Communication in Physical Sciences 2018, 3(1): 76-84

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Production of Activated carbon derived from Banana peel for the removal of Cd^{2+} and Cr^{6+} in Brewery wastewater

Gideon Wyasu

Received 24 January 2018/Accepted 26 December 2018/Published online: 27 December 2018

Abstract: *Heavy metal pollution of waste water has significant impact on the environment. This study was designed to investigate the use of activated carbon produced from local raw materials (banana peels) for the adsorption of Cd^{2+} and Cr^{6+} from waste water discharge from Brewery industry. Batch adsorption experiment was used for the study and the results obtained indicated that the adsorption increases linearly with increase in temperature, which pointed toward chemisorption mechanism. Initial increase succeeded by decrease after critical values were observed for influence of pH and adsorbent dosage on the adsorption. The adsorption behaviour of the cadmium and chromium ions fitted the Langmuir and Freundlich adsorption models, which also confirmed that the produced activated carbon adsorbed cadmium ion better than chromium ion.*

Key Words: *Environmental pollution, Cd^{2+} and Cr^{3+} brewery waste water, remediation, adsorption, activated charcoal, banana peel*

Gideon Wyasu
Department of Chemistry, Kaduna State University
Kaduna State, Nigeria
E-mail: wyasug@yahoo.com

1.0 Introduction

In Nigeria and other developing Countries, the management of heavy metals pollution is generating several evidences that call for precautional approach in managing heavy metal containing wastes generated by agricultural, domestic and industries wastes (Wyasu, 2016). Heavy metals concentration in an environment normally create potent future risk because it has the capacity to bioaccumulate and be magnified (I,e biomagnification) from a nontoxic level to a toxic level (Odoemelam and Eddy, 2009;). They are carcinogenic and at concentration above certain threshold value for the respective metal ion, short and long term toxicity impact manifest, whicg will ultimately lead to death (Ekwemengbo *et al*., 2011; Bryce-Smith *et al.,* 1997; Eddy and Udoh, 2004; Odoemelam *et al*., 2018; Boekx, 1986; Clarkson and Marsh, 1976 and Erickson *et al.,* 1983). Globally, much is published and research on the generation of heavy metals that its control. However, several approaches have been adopted in recent times to remove heavy metals from industrial waste water before they are discharged to the water body or other part of the environment (ref). These include membrane filtration, reverse osmosis, ion exchange, chemical precipitation, electrodialysis, electrochemical treatment, and adsorption (Kratochvil and Volesky,1998; Butter et al., 1998). However, adsorption has been found to be one of the best methods because it may be efficient, cost effective, easily accessible and can be operated within green chemistry requirements (ref). Several plant materials have been found to be good adsorbent for the removal of heavy metal ions from solution. Eddy (2009) modified *Cyperus esculentus* shell for adsorption of Zn^{2+} ion from aqueous solution and reported good adsorption efficiency. Okwunodulu and Eddy. (2014) reported that modified Cola *nitida* waste is an effective adsorbent for the removal of lead and cadmium ions from aqueous solution. Eddy and Odoemelam (2009) also reported similar findings on the use of modified tiger nut shell. Others include sorghum waste (Essien and Eddy, 2015), *Helix aspera* (Ekop and Eddy, 2009), kola nut pod (Uchechukwu *et al*., 2018), fluted pumpkin seed coat (Uchechukwu *et al*., 2015), etc.

Activated charcoal is one of the most commonly known adsorbents for the removal of heavy metal from aqueous solution (Eddy and Odoemelam, 2009). Activated carbon are amorphous form of carbon in which its production has been done to enhance a high degree of porosity and surface area, making it the most versatile adsorbent to be used for effective removal of organic contaminant (Monika et *al.,* 2009) and for removal of a wide range of substances from both liquid and gases (Abram, 1973). It can be prepared from animal or agricultural wastes as well as various nutshells. Agriculture wastes such as coconut shells, banana peels, oil palm nut shells, rice husks, olive waste cakes, and guava seeds have been reportedly used (Oladunmi *et al*., 2012).

Banana plant is common in the Nigerian environment and it grows to about 2 to 3rn in height and has evergreen leaves and produce fruits in which lies a number of fruits (Battle and Tous, 1997). The fruits are edible but the peels litters our communities with corresponding negative environmental impact.

