

Removal of Lead and Chromium from Aqueous Solution onto Flamboyant (*Delonix regia*) Pod Activated Carbon

S. I. Mustapha^{1*}, L. T. Adewoye¹, F. A. Aderibigbe¹, M. H. Alhaji^{2,3}, M. I. Adekola¹, I. A. Tijani¹

¹Department of Chemical Engineering, University of Ilorin, Ilorin, Nigeria.

²Nigerian Institute of Leather and Science Technology, Zaria, Nigeria.

³Department of Chemical Engineering and Energy Sustainability, Universiti Malaysia Sarawak (UNIMAS), Kota Samarahan, Malaysia.

ABSTRACT: The contamination of water by potentially toxic elements is considered a global problem. It calls for a safe, economic and technological approach in order to curb and prevent the devastating effect of the menace on both human and the aquatic life. In the light of this background, the adsorption potential of flamboyant pod activated carbon (FPAC) for the removal of chromium and lead from aqueous solution was studied. The effect of contact time, pH, initial concentration as well as adsorbent dosage on the removal efficiency of both metal ions was investigated via batch adsorption. Characterization of the FPAC adsorbent was done using Brunaur Emmett Teller and Fourier transform infrared spectroscopy. The maximum adsorption capacity Q_e was found to be 34.48 and 16.13 mg/g for Pb (II) and Cr (VI), respectively. The Langmuir isotherm model showed a better fit to the equilibrium data than the Freundlich isotherm model. The mechanism of adsorption for both metal ions onto the FPAC agrees well with pseudo second order kinetic model. The results showed that FPAC has excellent adsorption properties and thus can be used as an effective low-cost adsorbent for the removal of lead and chromium ions from aqueous solution.

KEYWORDS: Flamboyant pod, activated carbon, adsorption, lead, chromium.

[Received July 5 2017; Revised August 29 2017; Accepted October 3 2017]

I. INTRODUCTION

The pollution of water by the presence of toxic heavy metals has been a topic of global concern among environmental experts. The spontaneous increase in the pollution of water by toxic heavy metal has been attributed to the breakthrough in the advancement of technologies for industrial expansions (Jimoh *et al.*, 2012). Lead and chromium are among the priority toxic pollutants present in wastewaters which are released to the environment through various industrial operations. The main industrial sources of toxic metals in waste water include; metal finishing, electroplating, metallurgical, tannery, chemical manufacturing, mining, battery manufacturing industries and textile industries (Deepa and Suresha, 2014; Olayinka *et al.*, 2009).

Lead and chromium are considered among the top sixteen toxic pollutants whose exposure is carcinogenic to both humans and aquatic animals (Choudhary *et al.*, 2015). They have adversely affected the human health and cause many diseases and allergies such as encephalopathy seizures, mental retardation, anaemia, dermatitis, severe harm to kidneys, sensory system, and reproductive system (Barbooti, 2015; Dargahi *et al.*, 2016). The maximum allowable limits of lead and chromium in wastewater as indicated by the United States Environmental Protection Agency (USEPA) are 0.1

mg/l and 1.0 mg/l, respectively (Qaiser *et al.*, 2009). As a result of the highly toxic nature of these metals even at low concentrations, there is increasing interest in the development of techniques for their removal from contaminated waters prior to their discharge into the environment.

The adsorption phenomenon is one of the physicochemical treatment processes observed to be effective for heavy metals removal from aqueous solutions. This technology has been widely preferred to other conventional methods such as ion – exchange, chemical precipitation, electro dialysis, membrane separations, reverse osmosis and solvent extraction in the removal of pollutants from wastewater due to its cost effectiveness, simple to design, ease of operation, availability and environmental friendliness (Adebisi *et al.*, 2017). Various adsorbents such as clay mineral (Barbooti, 2015), activated carbons from agricultural waste materials (Amarasinghe and Williams, 2007; Choudhary *et al.*, 2015; Garba *et al.*, 2016; Olayinka *et al.*, 2009; P. Sarma *et al.*, 2015), magnesium oxide nanoparticles (Dargahi *et al.*, 2016), vegetable waste biomass (Nadeem *et al.*, 2014) as well as biological adsorbents (Ali and Alrafai, 2016; Deepa and Suresha, 2014; Lima *et al.*, 2013) have been reported in the literature for lead and chromium removal from wastewater.

These adsorbents have been found to be effective for the removal of targeted pollutants with removal efficiencies ranging from 70 to 99.9% at varied adsorption process

*Corresponding author's e-mail address: mustapha.si@unilorin.edu.ng

conditions. During the past few decades, considerable attention has been devoted to the development of unconventional materials such as agricultural waste materials for the removal of various pollutants from wastewater due to their abundant nature, selectivity, high adsorption capacity, and easy regeneration (Zhou *et al.*, 2015).

In spite of the good performance of these adsorbents in batch adsorption process, their application at the pilot and industrial scale columns are still very challenging. Developing cost effective adsorbents that can work at conditions such as pH 7.0, normal temperature with short contact time will be a logical approach to tackling the challenges of transferring the batch mode adsorption conditions to column operations (Ali *et al.*, 2012). Besides, a single adsorbent cannot be effectively used for the removal of all kind of pollutants.

The capacity of adsorbents depends largely on the type of starting material or precursor, processing method, quantity and the preparation conditions (Zhou *et al.*, 2015). Although some works have been reported on the development of adsorbents from agricultural waste materials; however, there is still need for further research on the potential of other available agricultural waste material toward the complete removal of targeted pollutants with the capability to work at column operations.

