

## Sorption of lead from aqueous solution by chemically modified carbon adsorbents

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Received 1 September 2005; received in revised form 29 May 2006; accepted 30 May 2006

Available online 6 June 2006

### Abstract

An indigenously prepared, steam activated and chemically modified carbon from husk and pods of *Moringa oleifera* (*M. oleifera*), an agricultural waste, was comparatively examined as an adsorbent for the removal of lead from aqueous solutions. Studies were conducted as a function of contact time, initial metal concentration, dose of adsorbent, agitation speed, particle size and pH. Maximum uptake capacities were found to be, 98.89, 96.58, 91.8, 88.63, 79.43% for cetyltrimethyl ammonium bromide (CTAB), phosphoric, sulfuric, hydrochloric acid treated and untreated carbon adsorbents, respectively. Bangham, pseudo-first- and second-order, intra-particle diffusion equations were implemented to express the sorption mechanism by utilized adsorbents. Adsorption rate of lead ions was found to be considerably faster for chemically modified adsorbents than unmodified. The results of adsorption were fitted to both the Langmuir and Freundlich models. Satisfactory agreement between the metal uptake capacities by the adsorbents at different time intervals was expressed by the correlation coefficient ( $R^2$ ). The Langmuir model represented the sorption process better than the Freundlich one, with  $R^2$  values ranging from 0.994 to 0.998.

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**Keywords:** Activated carbon; Adsorption; *Moringa oleifera*; Chemical modification; Adsorption isotherms

### 1. Introduction

The pollution of water resources due to indiscriminate disposal of heavy metals has been causing worldwide concern for the last few decades. Unlike organic pollutants, the majority of which are susceptible to bio-degradation, heavy metals are non-degradable to harmless end products. They are toxic to aquatic flora and fauna even in relatively low concentrations. Metals, which are significantly toxic to human beings and ecological environments, include arsenic (As), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), manganese (Mn), cadmium (Cd), nickel (Ni), zinc (Zn) and iron (Fe), etc. Some of these are capable of being assimilated, stored and concentrated by human

body, causing erythrocyte destruction, nausea, salivation, diarrhea, muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity [1]. Lead, an element which has been used by man for years, can be regarded as a longstanding environmental contaminant. All the chemicals/compounds containing lead are considered as cumulative poisons that usually affect the gastrointestinal track, nervous system and sometimes both. The chief sources of lead in water are the effluents of processing industries. Apart from this lead is also used in storage batteries, insecticides, plastic water pipes, food, beverages, ointments and medicinal concoctions for flavoring and sweetening. Lead poisoning causes damage to liver, kidney and reduction in hemoglobin formation, mental retardation, infertility and abnormalities in pregnant women. Briefly, many states of health are linked to elemental imbalance because beyond the healthy levels they may cause anemia, headache, chills, diarrhea and poisoning leading to the dysfunction of kidneys, reproductive system, liver, brain and central nervous system also [2]. There are several

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methods for removing toxic/heavy metals from aqueous solutions, such as chemical precipitation, membrane filtration, ion exchange, biosorption and adsorption [3]. The use of activated carbon and biosorbents, to remove trace metals from aqueous system has been widely investigated [4,5]. In recent years, considerable attention has been devoted to the study for the economical removal of heavy metal ions from solution by adsorption using agricultural materials such as waste wool, nut wastes, tree barks, modified cotton and sawdust, etc. [1,3,6–8]. Many agricultural wastes and by-products such as husk, bark, hulls, etc. are low-cost (or of no economic value) materials. *Moringa oleifera* Lam is the most widespread species of the plant family Moringaceae, found widely in the sub-Himalayan tracks and is also distributed in Philippine, Cambodia, Central America, North South America and Caribbean Islands. It is also cultivated in India, Pakistan and Burma for its leaves, flowers and pods that have tremendous medicinal and food value. *M. oleifera* indigenous to subcontinent is a small or medium-sized tree, about 10 m high, found wild, and cultivated through out the plains. It can grow well in the humid tropics or hot dry lands, can survive destitute soils, and is little affected by drought [9]. In Pakistan, *Moringa* is represented by only two species; *M. concanensis* and *M. oleifera*. The former specie is not common and perhaps confined to only remote areas (Tharparker, Sindh). The latter *M. oleifera*, locally known as “Sohanjna” is grown and widely cultivated in the Punjab plains, Sindh, Baluchistan and North Western Frontier Province (NWFP) particularly, in temperate and tropical regions of the country. Flowers are white, fragrant and the fruits are usually 30–45 cm long. In some parts of the world *M. oleifera* is referred to as drumstick tree, horse-raddish tree, while in others it is also known as Kelor tree. In the Neil valley, the name of the tree is “Shagara al Rauwaq” which means, “tree for purifying” [10]. The dried seeds can be crushed to produce a high quality vegetable oil and the resulting press-cake mixed with water and strained to form a coagulant for water treatment. The residue containing seed husks is currently discarded as waste. Some preliminary investigations on the production of activated carbon from *M. oleifera* husk and pods have been reported. It is demonstrated that the simple steam pyrolysis procedure [11] can produce high quality microporous activated carbons from both the waste husks and pods of *M. oleifera* which can be chemically modified to improve their removal efficiency for Pb(II) from aqueous solutions. Chemical modification of carbon adsorbents by acids, bases and surfactants, etc. is an important method to enhance their metal uptake capacity [12]. Surface-active substance or surfactants are amphipathic substances with lyophobic and lyophilic groups making them capable of adsorbing at the interfaces between liquids, solids and gases. They form self-associated clusters, which normally lead to organized molecular assemblies, monolayers, micelles, vesicles, liposomes and membranes. Depending upon the nature of hydrophilic group, they can be anionic (negative charge), cationic (positive charge), non-ionic (no apparent charge) and Zwitterionic (both charges are present). Critical micelle concentration (CMC) of surfactant can be defined as the minimum concentration at which the molecules of surfactant start to form the aggregates [13]. Surfactants have potential applications ranging from mundane (washing cloths)

