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Biosorption of Phenols and Dyes on *Albizia lebbeck* (Rattle Seed) Pod: Equilibrium and Kinetic Studies

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Abstract

The study investigated the possibility of using Albizia lebbeck pod (rattle seed pods): a low-cost adsorbent for the removal of phenol, 2, 4, 6-Trichlorophenol (2,4,6-TCP), a cationic (Methylene blue) and an anionic (Methyl orange) dyes from aqueous solution. Batch adsorption studies were conducted to examine the influence of pH, temperature, initial metal ion concentration; sorbent dose and contact time on the biosorption of phenol, 2, 4, 6-Trichlorophenol (2,4,6-TCP), Methylene blue and Methyl orange dyes by Albizia lebbeck pod. Langmuir, Freundlich, and Temkin models were used for the study of equilibrium data while Pseudo-first order, Pseudo-second order, Elovich and Intra-particle diffusion models were used to examine the kinetic data. The biosorbent before and after use were characterized by Fourier Transform Infrared Spectroscopy, FTIR and the residual adsorbate concentration was determined using the Ultraviolet-Visible Spectrophotometer, while the amount adsorbed was calculated by difference. The trend in biosorption is in the order of 2,4,6-TCP ≻ phenol ≻ methylene blue ≻ methyl orange. Pseudo-first order favoured the biosorption process of phenol, while Pseudo-second order favoured the biosorption of 2,4,6-TCP. The result showed that the sorption capacity increased with increase in initial concentration of adsorbate and it was pH dependent. The FTIR revealed that the active groups that play significant role in the biosorption process are $-OH_{stretch}\ (hydroxyl)$, $C=C_{stretch}\ aromatic$, $C-H_{bending}$ *and the* $C-H_{stretch}$.

Keywords: Biosorption, *Albizia lebbeck* pod, 2,4,6-Trichlorophenol, Phenol, Methylene blue, Methyl orange.

Introduction

One of the major problems of the industrial waste is the great amount of wastewater produced and the high investment needed for the treatment of this effluent before it is released in the environment. Pollution of water is a major environmental problem. The self-purification capacity of surface water and changes in the availability of food; have been extremely threatened by industrial effluents which are major sources of pollutants in the aquatic ecosystems (Udiba *et al.,* 2014). Modern industry is to a large extent responsible for the contamination of the environment. Lakes, rivers and oceans are being overwhelmed with bacteria and waste matter. Among toxic substances reaching hazardous levels are heavy metals and organic pollutants (Vieira and Volesky, 2000). Wastewater and effluents from industries such as paint, pesticides, coal conversion, petrochemicals, textiles, petroleum and phenolic resin industries are major sources of phenols and dyes in aquatic environment (Handan *et al., 2005*). The health of about 40 million people in Nigeria is at risk due to the problem associated with inadequate water resources in Nigeria (World Health Organization, 1997). It has being observed that in Nigeria, many factories are located on river banks, using the river as open sewer for their effluents and the contamination of the surface water with organic substances from agricultural activities mostly occur in the rural areas (World Health Organization, 1997).

Phenolic compounds in wastewater causes a serious discharge problem due to their poor biodegradability, high toxicity and long term ecological damage. They are strictly regulated due to their high toxicity and harmless compounds have been used to substitute their use in industries to a great extent (Bayramoglu *et al.,* 2009). 2,4,6-Trichlorophenol also known as TCP, phenaclor, Dowicide-2S, Dowcide 2S and omal is a chlorinated phenol has been used as a fungicide, herbicide, insecticide, antiseptic, defoliant and glue preservative (Ogunniyi *et al*., 2000 and Agency for Toxic Substances and Disease Registry, 1990). It is a yellow solid or flakes with a strong, sweet odour, and decomposes on heating to produce toxic and corrosive fumes. It has an odour threshold of 0.0026 ppm. 2,4,6-TCP is carcinogenic in animals, causing lymphomas, leukaemia and liver cancer via oral exposure and has been classified as a Group B2 (probable human carcinogen) by the United States Environmental Protection Agency (US EPA). (USEPA, 2000 and the Carcinogenic Potency Database Project, 2007).

Synthetic dyes however are often highly toxic and carcinogenic. Dyes consist of two main groups of compounds - chromophores and auxochromes. Chromophores determine the color of the dye while the auxochromes determine the intensity of the color (Moussavi and Mahmoudi, 2009). Most of these dyes are of synthetic origin and toxic in nature with suspected carcinogenic and

genotoxic effects (Chatterjee *et al*., 2005; Daneshvar *et al*., 2007). The presence of these dyes even at a very low concentration is highly observable and undesirable. Therefore, dye removal has been a very important but challenging area of wastewater treatment (Hu *et al*., 2006). The effluents containing dyes are highly coloured and they cause serious water pollution. Many health related problems such as allergy, dermatitis, skin irritation, cancer, and mutations in humans are associated with dye pollution in water (Bhattacharyya and Sharma, 2004). Today there are more than 100,000 dyes with different chemical structures available commercially (Robinson *et al*., 2001). Dyes are broadly classified as anionic such as methyl orange, cationic such as methylene blue and non-ionic such as azo-dispersive dyes, depending on the ionic charge on the dye molecules. Cationic dyes are more toxic than anionic dyes (Hao *et al*., 2000).

Many methods such as chemical oxidation, adsorption, microbial degradation, ion exchange, precipitation and solvent extraction have been used for the removal of phenol, phenolic compounds and dyes from aqueous solution. Adsorption is being used extensively for the removal of a wide range of organic pollutants due to its simplicity and efficiency (Ahmed and Theydan, 2013 and Uddin *et al.*, 2007). Activated carbon is the most widely used adsorbent and has a high adsorption capacity for phenolic compounds, as a result of its high surface area per unit mass (Banat *et al.,* 2000). Different low cost sorbents have been explored by various researchers for phenols, phenolic compounds and dye removal from wastewater in their raw form or as an activated carbon from different starting materials such as palm seed coat (Rengaraj *et al.,* 2002), *Albizia lebbeck* seed pod (Ahmed and Theydan, 2013), rice husk, saw dust and Casuarina wood (Swamy and Devi, 2012; Batzias and Sidiras, 2007; Khattri and Singh, 2009), coconut husk (Vinod and Anirudhan, 2002; Jain and Shrivastava, 2008; Low and Lee, 1990; Gupta *et al*., 2010), coconut shell (Radhika and Palanivelu, 2006; De Sousa *et al*., 2010; Babel and Kurniawan, 2004), particle board waste (Girods et al., 2009) peanut shell (Tanyildizi, 2011), orange peels (Khaled *et al*., 2009; Arami *et al*., 2008), wheat shell (Bulut and Aydin, 2006), pineapple stem (Hameed *et al*., 2009), to mention a few.

However, in recent times, high cost and problem of regeneration of activated carbon in the adsorption of phenol, 2,4,6-TCP, methyl orange and methylene blue has led to the growing interest in other substitutes as low cost adsorbents. Biosorption has proven as an alternative efficient technique for the removal of pollutants (heavy metals and organics) from aqueous solutions and biosorbents derived from different plants and microorganisms have been used.

Theydan and Ahmed (2013) investigated the use of activated carbon from *Albizia lebbeck* seed pods for adsorption of para-chlorophenol and there is dearth of information on the use of *Albizia lebbeck* pods as a biosorbent for the removal of phenols. In this study, *Albizia lebbeck* pod is used as a biosorbent for the removal of phenol and 2, 4, 6-Trichlorophenol, methyl orange and methylene blue from aqueous solution. *Albizia lebbeck* seed pods are readily available high volume waste, thus makes it suitable as a low cost biosorbent.

Materials and Method
Material and Chemicals
Albizia lebbeck is a plant species native to tropical and subtropical regions of Africa, Australia and Asia. It is often simply called *"Indian Siris"* or *"Igbagbo"* in Yoruba language and **"Rattle seed pods"** in English language**.** The *Albizia lebbeck* pods were obtained from the site of University of Ibadan, Oyo state, Nigeria. The pods were hand-picked from around the tree and the seeds were removed from the pods. All chemicals (phenol, 2,4,6-Trichlorophenol, methylene blue, methyl orange, sodium hydroxide pellets, potassium bromide) used in this work were of analytical reagent grade and were used without further purification.

