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Biosorption of Cd and Pb in Textile Effluent Using *Musasapientum* (Banana) Peels

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Abstract:
The efficacy of using Musasapientum (banana) peels was tested for the removal of Cd and Pbusing batch experiments from textile industrial effluent. Standard spectophotometric techniques using AAS were adopted to assess the concentrations of the heavy metals before and after treatment of effluent with the biosorbent (banana peels).Metal sorption increasedproportionally with the equilibrium metal concentration. The adsorption capacity of banana peels on the metal ions was of the order: Cd >Pb, with percentage removal of metal ions as 99.93% for Cd and 99.64% for Pb. Biosorption equilibrium isotherms were plotted for metal uptake capacity (q) against residual metal concentration (C_f) in the sample and mathematically expressed by Langmuir and Freundlich models. The values of separation factor were between zero and one, indicating favorable sorption for the two metals (Cd and Pb) on the biosorbent. Peels of M. sapientum showed comparable biosorption capacity for Cadmium and Lead with other types of biosorbent materials found in literature and are cost effective, economical and eco-friendly in removal of these heavy metals from textile effluent sample.

Keywords: *Biosorption, Isotherm models, Cadmium, Lead, textile effluent, Musasapientum,*

1. Introduction

Heavy metals released into the environment have been increasing continuously as a result of industrial activities and technological developments and pose threats to human health (Zhexian*et al.*, 2006). Cadmium is a priority toxic pollutant in wastewater that is introduced into water from metal mining, melting, plating, batteries, pesticides, oil paint, pigments, textiles and alloys (Xiaomin*et. al.*, 2007; Guiqiu*et al.*, 2008). Large dosages of Cadmium in humans can result in tubular and glomerular damage; cause proteinurea, and anemia (Michael & Ayebaemi, 2005). The presence of Cadmium ions in the environment has become a potential threat to plant, animal, and human life due to their bioaccumulation tendency and toxicity and therefore they must be removed from municipal and industrial effluents before discharged into natural streams (Schiewer & Santosh, 2007).

On the other hand, Lead is among the most recycled non-ferrous metals and its secondary production has therefore grown steadily inspite of its declining prices. Its physical and chemical properties are applied in the manufacturing, construction and chemical industries. Acute effects of Lead are inattention, hallucination, delusions, poor memory, and irritability. Lead absorption in children may affect their development and also results in bone storage of it. It is associated with behavioural effects, nephropathy, and plumbism (Jarup, 2003).

The conventional way of treating or removal of heavy metals from wastewater includes precipitation, membrane filtration, ion exchange, adsorption and co-precipitation. These methods have found limited applications because of their high capital and operational cost. Studies on the treatment of effluent-bearing heavy metals have revealed adsorption to be highly effective for the removal of these metals from wastewater.

In recent time, new approaches involving the use of inexpensive and efficient alternatives in removing heavy metals from wastewater have been reported (Badmus*etal.,* 2007). Agricultural wastessuch as sugar bagasse, Rice husk, Saw dust, Coconut husk, Neemhusk (Surchi, 2011), and Rice husks (Uttam & Rajesh, 2013). Banana peels have been found to adsorb heavy metal ions such as Cu (II) ion (Hossian *et al*., 2012).

In general an absorbent can be termed inexpensive if it requires little processing, is abundant in nature or is aby-product or waste materials from another industry (Nasim*et al.,* 2004). In Nigeria, huge amount of agricultural wastes are generated daily which cause

environmental and disposal problems. Application of these wastes as adsorbents offers highly effective technological means for dealing with pollution by heavy metals and solving their disposal problems. There is therefore, an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of heavy metals, studied.
Thisstudyaimed at the feasibility of using banana peels for Cadmium and Lead removal from textile effluent.

2. Methodology

2.1. Collection of Effluent Sample
Textile effluent sample used for this research work were collected from the outlet of Tie and Dye, Ama-Hausa, Owerri, Nigeria using clean 4 liters plastic Can.

2.2. Preparation of Bio-Sorbent Precursor
Ripe and unripe bananas used for this research work were bought from the local market in Yenagoa, Nigeria. The bananas were washed in tap water to remove sand and other debris and were peeled. The banana peels were sun-dried for 8days. They were washed again after sun-drying to remove the dirt adhered during the sun drying process. Wetted biomass was air-dried to remove free water from the surface, and dried in an oven for 4 hours at 50°C.The crispy peels were pulverized separately into fine powder using a sterilized milling machine. The pulverized peels were sieved through a 0.25mm sieve size and stored in air-tight bottle prior to laboratory investigations at room temperature.