Flamboyant pods (*Delonix regia*), a blooming tree species from the *Fabaceae* family, is known for its fern-like leaves and colourful display of flowers. After a period of maturation, the pods gradually fall off the trees and large quantities of the pods generated constitute environmental nuisance. Conversion of these low-value agricultural wastes (flamboyant pod) into useful material that can remove toxic heavy metals from wastewater would constitute a significant contribution to the search for cheaper adsorbent materials.

Hence, the study's aim was to evaluate the efficiency and effectiveness of sulphuric acid activated flamboyant pod for the removal of lead and chromium ion from aqueous solution. Consequently, the effects of various adsorption process factors such as contact time, pH, initial metal ion concentration and adsorbent dosage were investigated via batch adsorption process. Also, the adsorption isotherms and kinetics parameters were evaluated and reported.

II. MATERIALS AND METHODS

A. Preparation of Adsorbent

Flamboyant pods were collected from different locations within the University of Ilorin, Kwara State, Nigeria. The collected materials were completely washed with distilled water in order to remove dust and other adhering impurities. The washed flamboyant pods were dried at 80 °C for 24 hrs, ground and separated using sieve size of 225 µm. The uniform particle size biomaterial was subjected to carbonization process in a muffle furnace at a rate of 20 °C/min from room temperature to 500 °C and maintained at this temperature for 1.5 hours (Vargas *et al.*, 2011). A sample (400 g) of the calcined flamboyant pod was soaked in an excess of 0.2 M H₂SO₄ (purity 85%) solution for 24 hours.

This was then separated using sieve size of 65 µm and rinsed with distilled water to obtain a pH of 7; it was oven dried at 110 °C for 3 hrs and finally packaged in an airtight container for further use. The carbon prepared from flamboyant pods and activated with sulphuric acid was labelled as FP and FPAC, respectively. All the chemicals and reagents utilized were of analytical grade. Distilled water was used for all experimental work including the preparation aqueous solutions of lead and chromium metal ions. The desired pH of the aqueous solutions was adjusted using 0.1 M NaOH and 0.2 M H₂SO₄.

B. Preparation of Aqueous Solution

The stock solutions of Cr (VI) and Pb (II) metal ions of 1000 mg/ L concentrations were prepared by dissolving, 2.827 g of K₂Cr₂O₇ (Sigma – Aldrich) and 1.6 g of Pb(NO₃)₂ (Merck Germany), respectively in one litre of distilled water. Subsequently, the stock solutions were further diluted to obtain working solutions of the desired initial concentrations of lead (II) and chromium (VI).

C. Characterization of Adsorbent

The Brunaur Emmett Teller (BET) and Fourier transform infrared spectroscopy (FTIR) techniques were used to characterize the prepared adsorbent. The surface area and porosity measurement of the FP and FPAC were carried out using Quantachrome NOVA 4200e UK, surface area and pore size analyzer. The sample in the form of powder was loaded in a bulb ended quartz tube and heated in the furnace to about 350 °C for outgassing under the flow of liquid nitrogen for about 8 hours in order to remove moisture and contaminants. Fourier transform infrared (FTIR) spectroscopy technique was used to establish the presence of surface functional groups responsible for the lead and chromium adsorption. The FTIR analyses before and after metal ion adsorption were carried out on the samples using Perkin - Elmer spectrum with a resolution of 4 cm⁻¹ in the range of 4000 - 500 cm⁻¹.

D. Adsorption Experiments

Batch adsorption studies were conducted to examine the effect of solution pH, contact time, metal ion initial concentration, and adsorbent dosage on the removal of lead and chromium ion onto FPAC by studying one of the factors at a time and keeping other factors fixed. Different doses of adsorbents ranging from 10 – 50 mg were separately mixed with 25 mL of aqueous solution put into 100 mL Erlenmeyer flasks containing different initial concentrations (between 5–25 mg/L) for both chromium and lead ion. The pH of the solution was varied between the pH value of 5 and 9 using either 0.1 M NaOH or 0.2 M H₂SO₄.

The mixture was shaken constantly using an orbit shaker at 140 rpm speed for varying contact time interval from 20 to 70 mins. The mixture was then filtered and the residual concentration of metal ions was analyzed using Atomic Absorption Spectrophotometer (AAS) (BUCK Scientific ACCUSYS 211). The percentage removal of the lead and chromium ions was determined by using eqn (1).

$$\% \text{ Removal} = \frac{(C_o - C_e)}{C_o} * 100 \quad (1)$$

Where; C_o and C_e (mg/L) are the concentrations of Pb (II) and Cr (VI) in the aqueous solution at initial stage and at equilibrium, respectively.