This research studied the adsorption of heavy metals (Cd^{2+} and Cr^{6+}) from Brewery wastewater with the used of activated carbon from Banana peel. This aim shall be achieved by by implementing batch adsorption experiments towards evaluation equilibrium adsorption isotherms, adsorbent dosage, temperature and pH of the solution in order to ascertain the optimum conditions as well as the feasibility of the adsorption process.

2.0. Materials and Methods

2.1. Sample collection and treatment

Banana peel were removed from banana fruit, ~~was~~ collected from a farm land in Kamazou. Chikun Local Government Area of Kaduna State. After collection, it was taken to Biological Science Department, Kaduna State University, where it was authenticated and identified. The samples were washed several times with distilled and deionized water remove impurities. The samples were dried to constant weight and re-dried in the oven at 60 °C for 24 hours. The dried samples were grounded with the aid of a pestle and a mortar before been

2.2. Preparation of activated carbon from banana peel

The adsorbent was prepared using the method ~~as~~ described by Hanafiah *et al*. (2006). 200 g of the sieved material ~~above~~ was mixed with 300 cm^3 of 1M phosphoric acid (purity 85%, Merck, Germany) in a plastic container. The mixture was transferred into copper crucibles and heated in an oven at 105 °C for 30 minutes, stirred and was removed and left overnight. After cooling, the activated banana peel was repeatedly washed with distilled and de-ionized water until the pH of the filtrate was 7. It was dried in the oven at 105 °C for 1 hour and stored in a desiccator (Oladunmi *et al*., 2012).

2.3 Batch adsorption experiment

The batch adsorption experiment was carried out as reported elsewhere (Zare *et al* .2014). The method was applied to study the effect of different temperatures (30 to 60 °C), adsorbent dosage (0.4 to 1.2 g), pH (2 to 10) and initial concentration. 10 g of the adsorbent was used in each case and the volume of the solution was 200 ml. The equilibrium concentration of dye adsorbed was calculated using the following equation (Adedirin et al*.,* 2011a),

$$q_e = \frac{C_0 - C_e}{C_0} \times \frac{V}{m} \quad (1)$$

where C_0 is the initial concentration of the dye, C_e is the equilibrium concentration of the dye, V is the volume of solution and m is the mass of the adsorbent.

3.0. Results and Discussion

3.1. Effect of adsorbent dosage

Fig. 1. shows plots for the variation of the amount of chromium and cadmium ions adsorbed (mg/g) with adsorbent dosage.

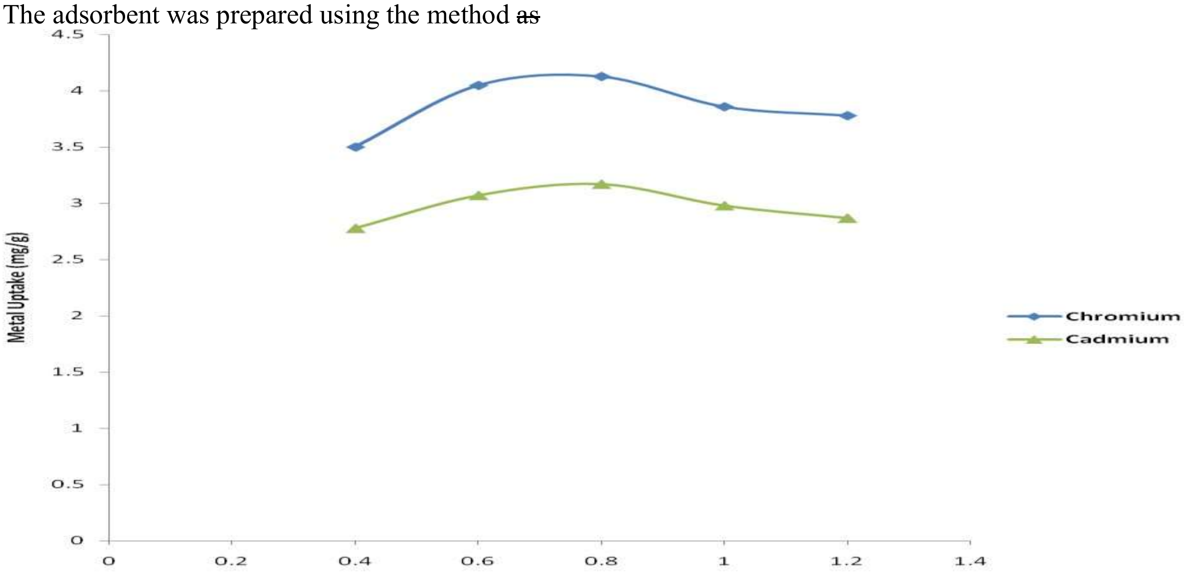

Fig. 1: Variation of the amount of Cd^{2+} and Cr^{6+} adsorbed with adsorbent dosage