2.3. Batch Experiment
Different concentrations of the pulverized peels were used: 1g, 2g and 4g, and each mixed with 400ml of the effluent per concentration. The sample was placed in the conical flask apparatus and stirred at 120rpm speed using rotary shaker at room temperature to obtain homogenous mixture for 2 hours. After 2 hours of mixing, the sample was allowed to settle for 10 hours and filtered using Whatman no.1 filter paper to remove the biosorbent precursors. The treated effluent was then analyzed for heavy metals.

2.4. Analysis of Heavy Metal Concentrations
Heavy metal concentrations of the effluents were analyzed using Atomic Absorption Spectrophotometer (AAS). The concentration of metal ion in the sample was measured by spraying to the flame generated by the AAS. The absorbance of these ions measured at different wavelengths and standard calibration curves plotted (APHA, 1998).

2.5. Efficiency Calculation
Removal efficiency was calculated on the heavy metal ions as percentage removal. This was computed by subtraction of the initial concentration from the final concentration multiplied by 100 divided by the initial concentration.

2.6. Adsorption isotherm study
Adsorption isotherms studies were conducted by varying the adsorbent dose with 1g, 2g and 4g in 400ml of the industrial effluent sample. It was placed in rotary shaker for 2 hours. The equilibrium data was fitted with Langmuir and Freundlich isotherm models and the applicability was judged with the correlation coefficient (R^2).

2.7. Calculation of Metal Uptake
The quality of biosorbent is judged by the metal uptake (biosorption capacity), q. Amount of metal bound by the biosorbent which disappeared from the solution was calculated based on the mass balance for the biosorbent in the system.

$$q = \frac{V\,(C_i - C_f)}{S}$$

q = Metal ion uptake capacity (mgg^{-1})
C_i= Initial concentration of metal in solution, before the sorption analysis (mgL^{-1}).
C_f= Final concentration of metal in solution, after the sorption analysis (mgL^{-1}).
S = Dry weight of biosorbent (g)
V = Solution volume (L)
The difference between the initial metal ion concentration and final metal ion concentration was assumed to be bound to the biosorbent.

2.8. Langmuir and Freundlich Models
Tocharacterize biosorption for the industrial wastewater, Langmuir and Freundlich models are used. The Langmuir model makes assumptions such as monolayer adsorption and constant adsorption energy while the freundlich model deals with heterogeneous adsorption.
Langmuir equation of adsorption isotherm is:
$1/q = 1/q_{max} + 1/(b.\ q_{max})(C_f)$
Where qmax and b are the Langmuir constants.

The Freundlich equation of adsorption isotherm is:

Log q = log K + (1/n) log Cf

Where q is the amount adsorbed per unit mass of adsorbent and Cf is equilibrium concentration. The plot of log q vs log Cf is linear and constants K and n evaluated from slopes and intercepts (Langmuir, 1918).

2.9. Separation Factor

The shape of the isotherm can be used to predict whether adsorption system is favorable or unfavorable in a batch adsorption system. Accordingly, the essential feature of Langmiur isotherm was expressed in terms of dimensionless constant called the separation factor. It is defined by the following relationship:

$$SF = 1/(1+bCi)$$

Where *SF,* is a dimensionless equilibrium parameter or separation factor; b, constant from Langmuir equation;and Ci, initial metal ion concentration. The parameter, *SF,* indicates the shape of the isotherm and nature of the sorption process. If

SF > 1,i.e unfavourable isotherm

SF = 1,i.e linear isotherm

SF = 0,i.e irreversible Isotherm

0 <*SF* < 1,i.e favourable isotherm (Horsefall & Spiff, 2005).

3. Results

3.1. Heavy metals analysis

Mean heavy metals concentrations of untreated textile effluent samples were 1.3737 for Cd and 1.2736mg/l for Pb. After treatment, their concentrations were reduced as in Tables1and 2.

