

Adsorption Efficiency of Chitosan-Coated Carbon for Industrial Effluent Treatment

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Abstract– Removal of heavy metals from industrial wastewater prior to discharge into the environment is essential to prevent pollution. The present study compared the efficiencies of flamboyant plant pod char (FPPC) with Chitosan modified flamboyant plant pod char (MFPPC) and Activated Carbon (AC) for the removal of Pb (II) and Cd (II) from aqueous solution. Presence of C, K, Ca, Mg, Al, Si, P and Cl were revealed by Rutherford backscattering spectrometry (1.7 MeV Tandem Accelerator) as part of the constituent of the adsorbent while Scanning Electron Microscope (SEM) reveal the morphology of the adsorbent. Batch adsorption experiments were performed with the view of assessing the removal efficiency under the various factors such as the effects of initial concentration, adsorbent dose, pH, and contact time. The adsorbent exhibits good adsorption efficiency for Pb (II) and Cd (II) at pH 6.8 with optimum contact time of 60 to 90 min even at trace concentration. Experimental data were analysed using Langmuir and Freundlich adsorption isotherms. The isotherm study showed that the adsorption equilibrium is well-fitted to the Langmuir and Freundlich isotherm. The order of metal ion selectivity by the adsorbent (modified and unmodified) was: Pb (II) > Cd (II). Flamboyant plant pod char could be successfully utilized for removal of heavy metals from industrial effluents while solving the problem of disposal of plant waste materials.

Index Terms— chitosan, cadmium (II), lead (II), heavy metal, adsorption, industrial effluent, flamboyant plant pod char, SEM.

1 Introduction

Thousands of organic, inorganic, and biological pollutants have been reported as water contaminants (Qu *et al.*, 2013). Some of them have serious side effects and toxicities with a few being lethal and carcinogenic (Ali and Aboul-Enein, 2006; Ali *et al.*, 2009). These pollutants are very dangerous for all of us, aquatic conditions, and the ecosystem of the earth as a whole (Ali, 2012). Some heavy metals are notorious water pollutants with high toxicity and carcinogenicity (Duffus, 2002).

It is very important to treat wastewater before discharging it into water bodies to preserve the natural conditions of the environment and most importantly human lives. For a few decades, different methods have been developed and used for water treatment (Gupta and Nayak, 2012; Peijnenburg *et al.*, 2015): the most important methods are screening, filtration, centrifugation, ultra-filtration, crystallization, sedimentation and gravity separation, flotation, precipitation, coagulation, oxidation, solvent extraction, evaporation, distillation, reverse osmosis, ion exchange, electro dialysis, electrolysis, adsorption, etc. (Ali, 2012).

Adsorption (a process in which pollutants are adsorbed on the solid surface) is considered as one of the suitable water treatment methods due to its ease of operation and the availability of a wide range of adsorbents. Besides, adsorption can also be applied for the removal of soluble and insoluble organic, inorganic, and biological pollutants. Additionally, adsorption can also be used for source reduction and reclamation for potable, industrial, and other water purposes. A molecule (pollutant) adhered to the solid surface is called an adsorbate, and the solid surface as an adsorbent (Alade *et al.*, 2012). Adsorption is controlled by various parameters such as temperature, nature of the adsorbate and adsorbent, and the presence of other pollutants along with the experimental conditions (pH, concentration of pollutants, contact time, particle size, and temperature) (Ali, 2012).

Adsorption processes, using industrial activated carbon, have been attempted to remove organic pollutants but the challenge of regenerating the spent adsorbent and the related high cost of the regeneration process have not given the adsorption process the deserved extensive applications (Johns *et al.*, 1998; Wartelle and

Marshall, 2001; Alade *et al.*, 2012). The high cost of coal-based activated carbons has stimulated the search for cheaper alternatives. Low cost and non-conventional adsorbents include agricultural by products such as nut shells, wood, bone, peat processed into activated carbons, and biomass such as *Aspergillus terreus*, *Pseudomonas* sp., *Rhizopus arrhizus* have been reported to be important adsorbents for the removal of metals and organics from municipal and industrial wastewater (Amuda and Ibrahim, 2006). Hence, natural materials have been investigated as potential industrial adsorption media. The use of natural adsorbents in wastewater treatment have received increasing attention and currently offer a very attractive method for pollution remediation (Rafatullah *et al.*, 2010).

