose and also the efficiency of unripe banana (*Musa sapientum*) peel biomass in removing Cd(II) and Cr(VI) ions from aqueous solutions.

2. MATERIALS AND METHODS

2.1 Adsorbent: Preparation and Collection

Banana *(musa sapientum) peel* biomass (Fig. 1) was collected from local market in Elebele community, Ogbia Local Government Area, Bayelsa State, Nigeria. Then washed and dried for fifteen days and crushed using a blender. The powdered material was sieved using a 106μm mesh Tyler sieve, to obtain a fine biomass. 500 g, of the sieved adsorbent was soaked in 250 ml 0.3 M HNO3 solution for 24 h, and later washed thoroughly with distilled water until a pH of 7.0 was attained. The rinsed adsorbent was then air dried for 12 h, ground and sieved for use [20].

Figure 1: Banana (*musa sapientum*) peel biomass

2.2 Reagents and Chemicals

All the reagents used were of analytical grade and distilled water was used in sample preparation. A 1.79 g of cadmium chloride $CdCl_2$ and 5.65 g of potassium dichromate, $K_2Cr_2O_7$ stock solution of 1000 mg/L concentration was prepared, and the working solution were made by diluting the stock solution using double distilled water. The range in concentration of cadmium (II) and chromium (vi) ions prepared from stock solution varied between 50 to 300 mg/L. The desired pH was adjusted to and maintained using concentrated 1M NaOH and 1M HCl.

2.3 Determination of Contact Time

1.5 g of the adsorbent was weighed and introduced into four 250mL conical flasks. 50mL of 100mg/L concentration of Cd2+ and Cr6+ solutions prepared in distilled water from the stock solution was added to the biomass. The pH of these suspensions was adjusted to 7.0. The flasks were labeled for time interval of 30, 60, 90 and 120 minutes. The flasks were tightly covered with cellophane and shaken for the appropriate time intervals on an electric shaker at 250 rpm. The suspension was filtered through Whatman No 1 filter paper and centrifuged for 5minutes. The supernatants obtained were analyzed for residual cadmium and chromium.

2.4 Effect of Adsorbent Dosage

100 mg/L of metal ion solutions of Cd2+ and Cr6+ was added to each of the conical flasks at pH of 7. A known amount the absorbent 1.5 g, 2.0 g, 2.5 g, 3.0 g, and was added into each flask and agitated intermittently for the period of 80 minutes. The mixture was shaken thoroughly at 250 rpm with an electric shaker. The suspensions were filtered through Whatman No 1 filter paper, centrifuged for 5 minutes and analyzed for initial and final concentrations of cadmium and chromium ions. The procedures used are similar to those earlier reported [21].

2.5 Determination of Optimum pH For Adsorption

The effect of pH on the amount of Cd2+and Cr6+ metal ions was analyzed over the pH range from 2, 4, 6 and 8. 100 mL metal ions concentration of 100 mg/L was measured into four 250 ml conical flasks and 1.5 g of the biomass was added and the pH of the solutions in the flask was adjusted with 1 M HCl and 1 M NaOH solutions. The mixture was shaken thoroughly at 250 rpm with an electric shaker for 80 minutes. The suspension was filtered using Whatman No. 1 filter paper to remove suspended adsorbent. Initial and final concentrations were analyzed for residual cadmium and chromium.

2.6 Effect of Initial Metal Ions Concentration

Batch adsorption experiments were performed by contacting 1.5g of the adsorbent with 100 mL of aqueous solutions of different initial concentrations (50 mg/L, 100 mg/L, 200 mg/L, and 300 mg/L) at pH 7 for cadmium and chromium followed agitation at 250 rpm with an electric shaker for 80 minutes. The suspension was filtered through Whatman No. 1 filter paper to remove any suspended adsorbent. Initial and final concentrations of cadmium and chromium ions were determined by AAS, while the amount adsorbed was calculated by difference. The percentage and capacity adsorption of adsorbent powder were estimated by the following equations:

$$\% R = \frac{Co-Ce}{Co} X\ 100 \quad (1)$$

$$Qe = \frac{V(Co-Ce)}{m} \quad (2)$$

Where,
V = Volume of solution (L)
M = mass of adsorbent (mg)
Co = Initial Concentration
Ce = Final Concentration at equilibrium (mg/L)
Qe = Adsorption capacity at equilibrium (mg/g)