Heavy Metals	Before Treatment	After Treatment			WHO (2014) Standards
		1g	2g	4g	
Cd (mg/l)	1.3737	0.0001	0.0001	0.0069	0.0003
Pb (mg/l)	1.2736	0.0001	0.0045	0.0091	0.0001

Table 1: Mean concetrations of Cd and Pb in textile effluent before and after treatment with ripe banana peels.

Heavy Metals	Before Treatment	After Treatment			WHO (2014) Standards
		1g	2g	4g	
Cd (mg/l)	1.3737	0.0001	0.0001	0.0076	0.0003
Pb (mg/l)	1.2736	0.0001	0.0030	0.0076	0.0001

Table 2: Mean concentrations of Cd and Pb in textile effluent before and after treatment with unripe banana peels.

3.2. Efficiency Calculation

Efficiency of percentage removal of Cadmium and Lead in the effluent samples was calculated. The result showed that Cr had the highest percentage removal with both ripe and unripe banana peels in textile effluent sample. The concentration of peels at which purification was best achieved was also ascertained by the efficiency calculation. It was observed that 1g of banana peel was the best concentration for purification as it appeared that the higher the concentration, the lower the purification efficiency (Figures 1 and 2).

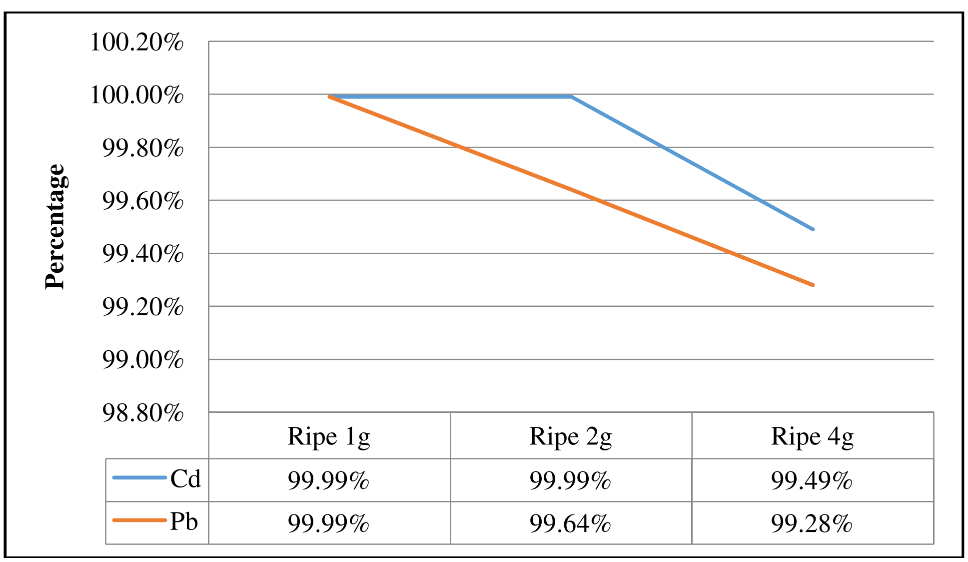

Figure 1: Efficiency of percentage removal of Cd and Pb in textile effluent sample.

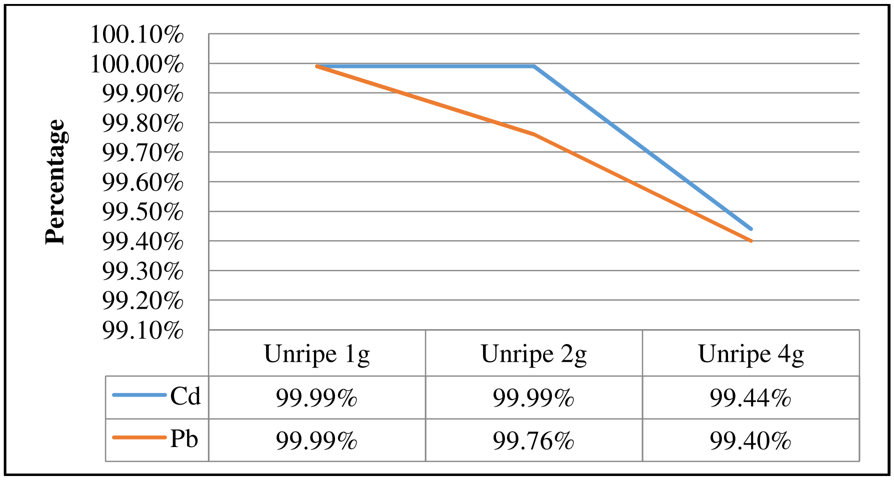

Figure 2: Efficiency of percentage removal of Cd and Pb in textile effluent sample.