Agricultural wastes are vast abundant raw material whose potential is still under-utilized. Activated carbon prepared from peanut hulls, an agricultural waste by-product has been used for the adsorption of cadmium from synthetic wastewater. Modification of agricultural waste or (biochar) with Chitosan gives an improved performance to the waste to remediate heavy metal. Chitosan (2-acetamido-2-deoxy-B-d-glucose-(N -acetyl glucosamine) is produced commercially by deacetylation of chitin using sodium hydroxide in excess as a reagent and water as a solvent (Amuda *et al.*, 2007). Chitin is the structural element in the exoskeleton of crustaceans (such as crabs and shrimp) and cell walls of fungi.

Chitosan is an important additive in the filtration process. Sand filtration can remove up to 50% of the turbidity alone, while the chitosan with sand filtration removes up to 99% turbidity (Woodmansey, 2002). Chitosan is also useful in other filtration situations, where one may need to remove suspended particles from a liquid. The chitosan used for this research was extracted from natural source (periwinkle shell). This present communication is devoted to study the adsorption efficiency of flamboyant plant pod modified with chitosan extracted from periwinkle shell for removal of Pb (II) and Cd (II) from industrial effluent.

2 Materials and Methods

2.1 Flamboyant Plant Pod Char preparation

The flamboyant pod used for this study was collected within the Obafemi Awolowo University Ile-Ife, Osun State. Periwinkle shell was obtained from backyard dumpsites in Uyo, Akwa-Ibom State. Activated carbon (GAC F-300) by Boncaki Nigeria Limited Lagos, Nigeria was purchased commercially. The agricultural wastes were dried ground and sieved to particle size less than 300 μm . Less than 2 mm size fraction of periwinkle shell and of the flamboyant plant pod were used (Okoya et al., 2014). 100 g of the sieved sample was placed in a furnace (Carbolite RHF 1600) at 500 $^{\circ}\text{C}$ for 1h. The carbonaceous substance was allowed to cool to room temperature in an air tight crucible.

2.2 Activation of Flamboyant Plant Pod Char

The charred samples were soaked in 2% H_2SO_4 (v/v) and placed in an oven at a temperature of 110 $^{\circ}\text{C}$ for 24 h. The treated sample was washed with distilled water until the solution was not acidic. Then, the char was soaked in 2% NaHCO_3 (w/v) to remove the residual acid. The sample was finally dried in an oven at 110 $^{\circ}\text{C}$, cooled at room temperature and stored in a desiccator until use (Kadirvelu et al., 2001).

2.3 Characterization of the adsorbent

Scanning Electron Microscope (SEM) (High resolution SEM-Carl Zeiss) was used to study the surface morphological characteristics of the flamboyant plant pod char. Rutherford backscattering spectrometry (RBS) (1.7 Mev Tandem Accelerator) was used to determine the elemental composition of the adsorbents (Goel et al., 2005; Mohan and Gandhimathi, 2009).

2.4 Chitosan Preparation

Periwinkle shell (50 g) after being washed, sun dried, ground and sieved to 2 mm particle size, was deproteinized with 4% (w/v) NaOH with constant stirring for 6 h at 80 $^{\circ}\text{C}$. Thereafter, it was demineralized in 5% (v/v) HCl with constant stirring for 1 hour at room temperature. The sample was thoroughly washed until its acid free. The demineralized periwinkle particles was refluxed in acetone for 3 hours at 60 $^{\circ}\text{C}$ to decolourize it. The content was filtered and dried, to get a snow white residue called chitin. The chitin was deacetylated in 50% (w/v) NaOH solution by constant stirring at 30 $^{\circ}\text{C}$ for 4 hours to produce chitosan.

2.5 Chitosan Gel Preparation

About 5 g of chitosan was slowly added to 100 ml of 10 % (w/v) oxalic acid with constant stirring. The mixture was also heated to 40-50 $^{\circ}\text{C}$ to facilitate mixing. A chitosan-oxalic acid mixture was formed (a whitish viscous gel).

2.6 Adsorbent Modification

The chitosan gel (100 ml) was diluted with water (~500 ml) and heated to 50 $^{\circ}\text{C}$. 50 g of flamboyant plant pod char was slowly added to the diluted gel, and mechanically agitated using a shaker (Flash Shaker SF1) operated at 200 osc/min for 24 h. The gel coated adsorbent were washed with distilled water, dried, and the soaked in 0.5 % (w/v) NaOH solution for 3 h. It was then extensively rinsed with distilled water and dried in an oven at 102 $^{\circ}\text{C}$ for 2 h, cooled at room temperature and stored in desiccator.