Biomass preparation
The adsorbent was prepared according to the method described by Raju *et al.*, 2012 with some modifications. The *Albizia lebbeck* pods were washed twice with tap water and once with distilled water to remove the adhering dirt. It was sun-dried for one week; the dried pods were crushed into powdery form using a mechanical grinding machine. The dried meal was sieved using a 425 µm sieve which was used for the biosorption studies. The meal was divided into two portions and stored in an air-tight container prior to further treatment.

Activation of biosorbent
A portion of the dried meal required for the biosorption of dyes (methylene blue and methyl orange) was soaked in ethanol for 48 hours in order to get rid of any trace of dye present, then meals were dried in the oven at 105°C for 12 hours. The meal was stored in an air-tight container prior to use and called ethanol treated *Albizia lebbeck* pod (EALP).

The second portion of the meal was treated for further chemical modification which was carried out by soaking known volume of 1 M sodium hydroxide (NaOH) for 24 hours after which the soaked biosorbents was filtered and washed with deionized water until the pH of the filtrate was approximately ~7. The residue was then air-dried for 12 hours, and then in the oven at 80°C for 3 hours. The chemically treated pods were then stored in an air-tight container prior to use and labelled TALP which corresponds to 1 M, of sodium hydroxide (NaOH) treated *Albizia lebbeck* pod.

Characterization of biosorbents
In determining the vibration frequency changes in the functional groups in the biosorbents, Fourier transform infrared spectroscopy was used. The spectra were collected by Perkin-Elmer spectrometer (Perkin-Elmer Spectrum BX11) within the range of wave number of 400-4000 cm^{-1}. The samples of the biosorbent were first mixed with KBr and then ground in an agate mortar at an approximate ratio of 1/100 for the preparation of pellets (weight of 100 mg). Prior to FTIR analysis, the resulting

mixture was pressed at 5 ton for 5 minutes and cast into disk. All spectra were plotted using the same scale on % Transmittance through Perkin-Elmer Spectrum 10.4.3.

Biosorption experiments
Biosorption experiments were optimised at the desired pH value and contact time in a centrifuge tubes containing 50 mL of adsorbate solution (30 mg/L phenol, 50 mg/L 2,4,6-TCP and 10 mg/L methyl orange and methylene blue) with 0.1g of the biosorbents. The pH was adjusted with either 0.1M HNO_3 or 0.1M NaOH. The centrifuge tubes were shaken in a temperature controlled reciprocating shaker at 300rpm for 120 minutes. The solution was filtered using Whatman filter paper No 4. The residual equilibrium concentration of the filtrates was analysed using a UV-Visible Spectrophotometer (Spectrum lab 752s) at wavelengths of 296 nm for 2,4,6-TCP, 270 nm for phenol, 465 nm for methyl orange, and 660 nm for methylene blue.   The amount of adsorbate sorbed at equilibrium condition, q_e (mg/g) was calculated using the equation

$$q_e = (C_o - C_e)\frac{V}{w}$$ (1)

Where, q_e is the amount of adsorbate biosorbed at equilibrium condition (mg/g),V is the volume of the solution used (L), W is the mass of biosorbent used, C_o and C_e is the initial and equilibrium adsorbate concentration (mg/L) in solution respectively.

Throughout the study, the contact time was varied from 15 to 360 min, the pH from 2 to 10, the initial metal concentration from 7.5 to 300 mg/L, and the biosorbent dosage from 100 mg to 2000 mg.

Results and discussion
FT-IR analysis
The FT-IR spectroscopy method was used to obtain information on the functional group present in both untreated (neat form), Ethanol treated *Albizia lebbeck* pod (EALP) and 1 M-NaOH treated *Albizia lebbeck* pod. The FT-IR spectra for UALP, EALP and TALP in their raw state and where the biomass was loaded with phenol, 2, 4, 6-TCP, methyl orange and methylene blue are presented in Figure 1, 2 and 3. Peaks appearing in the native and loaded biomass were assigned various functional groups and bands in accordance with their respective wave numbers cm^{-1}. The absorption band between $3600-3900$ cm^{-1} is due to the traces of moisture in the biosorbents. The broad peak at 3338 cm^{-1}(UALP), 3418 cm^{-1} (EALP) and 3432 cm^{-1}(TALP) was assigned to –OH stretch due to inter and intra-molecular binding of polymeric compounds such as alcohols, phenols, and carboxylic acids, as in pectin, cellulose and lignin. The very broad peak of UALP and a shift to a lower frequency can be attributed to hydrogen-bonding. The peaks at $2923.55-2723.5$ cm^{-1}, $2922.97-2853.01$ cm^{-1}and $2923.78-2851.5$ cm^{-1} on UALP, EALP and TALP corresponded to the C-H stretching vibrations. The peaks at $1733-1646$ cm^{-1}on UALP, $1733-1510$ cm^{-1} on EALP and $1637-1508$ cm^{-1}on TALP were assigned to C=O vibrations. The pectin peaks at 1376 cm^{-1}, 1377 cm^{-1}and 1381 cm^{-1}were identified in the biosorbents UALP, EALP and TALP respectively. The peaks at 1460 - 1150 cm^{-1} band in UALP spectra, 1424-1161 cm^{-1} in EALP and 1459-1234 cm^{-1} band in TALP spectra were assigned the C-O-H stretching in alcohols. The peaks at 1033-1150 cm^{-1} on UALP, 1036-1161 cm^{-1} on EALP and 1061-1234 cm^{-1} on TALP are due to C-O stretching vibrations.

