

## Evaluation of Lead(II) Removal by Carbon Derived from Gingelly Oil Cake

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Carbon was derived from gingelly oil cake by thermal activation method and its Pb(II) removal capacity was compared with commercial activated carbon. The effect of experimental parameters such as pH, initial concentration, contact time and adsorbents dosage were studied. The data were fitted with Langmuir, Freundlich and Temkin models to describe the equilibrium isotherms. The kinetic data fitted well with Lagergren pseudo first order and pseudo second order models. The maximum adsorption capacity for Pb(II) calculated from Langmuir isotherm was found to be 105.26 mg/g for thermally activated carbon. R<sup>2</sup> values showed that the experimental data fit well with Freundlich isotherm and pseudo second order kinetics. FT-IR analysis was used to obtain information on the nature of possible interaction between adsorbent and metal ions. SEM images confirmed the adsorption of Pb(II) onto thermally activated gingelly oil cake adsorbent through the morphological observation. Thermodynamic study further showed the feasibility and spontaneous nature of the adsorption. The carbon was also tested for the removal of Pb(II) from lead battery synthetic wastewater. Therefore, it has been concluded that carbon derived from gingelly oil cake can be evaluated as an alternative adsorbent to treat wastewater containing Pb(II) ions.

**Key Words: Pb(II) removal, Gingelly Oil Cake, Thermally Activated Gingelly Oil Cake, FT-IR, SEM, Adsorption isotherms, Kinetics.**

### INTRODUCTION

Heavy metal ions are extremely toxic and harmful even at low concentrations, which can seriously affect plants and animals and have been involved in causing a large number of afflictions<sup>1-3</sup>. Therefore, the elimination of these metals from water and wastewaters is important to protect public health. Traditional technologies for removal of heavy metals from wastewaters include chemical precipitation, ion-exchange, membrane separation, reverse osmosis, evaporation and electrolysis<sup>4-6</sup>. However, most of them do not exhibit high treatment efficiency, especially at metal concentrations in the range of 0.01-0.10 g/L<sup>1</sup>. Precipitation methods are particularly

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reliable but require large settling tanks for the precipitation of voluminous alkaline sludges and a subsequent treatment is also needed. Ion-exchange has the advantage of allowing the recovery of metal ions, but is expensive and sophisticated. In this connection, activated carbons are widely used because of their high adsorption abilities for a large number of heavy metal ions<sup>7</sup>. However, the price of activated carbons is relatively high, which limits their usage. This has led many researchers to search for low cost materials such as coal, fly ash, agricultural wastes and biosorbents<sup>8</sup>.

Lead, a toxic heavy metal, is widely used in many important industrial applications, such as storage battery, printing, pigments, fuels, photographic materials and explosives manufacturing<sup>2</sup>. Its presence in drinking water above the permissible limit (0.05 mg/L) may cause adverse health effects such as anemia, encephalopathy, hepatitis, nephritic syndrome and mental retardation<sup>3</sup>.

Agricultural solid waste by-products such as fruit stones<sup>9,10</sup>, coconut shell<sup>11,12</sup>, bagasse<sup>13,14</sup>, nut shells<sup>15,16</sup>, coir pith<sup>17,18</sup>, rice husk<sup>19</sup>, shells of lentil, wheat and rice<sup>20</sup> have been used as raw materials to prepare activated carbons. These solid wastes are not only cheap but also easily available. In this connection, gingelly oil cake which was available in large quantities from oil industries, has been procured and processed for the preparation of thermally activated gingelly oil cake (TAGOC) and its efficiency to remove Pb(II) from aqueous solution and lead battery wastewater (synthetic) was evaluated in relation to commercial activated carbon (CAC).

The influence of parameters governing adsorption of Pb(II), such as contact time, initial concentration, pH, adsorbent dose *etc.*, on thermally activated gingelly oil cake and commercial activated carbon were investigated in batch mode. The kinetic data were fitted to pseudo first order and pseudo second order models. The isotherm equilibrium data were fitted to Langmuir, Freundlich and Temkin model.

## EXPERIMENTAL

The atomic absorption spectrometer (AAS) of electronic corporation of India Ltd., (Hyderabad, India), model-SL163, was used for the determination of Pb(II) concentration. The fourier transform infrared spectroscopy (FT-IR) spectrum was recorded with a Shimadzu 8400 S model. Scanning electron microscopic (SEM) studies were performed using JOEL-6360 instrument. Adsorbents were analyzed using ARL-Advant XP-X ray fluorescence spectrometer (XRF) and LECO carbon and sulphur, LECO nitrogen and oxygen analyzers. BET isotherm studies were conducted using BET instrument model ASAP 2020. The pH was measured with a systronics digital pH meter model 335. A thermally controlled mechanical shaker with a speed of 200 rpm was used for batch studies.

All the chemicals used in the present study were of analytical reagent grade (SD fine chem., Mumbai, India) and distilled water was used for diluting the solutions. Stock aqueous solution 1000 mg/L of Pb(II) was prepared by dissolving 1.59 g of Pb(NO<sub>3</sub>)<sub>2</sub> in 100 mL of distilled water. Pb(II) solutions of desired concentrations

were prepared by adequate dilution of the stock solution. The pH was adjusted with 0.1 M HNO<sub>3</sub> or KOH.

**Preparation of thermally activated gingelly oil cake (TAGOC):** Gingelly oil cake was washed several times with distilled water to remove any surface and soluble impurities and then dried at 110 °C. About, 20 g of the dried material was taken in a silica crucible and carbonized slowly in a muffle furnace at a temperature of 600-700 °C. As soon as the production of char was complete, the furnace temperature was raised slowly to 800-850 °C for thermal activation for a period of 0.5 h and thermally activated gingelly oil cake (TAGOC) thus obtained was used for all experiments. Commercial activated carbon (SD fine chem., Mumbai, India) was procured from the market. Both CAC and TAGOC were powdered and sieved to a particle size of ASTM 80-120 and used for batch experiments.