2.7 Batch Biosorption Studies

Batch adsorption studies were carried out using 1.0 g of the adsorbent and 50 ml of the Pb^{2+} and Cd^{2+} solutions with constant shaking using a shaker (Flash Shaker SF1) operated at 300 osc/min. The following parameters were investigated; Initial metal ion concentration (1, 2, 5, 10 and 20 mg/L), Biosorbent dose (0.5, 1.0,

1.5, 2.0 and 2.5 g), pH (3.5, 4.5, 5.5, 6.5 and 7.5) and Contact time (15, 30, 45, 60 and 90 min). The mixture was filtered using Whatman no.1 and the filtrate was analysed using atomic absorption spectroscopy (AAS).

The removal efficiency (E) of adsorbent on Cr (IV) are measured as follows:

$$\text{Adsorption Efficiency} = \frac{(C_0 - C_1)}{C_0} \times 100\% \quad (1)$$

Where:

C_0 is the initial concentration before adsorption

C_1 is the final concentration of metal solution (mg/L) in the filtrate after adsorption.

2.8 Data Evaluation

The amount of metal adsorbed by the adsorbent was calculated using a mass balance equation

$$Q = v (C_i - C_f)/m \quad (2)$$

where Q is the metal uptake (mg metal per g biosorbent), v is the liquid sample volume (ml), C_i is the initial concentration of the metal in the solution (mg/L), C_f is the final (equilibrium) concentration of the metal in the filtrate (mg/L) and m is the amount of the added biosorbent on the dry basis (g).

2.9 Adsorption Isotherm

Adsorption of metals from 50 ml of metal solution was carried out at different initial metal ion concentrations ranging from 1 to 25 mg/L; pH of 3.5 to 7.5, at 300 osc/min with the optimum agitation period of 60 min (optimum conditions of all pertinent factors was used) while maintaining the adsorbent dosage at 1.0 g. Langmuir and Freundlich models were applied to the adsorption isotherm and different constants were generated (Freundlich, 1906; Langmuir, 1916).

The Langmuir model:

$$Q = Q_{\text{max}} \frac{bC_f}{1+bC_f} \quad (3)$$

Where Q_{max} is the maximum metal uptake under the given conditions, b a constant related to the affinity between the biosorbent and sorbate.

The linearized equation of Langmuir model is commonly represented by:

$$1/Q = 1/Q_{\text{max}} (1/b C_f + 1) \quad (4)$$

The maximum metal uptake can be obtained if a plot of $1/Q$ against C_f is made. The second model is Freundlich model which mathematical equation can be written as in equation 3.

The Freundlich Model:

$$Q = k C_f^{(1/n)} \quad (5)$$

Where k and n are Freundlich constant, which correlated to the maximum adsorption capacity and adsorption intensity, respectively.

Linearized Freundlich equation of equation 3 take the form (eqn 4)

$$\text{Log } Q = \text{Log } k + 1/n \text{ log } C_f \quad (6)$$

A plot of $\text{log } Q$ against $\text{log } C_f$, will give a straight line which will confirm the Freundlich Isotherm.

3 RESULTS AND DISCUSSION

3.1 Characterization of Adsorbent and Chitosan

Table 1 shows the presence of elements (O, Na, Mg, Al, Si, P, S, Cl, K, Ca, and Fe) other than carbon itself. Although carbon had the highest proportion, the presence of these other elements can enhance the adsorption through the following adsorption mechanism: ion exchange, chelation, co-ordination and complexation reactions (Porath and Olin, 1983; Inoue et al., 1993; Yu et al., 2003).

Scanning electron micrographs (SEM) clearly revealed the surface texture and morphological characteristics of the flamboyant plant pod char (Fig. 2). The distinctive irregular appearance of the adsorbents reveals the adsorption sites which encourage retention of metals onto the surface of the adsorbent (Farinella et al., 2007; Vimonses et al., 2009; Benyoucef and Amrani, 2011; Okoya et al., 2014; Selvaraju and Bakar, 2016).

The functional groups of the chitosan were determined using Fourier Transform- Infra Red microscope (FTIR). Fig. 3 shows the functional groups present in the chitosan extracted from periwinkle shell. The presence of C—O was confirmed by the stretching frequency at 1082 cm⁻¹; 1492 cm⁻¹ peak confirms the presence of CH₂; likewise 1467.54 cm⁻¹ stretching frequency should be attributed to amine (—NH₂) of chitosan (Zhao et al., 2014). The detected peak frequencies agrees with the functional groups of chitosan, hence complete deacetylation of chitin to chitosan.