Concentrations of Cd^{2+} and Cr^{6+} adsorbed is seen to witnessed a significant rise at initial stages upto a critical dosage amount (at about 0.8 g) after which, further increase in adsorbent dosage did not lead to increase in extent of adsorption. Maximum adsorption capacities were observed to be 3.18 mg/g (63%) and 4.12 mg/g for cadmium and chromium ions respectively. Influence of adsorbent dosage on the amount of dye has been reported by various authors (Gupta and Rastogi, 2017). In some trends, adsorbent dosage were observed to linear with with respect to adsorbent dosage. In others, complete decrease in adsorption capacity with adsorbent dosage were observed. Finally, situations similar to the present results have also been reported elsewhere (Dakiky *et al*., 2002; Acharya *et al*., 2009; (Adedirin et al., 2011b). According to Odoemelam *et* al. (2018), variation of equilibrium amount of dye adsorbed with adsorbent dosage depends on the number of available active sites available on the surface of the adsorbent. Eddy (2009) observed that although the number of adsorption sites available maybe constant for a given mass of the adsorbent, only those sites that have been activated to adsorbed will be occupied by the adsorbent. Therefore, the observed trend implies that further increase in adsorbent dosage beyond 0.8 g seems to have deactivated some of the adsorption sites thus reducing the number available for adsorption. The optimum dosage for maximum absorption of chromium and cadmium ions was the same which indicates that the surface activation maybe independent of the type of heavy metal in contact.

3.2 Effect of temperature

Effect of temperature on the adsorption of chromium and cadmium ions was demonstrated by the plots showing the variation of amount of heavy metals ion adsorbed with temperature, which is shown in Fig. 2