**Batch adsorption studies:** 100 mL of Pb(II) solution with desired concentration adjusted to a desired pH were taken in polythene bottles of 300 mL capacity and 0.1 g of adsorbent was added to it. The solutions were agitated for a predetermined period at 30 ± 1 °C and then carbon particles were separated by using centrifuge and the supernatant liquid was analyzed for Pb(II) by AAS. Blanks were used for control in all the experiments. Adsorption isotherm and kinetic studies were carried out with different initial concentrations of Pb(II) by maintaining the adsorbent dosage at constant level. Adsorption isotherm studies were made after an agitation period of 24 h.

**Analytical method:** The concentration of unadsorbed Pb(II) in the supernatant liquid was determined by using an AAS with an air-acetylene flame. The hollow cathode lamp was operated at 15 mA and analytical wavelength was set at 217 nm.

**Metal uptake:** The removal efficiency (E) of the adsorbents on Pb(II) was calculated by using the following expression.

$$E (\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

where, C<sub>o</sub> and C<sub>e</sub> are the initial and equilibrium concentrations (mg/L) of Pb(II) solution.

FTIR spectroscopy was used to detect vibration frequency changes in these adsorbents before and after Pb(II) uptake. The spectra were collected by Shimadzu spectrometer within the range of 4000-400 cm<sup>-1</sup> to determine various surface functional groups.

## RESULTS AND DISCUSSION

**Properties of the adsorbents:** Table-1 shows the characteristics of adsorbents including proximate and elemental analyses and Table-2 shows the XRF analysis of these adsorbents. Proximate analysis was carried out according to Indian standard methods of test for coal and coke (IS)<sup>21</sup>. As inferred from comparison of the results in Table-1, noticeable changes occurred due to activation process, which in

TABLE-1  
PHYSICO-CHEMICAL CHARACTERISTICS OF CARBON ADSORBENTS

Parameter	TAGOC	CAC
Moisture (%)	3.21	3.70
Volatile matter (%)	18.91	12.73
Ash (%)	34.94	1.19
Fixed carbon (%)	46.15	86.08
Iron content (%)	0.62	0.18
pH	11.30	7.60
Matter soluble in water (%)	7.10	4.80
Matter soluble in acid (%)	44.10	9.20
BD (gm/cm <sup>3</sup> )	0.84	0.74
Decolorizing power (mg/g)	30.00	90.00
BET Surface area (m <sup>2</sup> /g)	14.30	558.02
Pore volume (cm <sup>3</sup> /g)	0.04	0.32
Average pore size (Å)	117.34	23.00
Elemental analysis (%)		
Carbon	46.90	85.90
Sulphur	1.01	0.22
Nitrogen	0.94	0.11
Oxygen	13.35	4.99

TABLE-2  
XRF ANALYSIS OF CARBON ADSORBENTS

Component	TAGOC (%)	CAC (%)
Loss on ignition	64.200	98.430
CaO	8.190	0.183
P <sub>2</sub> O <sub>5</sub>	4.172	0.008
K <sub>2</sub> O	4.960	0.042
MgO	3.970	0.032
SO <sub>3</sub>	1.620	0.159
SiO <sub>2</sub>	2.060	0.161
Fe <sub>2</sub> O <sub>3</sub>	8.160	0.870
Cl	1.830	0.007
Al <sub>2</sub> O <sub>3</sub>	0.682	0.063
Na <sub>2</sub> O	0.003	0.064
ZnO	0.036	0.001
MnO	0.031	0.002
TiO <sub>2</sub>	0.052	0.002
CuO	0.011	0.005

turn depends upon activation atmosphere. In particular, ash content of TAGOC was markedly higher than CAC, which is in agreement with stronger oxidation conditions involved in the thermal treatment stage used in the preparation of former.

SEM is used to study the morphology and surface characteristics of adsorbent material. SEM images of TAGOC and CAC and Pb(II) loaded adsorbents, are shown in Figs. 1 (a-b) and 2(a-b), respectively. These images clearly indicate important

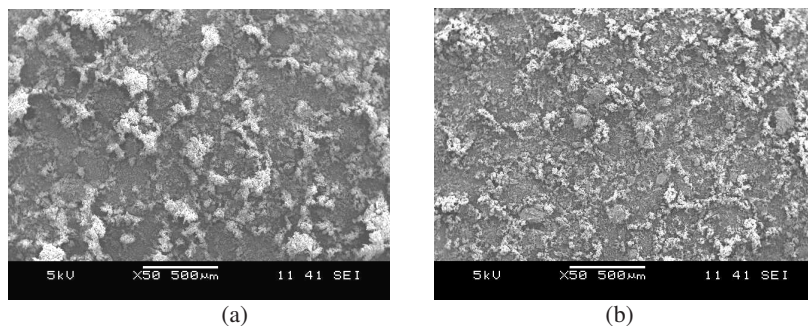


Fig. 1. SEM micrograph of (a) thermally activated gingelly oil cake (b) Pb(II) adsorbed thermally activated gingelly oil cake

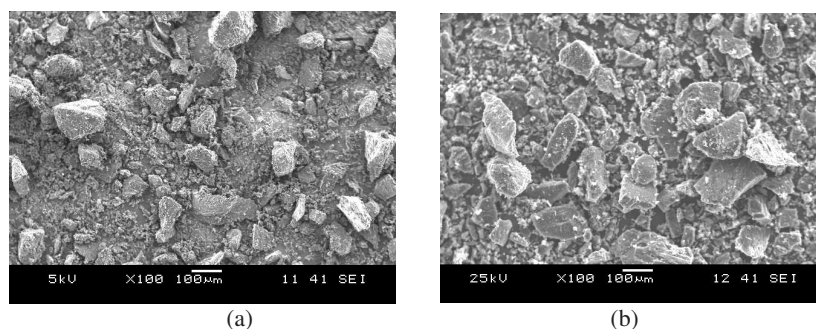


Fig. 2. SEM micrograph of (a) commercial activated carbon (b) Pb(II) adsorbed commercial activated carbon

morphological observations. Coverage of the surface of adsorbents due to adsorption of Pb(II), presumably leads to the formation of white layer (cloud) of uniform thickness and coverage may be visualized. It could be seen that many pores were available on the surface of the adsorbents. However, after the adsorption of Pb(II) on the surface of the adsorbents, the number of pores were reduced due to metal ion loading.