Table 1: Elemental composition of Sawdust and Flamboyant pod

Element	Flamboyant pod	
	Weight%	Atomic%
C	44.27	57.29
O	34.2	33.23
Na	0.38	0.26
Mg	0.82	0.52
Al	1.5	0.86
Si	2.9	1.61
P	0.83	0.41
S	0.43	0.21
Cl	1.18	0.51
K	10.22	4.06
Ca	1.7	0.65
Fe	1.61	0.42

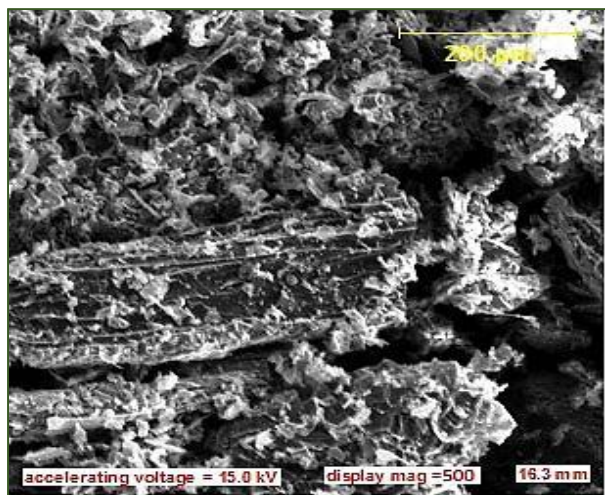


Fig. 2: Flamboyant plant pod char SEM image

The functional groups of the chitosan were determined using Fourier Transform- Infra Red microscope (FTIR). Fig. 4.1 shows the functional groups present in the chitosan extracted from periwinkle shell.

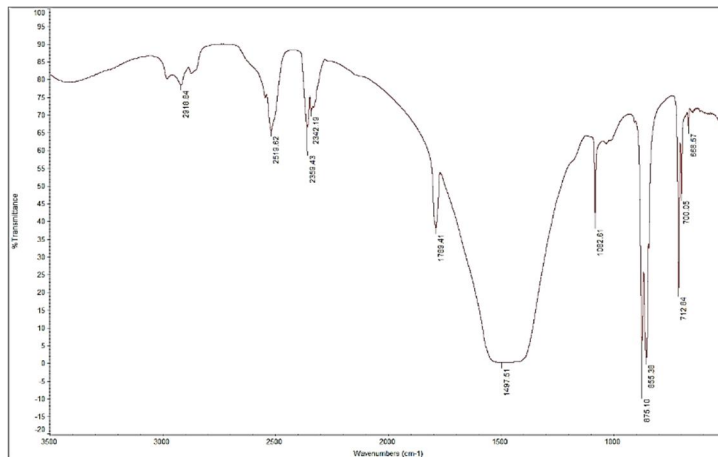


Fig. 3: FTIR of chitosan extracted from periwinkle shells

3.2 Effect of initial concentration on removal efficiency

Fig. 4 shows the adsorption of Pb²⁺ by FPPC and MFPPC with varied initial concentration of metals, while other conditions were kept constant. Although, the adsorption of Pb²⁺ was observed to be generally high, the removal efficiency increased with the initial concentration with best efficiency at 20 mg/l. As shown in Fig. 4, the efficiency of the modified adsorbent is higher than the unmodified adsorbent. The implication is that the enhancement with chitosan increases the binding site available for the uptake of the metals by the adsorbents.

Fig. 5 shows the adsorption efficiency of FPPC, MFPPC and AC for Cd²⁺ removal from industrial effluent. The trend of Cd²⁺ removal is similar to that of Pb²⁺ with best efficiency at 20 mg/l; the removal efficiency of Cd²⁺ is generally lower compared to Pb²⁺. The high adsorption of Pb²⁺ may be attributed to its higher selectivity. The order of metal selectivity is Pb²⁺ > Cd²⁺.

Although, industrial activated carbon has the highest removal efficiency, the natural adsorbents exhibited a relatively high removal efficiency. The inexpensive and abundance nature of the natural adsorbents (MFPPC and FPPC) make them more suitable for adsorption.