3. RESULTS AND DISCUSSION

3.1 The Effect of pH

Table 1-2 summaries the results of pH study of the adsorption of Cd (II) and Cr (VI) on unripe banana (musa sapientum) peel biomass, while percentage removal of the metal ions are graphically represented in Fig. 2. The result of the pH study revealed that maximum adsorption occurred at pH 8 for Cd(II) and pH 2 for Cr(VI). For the different pH range 96.6% of Cd (II) and 43.1% of Cr (VI) was removed. The percentage of Cd (II) adsorbed was higher than the percentage for Cr (VI), this indicates that banana (musa sapientum) peel biomass is more favourable for the removal of Cd (II) than Cr (VI) in solution. The pH affects the surface charge of the adsorbent, degree of ionization and specification of adsorbate [22-24].

Table 1: Effect of pH on the removal of cadmium from aqueous solution

pH	Co (mg/L)	Ce (x) (mg/L)	Co-Ce (x) (mg/L)	Qe (Cd (mg/g)	% Cd
2	50	3.923	46.077	1.5359	92.2
4	50	4.677	45.323	1.5107	90.7
6	50	3.143	46.857	1.5619	93.7
8	50	1.718	48.282	1.6094	96.6

Table 2: Effect of pH on the removal of chromium from aqueous solution

pH	Co (mg/L)	Ce (x) (mg/L)	Co-Ce(x(mg/L)	Qe (Cr) (mg/g)	% Cr
2	50	28.722	21.278	0.7092	42.5
4	50	28.444	21.556	0.7185	43.1
6	50	34.306	15.694	0.5231	31.3
8	50	35.860	14.14	0.4713	28.2

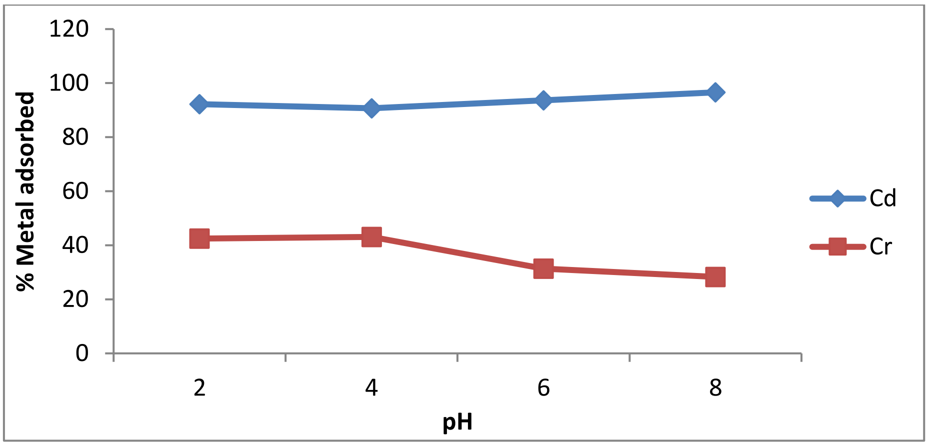

Figure 2: Effect of pH on the removal of metal ions from aqueous solution

3.2 Effect of Contact Time

The results of the effect of contact time on unripe banana (musa sapientum) peel biomass are presented in Table 3-4. The percentages of removal of the Cd (II) and Cr(VI) are represented graphically in Figs. 3. The adsorptive capacity of Cd (II) and Cr (VI) metal ions was observed to increase from 69.7%-70.5% and 4.7%-12.5%, when the contact time was increased from 30 to 120 minutes. Particle size and temperature affect sorption rate [25]. At a time interval of 30 minutes and an initial metal ion concentration of 50mg/L adsorption of the amount of Cd (II) and Cr(VI) ions removed by the biomass increased until a contact time of 60 minutes.