The FT IR spectra obtained before and after Pb(II) adsorption for TAGOC and CAC are shown in Figs. 3(a-b) and 4(a-b), respectively. Due to pyrolysis, some of the functional groups present on the surface of raw material disappear by dehydration and new functional groups may appear. The FT IR spectra of unloaded and Pb(II) loaded TAGOC in the range of  $4000-400\text{ cm}^{-1}$  were taken to find out which functional groups are responsible for adsorption. The FT IR spectrum of unloaded TAGOC indicated changes in the region of  $2400-500\text{ cm}^{-1}$  as compared to Pb(II) loaded TAGOC. Weak bands at  $1041-1024$  and  $1298\text{ cm}^{-1}$  may be assigned to C=O stretching of alcohols and carboxylic acids. The bands at  $1762$ ,  $1718$ ,  $1666$  and  $1298\text{ cm}^{-1}$  may be assigned to C=O groups. Peaks at  $3487$ ,  $3361$  and  $3299\text{ cm}^{-1}$  can be attributed to N-H groups. The peaks in  $3380-3361\text{ cm}^{-1}$  region were due to bounded hydroxyl groups (-OH). The stretching vibration of OH group was shifted from  $3380$  to  $3361$

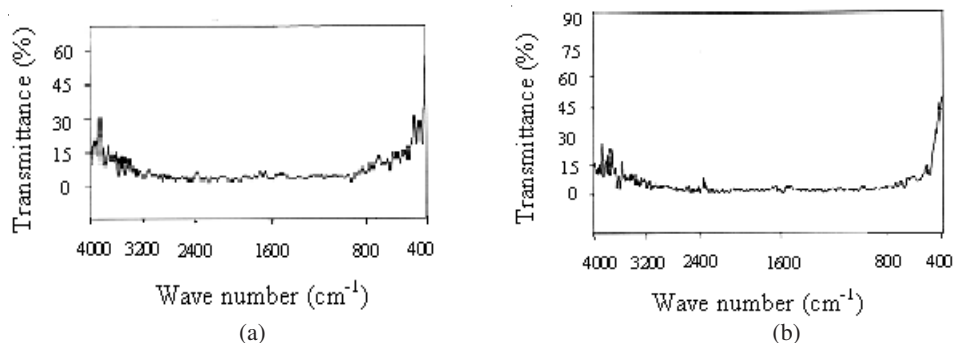


Fig. 3. FT IR spectrum of (a) thermally activated gingelly oil cake (b) Pb(II) loaded thermally activated gingelly oil cake

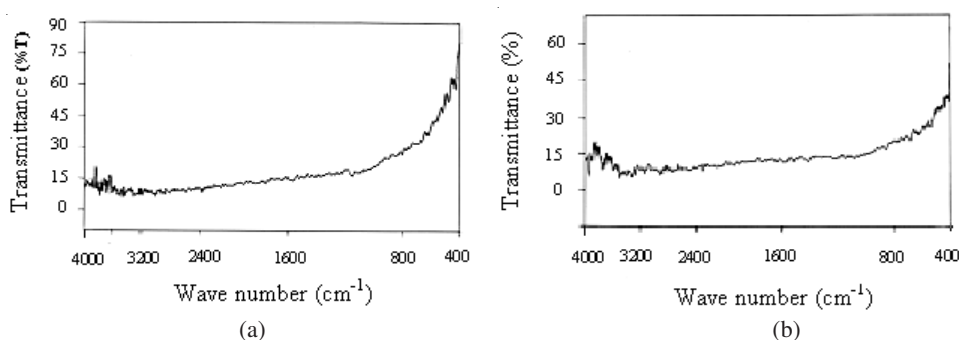


Fig. 4. FT IR spectrum of (a) commercial activated carbon (b) Pb(II) loaded commercial activated carbon

$\text{cm}^{-1}$  in the case of Pb(II) loaded spectra. These results indicate that ion-exchange mechanism operate between the hydrogen atoms of carboxyl (-COOH), hydroxyl (-OH) and amine (-NH) groups of the TAGOC and Pb(II) ions.

FTIR of CAC shows weak bands at 3803 and 3690  $\text{cm}^{-1}$  due to N-H groups. The peaks at 2918 and 2846  $\text{cm}^{-1}$  indicate the presence of C-H groups. Weak bands at 1053 and 1024  $\text{cm}^{-1}$  are due to C=O groups. Peaks in the range of 3600-3200  $\text{cm}^{-1}$  may be attributed to O-H groups of alcohols and phenols.

**Effect of contact time:** The adsorption kinetics is generally depicted by two phases: a rapid removal stage followed by much slower stages to reach equilibrium. The adsorption of Pb(II) by TAGOC and CAC was initially very fast and slowly reached equilibrium in around 0.5 h (Fig. 5). Thus, 1 h contact time was considered to be adequate for the adsorption of Pb(II) onto TAGOC and CAC. For an initial Pb(II) concentration of 10 mg/L and for a sorbent dosage of 0.1 g/100 mL, Pb(II) removal by TAGOC and CAC were found to be 99.0 and 95.5 %, respectively.