The equilibrium amount (Q_e) of lead and chromium ion removed per mass of adsorbent was evaluated using the equation 2:

$$Q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

Where; Q_e (mg g⁻¹) is the amount of metal ion adsorbed per unit mass of adsorbent at equilibrium. V (L) is the volume of the solution and W (g) is the mass of FPAC used. Each of the experiment was repeated twice and the mean values considered.

i. Effect of Contact Time

In order to investigate the effect of contact time, 25 mL of the aqueous solution containing 5 mg/L of initial metal concentration was taken into 100 mL Erlenmeyer flasks and 10 mg of the FPAC adsorbent was added. The mixture was shaken constantly using an orbit shaker at 140 rpm speed for varying contact time from 20 to 70 mins at 10 mins interval. At the end of each contact time period, the mixture was filtered and the residual of lead and chromium concentrations in solution were determined using AAS.

ii. Effect of pH

The effect of pH on adsorption of the metals was investigated by adding 10 mg of FPAC to 25 mL of the aqueous solution containing 5 mg/L of initial metal ion concentration. The pH of the solution was varied between the pH value of 5 and 9 using either 0.1M NaOH or 0.2M H₂SO₄. The blend was shaken for 30 mins and then filtered and the amount of metal ion adsorbed was determined.

iii. Effect of Initial Concentration

In order to investigate the effect of concentration on the adsorption of metal ion, 10 mg of FPAC adsorbent was added to 25 mL of the metal solutions of different initial concentrations (between 5–25 mg/L) for both chromium and lead ion. The resultant solution with the adsorbent in the flask was shaken for 30 mins at 140 rpm, filtered and analyzed.

iv. Effect of Adsorbent Dosage

In order to study the effect of adsorbent dose on the adsorption of lead and chromium, various doses of adsorbents ranging from 10 – 50 mg were separately mixed with 25 mL of aqueous solution put into 100 mL Erlenmeyer flasks containing 25 mg/L of initial metal ion concentration. The mixture was shaken constantly using an orbit shaker for 30

minutes at 140 rpm, filtered and the residual chromium and lead concentrations in solution were determined.

E. Adsorption Isotherm

The equilibrium relationship between the adsorbate concentration in the solution and on the surface of the adsorbent at a specified condition is described through adsorption isotherm models. The adsorption isotherms of Pb (II) and Cr (VI) ions onto FPAC were determined at different concentrations ranging from 5 to 25 mg/L on a fixed amount of adsorbent (FPAC). Langmuir and Freundlich isotherm models were used to describe the equilibrium characteristic of this adsorption study.

i. The Langmuir isotherm model

Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. The linearized form of the Langmuir isotherm model (Langmuir, 1918) is given as:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}} \quad (3)$$

Where; Q_{max} (mg/g) is the maximum monolayer adsorbent capacity and b (L/mg) is the Langmuir constant related to the energy of adsorption.

ii. The Freundlich isotherm model

Freundlich isotherm assumes heterogeneous adsorption surface and the linearized form of the Freundlich model (Clayton, 1926) is given as:

$$\ln Q_e = \ln k_f + (1/n) \ln C_e \quad (4)$$

Where; k_f (L/g) and n are the Freundlich isotherm parameters which reveal the capacity and intensity of the adsorption, respectively. The adsorption process is identified to be physical when $n > 1$, chemical when $n < 1$ or linear when $n = 1$. Generally, $n > 1$ suggests favourable adsorption (Garba *et al.*, 2016).

F. Adsorption Kinetics

Pseudo first-order and pseudo second order kinetic models were used to analyze the rate and mechanism of adsorption of the metal ions onto FPAC.

i. The Pseudo First Order Kinetic Model

The mathematical expression in linearized form for the pseudo first order model (Lagergren and Svenska, 1898) is given as:

$$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t \quad (5)$$

Where; k_1 (min⁻¹) is the pseud-first order rate constant, Q_e (mg/g) and Q_t (mg/g) are the amount of metal ion adsorbed per unit mass of FPAC adsorbent at equilibrium and at time t (min), respectively.

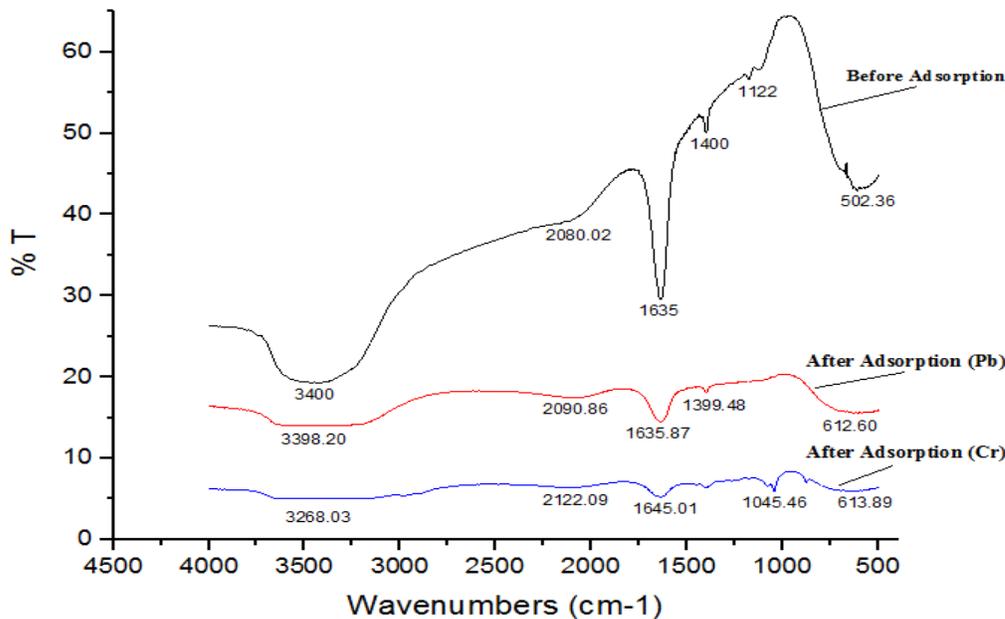


Figure 1: FT-IR of FPAC before and after Adsorption of the Metal Ions.

ii. The Pseudo Second Order Kinetic Model

The mathematical expression of pseudo second order model in linearized form (Ho and McKay, 1999) is given as:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{6}$$

Where; k_2 (g/mg min) is the model rate constant.