Table 3: Effect of contact time (minutes) on the removal cadmium

Time	Co (mg/L)	Ce (x) (mg/L)	Co-Ce (x) (mg/L)	Qe (Cd) (mg/g)	% Cd
30	50	14.884	35.116	1.1705	70.2
60	50	14.748	35.252	1.1750	70.5
90	50	15.123	34.877	1.1625	69.7
120	50	14.901	35.099	1.1699	70.2

Table 4: Effect of contact time (minutes) on the removal of chromium

Time	Co (mg/L)	Ce (x) (mg/L)	Co-Ce (x) (mg/L)	Qe (Cr) (mg/g)	% Cr
30	50	46.598	3.402	0.1134	6.8
60	50	45.733	4.267	0.1422	8.5
90	50	43.774	6.228	0.2076	12.5
120	50	47.653	2.347	0.0782	4.7

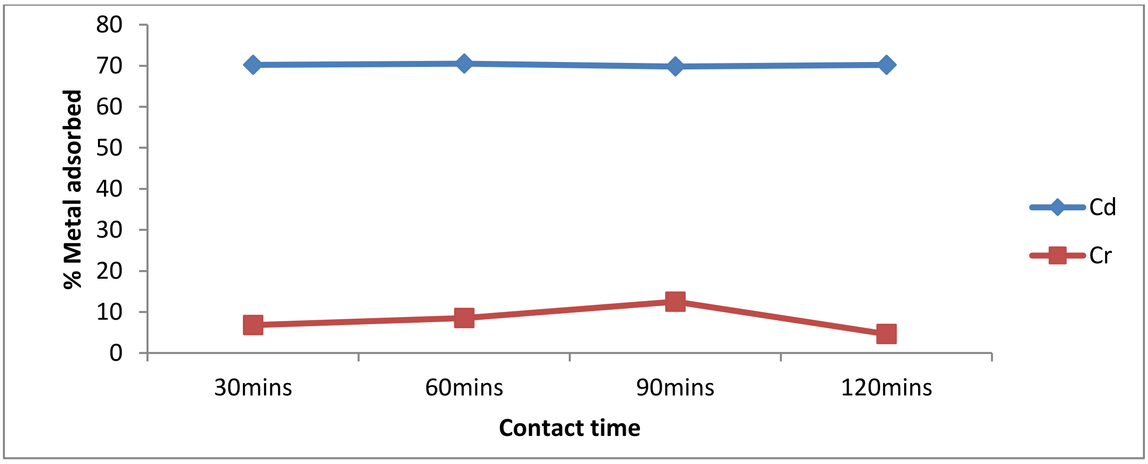

Figure 3: Effect of contact time on the removal of Cd(II) and Cr(VI) from aqueous solution

3.3 Effect on Absorbent Dose

The results of the effect of adsorbent dosage, banana (*musa sapientum*) peel biomass are presented in Table 5-6. The percentages of removal of Cd(II) and Cr(VI) ions are represented graphically in Figs. 4. In this study, five different adsorbent dosages were studied by varying the amount of adsorbent 1.5 to 3.0g. The plot(Fig. 5) showed increase in the adsorption percentage as dosage of the absorbent increases, for Cd (II), while Cr (VI) there was a certain decrease as adsorbent dose increases.

Table 5: Effect of adsorbent dose on the removal of Cd from aqueous solution

Adsorbent Dose (g)	Co (mg/L)	Ce(x) (mg/L)	Co-Ce(x) (mg/L)	Qe (Cd) (mg/g)	%Cd
1.5	50	16.573	33.427	1.1142	66.9
2.0	50	15.525	34.475	0.8618	68.9
2.5	50	15.456	34.544	0.6908	69.1
3.0	50	13.867	36.133	0.6022	72.3

Table 6: Effect of adsorbent dose on the removal of Cr from aqueous solution

Adsorbent Dose (g)	Co (mg/L)	Ce(x) (mg/L)	Co-Ce(x) (mg/L)	Qe (Cr) (mg/g)	%Cr
1.5	50	47.715	2.285	0.07616	4.5
2.0	50	45.652	4.348	0.10870	8.6
2.5	50	45.557	4.443	0.08886	8.8
3.0	50	45.405	4.595	0.07658	9.1