**Effect of pH:** The most important parameter influencing the sorption capacity is the pH of adsorption medium. Fig. 6, shows the effect of pH on the adsorption of

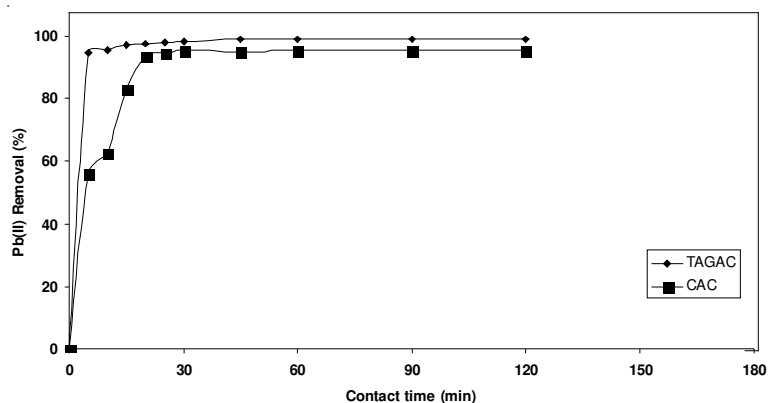


Fig. 5. Effect of agitation time on adsorption of Pb(II), (Pb(II) concentration 10 mg/L, adsorbents dosage 0.1 g/100 mL, pH 5)

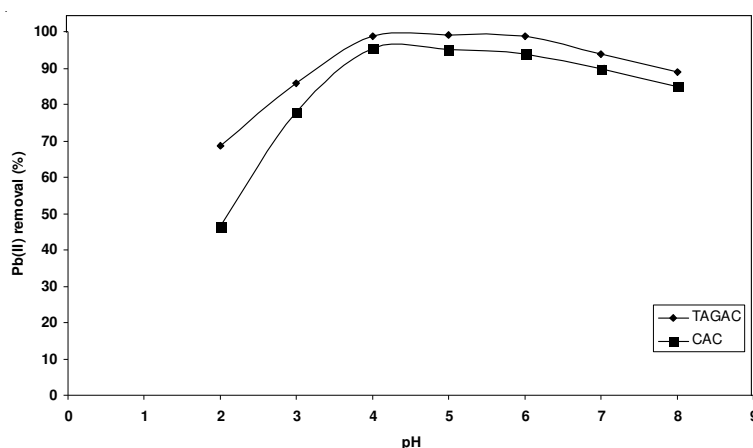


Fig. 6. Effect of pH on adsorption of Pb(II), (Pb(II) concentration 10 mg/L, equilibrated time 1 h, dosage 0.1 mg/100 mL)

Pb(II) by these adsorbents over a pH range 2-8. It could be seen that the metal adsorption was a function of pH. As the pH increases from 2-5, the percentage of adsorption increases. At low pH conditions, hydronium ions compete with Pb(II) for metal-binding sites on the adsorbents causing poor metal uptake. At higher pH values 3-6, there are lesser number of competing hydrogen ions and more ligands are exposed with negative charges, resulting in higher Pb(II) uptake. It may be noted that at low pH, the overall surface charge on the adsorbents becomes positive, which hinders the approach of positively charged Pb(II) cations. At higher pH ( $\text{pH} > 6$ ), Pb(II) tends to precipitate as hydroxyl complexes causing decrease in adsorption. A maximum removal of Pb(II) was achieved by TAGOC and CAC over the pH range of 3-6 for an initial Pb(II) concentration of 10 mg/L and for a carbon dosage of 0.1 g/100 mL. The values were found to be 86.0-98.8 % and 78-95.5 %, respectively.

respectively for TAGOC and CAC. The maximum Pb(II) uptake for TAGOC and CAC were observed at pH 5 and at pH 4, respectively. Hence, all further experiments were conducted at pH 5 for TAGOC and at pH 4 for CAC. From these data it could be observed that TAGOC was found to show more removal than CAC.

**Effect of adsorbent dose:** The effect of adsorbent dosage on the percentage removal of Pb(II) for these adsorbents has been shown in Fig. 7. It could be seen from the figure that the percentage removal increases very sharply with the increase in adsorbent dosage but after a certain value (0.1 g/100 mL), the removal was almost constant. This trend is expected because as the adsorbent dose increases the number of adsorbent particles increases and thus more Pb(II) is attached to their surfaces. A maximum removal of Pb(II) achieved by TAGOC and CAC at an optimum sorbent dosage of 0.1 g/100 mL for an initial concentration of 10 mg/L, at pH 5 and 4, respectively are 99.8 and 95 %.

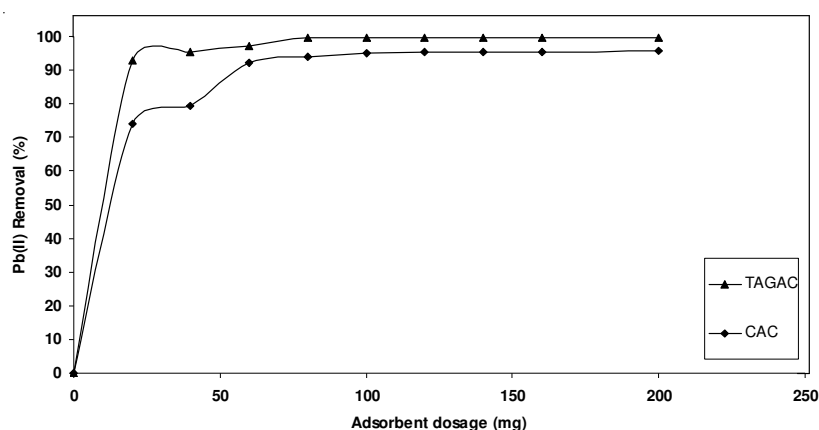


Fig. 7. Effect of adsorbents dosage on adsorption of Pb(II), (Pb(II) concentration 10 mg/L, equilibrated time 1 h, pH 5 for thermally activated gingelly oil cake and pH 4 for commercial activated carbon)