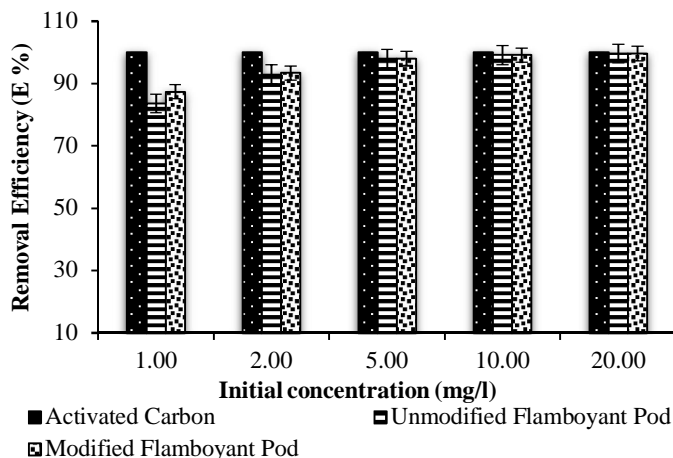


Fig. 4: Effect of initial concentration on Pb(II) removal [adsorbent dose = 1.0 g; contact time = 60 min; pH = 6.8; temp = 25°C]

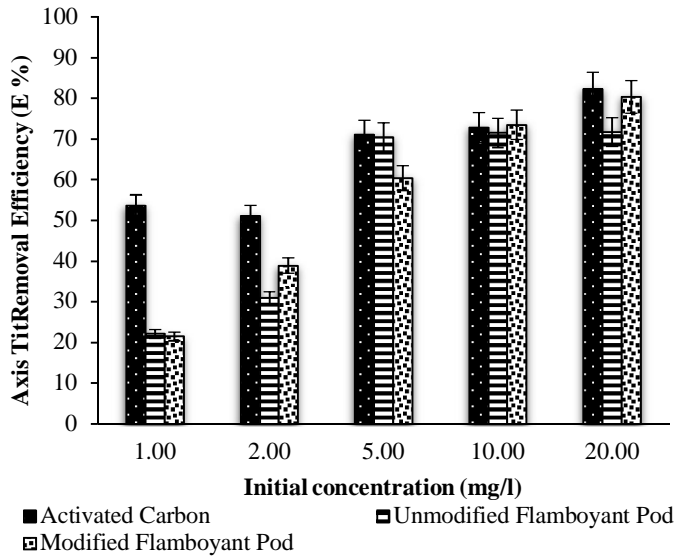


Fig. 5: Effect of initial concentration on Cd(II) removal [adsorbent dose = 1.0 g; contact time = 60 min; pH = 6.8; temp = 25°C]

3.3 Effect of pH on removal efficiency

The pH of effluent can greatly affect the adsorption capacity of the adsorbent. The adsorption as a function of pH was conducted at known initial concentration of 20 mg/L, adsorbent dose of 1.5 g, contact time of 60 min at 25 °C. The results of the investigation of the adsorption capacity of MFPPC and FPPC for Pb²⁺ and Cd²⁺ removal with varied pH are in shown in Fig. 6 and 7 respectively.

The results indicate that adsorption efficiency increases with increase in pH with the best efficiency at pH 7.5 for both metals. Higher pH values (alkaline) tend to favour adsorption efficiency (Demirbas et al., 2005; Jiang et al., 2010; Zhao et al., 2011; Deng et al., 2015; Choi et al., 2016). Same trend is observed for MFPPC; chitosan in itself has good adsorptive characteristics but because of its slight solubility at low pH, binding sites not readily available for sorption (Okoya et al., 2016a).

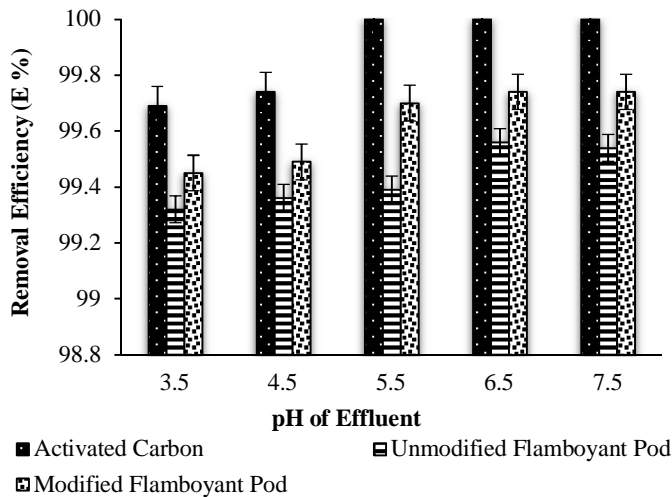


Fig. 6: Effect of pH on Pb(II) removal [Pb(II) Conc. = 25 mg/L; adsorbent dose = 1.0 g; contact time = 60 min; temp = 25°C]

