Removal of Heavy Metal Pb(II) Ions from Aqueous Solution Using Pentaclethra Macrophylla and Tetracarpidium Conophorum Seed Shells Based Activated Carbons: Equilibrium, Kinetics and Thermodynmamics Studies

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Authors' contributions

This work was carried out in collaboration between all authors. Authors CFOO and ODO designed the study, performed the statistical analysis, wrote the protocol, wrote the first draft of the manuscript and managed literature searches. Authors CCO and ICN managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Biosorption potentials of activated carbons from pentaclethra Macrophylla (PMAC) and Tetracarpidium Conophorum (TCAC) seed shells for the removal of Pb(II) from aqueous solution were investigated. The adsorbents were characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), X-ray fluorescence (XRF) and x-ray diffraction (XRD). The effects of particle size (0.2 - 1.2 mm), adsorbent dosage (0.2 - 3.0 g), initial pH of solution (2 - 8), initial Pb(II) concentration (100-500 mg/l), temperature (20ºC - 60ºC) and contact time (10 - 180 min) were studied. The percent Pb(II) uptake was found to increase with increase with increase in adsorbent dosage and contact time and decreased with increase in particle size, initial Pb(II) concentration and temperature. Optimum adsorption of Pb(II) was observed at pH 6. The biosorption equilibrium data were well represented by both Langmuir and the Freundlich

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models. Kinetic data obtained fitted the pseudo-second-order model very well with high correlation coefficient. The calculated thermodynamic parameters (ΔG, ΔH and ΔS) indicated that adsorption of Pb(II) onto PMAC and TCAC was exothermic, spontaneous and feasible in the temperature range studied. Results of this work showed that PMAC and TCAC could be used as low cost adsorbents for the removal of Pb(II) from aqueous wastewater.

NOMENCLATURES

PMAC : *Pentaclethra Macrophylla Activated Carbon*
TCAC : *Tetracarpidium Conophorum Activated Carbon*
SEM : *Scanning Electron Microscopy*
FTIR : *Fourier transforms infrared*
XRF : *X-ray fluorescence*
XRD : *X-ray Diffractometry*

1. INTRODUCTION

Contamination of the environment from a variety of sources has become an increasingly serious problem in recent years. Rapid industrialization has led to increased disposal of heavy metals into the environment. Heavy metals such as lead, copper, cadmium, zinc and nickel are among the most common pollutants found in industrial effluents. These metals, if present beyond certain concentration can be toxic to organisms, including humans [I,2]. Heavy metals cannot be degraded or rapidly detoxified biologically [3]. Lead is the one of the most toxic pollutant which cause severe environmental and health problems.

The major source of lead pollution in wastewaters is discharging of waste stream from acid battery manufacturing, pigments, metals plating and finishing, printing, lead mining, metallurgical alloying, gasoline additives, ceramics and glass industries [4,5,6]. The presence of lead in drinking water even at low concentration may cause such diseases as anemia, encephalopathy, hepatitis and nephritic syndrome [6]. Excess intake of lead by humans causes disruption in the biosynthesis of the hemoglobin level, a rise in blood pressure, kidney damage, miscarriages and abortions, brain damage, and diminished learning abilities in children. Furthermore, lead is a known carcinogen [2]. These lead containing effluents, therefore, must be adequately treated prior to discharge into receiving water bodies to ensure good human health and environmental quality [5,7].

Several physico-chemical treatments have been used for removing heavy metals such as ions exchange, chemical precipitation, coagulation/flocculation, membrane filtration, solvent extraction, sedimentation, biological operations, electrochemical processes and adsorption. Most of these processes are costly and lead to generation of sludge or formation of by-products [8,9]. Among all the techniques adsorption is more popular due to low operating cost, specific selectivity of the metals and no production of secondary toxic compounds [10]. Many non conventional adsorbents, such as agricultural and industrial solid wastes like activated carbon prepared from Moringa Oleifera, waste fruit cortex, red algae, coconut husk, tea leaves, cocoa shells, orange peel, maize cob, olive cake and soyabean hull [7] have been studied. Low cost adsorbents for wastewater treatment have shown great prospects as adsorbents due to their renewability, natural abundance, low cost and eco-friendly [11,12].

Pentaclethra macrophylla ((PM)*,* is a multiusage tree from Africa and belongs to the leguminous family; sub-family of mimosoideae found mostly in tropical Africa. It has been cultivated in Nigeria since 1937. The tree grows to about 21 m in height and about 6 m in girth. PM seeds are eaten in the form of salad across different African countries [13]. It is used as food, salt substitute, edible oil, seed craft, dye, fencing and palings, charcoal, carving bowls, medicine for convulsion, itching, lactogenicity and ornamental [14].

Tetracarpidium Conophorum (TC) is an economic plant widely cultivated for production of nuts which are regarded as delicacy and belongs to the Euphorbiaceae family. It is also used as ethnomedicine as a male fertility agent while the leaves are used for the treatment of dysentery. The oil from the nut has found use in the formulation of wood varnish, stand oil, vulcanized oil for rubber and leather substitute. Most of the studies on the plant had been on the nutritive value of the seeds which were as snack and delicacy [15].

The present paper is concerned with the preparation of activated carbons from PM and TC by chemical activation with H_3PO_4 and their effectiveness in the removal of Pb(II) from aqueous solution. The effects of particle size, initial pH of solution, adsorbent dosage, adsorbate concentration, contact time and temperature were investigated. The equilibrium and kinetic data of the adsorption process were then analyzed to study the adsorption isotherms, kinetics and thermodynamics of Pb(II) uptake on PMAC and TCAC.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 Preparation and characterization of *Pentaclethra macrophylla* and *Tetracarpidium conophorum* activated carbon (PMAC and TCAC)

PM and TC seed shells were obtained from Eke Awka market in Anambra State, Nigeria, and used in the preparation of activated carbons. The seed shells were washed with de-ionized water (pH 7.0) to remove dirt and other surface adhere particles, and then dried at 110°C for 12 hours to obtain a constant weight. Dried PM and TC seed shells were ground and sieved to 1- 3.0 mm particle size and stored for further use. A stock solution of 1000 mg/L Pb(II) was prepared from $Pb(NO_3)_2$ salt. Other concentrations of Pb(II) solution used in the experiments were prepared by appropriate dilution of the stock solutions. HCl and NaOH were used to adjust the pH of the test solution to the desired value. A pH meter (3305 and Hanna pH meter) was used for pH measurements. An atomic absorption spectrophotometer (AA 220FS model) was used for the determination of Pb(II) ions concentration before and after adsorption.

2.2 Preparation and Characterization of the Activated Carbon

The dried PM and TC seeds hulls were soaked in 60% H_3PO_4 for 24 hours at room temperature and carbonized at 500°C for 90 minutes using muffle furnace (Model SX-2.5-10). The carbonized samples were washed with de-ionized water until pH 7, filtered and dried in an oven at 105°C for 4 hours. The PM activated carbon (PMAC) and the TC activated carbon (TCAC) produced were allowed to cool to room temperature in a desiccator, sieved to different particle sizes and stored in an air tight container for Pb(II) adsorption.

The physicochemical properties of PMAC and TCAC were determined using methods described by Nwabanne and Igbokwe [16]. The surface area of each adsorbents was determined by agitating 1.5 g of activated carbon in 100 ml (0.1 L) of HCl that had been diluted to pH of 3. Then 30 g of NaCl was added while stirring the suspension after which the volume was made up to 150 ml with de-ionized water resulting in the change of the pH to 4 and V recorded. The surface area was then calculated using the following equation:

$$S(m^2/g) = 32V - 25 \qquad (1)$$

where:

  S = the surface area (m^2/g)
  V = Volume of NaOH used to raise the pH.

The surface functional groups on PMAC and TCAC were identified using FTIR (Shimadzu FTIR 8400 spectrophotometer). Scanning electron microscopy (SEM: Phenom Prox.) was used to determine the surface morphology of PMAC and TCAC. The diffraction pattern and inter planar spacing of PMAC and TCAC were determined on a powder x-ray diffractometer (Stchmabzu model 6000) with Cuk_α radiation having a scanning speed of 8000deg/min and tested at 40kV and 30 mA. X-ray fluorescence (XPF: municipal 4 model XRF spectrometer) was used to determine the chemical groups and oxides present in the adsorbents.