III. RESULTS AND DISCUSSION

A. Characterization of Adsorbent

The Brunauer Emmett Teller (BET) analysis of the calcined flamboyant pod (FP) and the sulphuric acid activated flamboyant pod (FPAC) are presented in Table 1. The BET surface area result as shown in Table 1 increased from 379.13 m²/g to 719.34 m²/g as a result of the effect of acid activation on the calcined flamboyant pod. The high value of surface area obtained is an indication that the FPAC may have better metal ion uptake capacity. This can be compared with the surface area of some commercial activated carbons found in the literature (Auta and Hameed, 2011; Ozcan et al, 2004). Also, based on the results obtained, both FP and FPAC adsorbents were found to be mesoporous (2 – 50 nm) in nature with the average pore diameter Dp of 3.17 nm and 2.94 nm, respectively.

The results of the FT- IR study carried out and the spectra are shown in Figure 1. The FT-IR spectra for the FPAC before adsorption, after adsorption of lead (II) and chromium (VI), are shown in Figure 1. The broad peak observed at 3400 cm⁻¹ corresponds to O-H stretching and N-H stretching presenting amino group (Krishnie *et al*, 2011; Kaiser *et al*, 2009).

A medium peak assigned as alkynes with stretches of C≡C was found around 2080.02 cm⁻¹. The sharp peak located at 1635 cm⁻¹ suggests the character of a typical carbonyl group (C=O) stretching from aldehydes and ketones. The presence of O-H, alkynes stretches of C≡C, along with the carbonyl group, confirms the presence of carboxylic acid groups in the adsorbent (Choudhary *et al*, 2015).

The peaks at 1400 cm⁻¹ and 1122 cm⁻¹ are associated with the C-H and C-O bonds. The FPAC after adsorption of Cr (VI) had its O–H/N-H at the broad peak of 3268.03 cm⁻¹ with C – H stretching vibrations of methyl radicals at the signal of 2980.46 cm⁻¹. After lead and chromium adsorption, the O-H, N-H, carbonyl and carboxylic functional groups were found on the FPAC with significant shifts in the bands suggesting that chemical interactions between the metal ions and the functional group occur on the FPAC surface (Deepa and Suresha, 2014; Duran *et al*, 2011; Ozcan *et al*, 2004; Kaiser *et al*, 2009). Hence, the main functional groups present in the FPAC adsorbent responsible for the adsorption activities of both lead and chromium are O-H, N-H, carbonyl and carboxylic groups.

Table 1: The BET Characterization of the Adsorbent.

Sample	BET surface area, S _{BET} (m ² /g)	Micropore surface area, S _{mic} (m ² /g)	Micropore volume, V _{mic} (cm ³ /g)	Pore Size, Dp (nm)
FP	379.13	346.10	0.123	3.17
FPAC	719.34	888.40	0.316	2.94

B. Adsorption Experiments

i. Effect of Contact Time

The removal efficiency of Pb (II) and Cr (VI) onto FPAC as a function of contact time in the range of 20 – 70 mins is shown in Figure 2. The figure reveals that the maximum removal efficiency of 98.4% and 94.4% for Pb and Cr ions, respectively was achieved within 20 – 30 minutes. This rapid adsorption process within the first 30 mins may be attributed to effective contact and availability of active adsorption sites (Choudhary *et al.*, 2015; Jimoh *et al.*, 2012).

After the equilibrium was attained at 30 mins, it was followed by a progressive drop in metal uptake. Slow pore intra – particle diffusion of the metal ion to the interior of the adsorbent and the electrostatic hindrance caused by already sorbed metal ion accounts for the subsequent slower sorption rate as the contact time increases. The trend of adsorption observed was Pb (II) > Cr (VI) as shown in Figure 2. This may be attributed to that fact that metal ion with smaller ionic radii diffuses faster than metal ion with larger ionic radii (Jimoh *et al.*, 2012). A similar trend was reported by Qaiser *et al.* (2009) who studied the potential of groundnut hull for the removal of lead (II) and chromium (VI) from wastewater.

ii. Effect of pH

The solution pH is an important controlling factor in heavy metal adsorption process which affects the surface charge of the adsorbent material, the degree of ionization and the specification of metals in the solution (Choudhary *et al.*, 2015). The pH of the solution was varied between the pH value of 5 and 9 and the effect of the pH on the percentage removal of Pb and Cr at initial metal ion concentration of 5 mg/L, the adsorbent dosage of 10 mg and contact time of 30 min is shown in Figure 3. As shown in the figure, it can be observed that the percentage removal of Pb increased from 94.5% to 99.1% between the pH of 5 and 6 while the percentage removal of Cr increased from 91.5% to 97.3% between the pH of 5 and 7. Further increase in pH leads to decrease in the percentage removal of both metal ions.

The maximum removal of 97.3% was attained at pH of 6.0 for lead (II) whereas, in the case of chromium (VI), the maximum removal of 99.1% was achieved at pH of 7.0. At low pH values, the competition for binding sites between the metal cations and protons may possibly be responsible for the reduced uptake capacity of the metal. However, with an increase in pH, the negatively charged adsorbent was expected to attract the positively charged lead and chromium ions (Sarma *et al.*, 2015). This electrostatic attraction may possibly be responsible for higher metal uptake at higher pH than at low pH value. Although, beyond pH 7, a slight decrease in the metal uptake was observed which might be due to numerous competition between OH⁻ and binding sites of FPAC.