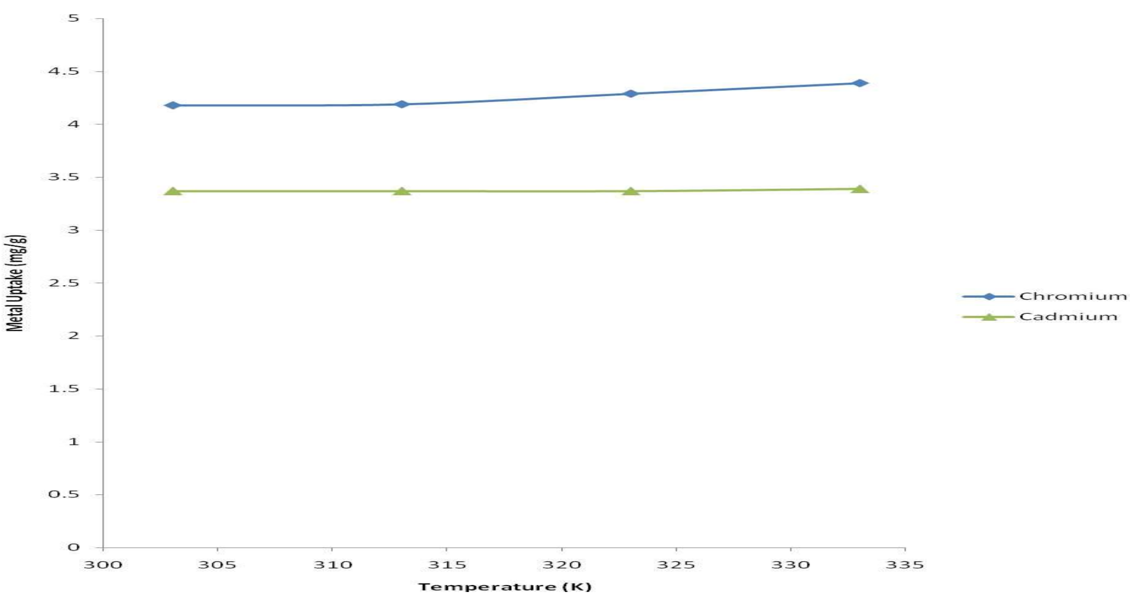

Fig. 2: Variation of amount of $Cd^{2=}$ and Cr^{6+} adsorbed with temperature

Temperature can affect the amount of metal ions adsorbed by affecting adsorption sites activation or deactivation depending on the mechanism of adsorption (i.e physical or chemical adsorption mechanism) (Bhatti, *et* al, 2007). In physical adsorption, increase in temperature decrease the number of adsorption sites activated and thus decrease the extent of adsorption while in chemical adsorption, increase in temperature increase surface activation and hence the amount of adsorbate adsorbed (Olayinka *et al*., 2009; Odoemelam *et al*., 2009). From Fig. 2, it is evidence that the amount of heavy metal adsorbed increase with increase in temperature, which suggest the mechanism of chemical adsorption. The uptake of chromium increase from 3.37 mg/g (67.4%) to 3.49 mg/g (69.8%) when the temperature was increase from 30 to 60 ºC. However, the uptake of cadmium ion (3.37 mg/g, 67.4%) was not significantly affected by the increment in temperature from 30 to 50ºC but increased slightly to 3.39 mg/g (67.9 %) when the temperature was increased to 60ºC. The results obtained follow trend similar to the one reported the adsorption of Cd (II) and Cr (VI) onto activated carbon derived from Locust Beans Husk (Oladunmi *et al*., 2012).

3.3 *Effect of solution pH*

Fig. 3. Depicts plots for the variation of amount of cadmium and chromium ions adsorbed with pH.