to very sophisticated (microelectronics). Surfactant's applications in the environmental industries are promising due to their biodegradability, low toxicity and effectiveness in enhancing bio-degradation and increasing the solubilization of sparingly soluble compounds. They have been used in industrially as adhesives, dispersants, flocculating, wetting and foaming agents, deemulsifiers and penetrants. They have also been used for mineral flotation and in the pharmaceutical industries [14]. They are used for these applications based on their abilities to lower surface tensions, increase solubility, detergency power, wetting ability and foaming capacity [15]. Typical desirable properties include solubility enhancement, surface tension reduction, and low critical micelle concentrations. Surfactants concentrate at interfaces (solid–liquid, liquid–liquid or vapour–liquid). An interfacial boundary exists between two immiscible phases. The hydrophobic portion concentrates at the surface while the hydrophilic portion is oriented towards the solution. However, more information is needed to be able to predict and model their behavior for better understanding of the involved mechanisms [16]. The physico-chemical characterization of carbonaceous porous materials (steam and chemically activated adsorbents like carbon, chars and composites) produced from agricultural wastes/by-products has been an established and productive field within carbon research for many years. Our recent efforts have focused on the chemical modification of activated carbon from *M. oleifera* for water and wastewater treatment. We are reporting an improved preparative strategy aimed at a much effective and cheaper activated carbon product that can significantly remove the heavy and trace metal contents from industrial effluents. Langmuir and Freundlich adsorption isotherms were studied to explain the sorption mechanism.

## 2. Experimental

All the chemicals used in this study are of analytical reagent grade and were utilized as received without further purification. Deionized water is used throughout the study. Aqueous solutions of lead nitrate, HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and CTAB were prepared from Pb(NO<sub>3</sub>)<sub>2</sub>, Merck, respective acid, Merck and CTAB (C<sub>16</sub>H<sub>33</sub>NCH<sub>3</sub>Br), Aldrich, respectively. Batch studies were performed with 30 and 45 mg/L of lead ions to investigate the extent of adsorption. The pH of each solution was adjusted to 5.8 ± 0.5 with 0.5 M NaOH or HCl. The stopper test tubes were agitated at 30 °C by orbital shaker at fixed speed, 160 rpm for various time intervals. The adsorbates were separated using Whatman filter paper and supernatant liquid was analyzed for residual concentration of lead by atomic absorption spectrometer (Perkin-Elmer, A Analys-300). Triplicate runs differing by less than 1% of all the tests were achieved assuring the reproducibility of the obtained data. The metal concentration retained by the adsorbent phase was calculated using the following relation:

$$Q_e = (C_0 - C_e)V/W \quad (1)$$

where  $Q_e$  is the equilibrium adsorption capacity,  $C_0$  the initial metal concentration,  $C_e$  the equilibrium metal concentration,  $V$  the volume of solution containing adsorbate and  $W$  is the mass

of adsorbent. Maximum metal uptake was achieved with initial metal concentration of 30 mg/L and the same concentration was utilized for further study. Micromeritics Gemini 2360 Analyzer was used to measure the, Brauner–Emmet–Teller (BET) surface area of the adsorbents which is fully automatic, single- or multi-point surface area analyzer. It uses a flowing-gas technique in which the analysis gas flows into a tube containing the adsorbent and into a balance tube simultaneously and provides rapid and accurate sample analysis for solid materials.