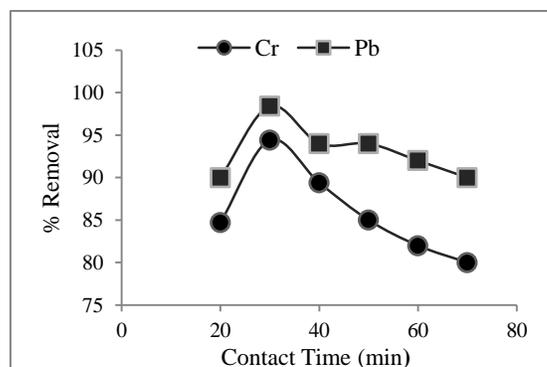


Figure 2: Effect of Contact Time on Adsorption of Pb/Cr on FPAC [Ambient Temperature = 30 °C; pH = 7; Metal ion conc. = 5 mg/L; Adsorbent dosage = 10 mg].

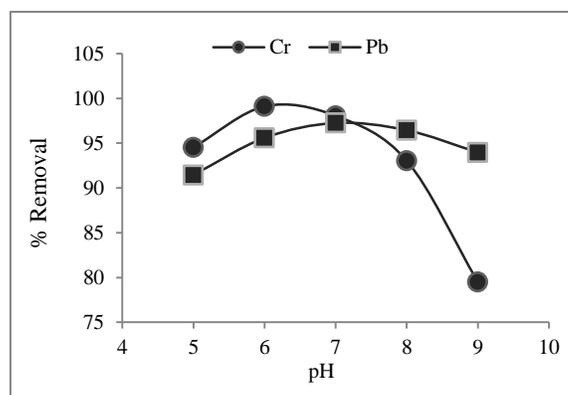


Figure 3: Effect of pH on Adsorption of Pb/Cr on FPAC [Ambient Temperature = 30 °C; Metal ion conc. = 5 mg/L; Adsorbent dosage = 10 mg; Contact time = 30 mins].

iii. Effect of Initial Concentration

The effect of initial metal ion concentration on the removal efficiency of FPAC was investigated and presented in Figure 4. The removal efficiency of lead decreased from 97.43% to 89.77% with an increase in the metal ion concentration. This can be attributed to the lack of sufficient surface area to accommodate more metal ions thereby leading to competition between metal ions to adsorb on the limited available active site of the adsorbent.

On the other hand, the removal efficiency of chromium increased from 74.76% to 99.6% with an initial metal ion concentration increased from 5 mg/L to 25 mg/L. This shows that more molecules of the chromium ions in solution competed for available binding sites of the adsorbent at higher concentrations than at lower concentrations. These findings agree well with previous studies carried out in similar work (Deepa and Suresha, 2014; Jimoh *et al.*, 2012; Olayinka *et al.*, 2009).

iv. Effect of Adsorbent Dosage

The effect of adsorbent dosage in the range of 10 mg to 50 mg at an initial metal ion concentration of 25 mg/L, pH of 7 and contact time of 30 min was investigated. As shown in Figure 5, the percentage removal of chromium ion increased from 89.5% to 99.7% with an increase in adsorbent dosage from 10 mg to 50 mg. This increase in chromium uptake as a result of an increase in adsorbent dosage was due to the availability of more number of active sites on the surface of FPAC for the adsorption of Cr (VI) (Krishna and Swamy, 2011).

A trend that is similar was observed for lead ion adsorption though the percentage removal increased from 92.5% to 97.2% as the dosage increases from 10 mg to 30 mg and thereafter decreased to 94.4% with a further increase in adsorbent dose to 50 mg. Thus, the percent adsorption of lead ion increased with the adsorbent dosage and reached an equilibrium value after certain dosage. The reason for the decrease may be due to aggregation or overlapping of the adsorption sites which could lead to an overall decrease in available binding sites (Choudhary *et al*, 2015; Nethaji and Sivasamy, 2014).

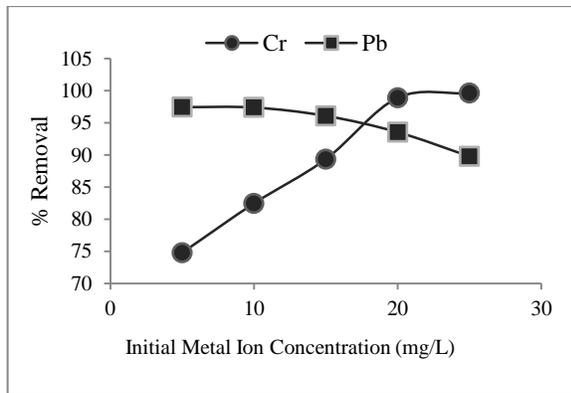


Figure 4: Effect of Initial Metal Ion Concentration on Adsorption of Pb/Cr on FPAC [Ambient Temperature = 30 °C; pH = 7; Adsorbent dosage = 10 mg; Contact time = 30 mins].

C. Adsorption Isotherm

The results of adsorption studies of Pb (II) and Cr (VI) at different concentrations ranging from 5 to 25 mg/L on a fixed amount of adsorbent are expressed by Langmuir and Freundlich isotherm models.