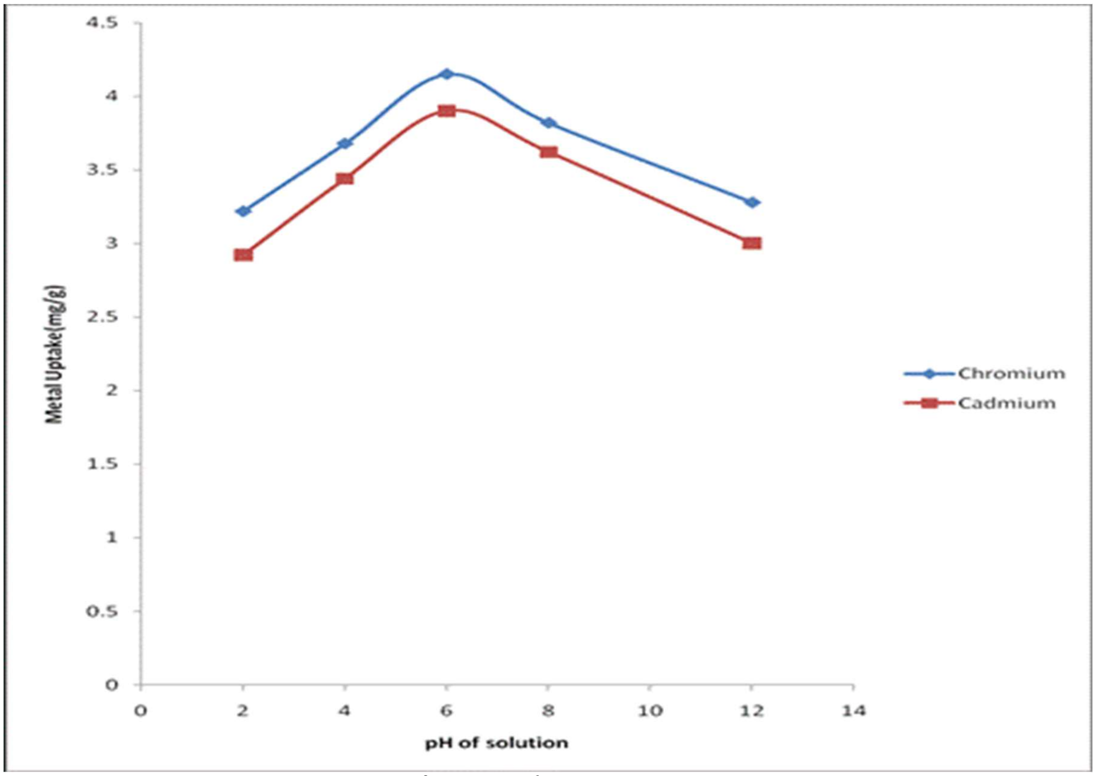

Fig. 3: Variation of the amount of Cd^{2+} and Cr^{6+} ion adsorbed with pH

The uptake and percentage removal of metals from the aqueous solution experienced three stages. In the first stage, metal up take increases with increase in pH. This was succeeded by an approach to critical value and finally be decrease in metal uptake with increasing pH. Several studies have concluded that pH can significantly influence the adsorption of heavy metals (Horsfall and Abia, 2003; Odiongbenyi, 2020; Zvinowanda *et al*., 2009). Fig. 3 reveals that increase in pH from 2 to 6 resulted in a corresponding increase in the uptake of cadmium from 2.08 to 3.15 mg/g while that of chromium increases from 3.22 to 4.15 mg/g respectively However, above pH values of 6 the adsorption capacity decreased with increment in pH. Degree of adsorption can be influence by protonation of the functional groups in the adsorbent. At acidic pH, protonation is higher but decreases at certain critical pH (Corapcioglu and Huang, 1987; Bansal and Goyal, 2008; Nazar *et al*., 2008) The minimum adsorption observed at ~~low~~ pH of 2 may be due to higher concentration and mobility of H^+ ions, which favoured H^+ adsorption compared to M^{2+} ions. pH can also affect the solubility of the metal ion in the solution suggesting that metal solution chemistry also play significant role in adsorption. Higher solubility may decrease the amount of metal ion adsorbing to the surface of the adsorbent. Therefore, at low pH, the hydroxonium ion might have competed strongly with the metal ion but as the pH gradually increases, the competition is gradually reduced and adsorption increase until optimum pH is approached. However, beyond the optimum pH, a progressive approach to alkalinity is established and negative charges dominated, leading to deprotonation and hence desorption. Consequently, the observed maximum adsorption capacity observed in the pH range of 6 and 8 might be due to partial hydrolysis of metal ions, resulting in the formation of $M(OH)^+$ which would be adsorbed to a greater extent on a less-polar carbon surface of the adsorbents compared to M^{2+} ions. (Oladunmi *et al*., 2012).

3.4 Adsorption isotherm

Experimental data obtained from this study were tested for best suited adsorption isotherms and the results obtained indicated that the Langmuir and Fruendlich isotherms best suited the adsorption of cadmium and chromium ions from aqueous solution.

The assumption establishin the Langmuir isotherm can be expressed according to the equation 2 which rearrange to equation 3 (Odiongenyi, 2020)

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (2)$$

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{b C_e q_{max}} \quad (3)$$

where q_e is the amount of adsorbate adsorbed per gram of dried adsorbent at equilibrium (mg adsorbate/g of dried adsorbent), q_{max} is a ~~the~~ constant defined as the maximum theoretical adsorption capacity for monolayer (mg/g) b is Langmuir constant or adsorption coefficient or the adsorption affinity (L/mg) for binding of adsorbate on the adsorbent sites, and Ce is equilibrium (residual) adsorbate concentration in solution after sorption (mg/L). The suitability of the Langmuir adsorption model to the adsorption of cadmium and chromium ions unto the activated carbon surface was confirmed by linear plots (with R^2 .0.9) obtained when 1/qe were plotted against 1/Ce as shown in Figs. 4 and 5.

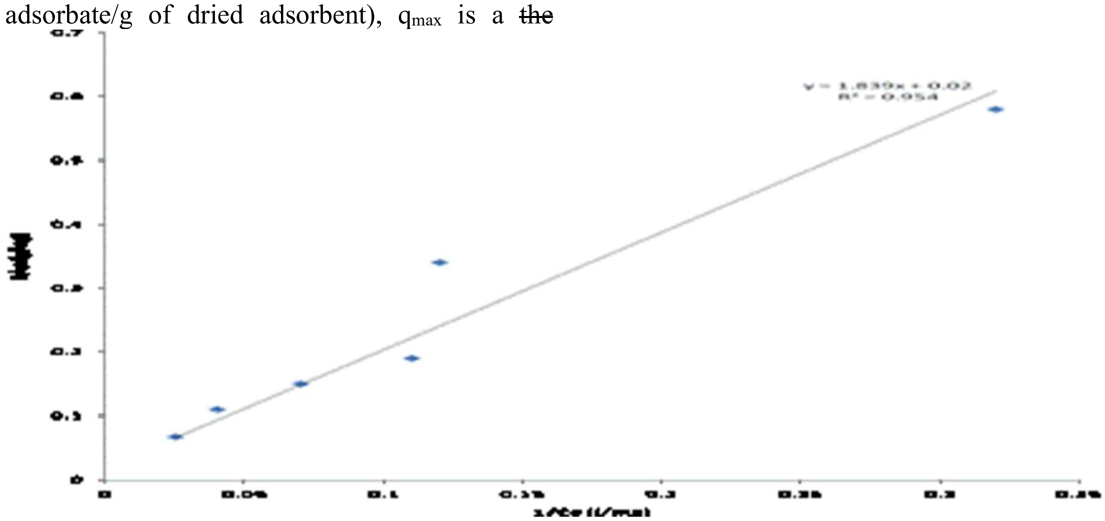

Fig.4: Langmuir isotherm for the adsorption of cadmium (II) unto activated carbon