**Adsorption isotherm:** The commonly used adsorption isotherms, such as Langmuir, Freundlich and Temkin have been applied for this study. The Langmuir equation is given as follows<sup>22</sup>.

$$1/q_e = 1/b + 1/ab \cdot C_e \quad (2)$$

where,  $C_e$  is the equilibrium concentration (mg/L),  $q_e$  is the amount adsorbed at equilibrium (mg/g) and 'a' and 'b' are Langmuir constants related to energy of adsorption (L/mg) and adsorption capacity (mg/g), respectively. Fig. 8 shows, Langmuir adsorption isotherm for adsorption of Pb(II) removal on both carbons after an equilibration time of 24 h. The linear plot of  $1/q_e$  versus  $1/C_e$  shows that the adsorption obeys the Langmuir model. The constants, 'a' and 'b' were determined from the slopes and intercepts. The Langmuir constants and correlation coefficients



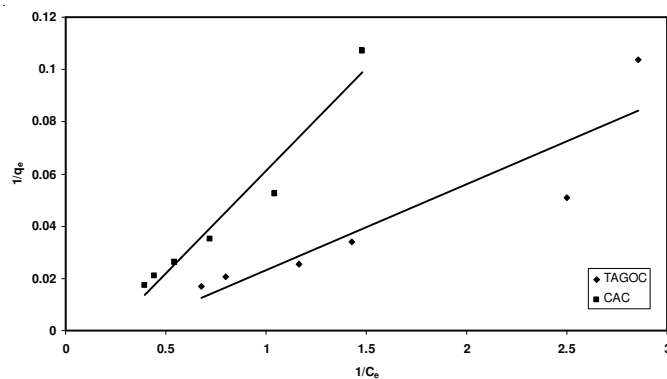


Fig. 8. Langmuir adsorption isotherm for adsorption of Pb(II), (adsorbent dosage 0.1 g/100 mL, temp. 30 °C, metal ion concentration 10-60 mg/L, contact time 24 h, pH 5 for thermally activated gingelly oil cake and pH 4 for commercial activated carbon)

( $R^2$ ) are given in Table-3. The  $R^2$  values indicate that Langmuir model fits well with experimental data. The Freundlich isotherm is represented by the following equation<sup>23</sup>.

$$\log x/m = \log K + 1/n (\log C_e) \quad (3)$$

TABLE-3  
LANGMUIR ADSORPTION ISOTHERM CONSTANTS

Adsorbent	a (L/mg)	b (mg/g)	$R_L$	$R^2$
TAGOC	0.290	105.26	0.0013	0.832
CAC	0.220	57.80	0.0032	0.955

where,  $C_e$  is the equilibrium concentration (mg/L) and  $x/m$  is the amount adsorbed per unit weight of adsorbent. The linear plots of  $\log (x/m)$  versus  $\log C_e$  show that the adsorption obeys the Freundlich isotherm. Fig. 9 shows, Freundlich adsorption

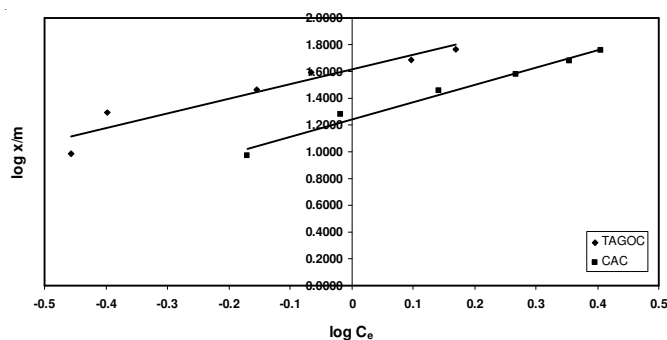


Fig. 9. Freundlich adsorption isotherm for adsorption of Pb(II), (adsorbent dosage 0.1 g/100 mL, temp. 30 °C, metal ion concentration 10-60 mg/L, contact time 24 h, pH 5 for thermally activated gingelly oil cake and pH 4 for commercial activated carbon)

isotherm for adsorption of Pb(II) onto TAGOC and CAC. The  $K$  and  $n$  values are calculated from the intercepts and slopes, respectively. The values of adsorption capacity ( $K$ ), adsorption intensity ( $n$ ) and correlation coefficient ( $R^2$ ) for these adsorbents are given in Table-4. The values of  $1 < n < 10$  show favourable adsorption of Pb(II) on the sorbent. The  $R^2$  values indicate that the Freundlich model also fits well with the experimental data.

TABLE-4  
FREUNDLICH ADSORPTION ISOTHERM CONSTANTS

Adsorbent	$K$ (mg/g)	$n$ (L/mg)	$R^2$
TAGOC	8.128	1.270	0.9865
CAC	6.026	1.462	0.9816

Temkin isotherm<sup>24,25</sup> is an empirical relationship, which gives a more satisfactory model of experimental data. It is represented by the equation

$$q_e = a_t + 2.3 b_t \log C_e \quad (4)$$

where,  $C_e$  is the equilibrium concentration (mg/L) and  $q_e$  is the amount adsorbed per unit weight of adsorbent. The values of  $a_t$  (mg/g) and  $b_t$  (L/mg) were obtained by plotting adsorption capacity and equilibrium concentration. The linear plots of  $q_e$  versus  $\log C_e$  show that the adsorption obeys the Temkin isotherm. Fig. 10 shows, Temkin adsorption isotherm for adsorption of Pb(II) onto TAGOC and CAC. The  $a_t$