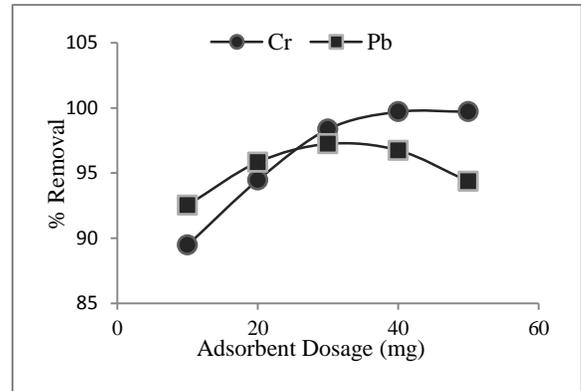


Figure 5: Effect of Adsorbent Dosage on Adsorption of Pb/Cr on FPAC [Ambient Temperature = 30 °C; pH = 7; Metal ion conc. = 25 mg/L; Contact time = 30 mins].

i. The Langmuir isotherm model

The Langmuir isotherm (Equation 3) was evaluated by plotting C_e/Q_e against C_e and straight lines shown in Figure 6 were fitted by regression for both Pb (II) and Cr (VI) adsorption data. The value of Q_{max} and b were evaluated from the slope and intercept of lines in Figure 6 and are presented in Table 2.

The dimensionless separation factor (R_L) was used to discuss the essential characteristics of Langmuir model which is given as:

$$R_L = \frac{1}{1 + bC_o} \tag{7}$$

Where C_o is the initial concentration of metal ion (mg/L) The value of R_L determined, gives information about the nature of adsorption.

It indicated the type of Langmuir isotherm to be favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).

As shown in Table 2, the values of R_L were found to be 0.046 and 0.031 for the concentration of 5 mg/L of Pb and Cr metal ions, respectively.

The values obtained in the range of 0 - 1 which indicates favourable adsorption. As presented in Table 2, the correlation coefficient values for both, Pb ($R^2 = 0.999$) and Cr ($R^2 = 0.906$) showed very good linearity to both metal ions. This is an indication of a strong positive relationship for the adsorption data.

Table 2: Langmuir and Freundlich Isotherms for Pb (II) and Cr (VI) Adsorption on FPAC.

Metal Ion	Langmuir isotherm model				Freundlich isotherm model		
	Q_{max} (mg/g)	b	R_L	R^2	k_f	n	R^2
Pb	34.48	4.14	0.046	0.999	25.30	3.28	0.945
Cr	16.13	6.21	0.031	0.906	17.10	3.53	0.492

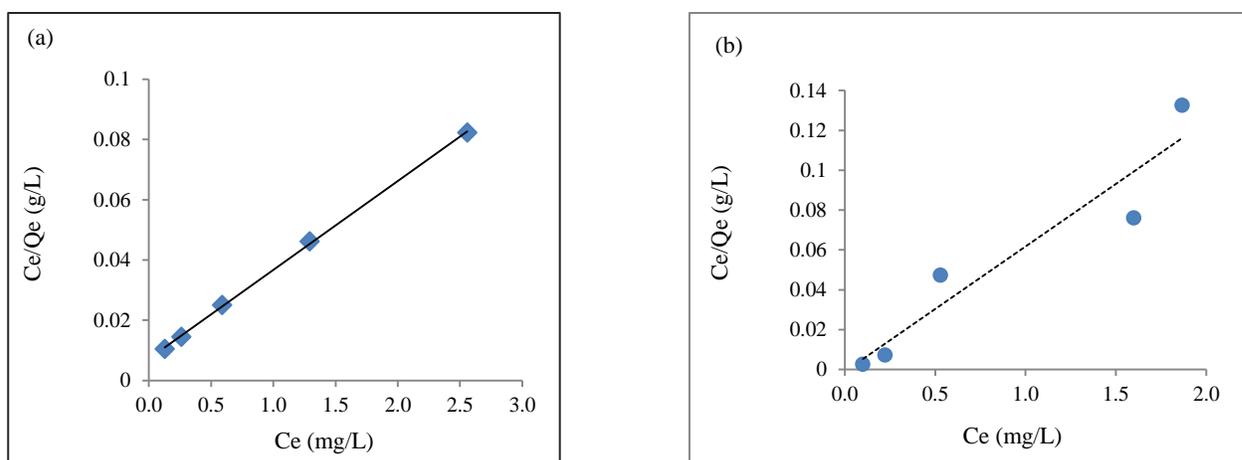


Figure 6: Langmuir adsorption isotherm plot for (a) Pb (II) (b) Cr (VI).

Table 3: Comparison of monolayer adsorption of Pb (II) and Cr (VI) onto various Adsorbents.

Adsorbents	Q_{\max} (mg/g)		References
	Pb (II)	Cr (VI)	
FPAC	34.48	16.13	This work
Magnesium oxide nanoparticles	21.78	16.44	(Dargahi <i>et al.</i> , 2016)
<i>Ficus nitida</i> leaves	-	21.0	(I. H. Ali and Alrafai, 2016)
Sorghum roots	-	20.703	(Choudhary <i>et al.</i> , 2015)
Vegetablewaste biomass	0.465	1.089	(Nadeem <i>et al.</i> , 2014)
<i>Araucaria cookii</i> leaves	37.03	-	(Deepa and Suresha, 2014)
Groundnut hull	31.54	30.21	(Qaiser <i>et al.</i> , 2009)
Biological activated dates stem	27.03	-	(Yazid and Maachi, 2008)
<i>Ficus religiosa</i> leaves	37.45	26.25	(Qaiser <i>et al.</i> , 2007)
Bagasse fly ash	2.5	4.35	(Gupta and Ali, 2004)

The maximum monolayer adsorption capacity (Q_{\max}) values of 34.48 mg/g for lead and 16.13 mg/g for chromium observed in this study compared well with some other adsorbents reported from literature as shown in Table 3.

ii. The Freundlich isotherm model

The Freundlich isotherm (Equation 4) was evaluated by plotting $\ln Q_e$ versus $\ln C_e$ and straight lines as displayed in Figure 7 were fitted by regression. The Freundlich model constants (k_f and n) values obtained from the slope and intercept of lines in Figure 7 are shown in Table 2.