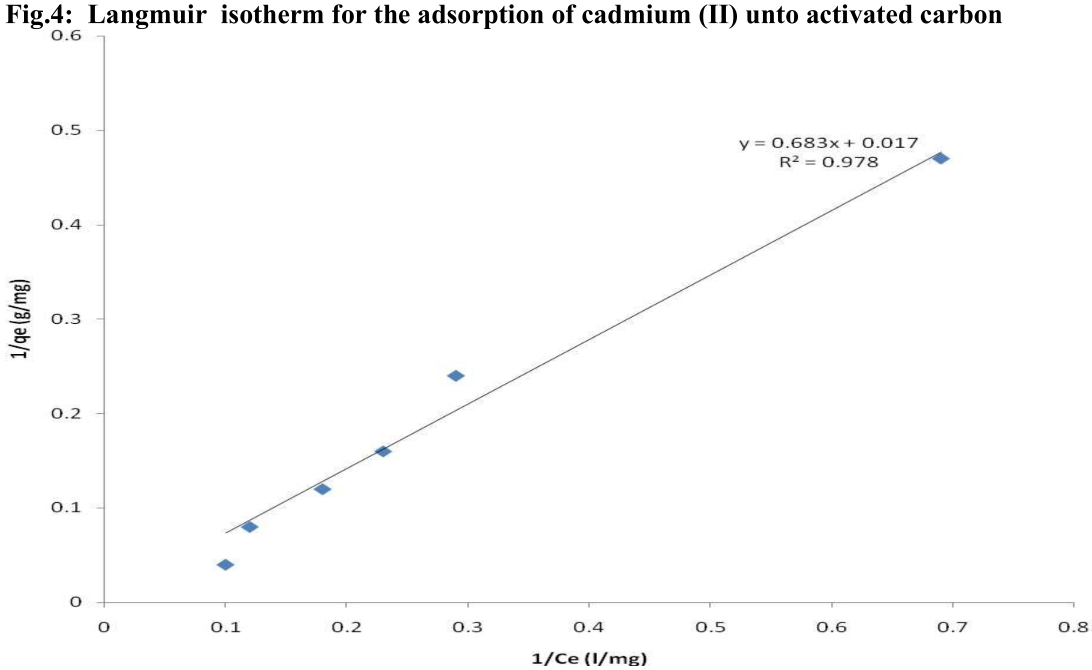

Fig. 5: Langmuir isotherm for the adsorption of chromium (IV) unto activated

Table 1: Langmuir and Freundlich parameters for the adsorption of cadmium and chromium ions unto the surface of activated carbon.

Metals	Langmuir Constant				Freundlich Constant		
	q_{max}(mg/g)	b (L/mg)	b (L/mol)	R^2	1/n	K_f(L/mg)	R^2
Cadmium	50.00	0.011	1236.5	0.954	0.838	0.6607	0.953
Chromium	58.80	0.025	1300.0	0.978	0.999	1.0000	0.957

Maximum metal uptake **(q_{max})** for Cd (II) and Cr (VI) are 50.0 mg/g and 58.8 mg/g respectively. Therefore, the order of adsorption can be deduced from Table I as follows: Cr (VI) > Cd (II) and this is in agreement with the trend in Fig. 6. This might be attributed to many factors ranging from available binding sites, binding sites affinity to the metal to be adsorbed. The maximum metal uptake (58.8 rng/g) obtained for Cr (VI) was higher than 11.08 mg/g reported by Gupta and Babu (2005) for tamarind seed as adsorbent s

One of the most essential components of the Langmuir adsorption model is the separation factor, which can be expressed according to equation 3

$$R_L = \frac{1}{1+bC_0} \quad (4)$$

where b is the Langmuir constant (l/mg), C_o is the initial metal ion concentration of the selected metal (mg/L). Favourable adsorption is certified ny this model when R_L is less between 0 and 1 (Mackay and Roberts, 1982). Fig. 6 shows a plot of separation factor versus concentration. The results obtained indicated that the separation factor were within the range that characterised favourable adsorption for both cadmium and chromium ions.