2.3 Batch Adsorption Experiment

The batch adsorption experiments were carried out using 0.5 g adsorbents and 100 ml of 100 mg/l Pb(II) solution in 250ml stoppered conical flasks on a temperature controlled water bath shaker set at 120 rpm. The initial concentration was taken as 100mg/l because below and after this initial concentration taken, the percentage removal was very high and same was observed during the calibration of the metal. The effects of adsorbents dosage, pH, contact time, initial Pb(II) concentration and adsorbent particle size on adsorption of Pb(II) onto PMAC and TCAC were investigated. Preliminary investigations showed that the concentration of Pb(II) remained constant after 60 minutes of contact with 0.5 g of PMAC and TCAC. The allowed contact time for equilibrium study was 120 min.

The effect of adsorbent dosages on Pb(II) removal from solution were investigated by varying the amount of PMAC and TCAC from 0.2 to 3.0 g. The effect of pH was investigated by adjusting the pH of the solution over a range of 2-8. The effects of contact time and kinetics on adsorption of Pb(II) were determined at different time intervals over the time range 10-80 min. temperature effects on Pb(II) uptake by PMAC and TCAC were studied by varying the temperature between 20℃ and 60℃. Similarly, the effect of adsorbent particle size on Pb(II) sorption on the adsorbents were investigated at particle size range 0.2- 1.2 mm.

At the end of each experiment, the adsorbent-solution mixture was centrifuged and the supernatant was analyzed for Pb(II) using atomic absorption spectrophotometer (AAS). The amount of Pb(II) sorbed onto PMAC and TCAC at time t, q_t, at equilibrium, q_e, percent Pb(II) adsorbed at time t, %q_t and at equilibrium %q_e were computed using equations (1), (2), (3) and (4), respectively.

$$q_t = \frac{(C_0 - C_t)}{W} V \qquad (2)$$

$$q_e = \frac{(C_0 - C_e)}{W} V \qquad (3)$$

$$\%q_t = \frac{(C_o - C_t)}{C_o} X \frac{100}{1} \qquad (4)$$

$$\%q_e = \frac{(C_o - C_e)}{C_o} X \frac{100}{1} \qquad (5)$$

Where C_o, C_t, and C_e are the initial concentrations, concentration at time t, and the concentration at equilibrium, respectively. V and W are the volume of the solution (l) and weight of carbon(g), respectively. The batch experiments were carried out in triplicate and the negative controls (with no adsorbents) were simultaneously carried out to ensure adsorption was by the adsorbents and not by the container. The values reported were the average of the three values.

3. RESULTS AND DISCUSSION

3.1 Characterization of Adsorbents

The characteristics result of the two adsorbents used in the present study was listed in Table 1. The surface area of PMAC (954.56 m^2/g) was larger than that of TCAC (916.17 m^2/g). The larger specific surface area of PMAC may mean

that PMAC was covered with more adsorption sites [17]. The iodine numbers for PMAC and TCAC were 764.53 and 652.31 m^2/g, respectively. Iodine number is the fundamental parameter for characterizing the performance of an activated carbon as it provides a good approximation of the entire surface available for the adsorption of the lower molecular compounds especially the microporosity [18]. The relatively high surface area of the PMAC and the TCAC may be due to the removal of most of the volatile matter during carbonization and oxidation process which leaves the adsorbents more porous and hence larger surface area.

The FTIR spectrum pattern of PMAC (Fig. 1a and Table 2) shows a number of absorption peaks reflecting the complex properties of the adsorbents. The peaks at 3926, 3797, and 3628 cm^{-1} is attached to O-H stretch in phenol and alcohols. The peaks at 3410 and 3235 cm^{-1} corresponded to the bonded –OH groups, while those around 3012 and 2902 cm^{-1} were assigned to C=H stretch in alkenes and C-H stretch in alkanes respectively. The peaks at 2677, 2566 and 2428 cm^{-1} were assigned to O-H stretch in carboxylic acids. The bands at 1985 and 1874 cm^{-1} were attributed to the aromatic combination while the peaks at 1607 and 1433 cm^{-1} were assigned to N-H blend in amines and O-H blend in carboxylic acids. Other significant band positions of PMAC are noted at 2780 cm^{-1} (indicative of methylamino, N-CH3, C-H stretch), 226 cm^{-1} 2(suggestive of aliphatic cyanide/nitrile), 2085 cm^{-1} (associated with transition metal carbonyl), 1316 and 1101 cm^{-1} (representing C-C stretch skeletal vibrations), 768 cm^{-1} (due to C-H bend [mono] in aromatics), 928 cm^{-1} (representing cyclohexane ring vibrations).

The FTIR spectra of TCAC displayed the following bands (Fig. 1b and Table 3). 3837, 3830, 3719 cm^{-1} and 3587 cm^{-1} (O-H stretch in phenols and alcohols), 3498 cm^{-1} (dimeric O-H stretch), 3395 cm^{-1} (polymeric O-H stretch), 3290 cm^{-1} (H-bonded O-H stretch), 3177, 3074 and 2950 cm^{-1} (O-H stretch in carboxylic acid). Other bands are in 1588 cm^{-1} which may represent the N-H bend in amides, in 1413 cm^{-1} which may be ascribed to C-H in-plane bend in alkanes and at 1272 cm^{-1} which may be associated with O-H in primary or secondary and/or in plane bend. From the FTIR spectra of PMAC and TCAC, it can be inferred that the adsorption of Pb(II) onto PMAC and TCAC were mainly due to the functional

4

groups such as the hydroxyl and carboxyl groups that may be the potential biosorption sites.

Scanning electron micrographs (SEM) of PMAC and TCAC are presented in Figure 2a and b, respectively. The micrographs seem to be rough with sponge like protrusions quite prevalent in adsorbents. High level of porosity was observed on both PMAC and TCAC. However, the PMAC seems more porous that the TCAC.

The x-ray diffraction (XRD) profiles of PMAC and TCAC are shown in Fig. 3a and b, respectively. The XRD spectrum of the carbons showed broad peaks which indicated the presence of high

content of amorphous form of carbon and little amounts of crystalline materials in the adsorbents.

Table 1. Physicochemical properties of PMAC and TCAC

Parameter/Adsorbents	PMAC	TCAC
Ash content (%)	5.87	5.39
Surface area (m^2/g)	954.56	916.17
Bulk density (g/cm^2)	0.43	0.47
Total pore volume	2.42	2.76
Iodine number (mg/g)	764.53	652.31
Moisture content (%)	3.63	4.52
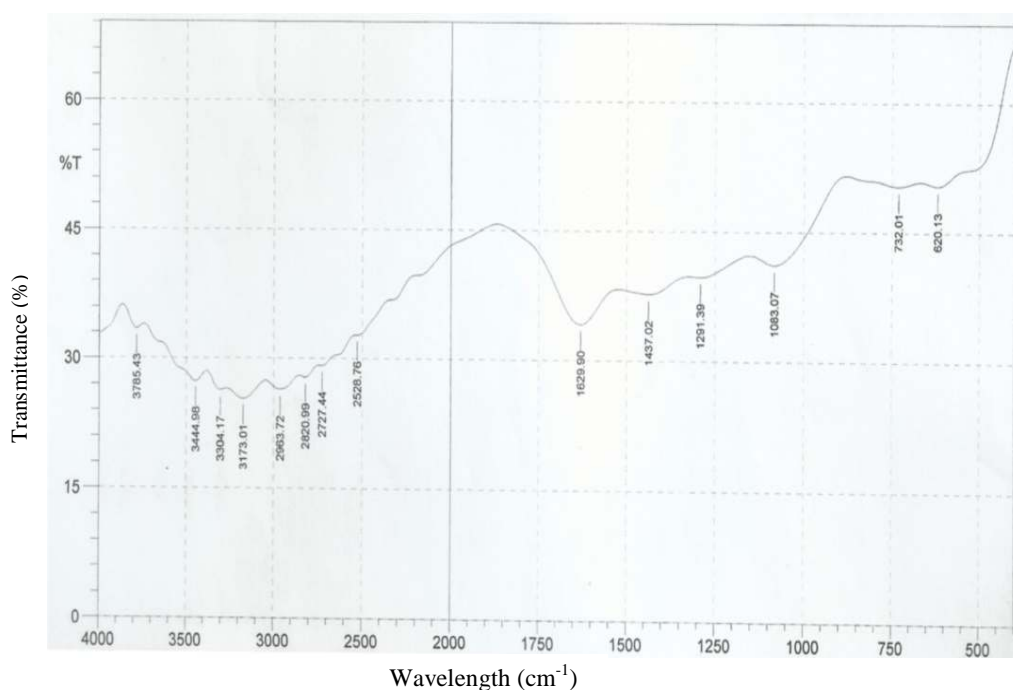
Wave number (cm^{-1})	Bond source
620.13	C-Cl, C-Br in alkyl halides and C-H bend in alkynes
732.01	Methylene -(CH2)*n*- rocking
1083.07	Primary amine, C-N stretch
1291.39	Aromatic primary amine, CN stretch
1437.02	Methyl C-H asymmetrical/symmetrical bend
1629.9	C=C stretch in alkenes
2528.76	O-H stretch in carboxylic acids
2727.44	O-H stretch in carboxylic acids
2820.99	C-H stretch in aldehyde, C-H stretch in alkane
2963.72	Methyl C-H asymmetrical/symmetrical stretch
3173.01	O-H stretch in carboxylic acids
3304.17	Hydroxyl group, H-bonded OH stretch
3444.98	Hydroxyl group, H-bonded OH stretch
3785.43	O-H Stretch in phenols and alcohols

