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REVIEW ARTICLE

ADSORPTION STUDIES OF PB2+ AND MN2+ IONS ON LOW-COST ADSORBENT: UNRIPE PLANTAIN (MUSA PARADISIACA) PEEL BIOMASS

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ABSTRACT

The capacity of unripe plantain (Musa paradisiaca) peel biomass to remove heavy metals, Pb(II) and Mn(II) from aqueous solution of lead trioxonitrate (v), Pb $(NO_3)2$ and potassium permanganate, $(KMnO_4)$ was investigated. Adsorption isotherms were determined by varying operating parameters such as effect of pH, initial concentration, adsorbent dose and contact time. Unripe plantain(Musa paradisiaca) peel was found to remove Pb and Mn ions in solution. Removal rate of Pb(II) and Mn(II) was found to increase steadily from pH 2 , however, Pb(II and Mn (II) removal decreases at pH 8. Langmuir and Freundlich models were applied to adsorption equilibrium data to find the best fitted amongst these models. Langmuir model type 1, with R^2 = 0.9823 best fitted for Pb (II) adsorption data. The separation parameter, R_L values were less than 1.0 i.e., 0.000903, 0.000451, 0.000225 and 0.000150 with corresponding initial concentrations of (50, 100, 200 and 300) mg/L respectively. This indicates that adsorption of Pb (II) ion on unripe plantain(Musa paradisiaca) peel biomass was favourable to Langmuir isotherm, while Freundlich model with R^2 = 0.9585 best fitted Mn (II) ion with (n) value of 1.03, which was favourable adsorption. Thus, the results of these findings showed that unripe plantain (Musa paradisiaca) peel biomass could be effectively and efficiently utilized for the removal of Pb (II) and Mn (II) ions from aqueous solution.

KEYWORDS

Unripe plantain, Musa paradisiaca, adsorption, Langmuir and Freundlich models.

1. INTRODUCTION

Currently, known modern techniques in existence and operational for the removal of environmental pollutants such as heavy metals, dyes etc., are relatively expensive and non-environment friendly, thus the need for an alternative and the remedy is low cost adsorbent like unripe plantain(*Musa paradisiaca*) peel biomass.

Adsorption as physico-chemical process has been a major industrial separation technique for the removal of heavy metal ions from aqueous solution for many years [1]. Chemical precipitation, electrochemical deposition, evaporation, cementation, membrane process, ion exchange and activated carbon adsorption are some usual or well-established techniques commonly used for removal of metal ions from water and waste-water [2,3].

The need of today is removal of heavy metals which has rank as major environmental pollutants [1]. The consistent desire that the levels of heavy metals be considerably reduced in industrial and municipal effluents to meet regulatory standards before final repository into the ecosystem was spurred due to their toxicity, persistence and bioaccumulative tendency in the environment.

The ability of low-cost materials (agricultural by-product or agrowastes) to remove various types of pollutants from water and wastewater is no more in doubt and a number are currently receiving attention [4].

There are varieties of low-cost materials that have been reported in literature for adsorption studies of heavy metals. These include: mango tree (*mangifera indica*) saw dust, teff straw (*eragrostis tef)* agricultural waste, Maize tassel based activated carbon bamboo-based activated charcoal and bamboo dust , formaldehyde and pyridine modified bean husks (Plantain (*Musa paradisiaca*) Wastesand *borassus aethiopium* and *cocos nucifera* [5-11]**.** In this study, unripe plantain **(***Musa paradisiaca*) peel biomass was recommended due to the fact that it's inexpensive and effective for the removal of environmental pollutants.

2. MATERIALS AND METHODS

2.1 Adsorbate Preparation and Experimental

Stock solutions of 1000mg/L of lead and managanese were prepared from potassium permanganate, (KMnO4), lead trioxonitrate (v), Pb (NO3)2 respectively in deionised water. The desired pH was adjusted to and maintained using concentrated 1M NaOH and 1M HCl. All reagents used in the experiment were of analytical grade.