Spectra of all used biosorbent (TALP & EALP) used for biosorption of phenol methyl orange, methylene blue and 2, 4, 6-TCP are shown in Figure 2 and 3. The peak at 2122.17 cm^{-1} on TALP, 2130.87 cm^{-1} and 2133.69 cm^{-1} on 2, 4, 6-TCP and phenol biosorbed on TALP respectively were assigned $C \equiv C$ stretching vibration frequency and was found to be absent in untreated *Albezia lebbeck* pod (UALP) which might be as a result of treatment by 1M NaOH; an alkali. The peak at 2136.68cm^{-1}on EALP, 2127.27 cm^{-1} and 2131.2 cm^{-1} on methylene blue and methyl orange biosorbed on EALP respectively were assigned $C \equiv C$ stretching vibration frequency. Peaks at 3425 cm^{-1}, 3417 cm^{-1}, 3418 cm^{-1} and 3406 cm^{-1} present on both EALP and TALP used for the biosorption of methylene blue, methyl orange, phenol and 2,4,6-TCP corresponded to the presence of $-OH_{stretch}$bands. Major shifts were not observed on the $C-H_{stretch}$, $C=O_{stretch}$,$C-H_{stretch}$ bands, but a shift to a lower frequency was observed upon biosorption on the $-OH_{stretch}$ band. The two peaks at 1595 – 1637 cm^{-1} on TALP used for biosorption of phenol and 2, 4, 6-TCP corresponded to the aromatic C=C stretch, which is a characteristic peak of aromatic compounds. Peaks at 1109 – 1112 cm^{-1} on the used biosorbents which is absent on the unused biosorbent (TALP) was assigned to the $C-H$ bend (In-plane) vibration of aromatic compounds. Also, peaks at 610 – 831 $cm^{-1}$and 613$-$898cm^{-1}on the used TALP and EALP respectively corresponded to $C-H$ bend (Out of plane) for aromatic compounds and it gives details about the aromatic pattern of substitution.
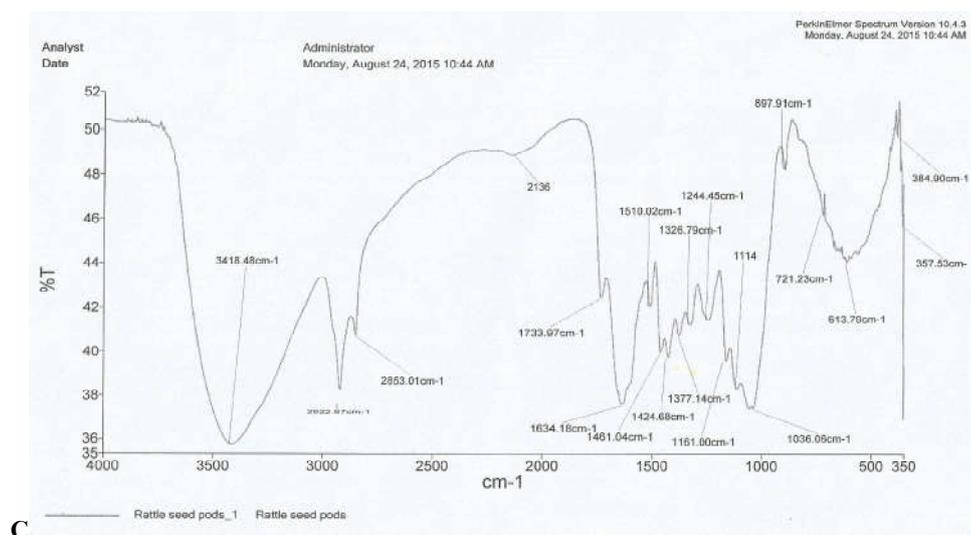
Effect of pH
The pH of the aqueous solution is an important controlling parameter in biosorption process because it provides an insight on the nature of the physicochemical interaction between solute in solution and adsorptive sites of the biosorbent (Aravindhan *et al*., 2009; Uddin *et al*., 2007).
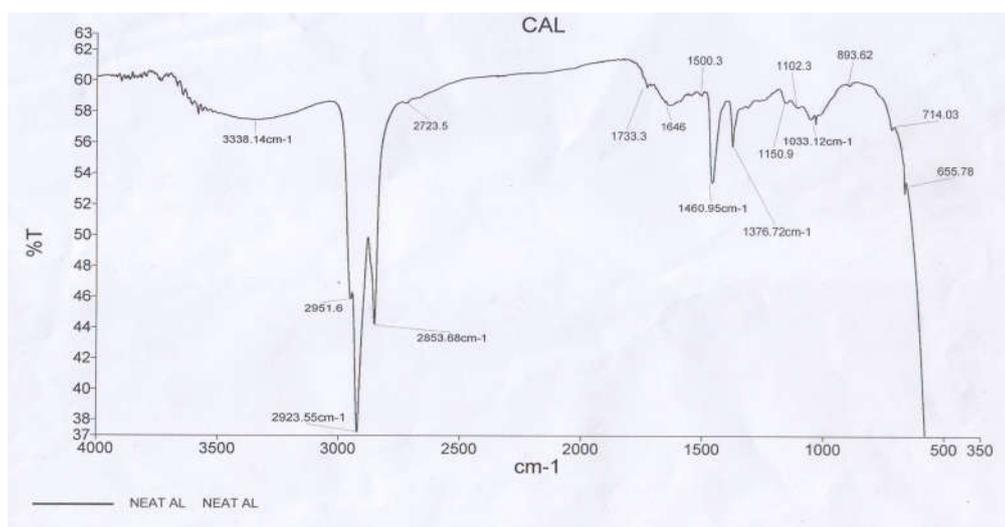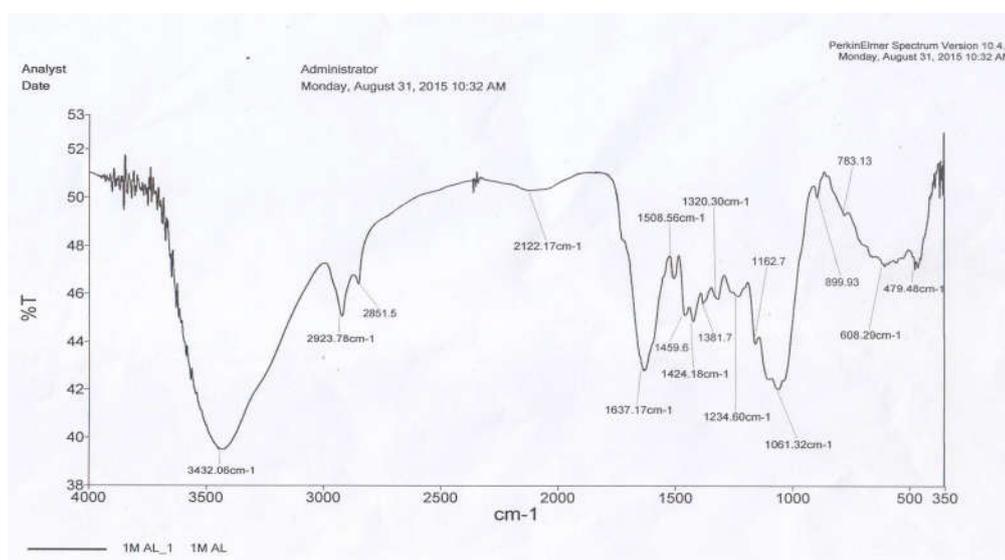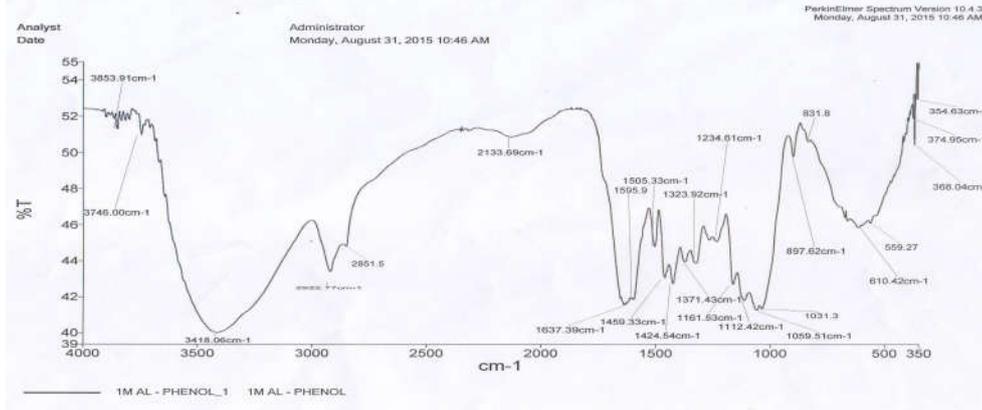
Fig 1: FT-IR spectrum of (a) untreated *Albizia lebbeck* pod (UALP) (b) 1.0 M treated *Albizia lebbeck* pod (TALP) (c) ethanol treated *Albizia lebbeck* pod (EALP)
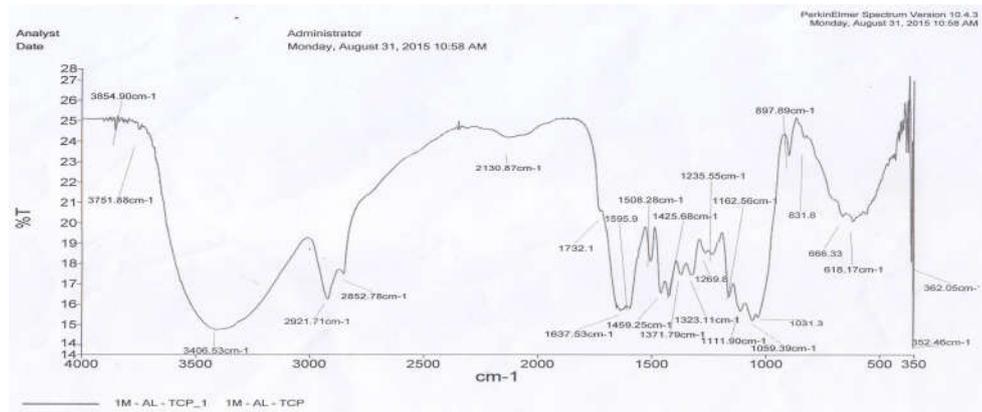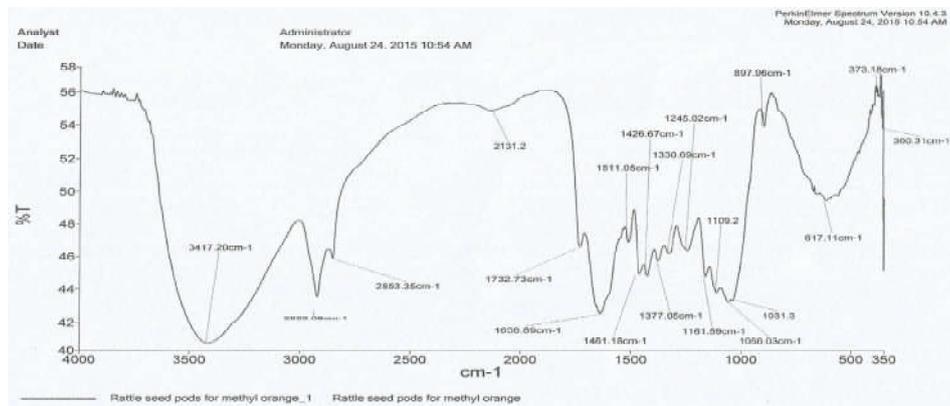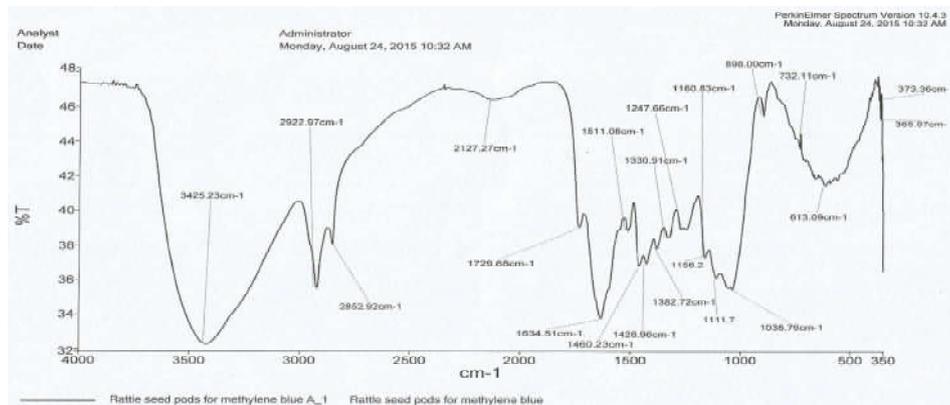
A