Fig. 1a and Table 2. FTIR spectra for PMAC
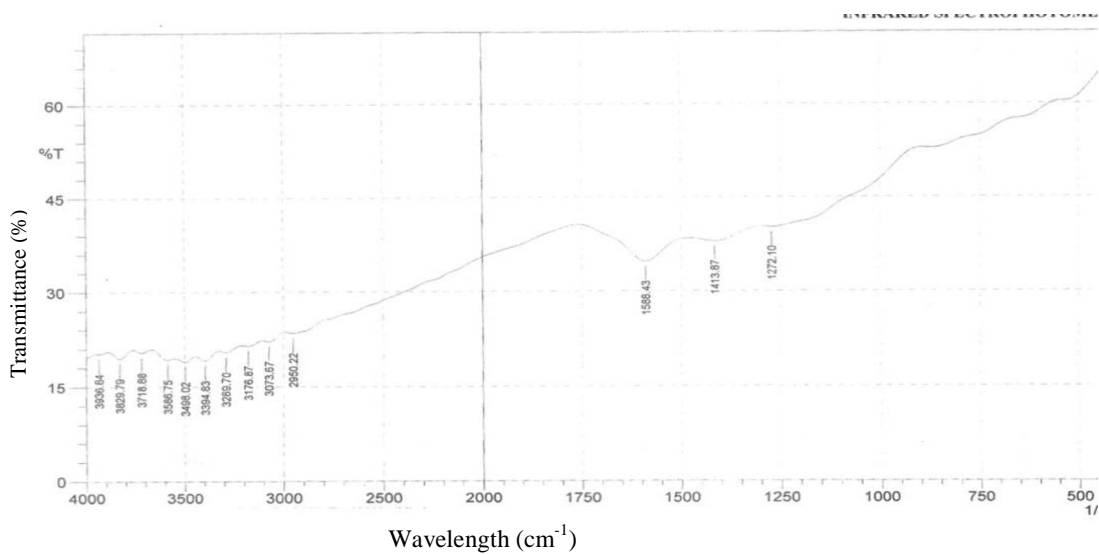
Wave number (cm^{-1})	Bond Source
1236.67	C – C Stretch in ketone, C-C(O)-C in ester
1431.23	Methyl C-H asymmetric bend
1585.58	C = C-C, Aromatic ring stretch
3293.56	O– H, Normal polymeric OH stretch
3472.95	O – H, Dimeric OH stretch
3648.48	O – H stretch in phenols and alcohols
3842.33	O – H stretch in phenols and alcohols
3959.03	O – H, stretch in phenols and alcohols

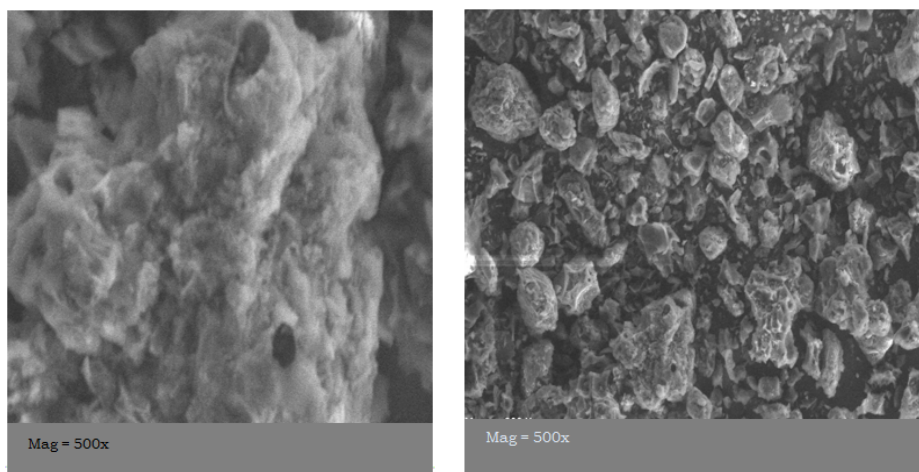**Fig. 1b and Table 3. FTIR spectra for TCAC**

Fig. 2a. SEM micrograph of PMAC (before and after adsorption)

3.2 Effect of Particle Size

The effect of particle size of PMAC and TCAC on Pb(II) uptake are presented in Figure 4 from where it can be seen that the % Pb(II) absorbed decreased with increase in particle size for both PMAC and TCAC. The %Pb(II) was higher for PMAC at smaller particle sizes while TCAC was slightly higher at larger particle sizes. There was only a slight decrease in %Pb(II) adsorption on

PMAC between 0.2 and 0.3 mm particle sizes and an increase in Pb(II) uptake on TCAC between these particle sizes. The decrease in %Pb(II) adsorbed became pronounced between 03-1mm for both adsorbents and became even more pronounced after 1mm particle size. The percentage of Pb(II) adsorbed at equilibrium on PMAC and TCAC decreased from 99.5% to 91% and from 99% to 91.5%, respectively, when the particle size of the adsorbents was increased from 0.3 to 1.2 mm. The higher biosorption with smaller biosorbent particles could be attributed to the fact that smaller particles provided a larger specific surface area.
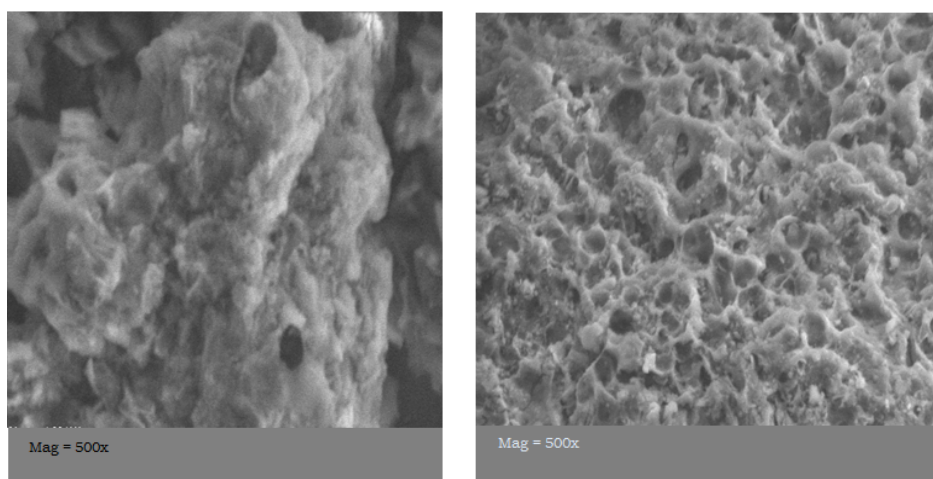
3.3 Effect of Solution pH

The solution pH is an important parameter in the adsorption of metal ions from aqueous solution because it affects the solubility of metal ions, concentration of the counter ions on the functional groups of the adsorbents and the degree of ionization of the adsorbate during reaction [5,19]. Pb(II) removal was studied as a function of pH over a pH range of 2-8 on PMAC and TCAC at the initial Pb(II) concentration of 100mg/l as shown in Fig 5. The figure shows that the percentage removal of Pb(II) was dependent on the initial pH of the solution. The removal of Pb(II) onto PMAC and TCAC were 84% and 62%, respectively, at pH 2, and increased to 99% and 96%, respectively, for the adsorbents as the pH was raised to 6. The percentage Pb(II) adsorbed then decreased sharply to 30% and 20%, respectively, for these adsorbents as the pH was further increased from 6 to 8. Similar behavior has been reported by various researchers.

The low level of Pb(II) uptake at low pH values could be attributed to the increased concentration of hydrogen (H^+) ions which competed with Pb(II) for binding sites on the adsorbent mass. In addition, at low pH the overall surface charge on the adsorbents is also positive and inhibited the approach of positively charged metal ions. As the solution pH is increased, the completion of H^+ and Pb(II) decreases and the surface active sites of the adsorbents became more negatively charged. The electrostatic attractive force between the adsorbents and the Pb(II) therefore, became prominent. The decrease in percentage Pb(II) uptake at pH above 6 may be due to the precipitation of lead hydroxide which reduced the percentage Pb(II) adsorbed [16].