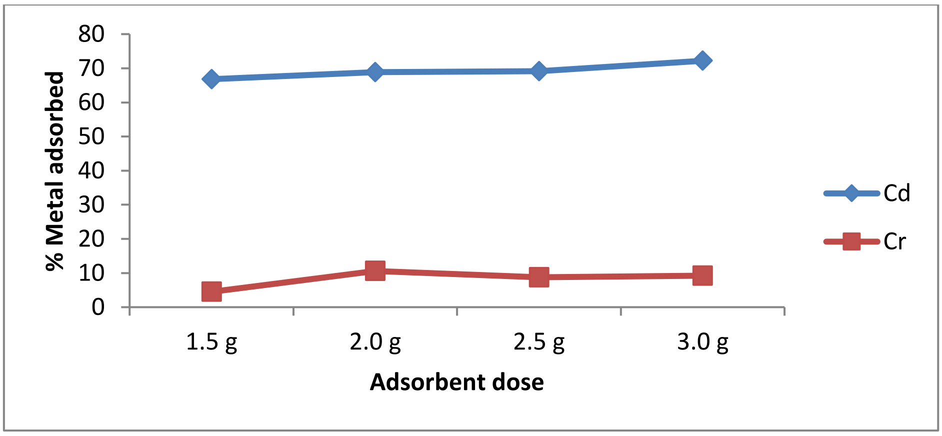

Figure 4: Effect of Adsorbent dose on the removal of Cd and Cr from aqueous solution

3.4 Effect of Concentration

The results of the effect of initial concentration on banana (musa sapientum) peel biomass are presented in Table 7-8. The of removal of Cd (II) and Cr(VI) ions are represented graphically in Figs. 5. The amount of Cd and Cr adsorbed increased at a steady rate with increasing initial metal ion concentrations from 50mg/L to 300 mg/L. The percentage removal is 97.6% for Cd (II) and 85.8% for Cr (VI) respectively. The equilibrium adsorption capacity (*Qe*), increased with increasing initial adsorbate concentrations. As the initial concentration of adsorbate increases from 50 mg/L to 300 mg/L, the equilibrium adsorption capacity of the adsorbate onto musa sapientium increased from 1.63 mg/g to 9.76 mg/g. This indicates that the initial concentration strongly affects adsorption capacity. This result is in agreement with those reported by a researcher [26].

Table 7: Effect of concentration on the removal of cadmium from aqueous solution

Co (mg/L)	Ce(x) (mg/L)	Co-Ce(x) (mg/L)	Qe (Cd) (mg/g)	% Cd
50	1.243	48.757	1.6252	97.5
100	1.668	98.332	3.2771	98.3
200	4.657	195.343	6.5114	97.6
300	7.139	292.861	9.7622	97.6

Table 8: Effect of concentration on the removal of chromium from aqueous solution

Co (mg/L)	Ce(x) (mg/L)	Co-Ce(x) (mg/L)	Qe (Cr) (mg/g)	% Cr
50	25.788	24.212	0.8071	48.4
100	35.161	64.839	2.1613	64.8
200	41.843	158.157	5.2719	79.0
300	42.360	257.64	8.5880	85.8

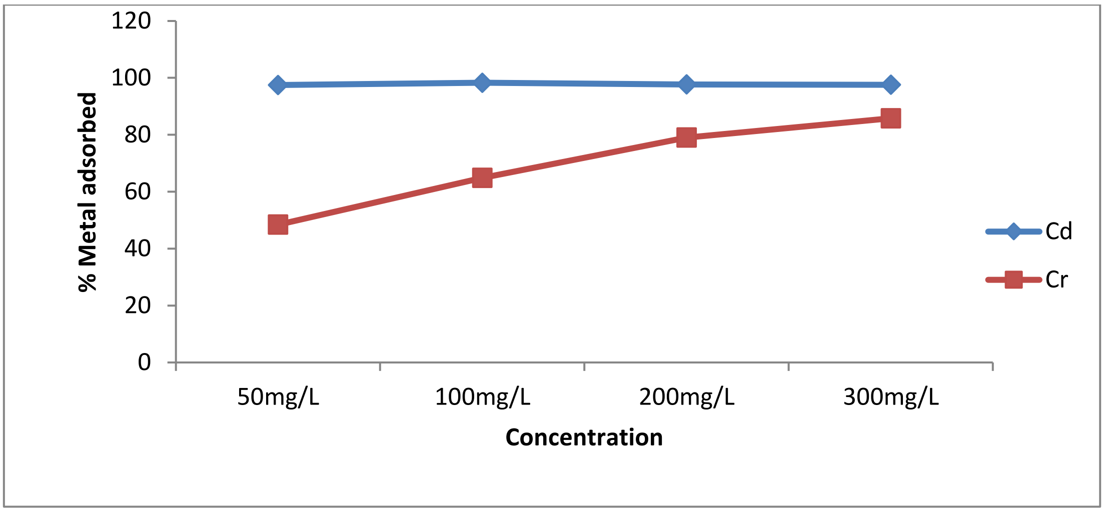

Figure 5: Effect of Concentration on the removal of Cd and Cr aqueous solution

3.5 Adsorption Isotherm

Some commonly used Isotherms are Langmuir, Freundlich, Temkin and Redlich-Peterson etc. However, for the purpose of the study, emphasis is restricted to the use of Langmuir and Freundlich models to describe the adsorption process of Cd (II) and Cr (VI) ions onto unripe banana (musa sapientum) peel biomass.