Fig 2: FT-IR spectrum of 1.0 M NaOH treated *Albizia lebbeck* pod bound with (a) phenol (b) 2, 4, 6-TCP

A

B

Fig 3: FT-IR spectrum of ethanol treated *Albizia lebbeck* pod bound with (a) methyl orange (b) methylene blue

Figure 4 shows the effect of initial pH in the range of 2-10 on the biosorption of 30 mg/L phenol, 50 mg/L 2,4,6-TCP on TALP and 10 mg/L methyl orange and methylene blue on EALP. The biosorption capacity of phenol, 2,4,6-TCP and methyl orange on the biosorbent decreased as the pH increased from 3-10 while that of methylene blue increases as the pH increased from 2.0 – 9.0. The maximum uptake was observed at pH 3.0 for both phenol and 2,4,6-TCP while it was pH 2.0 and 9.0 for both methyl orange and methylene blue respectively. The result clearly showed that the biosorption capacity is highly pH dependent. Phenol and 2, 4, 6-TCP have pKa values of 9.90 and 6.23 respectively, hence they only exist as anions at high pH values. The decrease in sorption capacity of the biosorbent towards phenol and 2,4,6-TCP as the pH increased over the range 6-10 can be explained as being a result of higher electrostatic repulsion between the sorbate and sorbent. The molecular form dominates in acidic solution, whereas the anionic form is the predominant specie in alkaline media. At low pH values, the surface of the biosorbent would be surrounded by the hydronium ions which enhance the phenol and 2,4,6-TCP interaction with the binding sites of the biosorbent by greater attractive forces (Kumar and Boddu, 2009). This observed pH trend for sorption of methylene blue can be explained by the electrostatic interaction of cationic dye (methylene blue) with negatively charged surface of the adsorbent (*Albizia lebbeck*).The negative charge on biomass increased with increasing pH, which was reported by Ucun *et al.*, 2003. In addition, lower adsorption of methylene blue at acidic pH might be due to the presence of excess H^+ ions competing with cationic dye for the available adsorption sites (Bestani *et al.,* 2008; Vadivelan and Kumar 2005). That of methyl orange can be explained by the electrostatic interaction of anionic dye, methyl orange with positively charged surface of the adsorbent (*Albizia lebbeck*). Also, lower adsorption of methyl orange at basic pH might be due to the presence of OH^- ions competing with dye anions for the available adsorption sites.

Furthermore, Figure 4 shows that the maximum biosorption capacity of phenol and 2,4,6-TCP on TALP were found to be 8.36 and 10.875 mg/g at pH 3.0 respectively while it was 3.825 and 4.642 mg/g at pH 2.0 and 9.0 for both methyl orange and methylene blue respectively. This is in agreement with the result obtained by Zazouli et al., 2013 and Hameed *et al.,* 2008. Similar results were also obtained by Uddin *et al.,* 2007 and Omar *et al*., 2012, where the biosorption capacity of phenol was found to decrease as the pH increases.
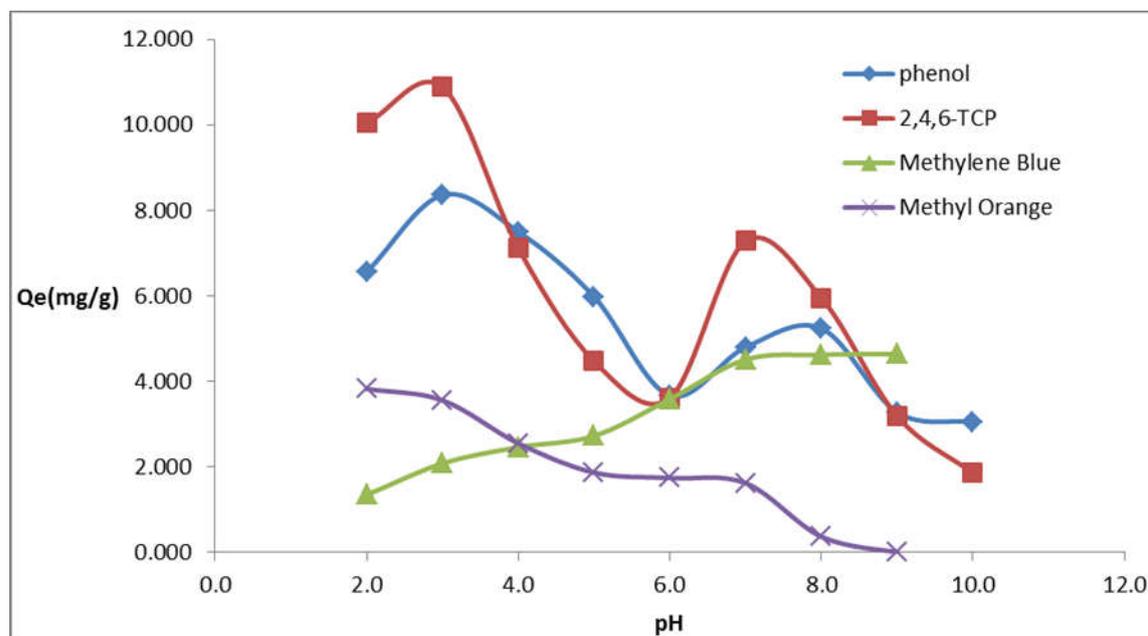

Fig 4: Effect of pH on the Biosorption of phenol, 2,4,6-TCP, methylene blue and methyl orange on *Albizia lebbeck* pod.