Table 4. XRF result of PMAC and TCAC

Chemical constituent	Carbon type/composition (%)	
	PMAC	TCAC
SiO_2	5.9	13.6
P_2O_5	2.7	4.3
Cl	1.6	Nil
K_2O	11	28.8
CaO	31.2	34.9
Cr_2O_3	1.4	0.07
MnO	0.2	0.19
Fe_2O_3	9	7.4
NiO	1.2	2.3
CuO	1.1	1.3
ZnO	1.3	0.3
MgO_3	3.2	1.86
Re_2O_7	3.08	Nil
SO_3	Nil	1.2
CdO	27	Nil
Rh_2O_3	**Nil**	3.7

Fig. 2b. SEM micrograph of TCAC (before and after adsorption)
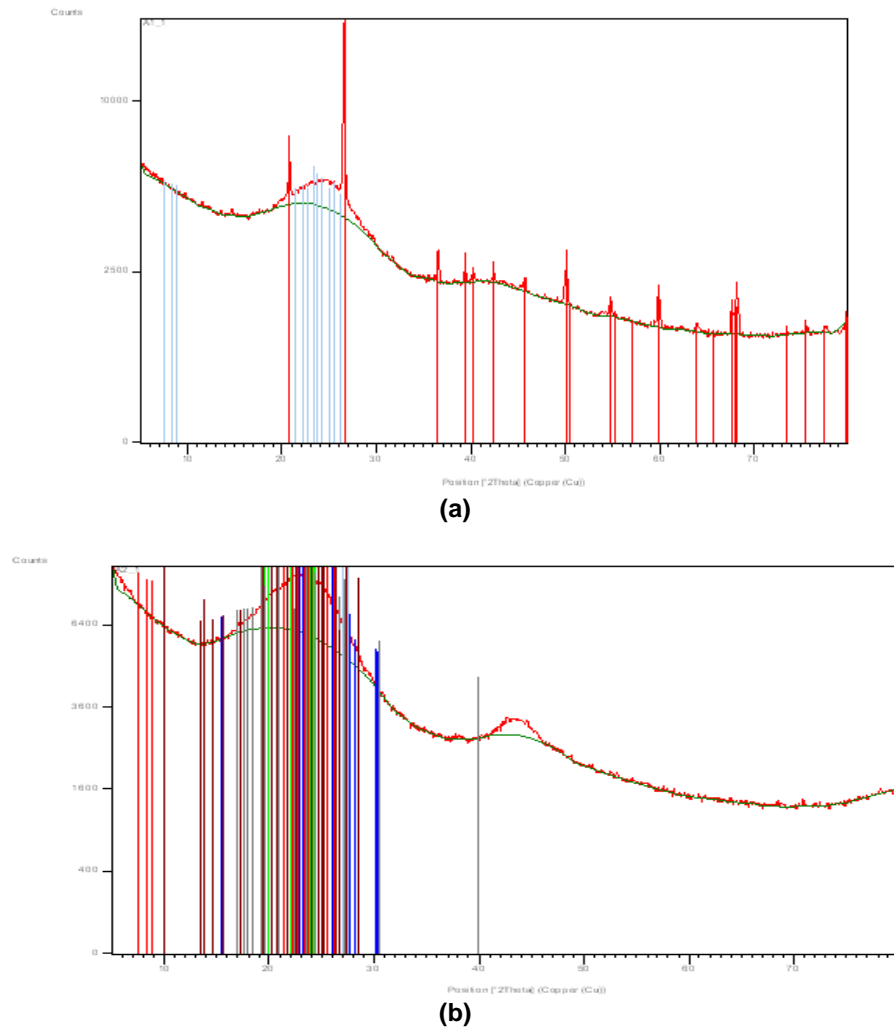
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(a)

(b)

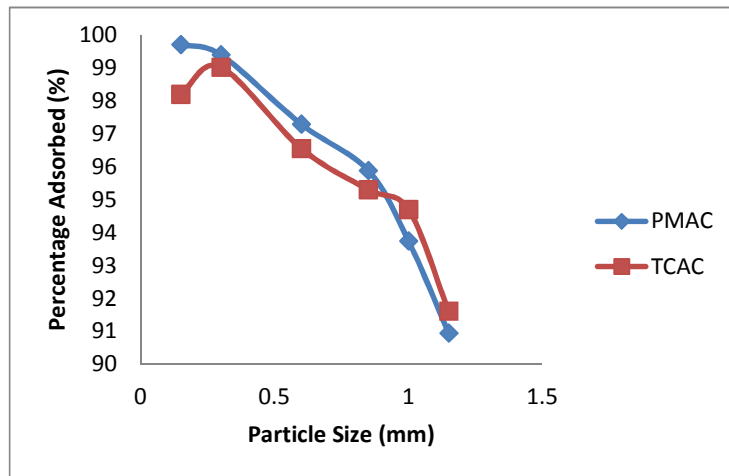**Fig. 3. XRD of activated carbons (a) PMAC, (b) TCAC**

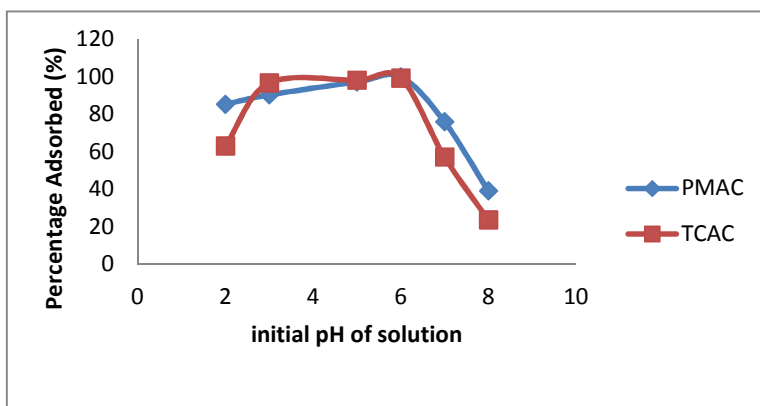**Fig. 4. Effect of particle size on Pb(II) adsorption by PMAC and TCAC**

Fig. 5. Effect of initial solution pH on Pb(II) adsorption by PMAC and TCAC
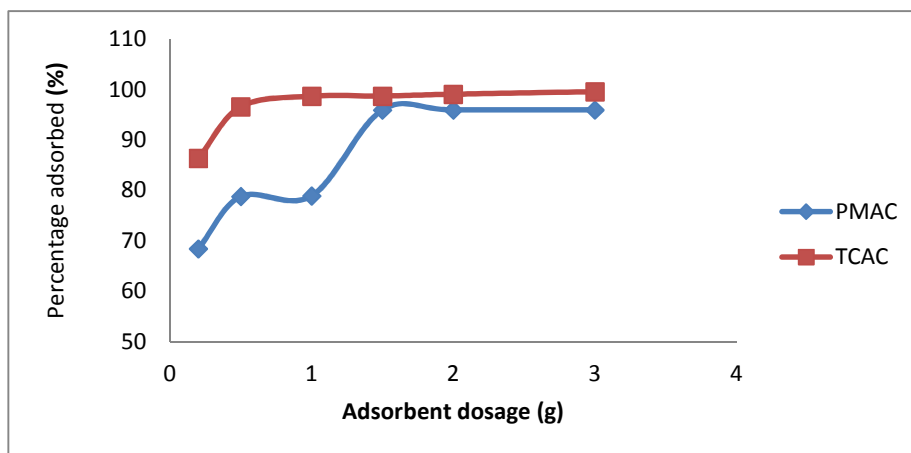

Fig. 6. Effect of adsorbent dosages on Pb(II) adsorption on PMAC and TCAC

3.4 Effect of Adsorbent Dosage

Fig. 6 shows the effect of increasing the dosages of PMAC and TCAC on the percent removal of Pb(II) at initial Pb(II) concentration of 100 mg/l. From this figure, it was observed that the percent Pb(II) adsorbed by PMAC reached 94% with an optimum dosage of 1.5 g while for TCAC, the amount adsorbed was 93% at optimum dosage of 1.0 g. The increase in percent Pb(II) with increase in adsorbents dosages could be due to an increase in the number of possible binding sites and surface area resulting from increasing dosage of the adsorbent [20]. Further increase of the adsorbents beyond the optimum dosages did not change the amount of Pb(II) ions adsorbed. This can be explained by the decreased active binding sites on the adsorbents due to the particles interactions, such as aggregation, resulting from high sorbent concentration [21,22].