A working concentration of 50mg/L was prepared from the stock and used for a series of batch adsorption for both metal ions with respect to effect of pH, contact time, effect of initial metal ions concentration and effect of adsorbent dosage. The procedure for effect of pH, contact time, effect of initial metal ions concentration and effect of adsorbent dosage determination was similar to that reported previously [3,5,12].

The mixtures were filtered to obtain the filtrates which were stored in plastic bottles and further analyzed for metal ion concentration in atomic absorption spectrophotometer.

Langmuir, Freundlich, Temkin etc are Isotherms commonly used, however, for the purpose of this study, Langmuir and Freundlich models were used to describe the heavy metal absorption process. The percentage and capacity adsorption of adsorbent powder were estimated by the following equations:

The percentage removal (%) can be calculated as follows:

$$\% R = \frac{Co-Ce}{Co} X\ 100 \quad \text{.......................................} \quad (3)$$

The amount of adsorption at equilibrium, qe (mg/g), was calculated by

$$Qe = \frac{V(Co-Ce)}{m} \quad \text{..} \quad (4)$$

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)

2.2 Instrumentation and Statistical Analysis of Data

In this study, raw data was used in calculating the various adsorption parameters of Langmuir and Freundlich models using Microsoft Excel 2010. The heavy metal concentrations in each batch adsorption were determined by using an ANALYST 400 Perkin-Elmer AAS.

3. RESULTS AND DISCUSSION

Table 1-2 summaries the results of the batch adsorption of Pb (II) and Mn (II) ions on unripe plantain (*Musa paradisiaca*) peel biomass, with respect to effect of pH, contact time, effect of initial metal ions concentration and effect of adsorbent dosage., while percentage removal of both metal ions in the batch adsorption with respect to effect of pH, contact time, adsorbent dosage and initial metal ions concentration are graphically represented in Figure 1-4.

In this study, a pH range of 2–8 was recommended; it was observed that Pb (II) and Mn (II) ions were effectively adsorbed and maximum adsorption of Pb (II) and Mn (II) ions using unripe plantain(*Musa paradisiaca*) peel biomass occurred at pH 6. The pH affects the surface charge of the adsorbent, degree of ionization and specification of adsorbate [13-15]. The percentage of Pb (II) adsorbed was higher than the percentage for Mn (II), this indicates that unripe plantain (*Musa paradisiaca*) peel biomass is more favourable for the removal of Pb (II) than Mn (II) in solution. This results are in agreement with those reported by the researchers [10].

The recommended contact time for this study ranged from 30-120 minutes, at a time interval of 30 minutes and an initial metal ion concentration of 50mg/L adsorption of Pb(II) and Mn(II) ions by the biomass was observed. The results showed that the rate of uptake of the metal ions was quite rapid in the first 30 min, using unripe plantain (*Musa paradisiaca*) peel biomass, 58% for lead and 32.2 % for manganese. The adsorptive capacity of Pb(II) and Mn(II) metal ions was observed to increase from 49.20%-58.00% and 32.20%-36.0%, when the contact time was increased from 30 to 120 minutes. Particle size and temperature affect sorption rate [16]. These results are in agreement with those reported by the researchesr [10].

In this study, four different adsorbent dosages were recommended, 1.5g, 2.0g, 2.5g and 3.0g respectively. The results showed that the percentage of metal ion removal increased with increase in adsorbent dose from 1.5 to 3.0 g for both lead and manganese ions. The adsorption percentage of Pb (II) was: 53.1%, 42.91%, 39.9% and 46.7%, while that of Mn (II) were: 32.9 %, 36.0 %, 32.3 % and 32.0 % respectively.

The amount of Pb and Mn adsorbed increased at a steady rate with increasing initial metal ion concentrations, ranged from 50mg/L to 300 mg/L. The percentage removals are 95.58% to 99.26 for Pb (II) and 90.28% to 94.05 for Mn (II) respectively. These results are in concomitant with those reported by the researchers for heavy metals removal by low-cost adsorbents [10].