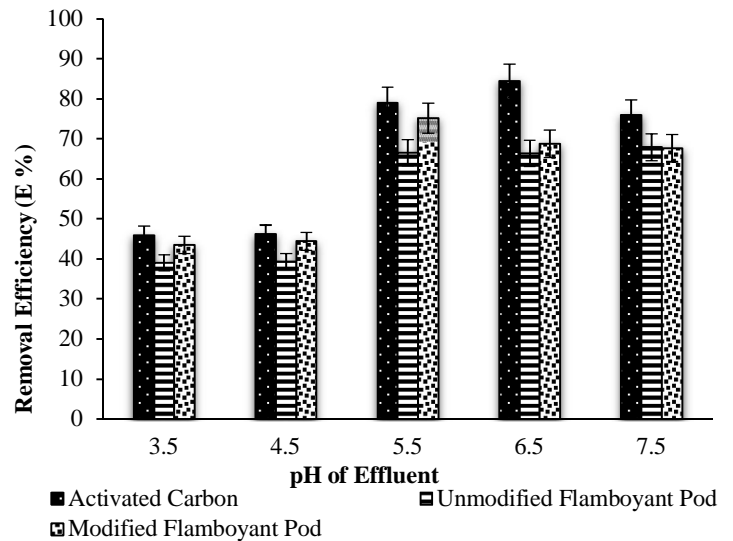


Fig. 7: Effect of pH on Cd(II) removal [Cd(II) Conc. = 25 mg/L; adsorbent dose = 1.0 g; contact time = 60 min; temp = 25°C]

3.4 Effect of adsorbent dosage on adsorption

Fig. 8 and 9 present the effect of varying adsorbent dosage on the adsorption of Pb²⁺ and Cd²⁺ respectively. The results of the effect of adsorbent dosage on the removal efficiency of lead (Pb²⁺) and cadmium (Cd²⁺) show that increase in adsorbent dosage increases adsorption efficiency with best efficiency at 2 g and 2.5 g dose respectively for Pb²⁺ and Cd²⁺. The increase in adsorption efficiency with increase in adsorbent dose as observed in this study is due to the greater availability of the exchangeable sites and increase in surface area at higher dose of the adsorbent (Asubiojo and Ajelabi, 2009; Dhabab, 2011; Gönen and Serin, 2012).

The chitosan modified adsorbent (MFPPC) exhibit greater efficiency over the unmodified adsorbent (FPPC) while commercial activated carbon shows the highest removal efficiency even at lesser dosage of about 0.5 g. Modification generally enhances the performance of the natural adsorbent (Amuda et al., 2007; Okoya et al., 2015; Okoya et al., 2016b). The trend of adsorption of Pb²⁺ and Cd²⁺ by the adsorbent is of the following order: activated carbon ≥ modified adsorbents ≥ unmodified adsorbents while the order of metal selectivity is Pb²⁺ > Cd²⁺.

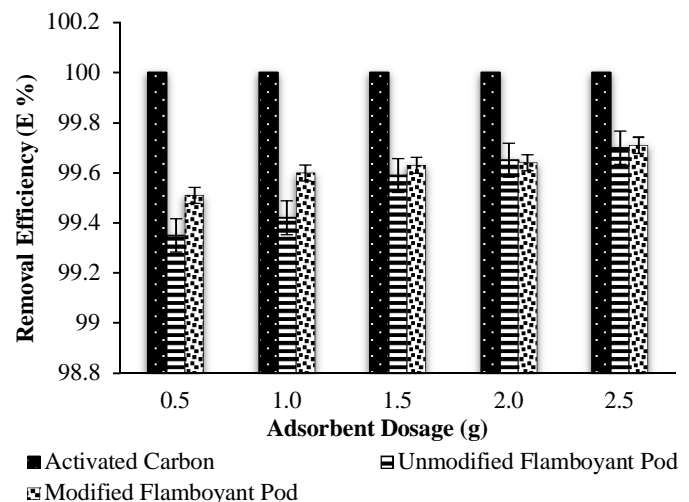


Fig. 8: Effect of adsorbent dosage on Pb(II) removal [Pb(II) Conc. = 25 mg/L; adsorbent dose = 1.0 g; pH = 6.8; temp = 25°C]