3.5 Effect of Adsorbate Concentration

The effect of initial Pb(II) concentration on percent Pb(II) adsorbed was investigated in the range 100-600mg/l using PMAC and TCAC. The results presented in Fig. 7 show that the percent Pb(II) removal was up to 98.5 and 99.5%, respectively, for PMAC and TCAC at 100 mg/l initial Pb(II) concentration. The figure also indicated that percent Pb(II) adsorbed decreased with increase in initial Pb(II) concentration. At 600mg/l initial Pb(II) concentration, the percent Pb(II) adsorbed was 60% and 83% for PMAC and TCAC, respectively. The high removal efficiency obtained at low Pb(II) concentration may be attributed to the availability of adequate adsorption site at the lower initial Pb(II) concentration while the low value obtained at higher initial Pb(II) concentration may be due to insufficiency of the adsorption site due to increase in the initial Pb(II)

concentration [23,24]. The figure showed also the adsorption capacity of the adsorbents at various initial Pb(II) concentrations in the range 100-600 mg/l. It is observed that the adsorption capacity increased with increase in initial Pb(II) concentration. The increase in adsorption capacity with increase in initial Pb(II) concentration can be explained by the higher driving force for mass transfer with increase in the initial Pb(II) concentration [25].

3.5 Effect of Contact Time

The percent Pb(II) adsorbed on PMAC an d TCAC was studied as a function of shaking time at 100 mg/l initial Pb(II) concentration, 30℃, 1.5 g adsorbent dose and pH 6. The results are

presented in Fig. 8. It can be seen from the figure that the percent Pb(II) adsorbed increased rapidly within the first 25 min of contact time. The percent Pb(II) uptake then gradually became slow between 25 and 60 min for PMAC and between 25 and 40 mins for TCAC. The percentage Pb(II) adsorbed thereafter became constant with increase in shaking time. The two step sorption profile obtained has been reported elsewhere [7, 26].

3.6 Effect of Solution Temperature

The effect of solution temperature on percent Pb(II) uptake onto PMAC and TCAC was investigated at various initial temperature and the results obtained were presented in Fig. 9. The
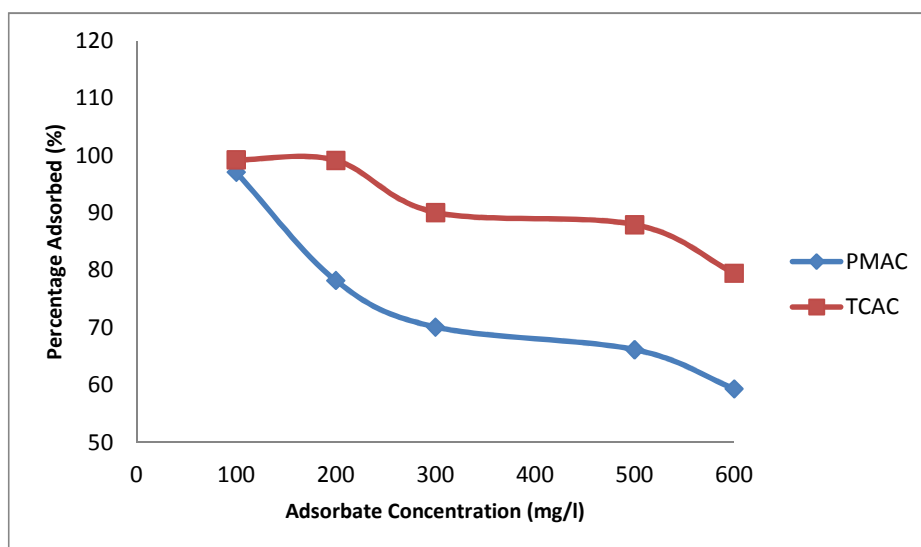
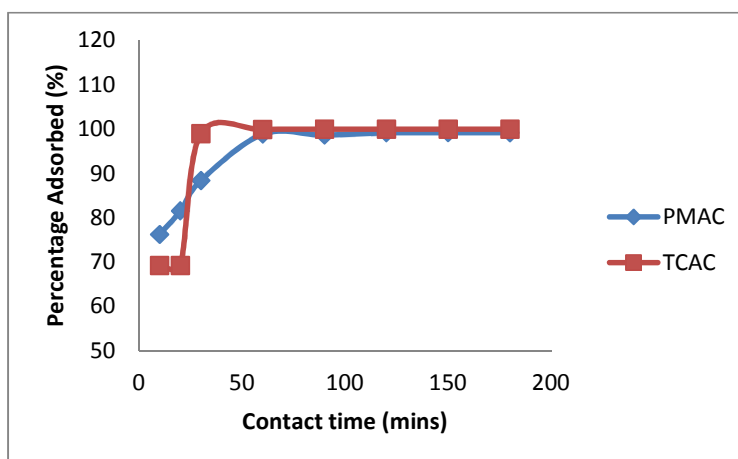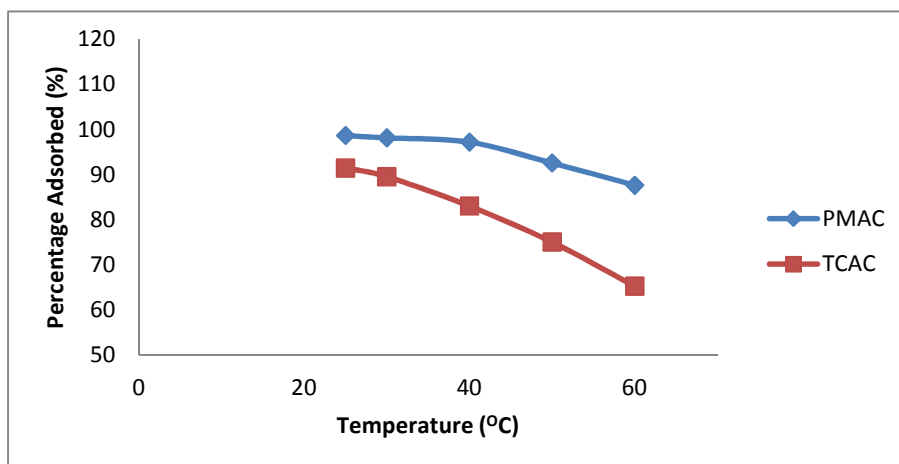**Fig. 7. Effect of adsorbate concentration on adsorption of Pb(II) onto PMAC and TCAC**

Fig. 8. Effect of contact time on Pb(II) adsorption by PMAC and TCAC

Fig. 9. Effect of Temperature on adsorption of Pb(II) by PMAC and TCAC

figure indicated that the percent Pb(II) adsorbed decreased from 98% and 96% to 84% and 63%, for PMAC and TCAC, respectively, when the solution temperature was increased from 20°C to 60°C. it could also be observed from the figure that very little decrease in percent Pb(II) adsorbed occurred between 20°C to 40°C for PMAC. The observed trend could be attributed to increased solubility of Pb(II) from the solid to the liquid phase. The decrease may also be due to decrease in equilibrium adsorption capacity of PMAC and TCAC for Pb(II) adsorbed with increase in temperature suggested that the adsorption occurred exothermically. Similar results were reported by other researchers [27,28].

3.7 Adsorption Isotherm

An adsorption isotherm represents the equilibrium relationship between the adsorbate concentration in the liquid phase and that of the adsorbents surface at a given condition. The data under study of adsorption isotherm are to be specific for each system and the determination of isotherm are to be carried out for every application [29]. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find suitable model that can be used for design purposes [30,31]. Adsorption isotherm is characterized by certain constant values which express the surface properties, sorption mechanisms and affinity of the adsorbent and can be used to compare the adsorptive capacities of the adsorbent for different pollutants [31,32,33]. In this study, data from the adsorption isotherm were tested with

Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm models.

The Langmuir model [34] is based on the assumptions of surface homogeneity, monolayer surface coverage and no interaction between adsorbed species. The linear form of the equation is expressed as

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \qquad (6)$$

Where q_e(mg/g) is the amount of Pb(II) adsorbed per unit weight of adsorbent at equilibrium, C_e(mg/l) the equilibrium concentration of Pb(II) in solution, Q_o(mg/g) is the maximum Pb(II) uptake and b is Langmuir constant related to the energy of adsorption. To confirm the favourability of an adsorption process to Langmuir isotherm, the essential features of the isotherm can be expressed in terms of a dimensionless constant; separation factor or equilibrium parameter, R_L, which is defined by the following equation [3, 9].

$$R_L = \frac{1}{1 + bC_o} \qquad (7)$$

where C_o(mg/l) is the initial amount of Pb(II) and b is the Langmuir constant. The value of R_L provides important information about the nature of adsorption. R_L value of zero implies irreversible adsorption; $0 < R_L < 1$ implies favourable adsorption process; $R_L = 1$ and $R_L > 1$ implies linear and unfavourable adsorption processes, respectively.