The n – values obtained were in the range of 3 to 4 for both metal ions which indicates a physical and favourable adsorption of Pb and Cr onto FPAC.

As shown in Table 2, the values of correlation coefficient (R^2) of both model revealed that the Langmuir isotherm model showed a better fit to the equilibrium data than the Freundlich isotherm model. Thus, the present adsorption of Pb and Cr onto FPAC can be interpreted as monolayer adsorption.

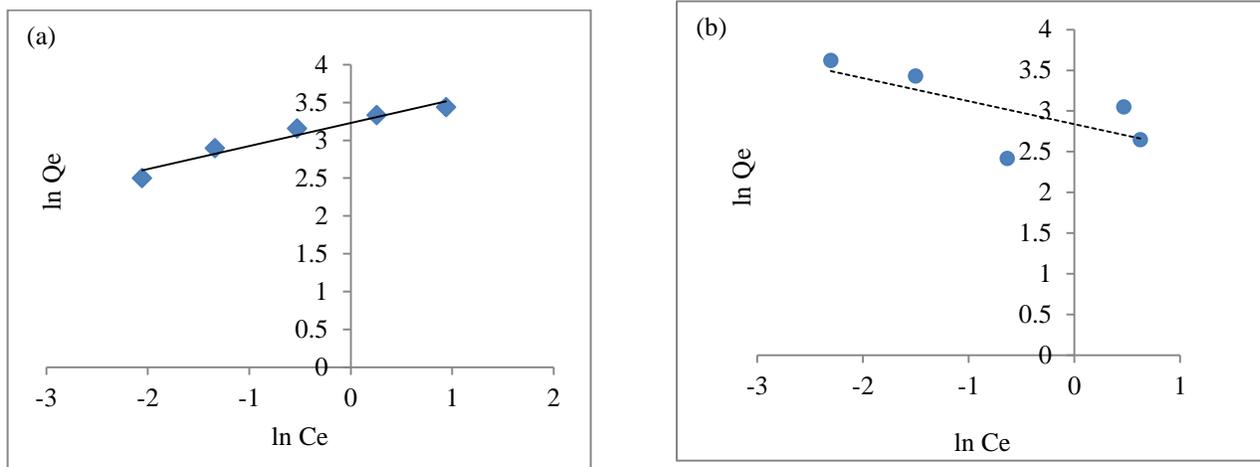


Figure 7: Freundlich adsorption isotherm plot for (a) Pb (II) (b) Cr (VI).

D. Adsorption Kinetics

Pseudo first-order (Equation 5) and pseudo second order (Equation 6) kinetic models were used to analyze the rate and mechanism of adsorption of the metal ions onto FPAC.

i. The Pseudo First Order Kinetic Model

The values of k_1 and Q_e were determined from the slope and intercept of lines of the plots of $\log(Q_e - Q_t)$ against (t) shown in Figure 8 and the respective values were presented in Table 4. The linear plots of $\log(Q_e - Q_t)$ versus t gave poorly fitted curves. Also, the values of experimental Q_e for both metal ions was observed to differ from the model Q_e values suggesting the mechanism of the adsorption was not well described by this kinetic model.

ii. The Pseudo Second Order Kinetic Model

The values of Q_e and k_2 were determined from the slope and intercept of lines of the plots of t/Q_t against time (t) as displayed in Figure 9. The Plots of t/Q_t against time (t) gave excellently fitted curves ($R^2 = 0.98$ for Pb (II); 0.99 for Cr (VI)). The parameters generated from the plots of pseudo second order kinetic model for the adsorption of Pb and Cr on FPAC are presented in Table 4. The value of Q_e from the plots for both metal ions (Table 4) conform to the experimental Q_e indicating that pseudo second order mechanism represented the data more appropriately. The applicability of this model suggested that the adsorption of Pb (II) and Cr (VI) onto FPAC was controlled by a chemical reaction between the metal ions and the active sites of the adsorbent.

The FTIR spectra of FPAC (Figure 1) before and after adsorption of Pb (II) and Cr (VI) also supported this argument.

Table 4: Pseudo-first order and Pseudo-second order kinetic model parameters for Pb (II) and Cr (VI) Adsorption onto FPAC.