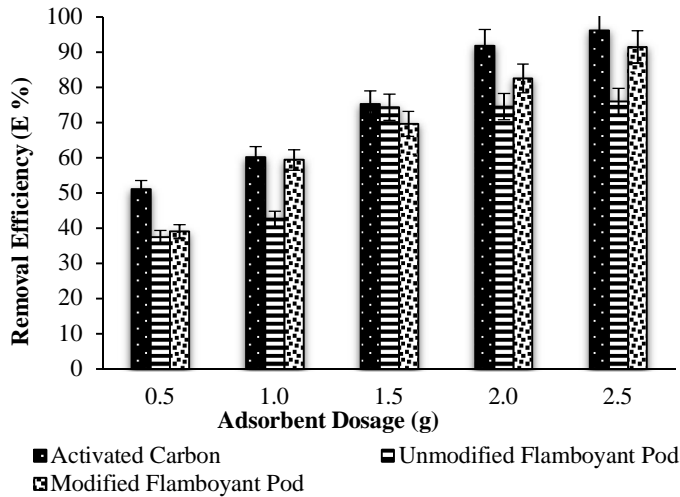


Fig. 9: Effect of adsorbent dosage on Cd(II) removal [Cd(II) Conc. = 25 mg/L; adsorbent dose = 1.0 g; pH = 6.8; temp = 25°C]

3.5 Effect of contact time on adsorption

Effect of contact time on adsorption efficiency of flamboyant pod char (modified and unmodified) were investigated in order to optimize the period for best adsorption result; the time was varied from 15 min to 90 min (15, 30, 45, 60 and 90 min). The impacts as presented in Fig. 10 and 11 for Pb²⁺ and Cd²⁺ respectively shows the contact time influence adsorption.

It was observed that the removal efficiency initially increased and then gradually remained constant with increase in agitation time and reached the equilibrium nearly at 60 min for both metals. This may be due to the initial availability of a large number of vacant sites for adsorption (Toor and Jin, 2012), later the adsorption capacity tailed off due to the saturation of vacant sites (Onundi et al., 2011).

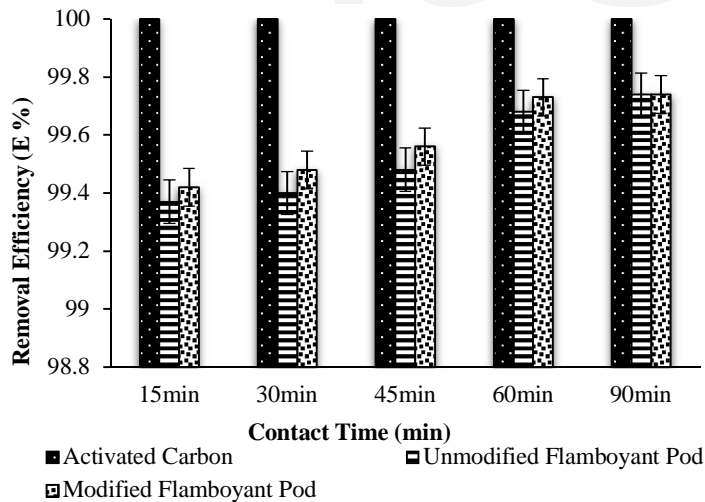


Fig. 10: Effect of contact time on Pb(II) removal [Pb(II) Conc. = 25 mg/L; adsorbent dose = 1.0 g; pH = 6.8; temp = 25°C]

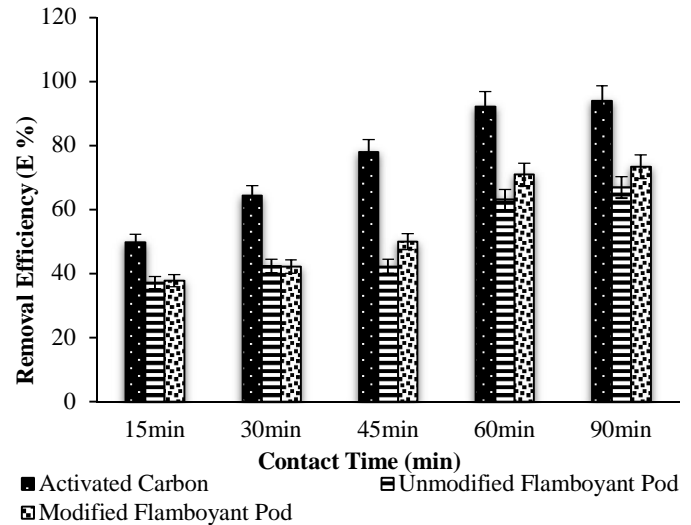


Fig. 10: Effect of contact time on Cd(II) removal [Cd(II) Conc. = 25 mg/L; adsorbent dose = 1.0 g; pH = 6.8; temp = 25°C]

3.6 Adsorption Isotherm

Adsorption isotherm is very useful in choosing the best carbon for adsorption or purification need (Ochonogor and Ejikeme, 2005). The isotherms of Freundlich and Langmuir have been widely used by several researchers (Okeola and Odeunmi, 2010; Okoya et al., 2016a). Adsorption capacity is usually predicted from equilibrium sorption isotherm (Kumar and Boobalan, 2013).