Effect of contact time
Figures 5 shows the biosorption data for the uptake of phenol, 2,4,6-TCP, methyl orange and methylene blue against agitation time at initial concentration of 30mg/L (phenol), 50mg/L (2,4,6-TCP) and 10mg/L (methyl orange and methylene blue) respectively. The result showed that 4 hours, 2 hours, and 6 hours are sufficient agitation time for phenol, 2,4,6-TCP and methyl orange and methylene blue to attain equilibrium respectively. However, the results also indicated that in the biosorption of 2,4,6-TCP and methylene blue, a higher sorption rate was observed at the initial period of 30 minutes and this was attributed to the increased number of vacant sites on the biosorbent (TALP& EALP) available at the initial stages, resulting in increased concentration gradient between adsorbate in solution and biosorbent surface (Uddin et al., 2007). Similar results were obtained for the biosorption of 2, 4, 6-Trichlorophenol on coconut husk based activated carbon and azolla (Zazouli et al., 2013; Hameed et al., 2008; Radhika and Palanivelu, 2006 and Chaliha and Bhattacharya, 2008). These results indicate that less residence time is required for the removal of 2,4,6-TCP compared to phenol and methyl orange.
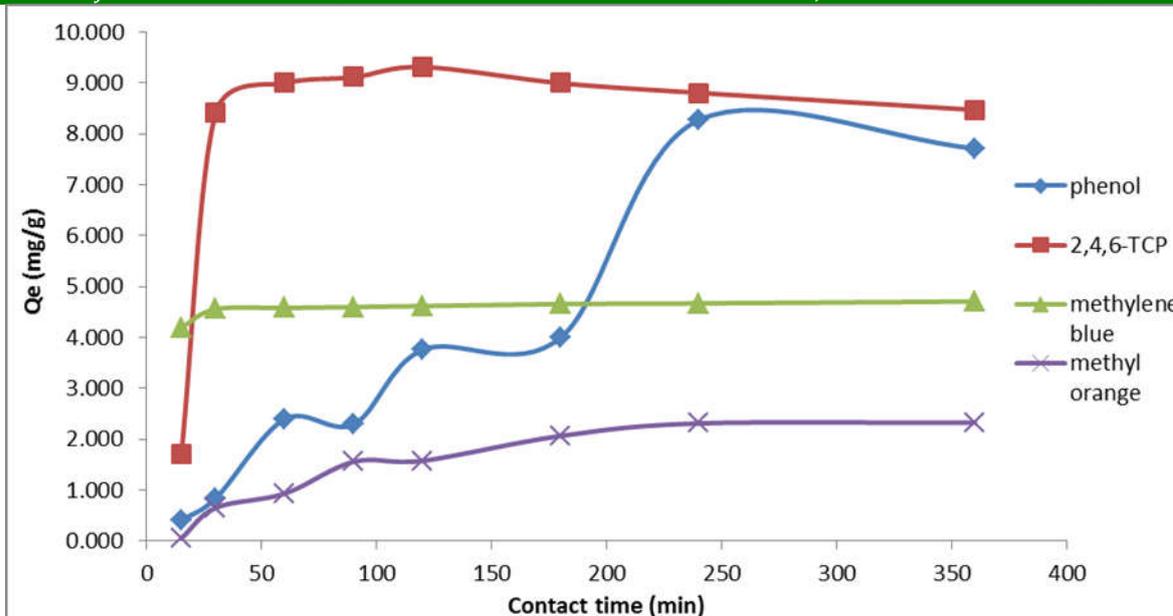
Fig 5: Effect of contact time on the Biosorption of phenol, 2,4,6-TCP, methylene blue and methyl orange on *Albizia lebbeck* pod.

Biosorption isotherm models
Equilibrium study on biosorption provides information on the biosorption capacity of the biosorbent. An isotherm is characterized by certain constant values which expresses the surface properties and affinity of the biosorbent and can also be used to compare the biosorptive capacities of the biosorbent for different pollutants (Uddin *et al*., 2007). Langmuir, Freundlich, Temkin isotherms will be used to determine the adsorption capacity of the biosorbents used in this study.

In 1916, Irving Langmuir proposed an isotherm named Langmuir isotherm. It is the most widely used simple two-parameter equation valid for monolayer adsorption onto a surface with finite number of identical site (Raju *et al.*, 2012).

The Langmuir equation is

$$q_e = \frac{q_o b C_e}{1 + b C_e} \qquad (2)$$

The linearized form of Langmuir equation can be written as

$$\frac{1}{q_e} = \left(\frac{1}{b q_o}\right)\frac{1}{C_e} + \frac{1}{q_o} \qquad (3)$$

Where, b is the Langmuir parameter related to free energy of adsorption (L/g), C_e is the Equilibrium concentration in the aqueous solution (mg/L), q_e is the equilibrium biosorption capacity (mg/g), q_o is the Langmuir parameter related to maximum biosorption capacity (mg/g).

It represents a practical binding biosorption capacity when the surface is fully covered with adsorbate molecules and assists in the comparison of biosorption performance, particularly in cases where sorbent did not reach its full saturation in experiments (Aksu and Yener, 2001).

The Langmuir constant q_o and **b** can be calculated by plotting $1/q_e$ against $1/C_e$ (a straight line graph). The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or Equilibrium parameter R_L, defined by

$$R_L = \frac{1}{(1 + b C_o)} \qquad (4)$$

Table 1: Values of the separation factor, R_L.

R_L Values	Biosorption
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

where, R_L is the Dimensionless constant separation factor (values shown in Table 1), **b** is the Langmuir constant (L/g), C_o is the initial solute concentration (mg/L). The separation factor calculated using Langmuir model constant yield the type of isotherm which was described by Weber and Chakravorti (Rao and Viraraghavan, 2002).

Table 2 showed regression values, R^2 ranges between 0.3427 and 0.999 for the biosorption of phenol, 2,4,6-TCP, and dyes (methyl orange and methylene blue) on *Albizia lebbeck* pod. The Langmuir isotherm regression value for phenol indicates that the correlation is not too satisfactory for the biosorption of phenol, while a low regression value for 2,4,6-TCP depicts that the

isotherm does not satisfactorily describe the biosorption process. The equilibrium parameter, R_L or the dimensionless constant separation factor was calculated for the biosorption of all the compounds on *Albizia lebbeck* pod. The result showed that the biosorption process is favourable, as the R_L values fall between the range of 0-1 ($0 < R_L < 1$). The biosorption capacities, q_o were found to be 7.71 mg/g, 6.80mg/g, 15384 mg/g and 370 mg/g for the biosorption of phenol, 2,4,6-TCP, methylene blue and methyl orange respectively on the biosorbent. The trend for biosorption is in order of methylene blue $>$ methyl orange $>$ phenol $>$ 2, 4, 6- TCP

Freundlich model is an empirical equation based on sorption on heterogeneous surface. It can be applied to multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. Freundlich isotherm is an empirical biosorption isotherm equation that can be applied in case of low and intermediate concentration changes (Foo and Hameed, 2010; Raju *et al*., 2012). The Freundlich isotherm is given as

$$q_e = K_F C_e^{1/n} \qquad\qquad (5)$$

Table 2: Isotherm parameters for phenol, 2, 4, 6-TCP, methyl orange and methylene blue biosorption by *Albizia lebbeck* pod

Model	TALP		EALP	
	Phenol	**2,4,6 TCP**	**MO**	**MB**
Langmuir				
Q_e (mg/g)	7.7101	6.7980	370	15384
K_L (L/mg)	0.1657	0.0249	4.67×10^{-3}	3.26×10^{-5}
R^2	0.8310	0.3427	0.9960	0.9990
R_L	0.4500 - 0.0387	0.7510- 0.2317	0.9554 - 0.4166	0.9903 - 0.9997
Freundlich				
K_F (mg/L)	1.8310	0.0732	2.28	11.02
N	2.87	0.86	1.19	1.69
1/n	0.35	1.16	0.84	0.59
R^2	0.8359	0.7829	0.990	0.845
Temkin				
K_T (L/mg)	0.8649	0.0789	0.9988	1.61
b_T (KJ/mol)	1.1890	0.3386	0.1017	0.1141
R^2	0.7363	0.8143	0.900	0.970

TALP   = *sodium hydroxide treated Albizia lebbeck pod*
EALP   = *ethanol treated Albizia lebbeck pod*
MO =   *methyl orange*
MB = *methylene blue*

The linearized form of Freundlich isotherm can be written as

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad\qquad (6)$$

where, K_F is the Freundlich constant indicating biosorption capacity (mg/g), n is the Freundlich constant indicating the biosorption intensity, C_e is the Equilibrium concentration in the aqueous solution (mg/L)). The value of K_f and **n** can be calculated by plotting ln q_e against ln Ce.