Metal ion	Pseudo – first order parameters			Pseudo – second order parameters		
	Q_e (mg/g)	k_1 (min^{-1})	R^2	Q_e (mg/g)	k_2 (g/mg min)	R^2
Pb	0.176	0.020	0.10	9.901	0.016	0.98
Cr	0.348	0.023	0.18	9.615	0.024	0.99

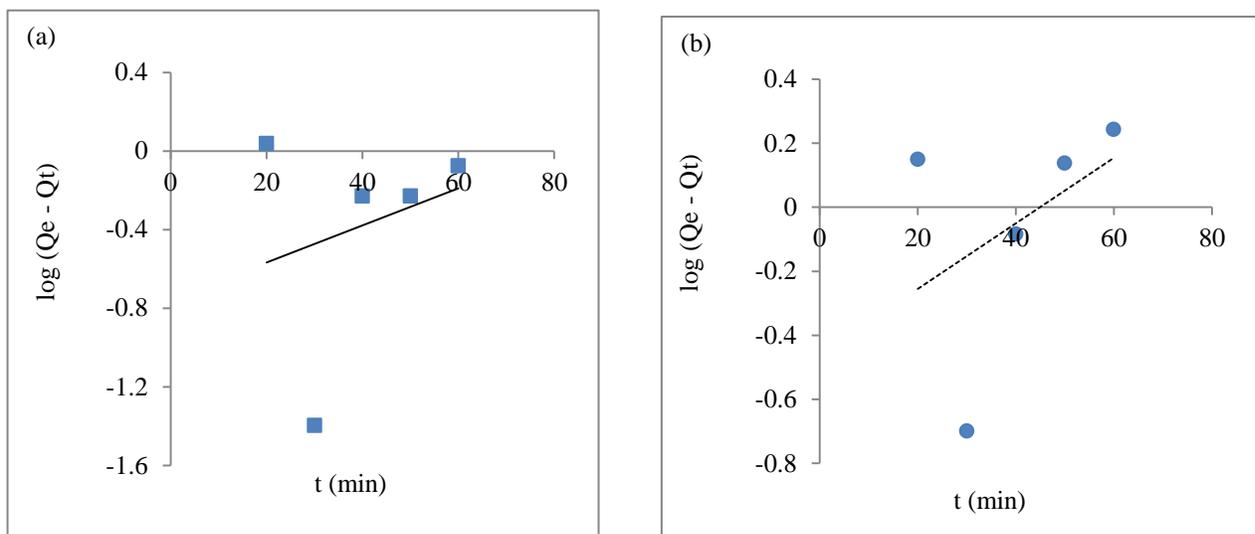


Figure 8: Pseudo – first order kinetic model plot for adsorption of (a) Pb (II) (b) Cr (VI).

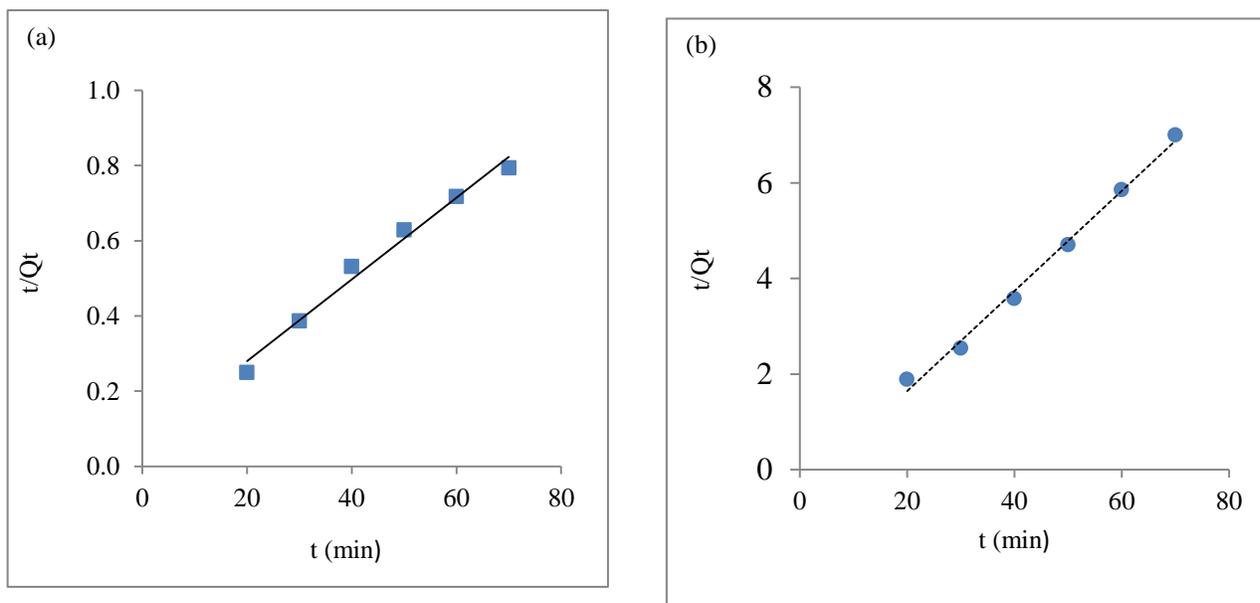


Figure 9: Pseudo – second order kinetic model plot for adsorption of (a) Pb (II) (b) Cr (VI).

CONCLUSIONS

The prepared sulphuric acid activated flamboyant pod is an efficient and cost-effective adsorbent for the removal of lead and chromium ion from aqueous solutions. The removal efficiency of Pb (II) and Cr (VI) was influenced by pH, contact time, initial metal ion concentration and adsorbent dosage. The maximum adsorption was at pH 6, contact time 30 mins, the adsorbent dosage of 50 mg with percentage removal of 99.7% of chromium and pH 7, contact time 30 mins, adsorbent dosage 30 mg with percentage removal of 97.2% of the lead metal ion. Langmuir model showed a better fit to the equilibrium data than the Freundlich isotherm model. The kinetics of adsorption for both metal ions was well represented by pseudo - second order kinetic model.

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