The Freundlich adsorption equation can be written according to equation 4 (Eddy and Ekop, 2005)

$$logqe = logKf + \frac{1}{n}logCe \quad (5)$$

where qe, is the amount of adsorbate adsorbed per unit weight of adsorbent, K_f is Freundlich constant, which is a measure of adsorption capacity (L/rng), Ce is equilibrium concentration of the adsorbent in solution (rng/L), n is a constant related to the adsorption efficiency and energy of adsorption or adsorption intensity of the adsorbent. From equation 4, a plot of log(q_e) versus log(C_e) should be linear if the Freundlich isotherm is obeyed. Fig. 7 and 8 shows Freundlich isotherms for the adsorption of Cd^{2+} and Cr^{6+} unto activated carbon produced from banana peel. Calculated values of R^2 were excellent (as listed in Table 1). The Freundlich adsorption-desorption constant and /n values were greater for cadmium ion adsorption than for the adsorption of chromium ion, hence the activated carbon comparatively adsorbed cadmium ion better than chromium ion.

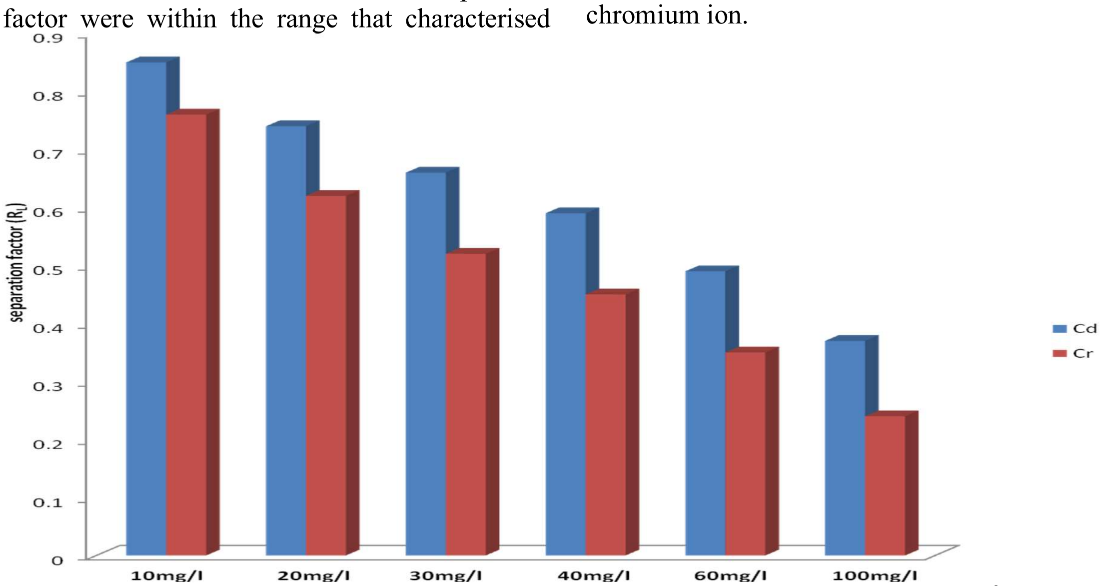

Fig. 6: Variation of separation factor with concentration for the ~~on~~ adsorption of Cd^{2+} and Cr^{6+}.