Table 1: Results of lead removal operating parameters of adsorption isotherm

Effect of pH					
pH	Co(mg/L	Ce. (X) (mg/L	Co-Ce (X) (mg/L)	Qe (mg/g)	% Pb
2	50	16.179	33.821	1.1274	67.6
4	50	12.580	37.42	1.2473	74.8
6	50	5.925	44.075	1.4692	88.1
8	50	7.251	42.749	1.4250	85.4
Effect of contact time					
time(min)	Co(mg/L)	Ce X(mg/L)	Co-Ce (X) (mg/L)	Co-Ce (X (mg/L)	%
30	50	20.997	29.003	29.003	58.0
60	50	21.643	28.357	28.357	56.7
90	50	25.358	24.642	24.642	49.2
120	50	24.147	25.053	25.053	51.7
Effect of adsorbent dose					
doses(g)	Co(mg/L	Ce (X) .mg/L	Co-Ce (X) (mg/L)	Qe (mg/g)	%
1.5	50	23.420	26.580	0.886	53.1
2.0	50	28.507	21.493	0.7164	42.9
2.5	50	30.042	19.958	0.6653	39.9
3.0	50	26.650	23.350	0.7783	46.7
Effect of concentration					
Conc (mg/L)		Ce(x)(mg/L)	Co-Ce(x)(mg/L)	Qe(Pb)(mg/L)	%
50		0.187	49.813	1.6604	99.26
100		0.104	99.896	3.3299	99.90
200		4.093	195.907	6.5302	97.85
300		13.491	286.509	9.5503	95.58

Table 2: Results of manganese removal operating parameters of adsorption isotherm

Effect of pH					
pH	Co(mg/L	Ce. (X) (mg/L	Co-Ce (X) (mg/L)	Qe Mn(mg/g)	% Mn
2	50	17.645	32.36	1.0787	64.72
4	50	15.961	34.04	1.1347	68.0
6	50	10.170	39.83	1.3277	79.6
8	50	26.482	23.52	0.784	47.0
Effect of contact time					
Contact	Co(mg/L)	Ce X(mg/L)	Co-Ce (X) (mg/L)	Qe Mn(mg/g)	% Mn
30	50	33.871	16.129	0.5376	32.2
60	50	31.983	18.017	0.6006	36.0
90 m	50	33.238	16.762	0.5587	33.5
120	50	33.706	16.294	0.5431	32.5
Effect of adsorbent dose					
doses(g)	Co(mg/L	Ce (X) .mg/L	Co-Ce (X) (mg/L)	Qe Mn(mg/g)	% Mn
1.5	50	33.537	16.463	0.5488	32.9
2.0	50	31.963	18.037	0.6012	36.0
2.5	50	33.844	16.156	0.5385	32.3
3.0	50	33.988	16.012	0.5337	32.0
Effect of concentration					
Conc.(mg/L).		Ce(x)(mg/L)	Co-Ce(x)(mg/L)	Qe(Mn)(mg/L)	% Mn
50		2.973	47.027	1.5676	94.054
100		8.418	91.582	3.0527	91.582
200		17.248	182.752	8.0917	91.376
300		29.154	270.846	9.0282	90.282