The sorption performance of FPPC and MFPPC were evaluated through the determination of adsorption isotherm with Pb²⁺ and Cd²⁺ for single metal sorption system as summarized in Table 2 and 3 respectively. Values of Q_{max} and b (Langmuir isotherms) are determined from the slope and intercepts of the plots of 1/Q against 1/C_f, while the values of K and n (Freundlich isotherms) are obtained from the intercept and slope of the graph between log Q versus log C_f.

The equilibrium experiment results of Pb²⁺ fitted well to the two adsorption isotherm. The results show that the adsorption process could be described well with both Freundlich and Langmuir isotherms.

The coefficient of correlation (R²) for both model falls within 0 < R² < 1 (Table 2 and 3). Although both models adequately describe the experimental data of the adsorption of Pb²⁺, Freundlich isotherm had a better fitting than Langmuir isotherm for all both FPPC and MFPPC. This is because the correlation coefficients of Freundlich isotherm (R²_F) is higher than the correlation coefficients of Langmuir isotherm (R²_L). The high correlation coefficient values (Table 2) for Freundlich and Langmuir isotherms confirmed the suitability of models (Amuda et al., 2007; Aggrawal et al., 2012; Okoya et al., 2015). In the case of Cd²⁺ adsorption, Langmuir isotherm and Freundlich isotherm exhibit similar trend for FPPC and MFPPC (Tables 3). Both models fit better for Cd²⁺ than Pb²⁺.

The magnitude of the adsorption capacity (K) and adsorption intensity (1/n) show that it is possible for an easy separation of heavy metal ion from aqueous solution and a high adsorption capacity. The Q_{max} value which is the maximum value of Q (the metal uptake in mg metal per g adsorbent) is important to identify the biosorbent highest metal uptake capacity and as such useful in scale-up considerations (Benguella and Benaissa, 2002; Pino et al., 2006). From this study it is therefore concluded that high capacities of Pb²⁺ and Cd²⁺ being adsorbed were observed for both FPPC and MFPPC.

Table 2: Langmuir and Freundlich constants for the adsorption of Pb²⁺ at 25°C

Adsorbent	Langmuir constants			Freundlich constants		
	b (L/mg)	Q _{max} (mg/g)	R ² _L	K	1/n	R ² _F
FPPC	-	4.39	0.85	7.76	-	0.94
	2.2760	37	02	25	0.2273	95
MFPPC	-	4.24	0.66	6.61	-	0.91
	2.8124	81	19	30	0.1794	85

R²= correlation coefficient.

Table 3: Langmuir and Freundlich constants for the adsorption of Cd²⁺ at 25°C

Adsorbent	Langmuir constants			Freundlich constants		
	b (L/mg)	Q _{max} (mg/g)	R ² _L	K	1/n	R ² _F
FPPC	1.7	136.9	0.8	69.8	0.4	0.8
	805	863	514	232	045	493
MFPPC	1.9	129.8	0.9	67.3	0.3	0.9
	250	701	141	597	648	960

R²= correlation coefficient.

4 CONCLUSION

This study showed that Agricultural wastes such as flamboyant pod and periwinkle shell, instead of constituting a nuisance to the environment could be processed to serve as cheaper, non-hazardous alternative adsorbents to the commercially expensive activated carbon for treating heavy metal contaminated wastewater. Best adsorption conditions for both flamboyant plant pod char and modified flamboyant plant pod char are 20 mg/l initial concentration for both metals; 2 g and 2.5 g dose respectively for Pb²⁺ and Cd²⁺; 7.5 pH for both metals; and 60 – 90 min contact time for both metals. The natural adsorbents exhibit a higher adsorption for Pb²⁺ and when modified with Chitosan gave improved adsorption for Cd²⁺ that is comparable to that of commercial activated carbon. The results of adsorption isotherms show that the adsorption of Pb²⁺ and Cd²⁺ by FPPC and MFPPC could be described well with both Freundlich and Langmuir isotherms.

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