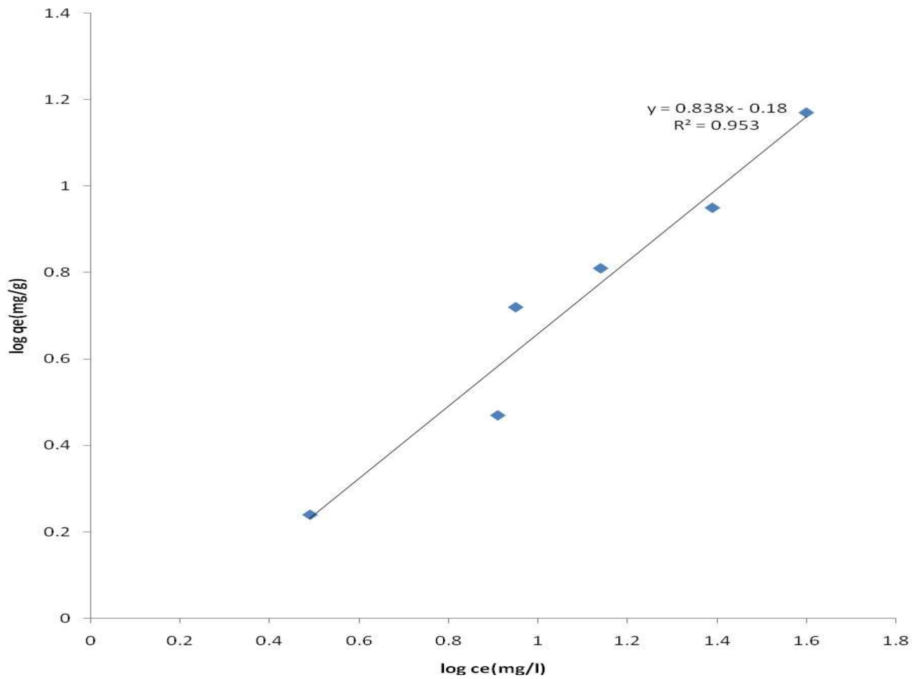

Fig. 7: Freundlich adsorption Isotherm for Cd (II) adsorption

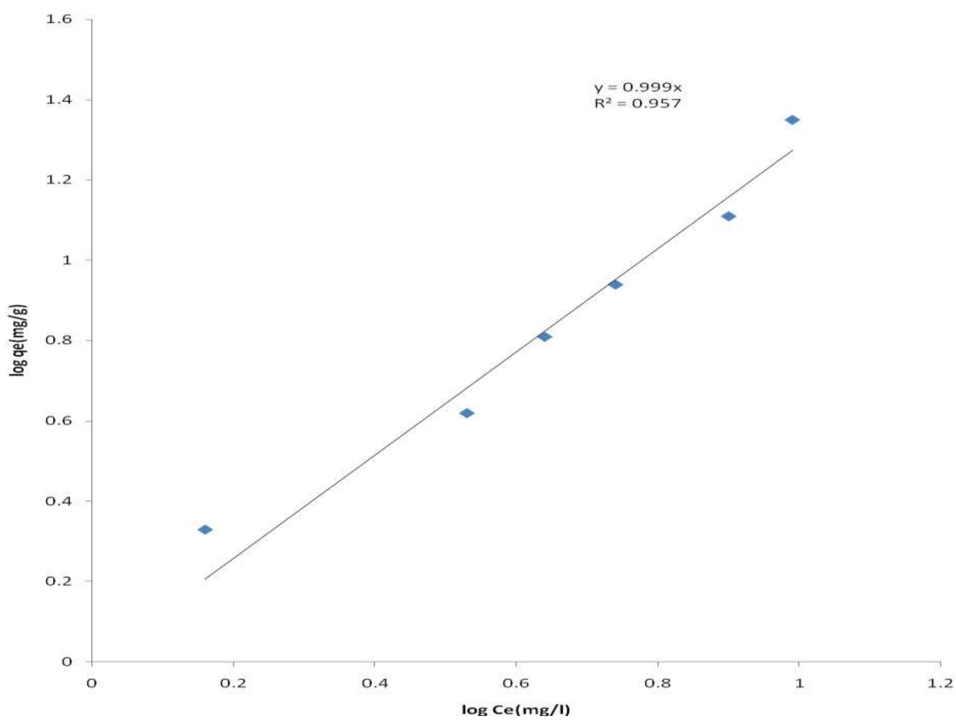

Fig. 8: Freundlich isotherm for the adsorption of Cr(VI) and Cd(II) unto activated charcoal

4.0 Conclusion

Based on the research, the following conclusions are drawn:

(i) Activated carbon produced from Banana peel is an effective adsorbent for Cd (II) and Cr (VI) removal from aqueous solution.

(ii) The optimum dosage for the removal of Cd (II) and Cr (VI) by activated carbon produced was found to be 0.8 g, recording adsorption capacity of 3.18 mg/g and 4.12 mg/g for Cd (II) and Cr (VI) respectively.

(iii) The uptake of cadmium and chromium increased when the solution's pH was increased from 2 to 6. For pH values above 6, the adsorption capacity decreased with increment in pH.

(iv) The two metals showed increased in adsorption capacity with increase in temperature.

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