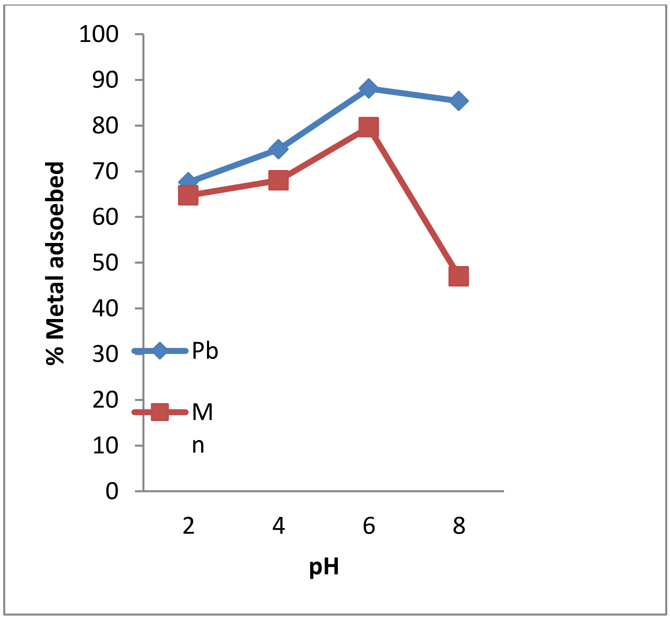

Figure 1: Effect of pH on the removal of Pb and Mn

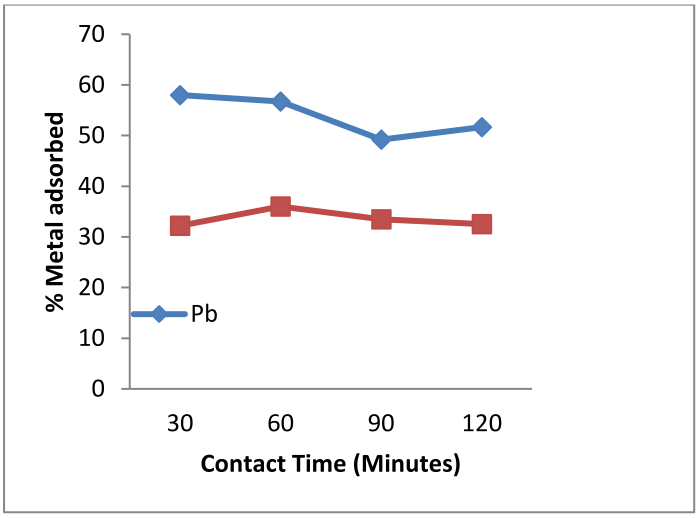

Figure 2: Effect of contact time on the removal of Pb and Mn

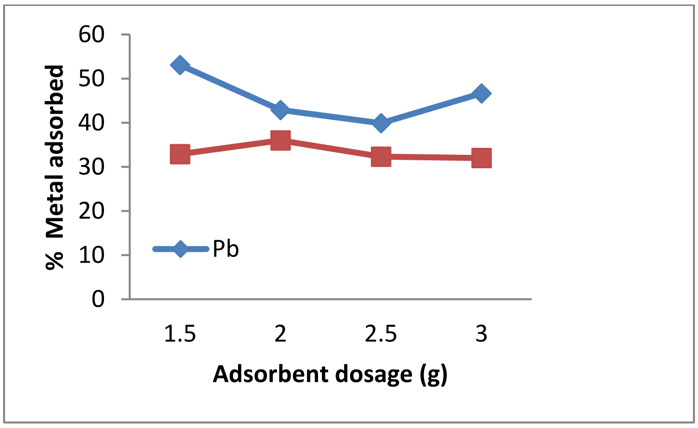

Figure 3: Effect of Adsorbent dose on the removal of Pb and Mn

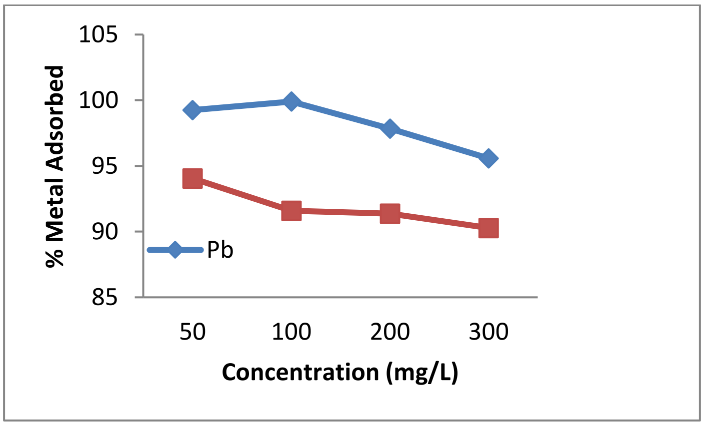

Figure 4: Effect of Concentration on the removal of Pb and Mn

3.1 Adsorption Isotherm

Adsorption is the ability of the adsorbate to adhere or attach to the adsorbent. The adsorption isotherm is an equation that shows the transfer of adsorbate from aqueous phase to the adsorbent phase at equilibrium condition. Some commonly used Isotherms are: Langmuir, Freundlich and Temkin etc. [17]. For the purpose of this study, the use of Langmuir and Freundlich models which are the earliest and simplest known relationships is emphasized.

3.2 Langmuir Isotherm

The essential features of a Langmuir isotherm can be expressed mathematcally in terms of a dimensionless constant, separation factor "R_L" which is used to predict the adsorption system, favourable or unfavourable and is given mathematically in equation 1 [18].

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