Langmuir Isotherm: The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor "R_L" which is used to predict the adsorption system is favourable or unfavourable and is given as [27].

$$RL = \frac{1}{1 + Kl * Co} \qquad 1$$

Where, C0 is the initial metal ion concentration in (mg/L,), $K_L$is the Langmuir equilibrium constant. The value of RL indicated the type of Langmuir isotherm to be irreversible

(RL =0), favourable (0<RL<1), linear (RL =1) or unfavourable (RL>1). The value of R_L was found less than one in all the cases for Cr(VI) Table 5. This confirms that the Langmuir isotherm model is favourable for adsorption for Cr (VI) onto banana (musa sapientum) peel biomass.

Freundlich Isotherm: This model proposes heterogeneous distribution of active sites, accompanied by interaction between adsorbed molecules. The linear form of isotherm can be represented as [28].

$$logQe = logKf + \frac{1}{n}\, x\, logCe \qquad 2$$

Where, K_F is a constant related to the adsorption capacity and n is related to the adsorption intensity of the adsorbent.

K_F and $\frac{1}{n}$ can be determined from the linear plot of log Qe versus log Ce. The evaluated constants are given in Table 5.

The results of the study (chromium and cadmium), reveals that the removal of Cr (VI) best fits with the Langmuir model (Fig. 6-7) with a higher coefficient of determination, i.e., R^2 =0.999. All the four types of Langmuir were plotted but Langmuir type (2) which is a plot of 1/qe vs1/Ce, seems to have a better regression coefficient than the others. While for Cd (II), it was shown that the plot best fits with the Freundlich model, which is a plot of log Qe versus log Ce(Fig.8-9), having a higher coefficient of determination, i.e., R^2 =0.949 with an (n) value which is the sorption affinity, n =1.1, thus n>1 and this shows favorable physical process. This is attributed to the active sites present more in cadmium. The evaluated constants are given in Table 9.

Table 9: Adsorption isotherm constants for adsorption of Cd (II) and Cr (VI) on unripe banana (musa sapientun) peel biomass

Metal	Cd	Cr
	Langmuir parameters	
Qmax (mg/g)	1.44	47.67
KL (L/mg	63.18	1.62
R^2	0.905	0.999
	Freundlich parameters	
K_f	1.23	1.87
$^1/_n$	0.927	4.371
n	1.1	0.2
R^2	0.949	0.941
	Pseud-second order parameters	
K_2	5.923	0.556
Qe	1.166	0.0785
H	8.064	0.00343
R^2	0.999	0.709