3.3. Adsorption Isotherm Study

The adsorption isotherm study was conducted and the equilibrium data was fitted in comparison with Langmuir and Freundlich isotherm models and the applicability was judged with the correlation coefficient (R^2) as shown in Tables 3.The plot of log q vs log Cf was positively linear, and constants K and n were evaluated from slopes and intercepts while 1/q vs 1/cf was negatively linear, and constants b and qmax, evaluated from slopes and intercepts as shownin Figures 3 – 6.

	Langmuir Isotherm Parameters				**Freundlich Isotherm Parameters**		
Metals	q_{max}	**b**	**RL**	R^2	**KF**	**n**	R^2
Cd	-0.0000005	0.0078	0.72	0.99	0.30	1.40	-3.7
Pb	-0.000007	0.0079	0.78	1.00	0.57	1.0	-6.2

Table 3: Comparison of Langmuir and Freundlich isotherms for Cd and Pbin Textile Effluent sample

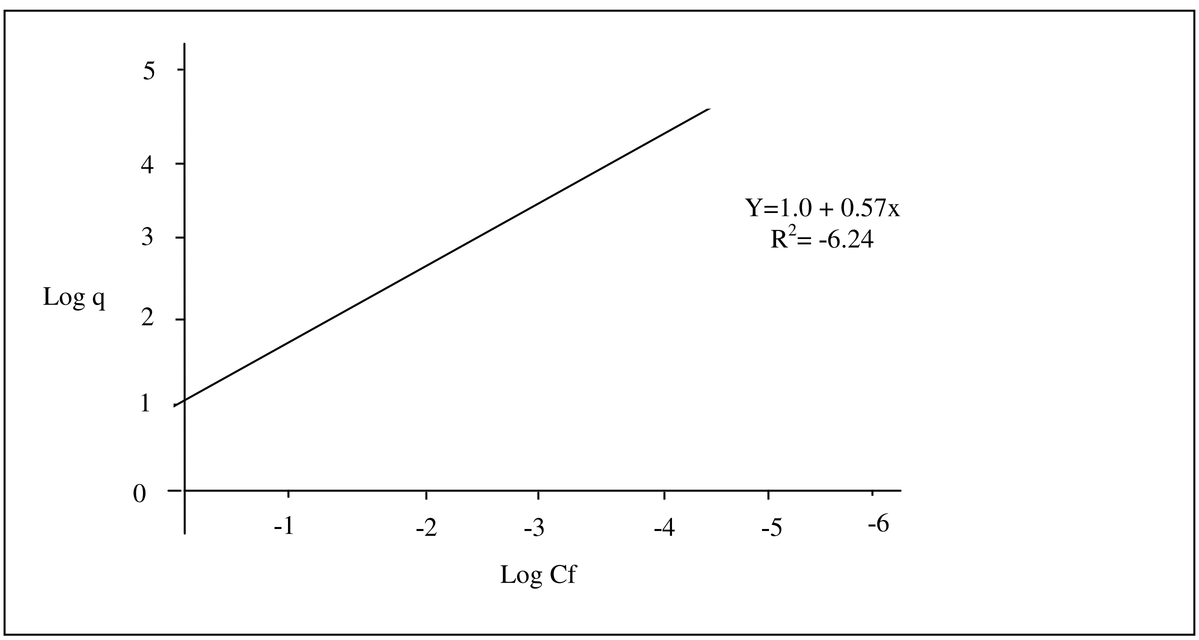

Figure 3: Freundlich Isotherm for Pb in Textile Effluent

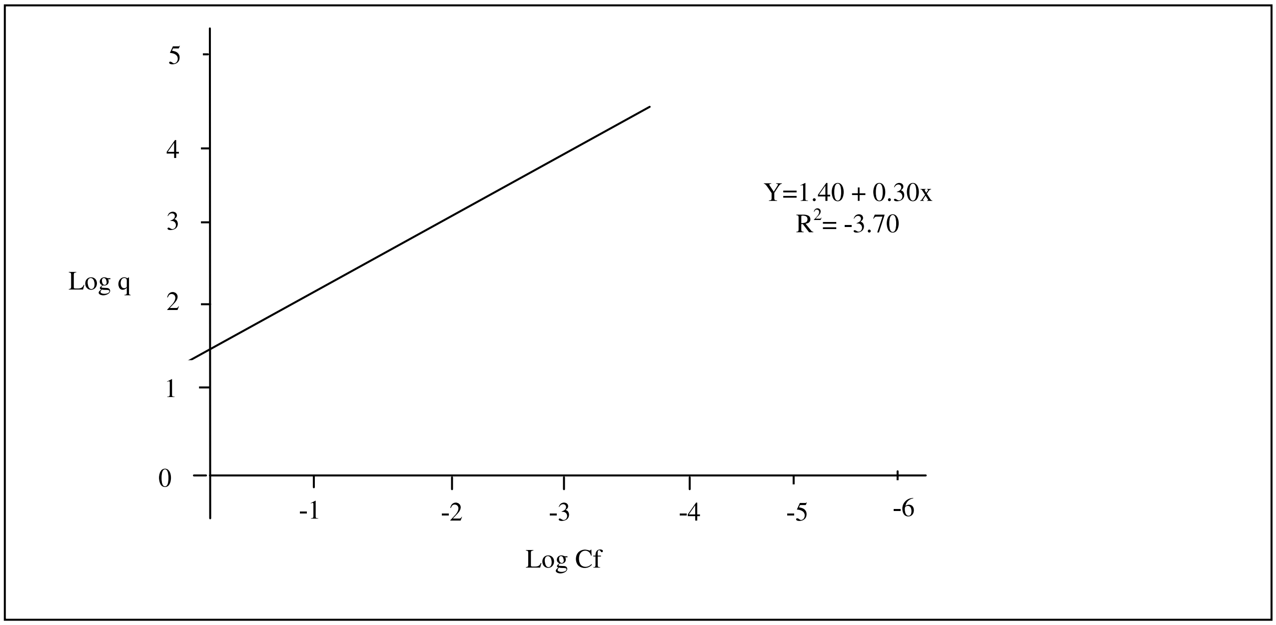

Figure 4: Freundlich Isotherm for Cd in Textile Effluent

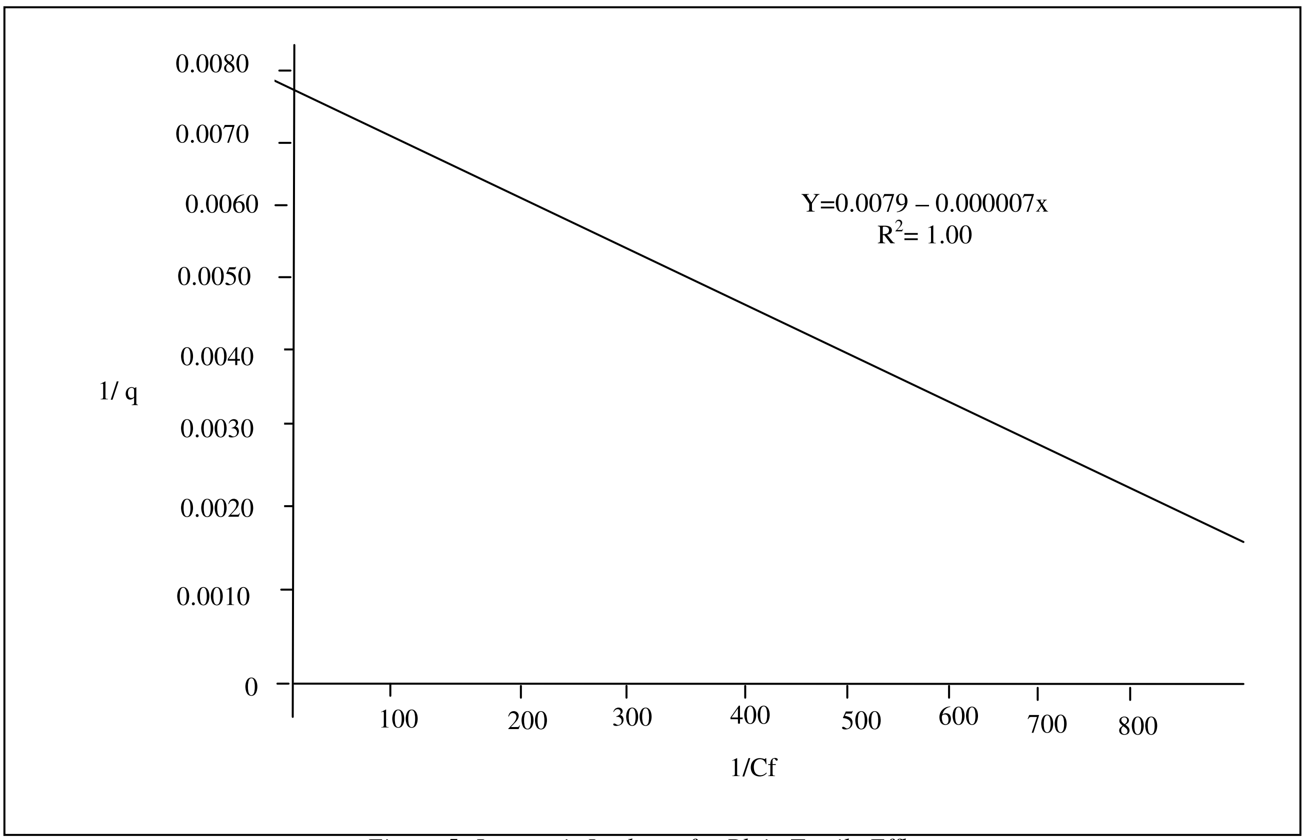

Figure 5: Langmuir Isotherm for Pb in Textile Effluent

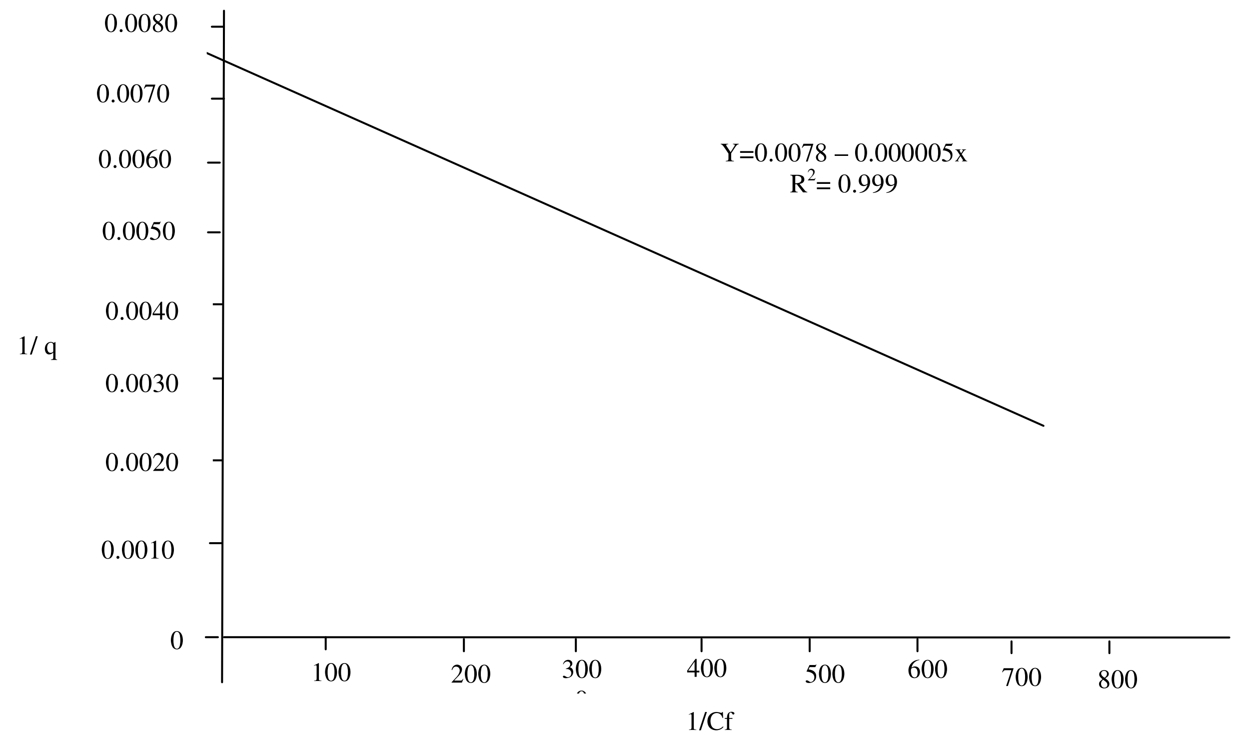

Figure 6: Langmuir Isotherm for Cd in Textile Effluent

4. Discussion