Where, Co is the initial metal ion concentration in (mg/L), K_L is the Langmuir equilibrium constant. The value of RL indicates the type of Langmuir isotherm. Irreversible (RL =0), favourable (0<RL<1), linear (RL =1) or unfavourable (RL>1).

Figure 5-6 presents the Langmuir Isotherm for biosorption of Pb (II) and Mn(II) ions onto unripe plantain (*Musa paradisiaca*) peel biomass. This confirms that the Langmuir isotherm model is more favourable to adsorption of Cr (VI) onto banana (musa sapientum) peel biomass. The value of R_L was found less than one in all the cases for Pb(II) and Mn(II). This confirms that the Langmuir isotherm model is favourable for adsorption of Pb(II) and Mn (II) onto unripe plantain**(***Musa paradisiaca*) peel biomass

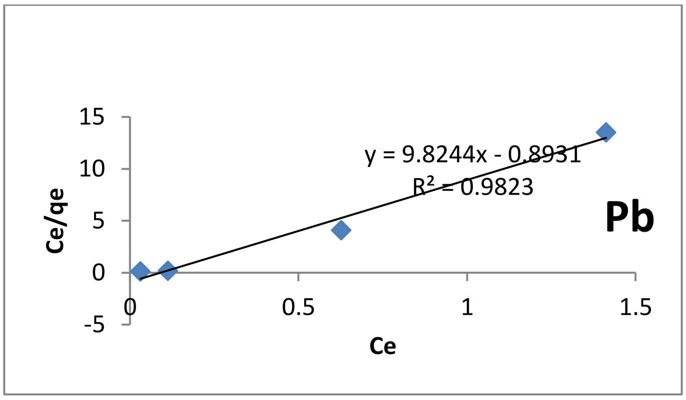

Figure 5: Langmuir isotherm (Ce/qe Vs Ce) for Pb removal

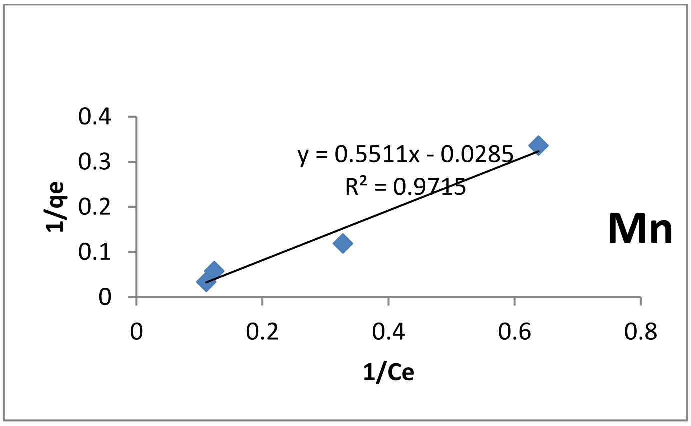

Figure 6: Langmuir isotherm (1/qe Vs 1/Ce) for Mn removal

3.3 Freundlich Isotherm

The Freundlich model named after the researchers is an empirical equation used to estimate the adsorption intensity of the sorbent towards the adsorbate [19]. This model suggested that the heterogeneous distribution of active sites and accompanied by interaction between adsorbed molecules [17].