Based on the regression values which ranges between 0.990 and 0.7829 obtained for the biosorption of phenol, 2,4,6-TCP, methyl orange and methylene blue on the biosorbent as shown in Table 2, the linear form of Freundlich isotherm appears to produce a reasonable model for the sorption of phenol, 2,4,6-TCP and the dyes (methyl orange and methylene blue). It can be seen that the trend in biosorption as seen in Table 2 is in order of methylene blue $>$ methyl orange $>$ phenol $>$ 2,4,6-TCP. This agrees with Langmuir adsorption isotherm. Some researchers found that Freundlich model gave a better fit than Langmuir model on the adsorption of phenols using different adsorbents and this is assumed to be influenced by the characteristics of the adsorbents used as well as the original nature of the adsorbates (Radhika and Palanivelu, 2006; Hameed 2007; Wu *et al*., 2005).

The Freundlich constant,**n** can also be a measure of the deviation from linearity. The result from this study showed that the n value for phenol, methyl orange and methylene blue biosorption is greater than 1, indicating that the biosorption bond becomes weak and the value of sorption capacity changes significantly with small changes in concentration (Akbal, 2005). The n value for biosorption of 2,4,6-TCP is less than 1 (n = 0.868) and this implies that increased adsorption modifies the sorbent in a manner that increases the sorption capacity, such as forming new sites.

Temkin and Pyzhev isotherm equation describes the behaviour of many biosorption systems on the heterogeneous surface. It is an early model describing the adsorption of hydrogen onto platinum electrons within the acidic solutions. The isotherm contains a factor that explicitly takes into account the adsorbent-adsorbate interactions and the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage (Ahmed and Theydan, 2013; Foo and Hameed, 2010).

The Temkin isotherm as shown in equation 6

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \qquad (7)$$

The linearized equation is

$$q_e = \beta \ln \alpha + \beta \ln C_e \qquad (8)$$

Where, $\beta = \frac{RT}{b_T}$ and $\alpha = K_T$ $\qquad (9)$

`*where, T is the absolute temperature in Kelvin, R is the universal gas constant 8.314 Jmol⁻¹K,* b_T *is the Temkin constant related to heat of sorption (J/mg), and K_T is the Temkin isotherm constant (L/mg).*

The heat of biosorption, b_T was found to be 1.189 KJ/mol, 0.3386 KJ/mol , 0.1141 KJ/mol and 0.1017 KJ/mol for phenol, 2,4,6-TCP, methylene blue and methyl orange respectively. The R^2 values ranges from 0.970 - 0.7363. It can be seen that the trend in heat of biosorption as seen in Table 2 is in order of phenol ≻ 2,4,6-TCP ≻ methylene blue ≻ methyl orange.

Biosorption kinetics
The rate of the biosorption process and potential rate-controllong step can be examined using the kinetic models, hence; these kinetic models are useful for the design and optimization of effluent treatment models. Pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion kinetic models were analysed for the mechanism of organic pollutants biosorbed by *Albizialebbeck* pod.

The Lagergren's pseudo-first order rate equation is generally expressed as

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad (10)$$

The integrated linear form of the model can be written as

$$\log_{10}(q_e - q_t) = \log_{10} q_e - \frac{K_1 t}{2.303} \qquad (11)$$

Where, q_t *is the biosorption capacity at time t (mg/g),* q_e *is the biosorption capacity at equilibrium (mg/g) and K_1 is the rate constant of pseudo first order biosorption (min⁻¹).*

A plot of $\log_{10}(q_e - q_t)$ versus t gives a linear line from which the values K_1 and q_e can be determined from the slope and intercept respectively (Theivarasu and Myslamy, 2010; Dang *et al.,* 2009).

The rate constants predicted equilibrium uptakes and the corresponding correlation coefficient for phenol, 2, 4, 6- TCP, methyl orange and methylene blue were computed into Table3. It can be concluded from the R^2 values in Table 3 that the biosorption mechanism of 2, 4, 6- TCP on the biosorbent does not follow the pseudo-first order kinetic order while that of phenol and the dyes follows the pseudo-first order kinetic order. Though, the calculated Q_e for the biosorbate is not equal to the experimental Q_e. The differences between the Q_e values might have been due to the time lag, possibly due to a boundary layer or external resistance controlling at the beginning of the sorption process (Mckay *et al.,* 1999). Vijayaraghavan *et al.,* 2006 reported that in most cases in the literature, the pseudo-first order model does not fit the kinetic data well for the whole range of contact time, and generally under estimate the Q_e values.

The pseudo-second order kinetics can be expressed as:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad (12)$$

The integrated form of the above model becomes

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \qquad (13)$$

where, q_e *is the amount of adsorbate biosorbed per unit mass of biosorbent at equilibrium (mg/g),* q_t *is the amount of the biosorbate biosorbed at contact time t (mg/g) and K_2 is the rate constant of pseudo-second order biosorption (mg/gmin⁻¹).*

A plot of t/q_t versus t gives a linear relationship from which q_e and K_2 can be determined from the slope and intercept of the plot respectively.

The pseudo-second order model is based on the sorption capacity on the solid phase, contrary to other well established models, it predicts the behaviour over the whole range of studies and it is in agreement with a chemisorption mechanism being the rate controlling step (McKay *et al.,* 1999). The pseudo-second order kinetics was used to fit the sorption data. The plots returned good linear plots for the dyes and 2,4,6 TCP. R^2 values shown in Table 3 range from (0.1802-1.0). The R^2 value (0.967) for biosorption of methyl orange, 1.0 for methylene blue and 0.963 for 2, 4, 6-TCP showed that the pseudo-second order model equation gave a better fit than the pseudo-first order which was found satisfactory for describing the biosorption of phenol with an R^2 value of 0.9677. In this model, the rate-determining step is a biosorption mechanism involving chemisorption, where biosorbate removal from solution is due to physicochemical interactions between biomass and biosorbate solution (Aksu, 2001). Similar results have been reported by Zazouli *et al.,* 2013; Hameed *et al.,* 2008.

The Elovich equation is another rate equation in which the biosorbent surface is heterogeneous (Ejikeme *et al.,* 2011) and it is given as

$$\frac{dq_t}{dt} = \alpha e^{-\beta} \qquad (14)$$

The linear form becomes

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad (15)$$

Where,α is the initial biosorption rate (mg/gmin^{-1}) and β is the desorption rate constant (mg/gmin^{-1}). A plot of q_t versus $\ln(t)$ *gives a linear trace with a slope (1/β) and an intercept of 1/β ln(αβ).*The regression value, R^2, ranges between 0.4924-0.975. The plot gave a satisfactory fit of the biosorption of 2,4,6-TCP when fitted. Based on this model, it can be seen that methyl orange gave the best fit and this is indicative of heterogeneity of biosorbent (*Albizia lebbeck*) surface used.

Table3: Kinetics parameters for the biosorption of phenol, 2, 4, 6-TCP, methyl orange and methylene blue on *Albezia lebbeck* pod.