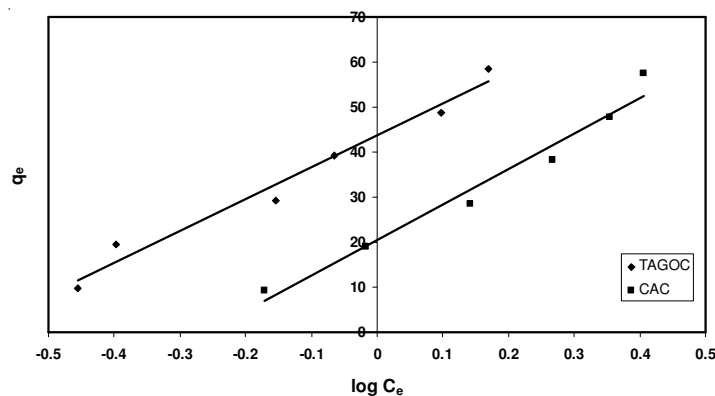


Fig. 10. Temkin adsorption isotherm for adsorption of Pb(II), (adsorbent dosage 0.1 g/100 mL, temp. 30 °C, metal ion concentration 10-60 mg/L, contact time 24 h, pH 5 for thermally activated gingelly oil cake and pH = 4 for commercial activated carbon)

and  $b_t$  values are calculated from the intercepts and slopes, respectively. The values of  $a_t$ ,  $b_t$  and correlation coefficient ( $R^2$ ) for various adsorbents are given in Table-5. The  $R^2$  values indicate that Temkin model also fits well with the experimental data. From  $R^2$  values of all the three models, it is clear that Freundlich model fits best with experimental data for both the adsorbents.

TABLE-5  
TEMKIN ADSORPTION ISOTHERM CONSTANTS

Adsorbent	$a_i$ (mg/g)	$b_i$ (L/mg)	$R^2$
TAGOC	43.681	30.7769	0.975
CAC	20.484	34.3883	0.968

**Separation factor ( $R_L$ ):** A dimensionless constant, separation factor ( $R_L$ ) can be used to predict whether a sorption system is favourable or unfavourable in batch adsorption process.  $R_L$  values between 0 and 1 represent favourable isotherm.  $R_L$  was calculated from Langmuir isotherm based equation as given by the following expression.

$$R_L = \frac{1}{(1 + aC_o)} \quad (5)$$

where,  $C_o$  is the initial concentration of Pb(II) and 'a' is the Langmuir constant.

The parameter,  $R_L$  indicates the nature of adsorption process as given below:  $R_L > 1$  = unfavourable isotherm,  $R_L = 1$  = linear isotherm,  $R_L = 0$  = irreversible isotherm,  $0 < R_L < 1$  = favourable isotherm.

The  $R_L$  values were found to be between 0 and 1 for both the adsorbents showing the sorption of Pb(II) on these adsorbents is favourable. From  $R_L$  values of Table-3, it is clear that the sorption process was favourable for Pb(II) removal for both the adsorbents at all concentrations investigated.

**Adsorption kinetics:** In order to clarify the adsorption kinetics of Pb(II) onto these adsorbents, two kinetic models, such as Lagergren's pseudo-first order and pseudo-second order models were applied to the experimental data.

The linearized form of the pseudo-first order rate equation of Lagergren is given as follows<sup>26</sup>.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where,  $q_e$  and  $q_t$  are the amount of the metal ions adsorbed (mg/g) at equilibrium and at time 't' (min), respectively and  $k_1$  is the pseudo-first order equilibrium rate constant ( $\text{min}^{-1}$ ). A plot of  $\ln(q_e - q_t)$  versus 't' gives a straight line with slope of  $k_1$  and an intercept of  $\ln q_e$ . Straight-line nature of the curves from the Figs. 11 and 13, show the applicability of pseudo-first order rate equation for both carbons.

The pseudo-second order model rate equation may be expressed as follows<sup>27</sup>.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where,  $k_2$  is the pseudo-second order adsorption rate constant ( $\text{g/mg min}^{-1}$ ). A plot of  $(t/q_t)$  versus 't' also produces straight line with slope of  $1/q_e$  and intercept of  $1/k_2 q_e^2$ . Straight line nature of curves from Figs. 12 and 14 show, pseudo-second order kinetics also is applicable for the adsorption of Pb(II) onto TAGOC and CAC.

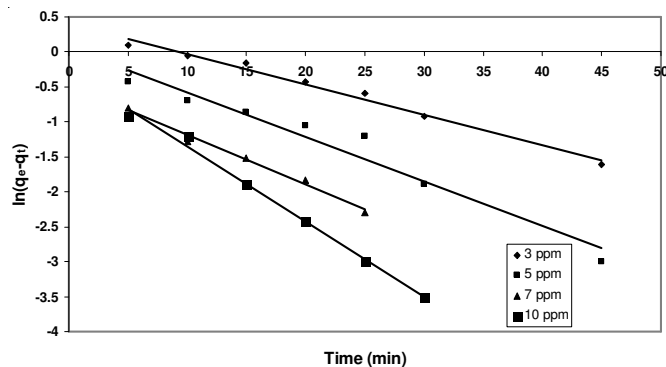


Fig. 11. Pseudo first order kinetics for the adsorption of Pb(II) on thermally activated gingelly oil cake (pH 5, adsorbent dosage 0.1 g/100 mL, Temp. 30 °C)