The Freundlich isotherm [35] is based on the assumption of heterogeneous surface with a

non-uniform distribution of biosorption heat over the surface. The linear form of the equation is

$$log\, q_e = log\, K_F + \frac{1}{n} log\, C_e \qquad (8)$$

where C_e is the equilibrium concentration of Pb(II), q_e the amount of Pb(II) adsorbed at equilibrium, K_F, and 1/n the Frendlich model constants indicating the adsorption capacity and adsorption intensity , respectively. In general, n > 1 suggests that the adsorbate is favourably adsorbed on the adsorbent.

The Temkin isotherm [36] assumes that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate-adsorbent interaction. The linear form of this model is given as

$$q_e = \frac{RT}{b_T} ln\, K_T + \frac{RT}{b_T} ln\, C_e \qquad (9)$$

where q_e is the amount adsorbed at equilibrium, K_T the Temkin isotherm energy constant and b_T a constant related to the heat of adsorption.

The Dubinin-Radushkevich (D-R) isotherm model [37] is often used to estimate the characteristic porosity and the apparent free energy of adsorption. The D-R isotherm does not assume heterogeneous surface or constant adsorption potential. It is, therefore, more general than the Langmuir isotherm [38]. The linear form of D-R equation is

$$ln\, q_e = ln\, q_m + \beta \varepsilon^2 \qquad (10)$$

where $\beta (mg^2 K/J^2)$ is a constant related to the adsorption energy and ε the Polanyi potential equal to RTln(1+1/C_e). The adsorption mean free energy, E (kJ/mol) is given as

$$E = \frac{1}{(2\beta)^{0.5}} \qquad (11)$$

The mean free energy (E) of adsorption specifies the adsorption mechanism whether it is physical or chemical. Physical adsorption process occurs if the value of E< 8 kJ/mol, while 8<E<16 kJ/mol describes chemical (ion exchange) adsorption mechanism.

The Langmuir, Freundlich, Temkin and D-R isotherm plots for the removal of Pb(II) onto PMAC and TCAC were presented in Figs. 10 to

13, respectively. The models constants and correlation coefficients (R^2) values obtained for the four isotherm models are shown in Table 2. On the basis of the figures and the correlation coefficients, The Langmuir and Freundlich models represented the equilibrium data better that the Temkin and the D-R isotherm models. Similar results were obtained by many researchers [39,40,41]. The Langmuir equation is intended for a homogenous surface and a good fit of this equation suggests monolayer adsorption. The Freundlich equation is suitable for homogenous and heterogeneous surfaces indicating a multilayer adsorption [39]. These might suggest that the adsorption of Pb(II) on PMAC and TCAC mainly takes place at specific homogenous sites and is confined to monolayer adsorption [39].

The value of Q_o obtained was 200mg/g at temperatures of 20℃ and 40℃ and 100mg/g at 60℃ for PMAC and 200 mg.g, 250mg/g and 100 mg/g at 20℃, 40℃ and 60℃, respectively for TCAC > the value of R_L at different temperatures were between 0 and 1, which showed favourable adsorption of Pb(II) on PMAC and TCAC at the conditions investigated. The K_F values obtained from the Freundlich isotherm were between 10.72 and 11.94(l/g) for PMAC and between 8.37 and 9.33 (l/g) for TCAC. It was observed that there was slight increase in K_F with increase in temperature. The values of n larger than 1 suggested than Pb(II) was favourably adsorbed on PMAC and TCAC.

3.8 Adsorption Kinetics

Kinetics analysis is required to get an insight into the rate of adsorption and the rate-limiting step of adsorption mechanism [42]. In order to analyze the sorption kinetics of Pb(II) onto PMAC and TCAC, the pseudo-first-order, the pseudo-second-order and the intraparticle diffusion models were applied to experimental data.

The linear form of the pseudo-first order equation [19] is expressed as:

$$log(q_e - q_t) = log\, q_e - \frac{k_1 t}{2.303} \qquad (12)$$

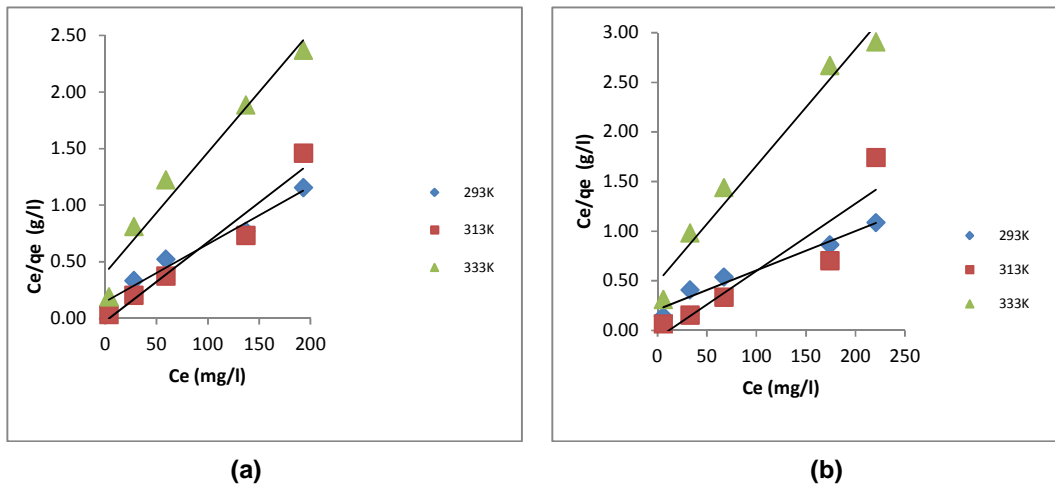where q_e and q_t are the amounts of Pb(II) adsorbed at equilibrium and at time t,

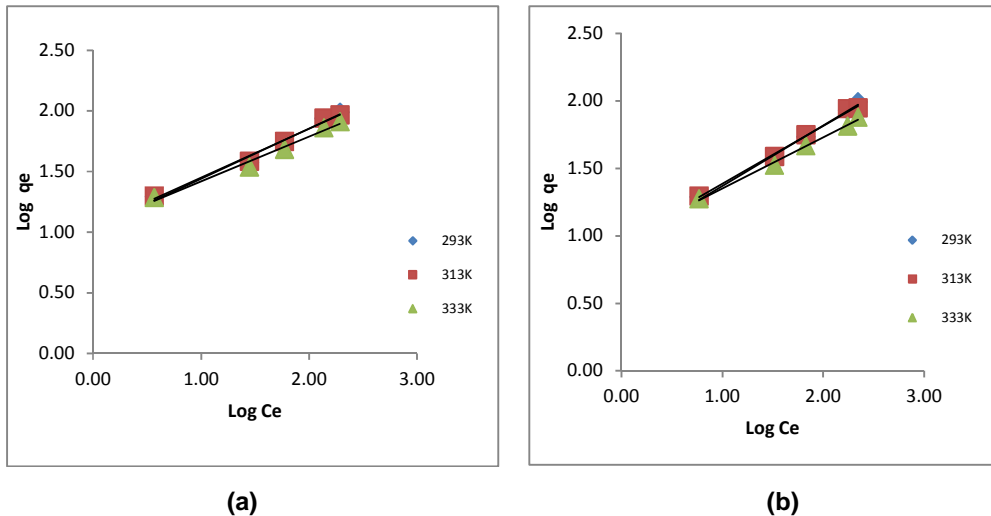**Fig. 10. Langmuir plot for Pb(II) adsorption onto (a) PMAC, (b) TCAC**

Fig. 11. Freundlich plot for Pb(II) adsorption onto (a) PMAC, (b) TCAC

respectively, and k_1 is the rate constant of first order adsorption (h^{-1}). The plot of $\log(q_e - q_t)$ against t provided a linear relationship from where k_1 and q_e were determined (see Fig. 14). The experimental and calculated values of q_e, k_1, and the correlation coefficients R^2 for various Pb(II) concentrations are presented in Table 6.

The linearized form of the pseudo-second-order kinetic equation [43] is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \qquad (13)$$

where k_2(g/mgh) is the rate constant of the second-order adsorption. The linear plot of t/q_t versus t (Fig. 15) gives $1/q_e$ as the slope and $1/k_2 q_e^2$ as the intercept. The values of the

experimental and predicted values of q_e, k_1 and correlation coefficient, R^2, for various Pb(II) concentrations are shown in Table 6.