The linear form of isotherm can be represented as [18, 19].

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

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 3.

Table 3: Adsorption isotherm constants for Pb (II) and Mn (II) on unripe plantain peel biomass

Metal	**Pb**	**Mn**
	Langmuir parameters	
Q^{max} (mg/g)	9.3	0.59
KL (L/mg	4.98	22.27
R^2	0.9823	0.9715
	Freundlich parameters	
K_f	0.239	0.641
$^1/_n$	0.9733	0.7787
n	1.03	0.2
R^2	0.9999	0.941

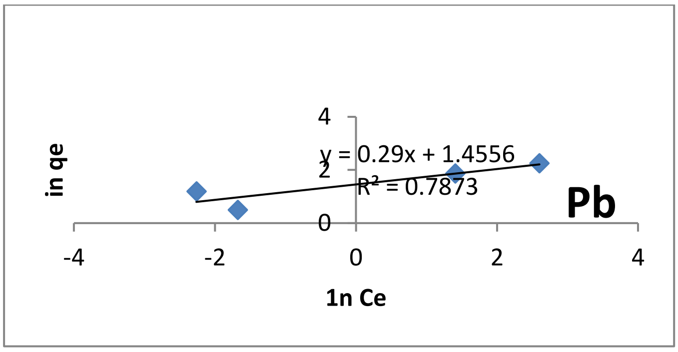

Figure 7: Freundlich isotherm (In qe Vs In Ce) for Pb removal

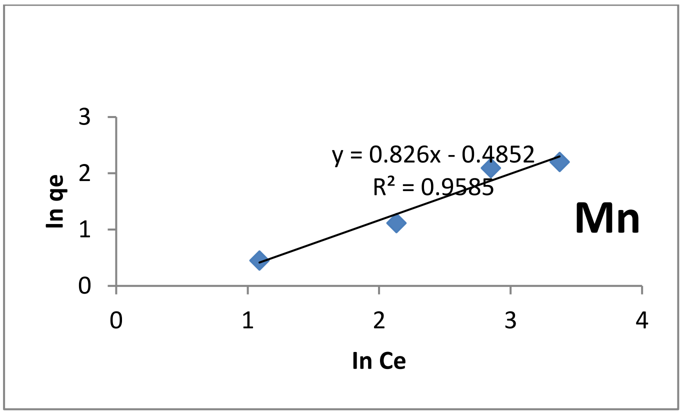

Figure 8: Freundlich isotherm (In qe Vs In Ce) for Mn removal

The results of the study (lead and manganese), reveals that the removal of Pb (II) best fits with the Langmuir model (Fig. 5-6) with a higher coefficient of determination, i.e., R^2=0.7873. 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 Mn (II), it was shown that the plot best fits with the Freundlich model, which is a plot of log Qe versus log Ce(Fig.7-8), having a higher coefficient of determination, i.e., R^2 =0.9585 with an (n) value which is the sorption affinity, n =1.03, thus n>1 and this shows favorable physical process. This is attributed to the active sites present more in Mn(II). The evaluated constants are given in Table 3. These observations are in agreement with those reported by the researchers [3,10,11,13-15].

4. CONCLUSION

The results of this study showed clearly that unripe plantain (*Musa paradisiaca*) peel biomass can be used as an effective adsorbent for the removal of lead and manganese ions from aqueous solution. The experimental data were best fitted to two different kinetic models, which are Langmuir and Freundlich Isotherms. Both Langmuir and Freundlich model fitted well for Pb (II) and Mn (II) ions with an R^2= 0.9823 and R^2 =0.9715. All the R_L values were less than one, thus indicating favorable adsorption. In emphasis, this study has further brought to spotlight that instead of other expensive materials; unripe plantain (*Musa paradisiaca*) peel biomass can be used as an effective adsorbent for the removal of heavy metal from aqueous solution.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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