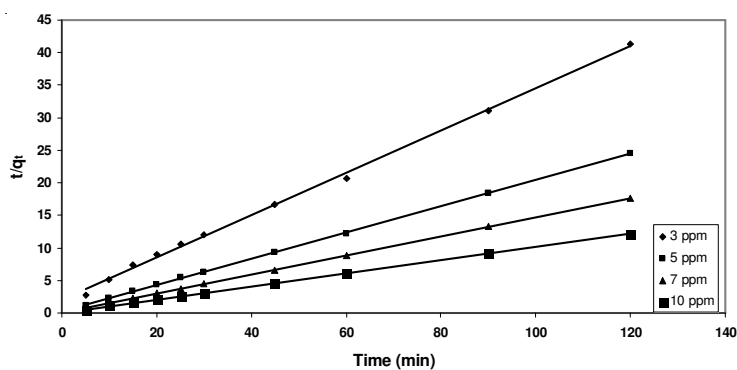


Fig. 12. Pseudo second order kinetics for the adsorption of Pb(II) on thermally activated gingelly oil cake (pH 5, adsorbent dosage 0.1 g/100 mL, Temp. 30 °C)

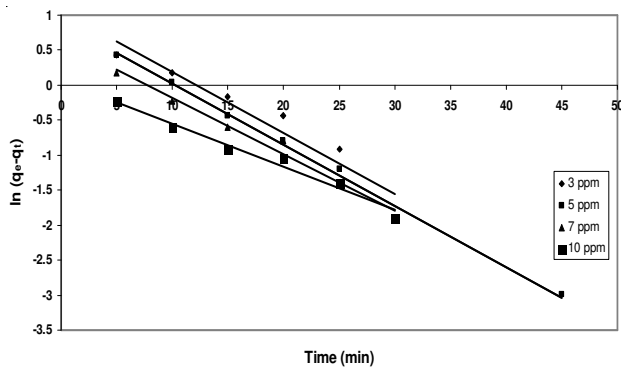


Fig. 13. Pseudo first order kinetics for the adsorption of Pb(II) on commercial activated carbon, (pH 4, adsorbent dosage 0.1 g/100 mL, Temp. 30 °C)

In order to compare quantitatively the applicability of kinetic models in fitting to data, the per cent relative deviation (P), was calculated as per the expression given below.

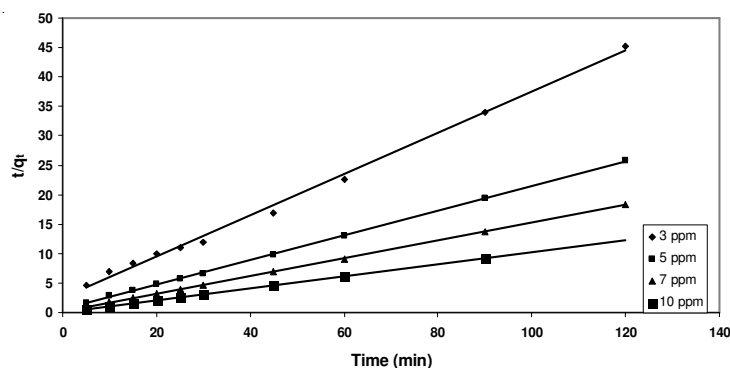


Fig. 14. Pseudo second order kinetics for the adsorption of Pb(II) on commercial activated carbon (pH 4, adsorbent dosage 0.1 g/100 mL, Temp. 30 °C)

$$P = \frac{100}{N} \sum \left[ \frac{\{q_e(\text{exp}) - q_e(\text{theo})\}}{q_e(\text{exp})} \right] \quad (8)$$

where,  $q_e(\text{exp})$  is the experimental value of  $q_e$  at any value of  $C_e$ ,  $q_e(\text{theo})$  is the corresponding theoretical value of  $q_e$  and  $N$  is the number of observations. It is found that lower the value of percentage deviation ( $P$ ) better is the fit. It is generally accepted that when  $P$  value is less than 5, the fit is considered to be excellent<sup>28</sup>. The results have been analyzed using the data from eqns. 6 and 7. The values of  $q_e(\text{theo})$  calculated from these models are compared with experimental values  $q_e(\text{exp})$  in Table-6. It is found that values of  $q_e(\text{theo})$  calculated from the pseudo-first order

TABLE-6  
PSEUDO-FIRST ORDER AND PSEUDO-SECOND ORDER KINETIC CONSTANTS

Adsorbent	Conc. (mg/L)	Pseudo-first-order kinetics					Pseudo-second-order kinetics				
		$k_1$ (1/min)	$q_e(\text{theo})$ (mg/g)	$q_e(\text{exp})$ (mg/g)	$R^2$	$P$	$k_2$ (g/mg/min)	$q_e(\text{theo})$ (mg/g)	$q_e(\text{exp})$ (mg/g)	$R^2$	$P$
TAGOC	10	0.1076	0.2709	9.85	0.9934	97.25	0.4601	9.8716	9.85	1.0000	0.2199
CAC	10	0.0621	0.0751	9.70	0.9766	99.23	0.1581	9.7656	9.70	1.0000	0.6765
TAGOC	7	0.0714	0.4738	6.80	0.9876	93.03	0.0013	6.8306	6.80	1.0000	0.4500
CAC	7	0.0805	0.6220	6.55	0.9827	90.50	0.0045	6.6445	6.55	0.9999	1.4430
TAGOC	5	0.0636	0.0584	4.90	0.9530	98.81	0.1458	4.9677	4.90	0.9999	1.3818
CAC	5	0.0875	0.8984	4.65	0.9949	80.68	0.0836	4.7778	4.65	0.9997	2.7490
TAGOC	3	0.0435	0.4078	2.90	0.9866	85.94	0.0536	3.0712	2.90	0.9983	5.9053
CAC	3	0.0871	1.0597	2.65	0.9264	60.01	0.0485	2.8645	2.65	0.9965	8.0947

kinetic model differed appreciably from the experimental values  $q_e(\text{exp})$ . The per cent relative deviation ( $P$ ) is also very high. On the other hand, values of  $q_e(\text{theo})$  are found to be very close to  $q_e(\text{exp})$  when pseudo-second order rate equation was applied. The per cent relative deviation ( $P$ ) is well within the range and also the values of correlation coefficients ( $R^2$ ) are very high in pseudo-second order kinetics.