Cadmium has cumulative and high toxic effects in all chemical forms. Cadmium was detected in textile effluent samples and percentage level of removal indicates that the peels removed Cd more than Pb. A similar study carried out by Wanna & Pairat (2009), recorded that banana peels had the highest Cadmium ions removal of 73.15%.Generally,1g and 2g of both ripe and unripe banana peels reduced the values of Cd and Pb in the textile effluent below World Health Organization standards while 4g are above the approved standards. Lead is expected to have low phytotoxicity because of its strong affinity to organic matter, under certain environmental conditions e.g., change in pH, it may become mobile (Badmus *et al*, 2007).

The adsorption capacity of banana peels on heavy metals in textile effluent samples in this research work wasof the order: Cd >Pb. Moreover, it could adsorb 5.71 and 2.18 mg/g of Cd^{2+} and Pb^{2+}, respectively (Anwar *etal*., 2010). The findings of this work are in consistent with reports of Annadurai*et al*. (2002), Anwar *et al.* (2010), Ashraf *et al*. (2011), and Memon*etal*. (2008). In a related studies by Ashraf *et al*. (2010), similar results were obtained using mango (*Mangifera indica* L). Cadmium has as been successfully removed from aqueous solutions by chitin using similar techniques (Benguela & Benaissa, 2002). Banana peels, which represent about 40% of total weight of the fresh fruit (Anhwange, 2008),are recognized to be economically viable and environmentally sound adsorbent for removal of heavy metals from contaminated waters (UNCTAD, 2012).