Table 6 shows that the correlation coefficients for pseudo-first-order kinetic model were low and the predicted values of q_e were not close to experimental q_e values. These observations suggests that the model is not suitable to describe Pb(II) sorption on PMAC and TCAC. The R^2 value for the pseudo-second-order kinetic model had higher (>0.995) values for the adsorbents and at all the concentrations investigated. In addition, the rate constants of the pseudo-second-order model decreased with increasing initial Pb(II) concentration. Similar results were obtained by other researchers (20,

43). The results indicated that the adsorption kinetic data was better represented by the pseudo-second-order model. This suggests that the adsorption of Pb(II) onto PMAC and TCAC is a chemisorptions process involving exchange or sharing of electrons mainly between metal ions and functional groups (mainly hydroxyl and carboxyl groups of the adsorbents) [44].

The intraparticle diffusion model [44, 45] was proposed to identify the adsorption mechanism and to predict the rate controlling step. The intraparticle diffusion equation is expressed as:

$$q_t = k_{id}t^{\frac{1}{2}} + c_i \tag{14}$$

where q_t(mg/g) is the amount adsorbed at time t, c_i(mg/g) the intercept, and k_{id}(mg/gmin$^{1/2}$) the intraparticle diffusion rate constant. Figure 16 shows the amount of Pb(II) sorbed versus $t^{1/2}$ at three different adsorbate concentrations with fixed amounts of PMAC and TCAC. The figures showed three distinct regions. The initial region of the curve (0-9 min) relates the adsorption on the external surface. The region after 9min is the gradual stage of adsorption which is the
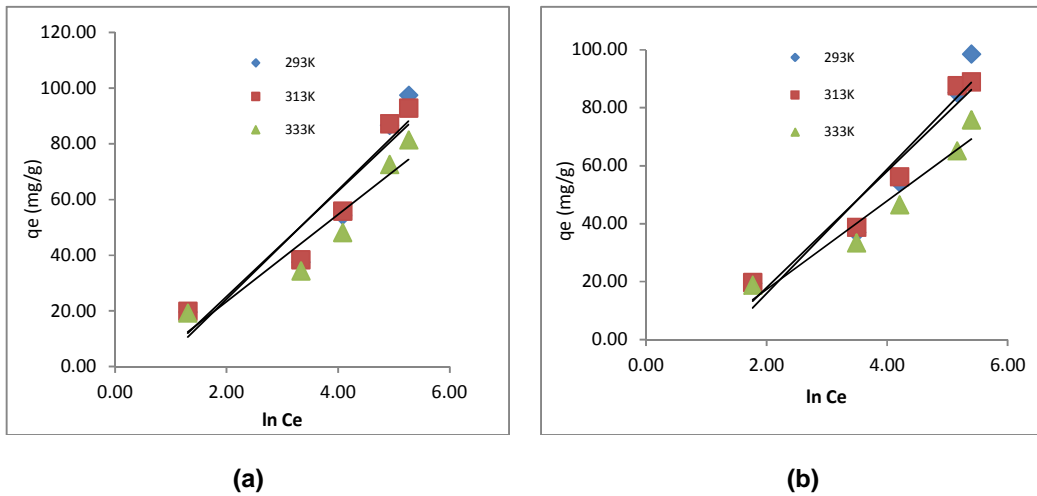

(a)

(b)

Fig. 12. Temkin plot for Pb(II) adsorption onto (a) PMAC, (b) TCAC

Table 5. Isotherm model parameters and correlation coefficients for Pb(II) adsorption on PMAC and TCAC at 20, 40 and 60°C

| Isotherm model	Temperature (K)					
	PMAC			TCAC		
	293	313	333	293	313	333
Langmuir						
Q_m (mg/g)	200.00	200.00	100.00	200.00	250.00	100.00
K_L or b (L/mg)	0.0342	0.2273	0.0252	0.0122	0.4444	0.0161
R_L	0.2260	0.0421	0.2842	0.4505	0.220	0.3831
R^2	0.971	0.991	0.959	0.997	0.967	0.962
Freundlich						
N	2.4331	2.4938	2.7100	2.2321	2.3310	2.6316
K_f (L/g)	10.7152	11.1686	11.1944	8.3753	9.0782	9.3325
R^2	0.983	0.987	0.984	0.993	0.995	0.995
Tempkin						
b_T (J/mg)	124.4763	137.7598	177.4719	113.4607	129.4024	181.1886
A	0.4689	0.5154	0.6079	0.2830	0.3311	1.0637
R^2	0.889	0.907	0.902	0.914	0.943	0.937
Dubinin-Radushkevich						
q_D (mg/g)	64.91	65.20	56.32	62.43	64.59	54.76
B (mol^2/KJ^2)	2×10^{-7}	2×10^{-7}	2×10^{-7}	3×10^{-6}	3×10^{-6}	3×10^{-6}
E (kJ/mol)	6.3×10^{-4}	6.3×10^{-4}	6.3×10^{-4}	2.5×10^{-3}	2.5×10^{-3}	2.5×10^{-3}
R^2	0.6673	0.696	0.673	0.796	0.837	0.817

| (a) | (b) |
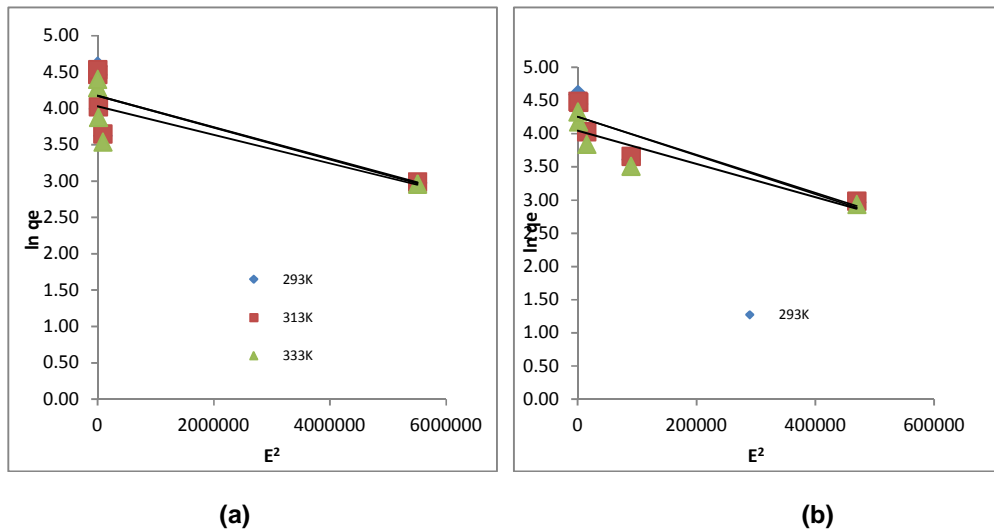
Fig. 13. D-R plot for Pb(II) adsorption on (a) PMAC, (b) TCAC
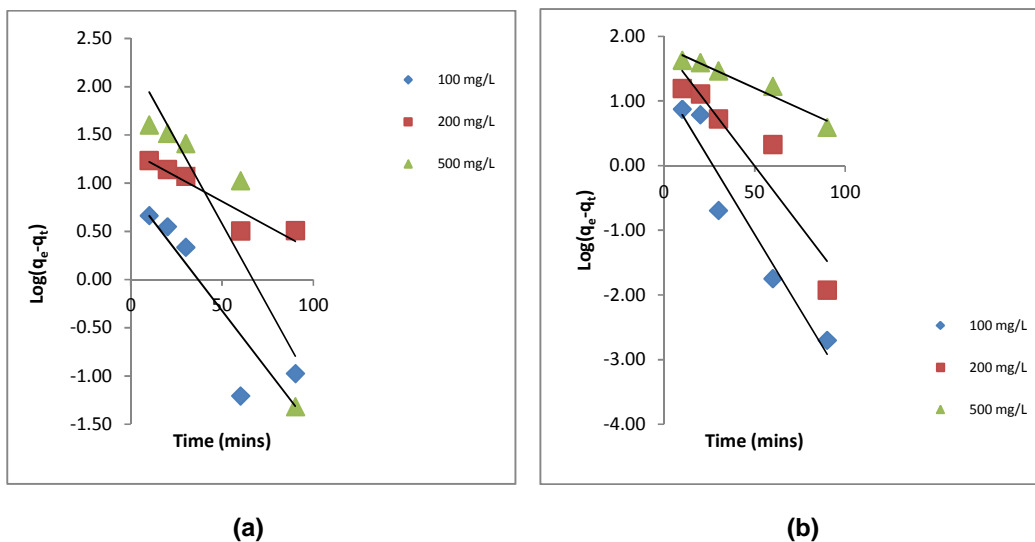

| (a) | (b) |

Fig. 14. Pseudo-first-order kinetic plot for Pb(II) adsorption on (a) PMAC, (b) TCAC

intraparticle diffusion and the third portion is the final equilibrium stage [46,47]. The intraprticle diffusion region followed the intraparticle diffusion model with high correlation coefficient (>). The lines, however, did not pass through the origin, indicating that intraparticle diffusion was not the only rate limiting step and the boundary layer diffusion controlled the adsorption to some degree [47]. The intraparticle diffusion model constants and correlation coefficients for adsorption of Pb(II) on PMAC and TCAC is presented in table 6. It can be seen from the table that the value of c_i increased with increase in initial Pb(II) concentration (100 – 500 mg/l)

which indicated an increasing boundary layer effect [48].