	TALP		EALP	
Model	**phenol**	**2, 4, 6 TCP**	**MO**	**MB**
Pseudo-first order kinetics/				
Q_e (mg/g)	10.06	1.138	2.71	0.30
K_1 (min)	0.0083	0.0021	-0.0023	-0.0046
R^2	0.9677	0.0556	0.855	0.871
Pseudo-second order kinetics				
Q_e (mg/g)	41.67	9.174	3.22	4.74
K_2(g/mg/min)	1.81×10^{-5}	7.14×10^{-3}	0.0027	0.1023
R^2	0.1802	0.963	0.967	1.0
$Q_{e\ experimental}$ (mg/g)	8.275	9.383	3.825	4.642
Elovich				
α (mg/g.min)	0.1326	1.9870	0.0552	3.47×10^{12}
β (g/mg)	0.3813	0.5666	1.31	7.75
R^2	0.8605	0.4924	0.975	0.755
Intra-particle diffusion				
K_d (g/mg/min)	0.5624	0.2828	0.153	0.024
C (mg/g)	-2.1154	5.0796	-0.21	4.32
R^2	0.9228	0.2944	0.909	0.596

The intra-particle diffusion model is expressed as

$$q_t = K_d t^{1/2} + C \qquad (16)$$

Where, K_d is the intra-particle diffusion rate constant (mg/gmin$^{-1/2}$), q_t is the amount of biosorbate at time t (mg/g) and C is the intercept (mg/g). A plot of q_t versus $t^{1/2}$ gives a linear relationship from which $K_d$value is determined from the slope and value of C (intercept) gives an idea about the thickness of boundary layer (Theivarasu and Myslamy, 2010). However, R^2 values from Table 3 shows fairly high values by the phenol and the dyes while 2, 4, 6-TCP displayed very low R^2 values. In general terms, the sorption process did not give a satisfactory fit with intra-particle diffusion model and that particle diffusion is not the only major process in the rate determining step.

Conclusion
The study revealed that the optimum binding of phenol and 2, 4, 6-TCP to the 1.0 NaOH treated *Albezia lebbeck* pod (TALP) occurred at a pH of 3.0 and that of methyl orange and methylene blue on ethanol activated *Albezia lebbeck* pod (EALP) occurred at a pH of 2.0 and 9.0 respectively, while the time required for the optimum binding of phenol and 2,4,6-TCP to TALP occurred at contact time of 240 and 120 minutes respectively and both dyes (methyl orange and methylene blue) occurred at contact time of 360 minutes. The equilibrium data for phenol fitted well into the Freundlich isotherm, 2,4,6-TCP fitted well into the Temkin isotherm while both dyes produced the best fit into Langmuir isotherm, on the other hand the linearity of the plot tested the representative nature of biosorption on the biosorbent. 1.0M NaOH treated *Albezia lebbeck* pod (TALP) bind more phenol than 2, 4, 6-TCP while the ethanol activated *Albezia lebbeck* pod (EALP) bind more methylene blue than methyl orange. The sorption of phenol on TALP conformed to pseudo-first order kinetic model while the sorption of 2,4,6-TCP on TALP and methylene blue on EALP conformed to the Pseudo-second order model suggesting that the rate determining step is chemisorption. The sorption of methyl orange on EALP conformed to Elovich kinetic model. The comparative goodness-of-fit of the kinetic isotherm used in producing kinetic model for the biosorption was in the order: Pseudo-second order ≯ Pseudo-first order ≯ Elovich ≯Intra-particle diffusion.The active groups that play a significant role in the biosorption of phenol and 2,4,6-TCP are the $-OH_{stretch}$ (hydroxyl), $-OH_{bending}$ vibration, $C-H_{stretch}$ and the $C-C_{stretch}$(Aromatic).The trend in biosorption of phenol, 2,4,6-TCP, methyl orange and methylene blue on *Albezia lebbeck* pod is in order of 2,4,6-TCP≯ phenol ≯ methylene blue ≯ methyl orange. It can be inferred that Rattle seed pods (*Albizia lebbbeck*) can be used as an effective low cost adsorbent for the removal of methylene blue and methyl orange from their aqueous solutions.

References

Agency for Toxic Substances and Disease Registry, (ASTDR). 1990. Toxicological Profile for 2,4,6-Trichlorophenol. U. S. Public Health Service, U.S. Department of Health and Human Services, Atlanta, G.A.

Ahmed, M. J., and Theydan, S. K. 2013. Adsorption of p-chlorophenol onto microporous activated carbon from *Albizia lebbeck* seed pods by one-step microwave assisted activation. *Journal of Analytical and Applied Pyrolysis,*100: 253–260.

Akbal, F. 2005. Sorption of phenol and 4-chlorophenol onto pumice treated cationic surfactant. *Journal of Environmental Management*, 74: 239-244

Aksu Z. 2001. Equilibrium and kinetic modelling of cadmium (II) biosorption by C. *vulgaris* in a batch system: effect of temperature. *Purification Technology* 21: 285-294.

Aksu, Z. and Yener, J. 2001. A comparative adsorption/biosorption study of mono-chlorinated phenols onto various sorbents. *Waste Management,21*: 695–702.

Arami, M., Limaee, N. Y., Mahmoodi, N. M., and Tabrizi, N. S., 2005. Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetic studies. *Journal of Colloid and Interface Science* 288, 371–376.

Aravindhan, R., Rao, J. R., and Nair, B. U. 2009. Application of a chemically modified green macro alga as a biosorbent for phenol removal. *Journal of Environmental Management, 90*(5): 1877–1883.

Babel, S., and Kurniawan, T.A., (2004). Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere* 54, 951–967.

Banat, F. A., Al-bashir, B., Al-asheh, S., and Hayajneh, O. 2000. Adsorption of phenol by bentonite. *Environmental Pollution,*107: 391–398.

Batzias, F. A., and Sidiras, D. K. 2007. Dye adsorption by prehydrolysed beech sawdust in batch and fixed-bed systems. *Bioresource Technology* 98, 1208–1217.

Bayramoglu, G., Gursel, I., Tunali, Y., and Arica, M. Y. 2009. Biosorption of phenol and 2-chlorophenol by *Funalia trogii* pellets. *Bioresource Technology,*100(10): 2685–2691.

Bestani, B., Benderdouche, N., Bestaali, B., Belhakem, M. and Addou, A. 2008. Methylene blue and iodine adsorption onto an activated desert plant. *Bioresource Technology*, 99(17): 8441-8444.

Bhattacharyya, K. G., Sharma, A. 2004. *Azadirachta indica* leaf as an effective biosorbent for dye: a case study with aqueous Congo red solution. *Journal of Environmental Management* 71, 217–229.

Bulut, Y., and Aydin, H. 2006. A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination* 194, 259–267.

Chaliha, S. and Bhattacharya, K. G. 2008. Catalytic wet oxidation of 2-chlorophenol, 2, 4-dichlorophenol and 2,4,6-trichlorophenol in water with Mn(II)-MCM41. *Chemical Engineering Journal* 139: 575-588.

Chatterjee, S., Chatterjee, S., Chatterjee, B. P., Das, A.R., and Guha, A.K. 2005. Adsorption of a model anionic dye, eosin Y, from aqueous solution by chitosan hydrogels. *Journal of Colloid and Interface Science* 288, 30–35.

Daneshvar, N., Ayazloo, M., Khataee, A. R., and Pourhassan, M. 2007. Biological decolourization of dye solution containing Malachite Green by microalgae Cosmarium sp. *Bioresource Technology* 98, 1176–1182.

Dang, V. B. H., Doan, H. D., Dang-Vu, T., and Lohi, A. 2009.Equilibrium and kinetics of biosorption of cadmium (II) and copper (II) ions by wheat straw. *Bioresource Technology* 100: 211-219.

De Sousa, D.A., de Oliveira, E., Nogueira, M.C., and Esposito, B.P. 2010. Development of a heavy metal sorption system through the P=S functionalization of coconut (Cocos nucifera) fibers. *Bioresource Technology* 101, 138–143.

Ejikeme, P. M., Okoye, A.I and Onukwuli, O. D. 2011. Kinetics and isotherm studies of Cu^{2+} and Pb^{2+} ions removal from simulated waste water by *Gambeya albida* seed shell activated carbon. *The African Review of Physics* 6:0017: 143-152

Foo, K. Y., and Hameed, B. H. 2010. Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal,*156: 2–10.