Therefore it could be concluded that the adsorption of Pb(II) onto these adsorbents is governed by pseudo-second order kinetics predominantly.

The free energy of adsorption ( $\Delta G^\circ$ ) can be related with the equilibrium constant  $K$  ( $\text{L mol}^{-1}$ ), corresponding to the reciprocal of the Langmuir constant, 'b', by the following equation,

$$\Delta G^\circ = -RT \ln b \quad (9)$$

where,  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the absolute temperature (K). Gibbs free energy change ( $\Delta G^\circ$ ) of various adsorbents is shown in Table-7. The negative values of  $\Delta G^\circ$  for all concentrations suggest that the Pb(II) adsorption process by these carbons is feasible and spontaneous in nature at all metal ion concentrations.

TABLE-7  
GIBBS FREE ENERGY OF ADSORPTION FOR ADSORBENTS

Adsorbent	a (L/mg)	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )
TAGOC	0.2896	-27.72
CAC	0.0410	-22.79

**Desorption studies:** Experiments were conducted to desorb Pb(II) from the spent sorbents using 0.01-0.25 N HNO<sub>3</sub>. Results showed that 99 % of Pb(II) could be desorbed from TAGOC with 0.05 N HNO<sub>3</sub> and 30 % of Pb(II) could only be desorbed from CAC with 0.1 N HNO<sub>3</sub>. After the extraction of Pb(II), these sorbents were washed with distilled water and their adsorption capacities were again tested. Five consecutive sorption-desorption cycles were carried out and the values are shown in Table-8. Results show that, the adsorption capacity of spent TAGOC and CAC in five cycles of operation are decreasing in the range of 99.9-27 % and 94-32 %, respectively. Experiments show that 0.05 and 0.10 N HNO<sub>3</sub> are best suitable for regeneration and recovery of valuable lead ions from TAGOC and CAC, respectively.

TABLE-8  
REMOVAL EFFICIENCIES OF ADSORBENTS

Cycle No.	TAGOC (%)	CAC (%)
1	99.9	94.0
2	92.0	52.0
3	56.0	46.0
4	38.0	36.0
5	27.0	32.0

**Application to wastewater:** Experiments with synthetic lead battery wastewater have been carried out to elucidate the adsorption capacity of the various sorbents. Results in Table-9, gives the characteristics of the synthetic wastewater applied for this study. The effect of varying adsorbents dosage on the removal of Pb(II) has been carried out under optimum time and pH. Fig. 15, shows the removal

TABLE-9  
CHARACTERISTICS OF LEAD BATTERY WASTEWATER (SYNTHETIC)

Parameter	Amount before treatment (mg/L)	Amount after treatment (mg/L)	
		TAGOC	CAC
Pb(II)	101.53	0.2	2.1
Chlorides	18.27	0.6	1.0
Calcium	20.48	0.8	1.2

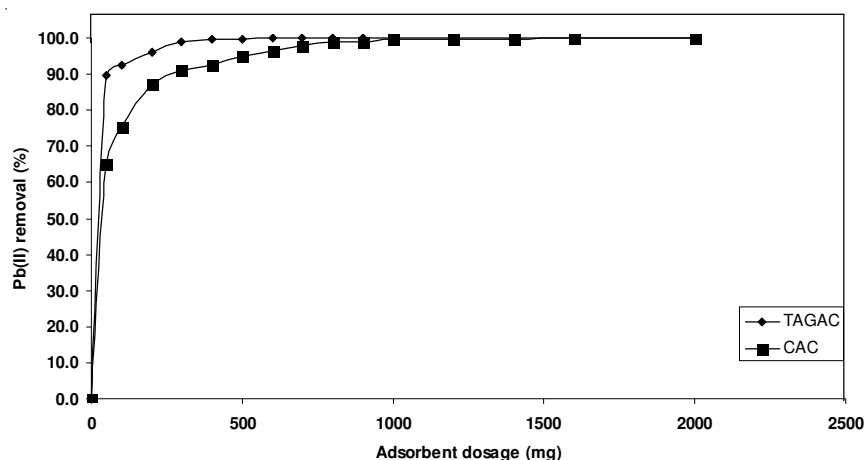


Fig. 15. Effect of adsorbents dosage on adsorption of Pb(II) from wastewater [(Pb(II) concentration 101.53 mg/L, equilibrated time = 1 h)]

of Pb(II) as a function of sorbent dosage for an initial concentration of 101.53 mg/L. It has been observed that 99 % removal of Pb(II) from wastewater could be achieved with a sorbent dose of 0.2 g/100 mL of TAGOC, but CAC requires a dosage of 0.9 g/100 mL. Hence it could be seen that TAGOC was found to be 4.5 times superior in the removal of metal ions from wastewater than CAC.

### Conclusion

Pb(II) removal could be achieved from aqueous solution at pH 5, at an adsorbent dose of 0.1 g by TAGOC to an extent of 99.8 and 95.5 % removal could be achieved at pH 4 at an adsorbent dose of 0.1 g by CAC. Furthermore, desorption of Pb(II) could effectively be achieved with 0.05 N HNO<sub>3</sub> by TAGOC whereas CAC required 0.1 N HNO<sub>3</sub>. Based on statistical considerations, R<sup>2</sup> values were found to be favourable for Freundlich isotherm for both the adsorbents and they follow pseudo-second order kinetics. Batch studies demonstrated that TAGOC showed excellent removal capabilities of Pb(II) and other metals from lead battery wastewater than CAC and maximum recovery of valuable lead could also be achieved. Therefore, it can be concluded that TAGOC derived from GOC can be evaluated as an alternative adsorbent to treat wastewater containing Pb(II) ions as GOC is a cheap, locally available material.

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