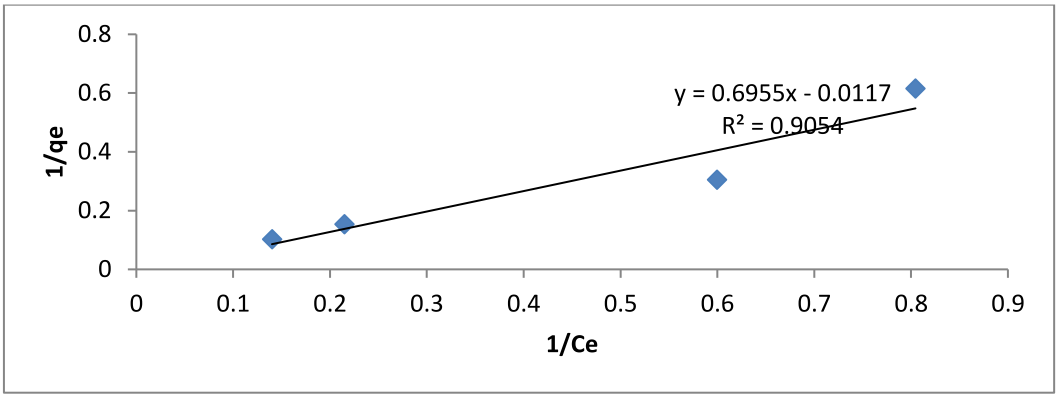

Figure 6: Langmuir isotherm for cadmium removal by unripe banana peel biomass

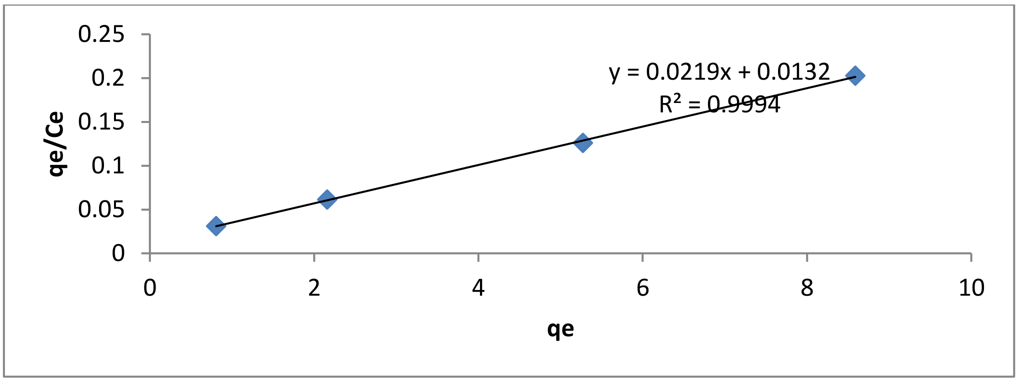

Figure 7: Langmuir isotherm for Chromium removal by unripe banana peel biomass

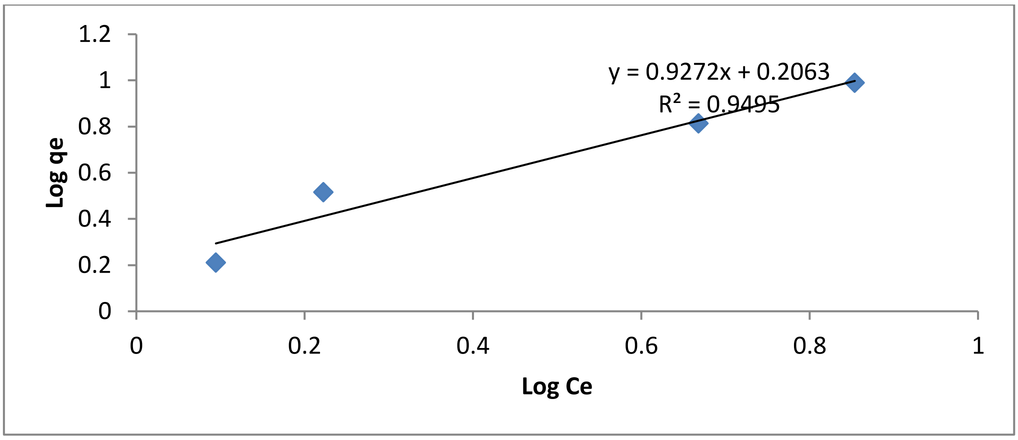

Figure 8: Freundlich isotherm for Cadmium removal by unripe banana peel biomass

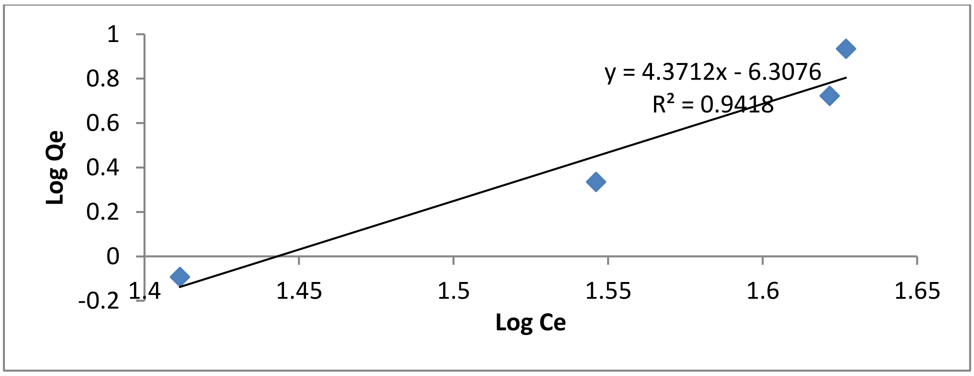

Figure 9: Freundlich isotherm for Chromium removal by banana peel biomass

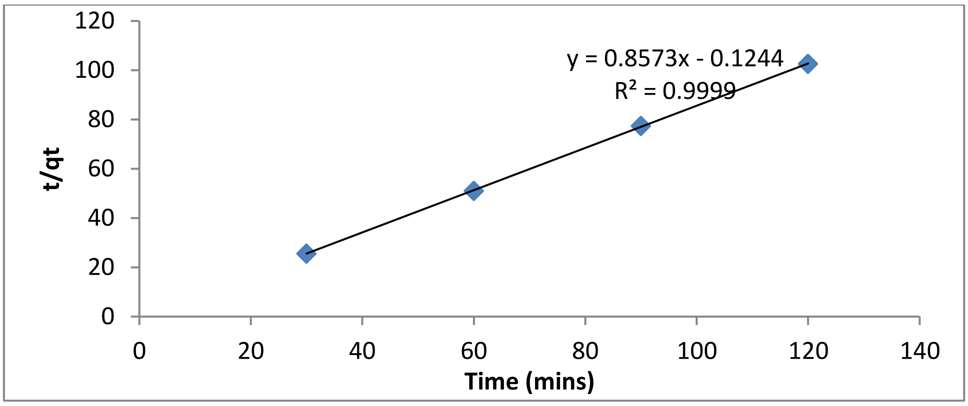

Figure 10: Pseudo second order for cadmium removal by banana peel biomass

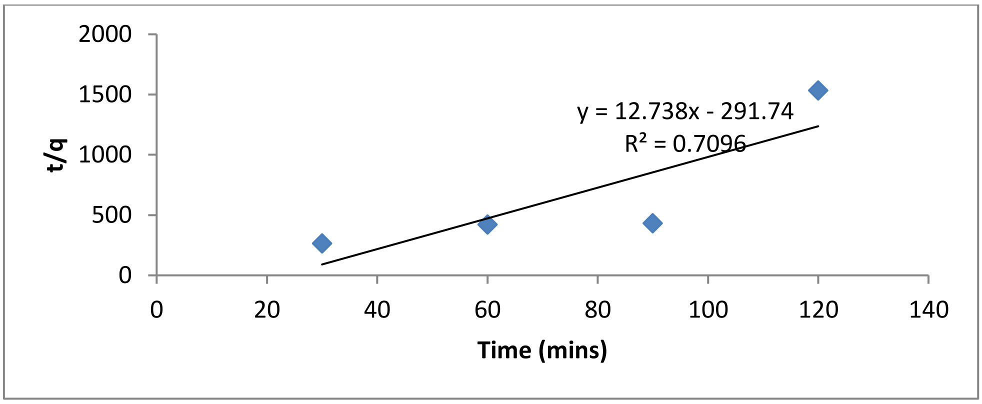

Figure 11: Pseudo second order for chromium removal by banana peel biomass

The kinetic study was performed based on pseudo-first order and pseudo-second order. The data indicated that the adsorption kinetics followed the pseudo-second order. The plots of the kinetics models applied to the data are represented in Fig. 10-11. Adsorption data fitted well to almost all models applied, as correlation coefficients were all greater than 0.70. For the kinetics plots, the pseudo-second order were the best correlated at 0.9999 for Cd (II) and 0.7096 for Cr(VI). This implies that the dominant rate limiting mechanism for sorption was the pseudo-second order.

4. CONCLUSION

The results of this study showed that unripe banana peel powder can be used as an effective adsorbent for the removal of cadmium and chromium ions from aqueous solution. The experimental data were fitted to three different kinetic models, which were Langmuir, Freundlich and Pseudo Second order. Langmuir model fitted well for the Cr (VI) ion with an R^2 = 0.999, having all the R_L values were less than one, with an adsorption capacity of 47.61mg/g. While for Cd (II) ion, fitted well for Freundlich model with R^2 =0.949, with an n value of 1.1, thus showed favorable adsorption. Pseudo Second order for Cd (II) and Cr (VI) ions were plotted, t/qt versus time (mins), had R^2 = 0.999 for Cd (II) and R^2 = 0.705 for Cr (VI). The parameter of qe was determined, 1.166 (mg/g) for Cd (II) and 0.0785 (mg/g) for Cr (VI) respectively. This study has shown that instead of other expensive materials; unripe banana peel biomass can be used as an effective adsorbent for heavy metal removal from aqueous solution.

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