3.9 Adsorption Thermodynamics

Thermodynamic parameters such as enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy change (ΔG) are important in deciding whether a reaction is spontaneous or not and could also provide indepth information regarding the inherent energy and structural changes after adsorption [7, 38]. The values of ΔS and ΔH were evaluated using the following relations.

$$ln\,K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (15)$$

where R(8.314 J/mol.K) is the universal gas constant, K_c is the equilibrium constant defined by q_e/C_e and T(K) the absolute temperature. The values of ΔS and ΔH were evaluated from the intercept and slope of lnK_c versus 1/T. The free energy change (ΔG) was estimated from equation [16].

$$\Delta G = \Delta H - T\Delta S \qquad (16)$$

The values obtained for ΔS, ΔH and ΔG for Pb(II) uptake onto PMAC and TCAC were presented in Table 7. The values of ΔG were negative which

reflects the spontaneous nature of the adsorption of Pb(II) onto PMAC and TCAC at the temperature range investigated. A more negative value obtained for ΔG at higher temperature showed that adsorption was more favourable at high temperature [19]. The negative values obtained for ΔH at the temperatures investigated signified that the process was exothermic and the magnitude of ΔH showed that it was physical in nature and involves weak forces [38,49,50]. The positive value of ΔS indicated that there were increased randomness at the solid/solution interface with some structured changes in the adsorbate and adsorbent during the adsorption process [9].
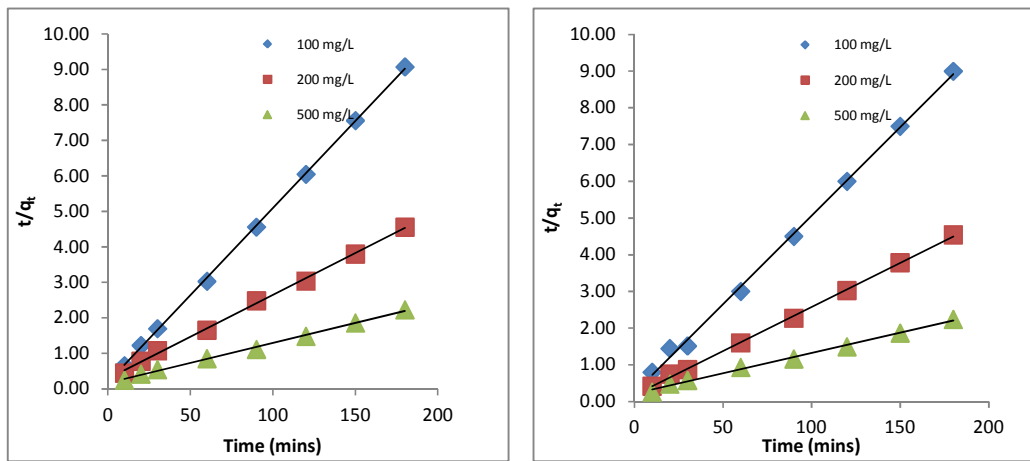

Fig. 15. Pseudo-second-order kinetic plot for Pb(II) adsorption on (a) PMAC, (b) TCAC
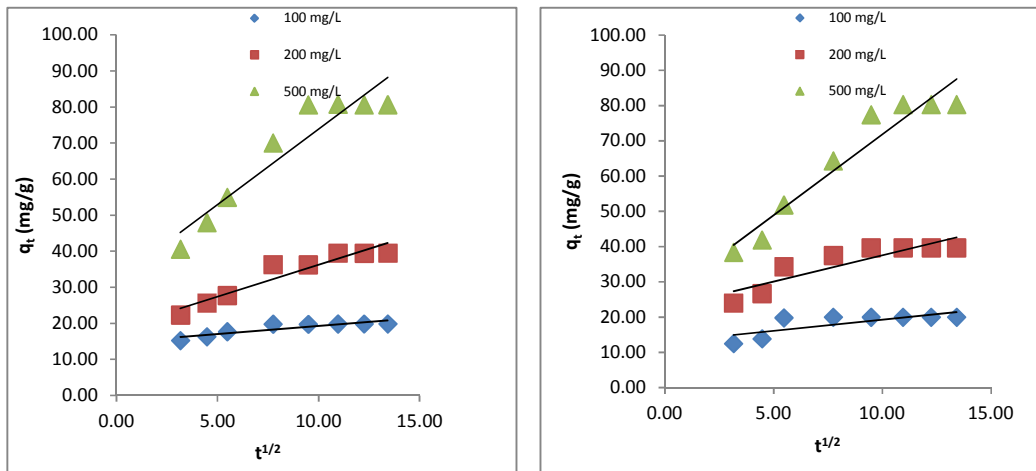

Fig. 16. Intraparticle diffusion kinetic plot for Pb(II) adsorption on (a) PMAC, (b) TCAC

Table 6. Kinetic model parameters and correlation coefficients for Pb(II) adsorption on PMAC and TCAC at 100, 200 and 500 mg/l

Kinetic models	Metal ion concentration (mg/L)					
	PMAC			TCAC		
	100	200	500	100	200	500
First-order						
K_1 (min^{-1})	0.0210	0.0230	0.0070	0.0470	0.0230	0.0070
R^2	0.758	0.918	0.818	0.741	0.918	0.877
Pseudo first-order						
K_1 (min^{-1})	0.0553	0.0230	0.0783	0.0276	0.0829	0.1059
q_e (mg/g)	8.1283	21.0378	191.8669	68.7068	68.3912	17.7419
R^2	0.822	0.889	0.826	0.944	0.883	0.936
Pseudo Second-order						
K_2 (g/mg min)	0.0137	0.0018	0.0007	0.0094	0.0032	0.0006
q_e (mg/g)	20.4082	43.4783	90.9091	20.8333	41.6667	90.9091
R^2	0.999	0.998	0.997	0.998	0.999	0.995
Intra particle and film diffusion						
K_d (g/mg min$^{1/2}$)	0.44	1.765	4.196	0.639	1.493	4.594
Δ	14.84	18.55	31.89	12.9	22.62	25.88
R^2	0.786	0.905	0.891	0.58	0.784	0.925

Table 7. Thermodynamic parameters for the adsorption of Pb(II) on PMAC and TCAC

Adsorbent	ΔH^0 (KJ /mol)	ΔS^0 (KJ /K /mol)	ΔG^0 (KJ /mol)		
			298K	313K	333K
PMAC	-1.60	0.024	-7.171	-8.014	-8.013
TCAC	-1.73	0.024	-11.03	-11.58	-12.32

4. CONCLUSIONS

Activated carbons were prepared from *Penthaclethra macrophylla* (PMAC) and *Tetracarpidum conophorium* (TCAC) seed shells by chemical activation with H_3PO_4. They were characterized and utilized for the removal of Pb(II) from aqueous solution of various concentrations (100 – 500 mg/l). The percent Pb(II) adsorbed increased with increase in adsorbent dosage and contact time and decreased with increase in particle size, initial Pb(II) concentration and temperature. Maximum adsorption of Pb(II) on the absorbents occurred at pH 6. The equilibrium data fitted the Langmuir and Freundlich isotherm well. The maximum adsorption capacities q_e, calculated from Langmuir model were found to be 200 mg/g for both adsorbents at 20°C, 200 and 250 mg/g for PMAC and TCAC, respectively at 40°C and 100mg/g for both adsorbents at 60°C. Kinetic studies showed that adsorption followed pseudo-second-order kinetic model and intraparticle diffusion was not the only rate controlling step. Thermodynamic calculations indicated that the process was feasible, spontaneous and exothermic. It can be concluded that PMAC and TCAC are efficient adsorbents for the removal of Pb(II) from aqueous solutions.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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