Girods, P., Dufour, A., Fierro, V., Rogaume, Y., Rogaume, C., Zoulalian, A., and Celzard, A. 2009. Activated carbons prepared from wood particleboard wastes : Characterisation and phenol adsorption capacities. *Journal of Hazardous Materials,*166: 491–501.

Gupta, V.K., Jain, R., and Shrivastava, M. 2010. Adsorptive removal of Cyanosine from waste water using coconut husks. *Journal of Colloid and Interface Science,* 347: 309–314.

Hameed, B. H., Tan, I. A.W., and Ahmad, A. L. 2008. Adsorption isotherm, kinetic modeling and mechanism of 2,4,6-trichlorophenol on coconut husk-based activated carbon. *Chemical Engineering Journal*, *144*(2): 235–244.

Hameed, B. H., Krishni, R. R., Sata, S. A. 2009. A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solutions. *Journal of Hazardous Materials* 162, 305–311.

Dursun, G., Handan, C. and Dursun, A.Y. 2005. Adsorption of phenol from aqueous solution by using carbonised beet pulp. *Journal of Hazardous Materials,*125: 175–182.

Hao, O. J., Kim, H., Chiang, P. C., 2000. Decolorization of wastewater. *Critical Reviews in Environmental Science and Technology* 30 (3), 449–505.

Hu, Q. H., Qiao, S. Z., Haghseresht, F., Wilson, M.A., Lu, G.Q. 2006. Adsorption study for removal of basic red dye using bentonite. *Industrial & Engineering Chemistry Research* 45, 733–738.

Jain, R., and Shrivastava, M. 2008. Adsorptive studies of hazardous dye Tropaeoline 000 from an aqueous phase on to coconut-husk. *Journal of Hazardous Materials* 158, 549–556.

Khaled, A., El Nemr, A., El-Sikaily, A., and Abdelwahab, O. 2009. Removal of Direct N Blue-106 from artificial textile dye effluent using activated carbon from orange peel: adsorption isotherm and kinetic studies. *Journal of Hazardous Materials* 165, 100–110.

Khattri, S. D., and Singh, M. K. 2009. Removal of malachite green from dye wastewater using neem sawdust by adsorption. *Journal of Hazardous Materials* 167, 1089–1094.

Kumar, N. S., Boddu, V. M. and Krishnaiah, A. 2009. Biosorption of Phenolic Compounds by *Trametes versicolor polyporus Fungus. Adsorption Scienceand Technology,27*(1): 31-46

Low, K.. S and Lee, C. K.1990. The removal of cationic dyes using coconut husk as an absorbent. *Pertanika* 13, 221–228.

McKay, G., Ho, Y. S., Ng, J. C. Y. 1999. Biosorption of copper from waste waters. A review. *Separation and Purification Methods* 28: 87-125

Moussavi, G., and Mahmoudi, M. (2009). Removal of azo and anthraquinone reactive dyes by using MgO nanoparticles. *Journal of Hazardous Materials*, 168, 806–812.

Ogunniyi, T. A. B., Oni, P. O., Juba, A., Asaolu, S.O and Kolawole, D. O. 2000. Disinfectants/antiseptics in the management of guinea worm ulcers in the rural areas. *Acta Tropical* 74(1): 33-38

Omar, H. A. 2012. Adsorptive removal of phenol from aqueous solution using natural and immobilized chitin by dithiazone. *New York Science Journal,5*(8): 47–55.

Radhika, M., and Palanivelu, K. 2006. Adsorptive removal of chlorophenols from aqueous solution by low cost adsorbent — Kinetics and isotherm analysis. *Journal of Hazardous Materials,*138: 116–124.

Raju, C. A. I., Kumari, R. S., Satya, C. V, Rao, P. J., and Bai, M. T. 2012. Biosorption performance of *Albezia lebbeck* pods powder for the removal of lead : Application of statistical method. *International Journal of Modern Engineering Research,2*(3), 1297–1305.

Rao, J. R., and Viraraghavan, T. 2002. Biosorption of phenol from an aqueous solution by *Aspergillus niger* biomass. *Bioresource Technology,85*: 165–171.

Rengaraj, S., Moon, S., Sivabalan, R., Arabidoo, V. and Murugesan, B. 2002. Agricultural solid waste for the removal of organics : adsorption of phenol from water and wastewater by palm seed coat activated carbon. *Waste Management,*22: 543–548.

Robinson T, McMullan G, Marchant R, Nigam P. 2001. Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*, 77(3): 247–255.

Swamy, A.V.V.S. and Devi, K. S. 2012. Biosorption of phenols. *International Journal of Engineering Research and Applications,2*(4): 262–265.

Tanyildizi, M.S., 2011. Modeling of adsorption isotherms and kinetics of reactive dye from aqueous solution by peanut hull. *Chemical Engineering Journal* 168, 1234–1240.

The Carcinogenic Potency Database Project. 2007. 2,4,6-Trichlorophenol (CAS 88-06-2), Rats and Mice: Cancer Test Summary. University of Berkeley. Retrieved from *www.toxnet.nlm.nih.gov/cpdb/chempages/2,4,6-TRICHLOROPHENOL.html* on November 19, 2015

Theivarasu, C., and Mylsamy, S. 2010. Equilibrium and kinetic adsorption studies of Rhodamine B from aqueous solutions using cocoa (*Theobroma cacao*) shell as new adsorbent. *International Journal of Engineering, Science and Technology,* 2(1): 6284-6292.

Ucun, H., Bayhan, Y. K., Kaya, Y., Cakici, A. and Algur, O.F. 2003. Biosorption of lead (II) from aqueous solution by cone biomass of *Pinus sylvestris*. *Desalination*, 154:233-238.

Uddin, M. T., Islam, M. S., and Abedin, M. Z. 2007. Adsorption of phenol from aqueous solution by water hyacinth ash, *ARPN Journal of Engineering and Applied Sciences,* 2(2): 11–17.

Udiba U.U., Gauje, B., Ashade, N.O., Ade-Ajayi, F. A., Okezie, V.C., Aji, B.M. and Agboun, T. D. T., 2014. An assessment of the heavy metal status of River Galma around Dakace industrial layout , Zaria , Nigeria. *Merit Research Journal of Environmental Science and Toxicology, 2*(8): 176–184.

United States Environmental Protection Agency. 2000. 2,4,6-Trichlorophenol 88-06-2. Retrieved from *www.epa.gov/ttn/atw/hlthef/tri-phen.html* on November 19, 2015

Vadivelan, V. and Kumar, K. V. 2005. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *Journal of colloid and interface science*, 286: 90-100

Vieira, R.H.S.F. and Volesky, B. 2000. Biosorption: a solution to pollution. *International Microbiology,* 3: 17-24.

Vijayaraghavan, K., Palanivelu, K., and Velan, M. 2006. Biosorption of Copper (II) and cobalt (II) from aqueous solutions by crab shell particles. *Bioresource Technology* 97: 1411-1419

Vinod, P., and Anirudhan, T. S. 2002. Effect of experimental variables on phenol adsorption on activated carbon prepared from coconut husk by single-step steam pyrolysis: Mass Transfer Process and Equilibrium Studies. *Journal of Scientific and Industrial Research,* 61: 128–138.

World Health Organization. 1997. Water Pollution Control: A Guide to the use of Water Quality Management Principles. Retrieved from *http://who.int/water-sanitation-health/resourcequality/wpcasestudy4.pdf?ua=1* on August 5th, 2015.

Wu, F. C., Tseng, R. L. and Juang. 2005. Comparisons of porous and adsorption properties of carbon activated by steam and KOH. *Journal of Colloid and Interface Science*, 283: 49-56.

Zazouli, M. A., Balarak, D., and Mahdavi, Y. 2013. Application of Azolla for 2,4,6-trichlorophenol (TCP) removal from aqueous solution. *Archives of Hygiene Sciences*. 2(4), 143-149.