Modelling the equilibrium data is fundamental for the industrial application of biosorption since it gives information for comparison among different biomaterials under different operational conditions, designing and optimizing operating procedures (Ashraf *et al*., 2010). To examine the relationship between uptake capacity (q) and aqueous concentrations (Ci) at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are the most widely used (Benguela and Benaissa, 2002). The Langmuir and Freundlich adsorption constants evaluated from the isotherms with correlation coefficients as obtained illustrate the relationship between absorbed and aqueous concentration at equilibrium. The Langmuir and Freundlich adsorption constants are evaluated from the isotherms with correlation coefficients. Both the models represent better absorption process due to high value of correlation coefficients (R^2). The results obtained can further be explained on the basis that the higher the constant b, the higher the affinity of the biosorbent for the metal ions; q_{max}, interpreted as the total number of binding sites that are available for biosorption, and q as the number of binding sites that are occupied by the metal ions at the concentration Cf. The equilibrium data was best fitted in both Freundlich and Langmuir isotherm models as shown in the correlation coefficient (R^2) values. Langmuir isotherm model better represented the sorption process for Pb than Cd due to high values of correlation coefficient(R^2). In the view of above mentioned comparison, the values of Freundlich constant K, represent the sorption. Thus, Freundlich model of sorption indicates the heterogeneity of biomass and Langmuir model shows homogeneity of biomass.

5. Conclusion

This research work shows that ripe and unripe banana peels are very effective for the removal of heavy metals from textile effluent. It can further be deduced that the unripe peels are more effective in metal removal than the ripe peels. In terms of the concentrations of the peels, it was observed that the lower the dose the more effective the adsorption process. The adsorption capacity of banana peels on heavy metals was Cd >Pb. The equilibrium data was best fitted in both Freundlich and Langmuir isotherm models as shown in the correlation coefficient (R^2) values, but better in Langmuir isotherm model. The cost implication of using conventional methods of heavy metal removal from textile industrial effluent is extremely high compared to using banana peels which is cost effective, economical and eco-friendly.

Although there is the need for further investigation to ascertain the best conditions for metal removal and the possibility for scale-up studies, the present findings have revealed the potential of this agro-waste for use in the bioremediation of polluted wastewater effluents.

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