### 2.1. Preparation and chemical modification of activated carbon

The raw materials (mature pods of *M. oleifera* containing seeds) required for the preparation of carbon adsorbents were collected from *M. oleifera* plants, within the campus of University of Agriculture, Faisalabad, Pakistan. Seeds were separated from husk and pods. Activated carbon was produced by following the similar processes as described by the Warhurst et al. [11], comprising heating the precursor (30 g husk material and 10 g pods) in a furnace to eliminate volatiles (carbonization) with concurrent activation by steam. This method is also reported by Gergova and Petrov [17] to be economical in producing effective carbons from materials such as apricot stones, grape seeds and coconut shells. Five samples of activated carbon were produced independently following the same procedure, dried in an oven overnight at 110 °C, mixed together, homogenized and sieved to 0.250, 0.149 and 0.074 mm sizes, respectively. Chemical modification of indigenously prepared activated carbon was done by immersing 5 g of adsorbent in 100 mL, 1N aqueous solution of each acid, i.e., HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> and critical micellar solution of CTAB for 4 h. Adsorbents were separated using Whatman filter paper, rinsed with deionized water, dried in an oven overnight at 110 °C, sieved to the required sizes and stored in desiccators for further applications.

## 3. Results and discussion

### 3.1. Textural characterization of adsorbents

SEM images of steam activated, hydrochloric, sulfuric, phosphoric acid and CTAB-modified activated carbon from husk and pods of *M. oleifera* are presented here.

It is quite obvious from the obtained SEM images (Fig. 1) that chemical modification of the carbon adsorbents significantly alters the physico-chemical properties and porosity of the materials. The porous structure characteristics and the pH values of aqueous suspensions of the carbon samples are summarized in Table 1. The obtained results have indicated that the surfaces of the modified carbon possess different physico-chemical properties as well as have the greater surface area (BET), as compared to the unmodified carbon adsorbents. CTAB-treated adsorbents were found to be having greater surface area followed by phosphoric, sulfuric, hydrochloric acid treated and unmodified adsorbents, respectively. Acids are responsible to provide the protons upon ionization in aqueous solutions which in turn can further open the pores of activated carbon which increases

Table 1  
Surface characteristics of the carbon adsorbents

Adsorbents	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	pH
Unmodified steam activated carbon	725.0	8.17
HCl-modified activated carbon	746.3	5.71
H <sub>2</sub> SO <sub>4</sub> -modified activated carbon	769.8	5.43
H <sub>3</sub> PO <sub>4</sub> -modified activated carbon	782.4	5.19
CTAB-modified activated carbon	814.2	7.24

the surface area of adsorbents. From the obtained results it is evident that phosphoric acid was susceptible to provide three protons as compared to the sulfuric and hydrochloric acid which can provide two and one protons, respectively, so the surface area was found to be greater for phosphoric, followed sulfuric and hydrochloric acid treated adsorbents. But in case of CTAB-treated adsorbents surface area was further increased due to the typical properties of the surfactants like adsorption, wetting, solubilization, etc. Being amphipathic in nature surfactant treated surfaces can offer much more surface area and wetting (water or oil wet) according to the requirement because surfactant molecules are capable to organize themselves accordingly [13]. It is well known that *M. oleifera* husk and pods contain lot of mineral contents like sodium, potassium, calcium, etc. [9,10]. Due to the presence of these metallic contents pH of the unmodified adsorbents was found to be alkaline in nature, whereas it was highly acidic in all the acid treated adsorbents and about neutral in case of CTAB-treated adsorbent. It reported that maximum removal of the lead from aqueous solutions can be achieved with pH 5.8 [3]. The pH of the adsorbents for all the sorption experiments was adjusted using dilute solutions of HCl or NaOH accordingly.

### 3.2. Effect of contact time and particle size

Three different particle sizes of untreated activated carbon, i.e., 0.250, 0.149 and 0.074 mm are utilized. It is presented in Fig. 2 that sorption increases with contact time from the solution under prescribed conditions (pH 5.8 ± 0.5, temperature 30 °C, shaking speed 160 rpm and initial metal concentration 30 mg/L) and becomes nearly constant after 120 min. Sorption capacity of untreated activated carbon is found to be maximum, 79.43, 76.8 and 70.19% for particle size 0.074, 0.149 and 0.250 mm, respectively, as shown in Fig. 1. It is well established that the sorption is related to available surface area and contact time hence the sample with particle size 0.074 mm has depicted maximum uptake capacity towards lead.

### 3.3. Effect of initial metal concentration and adsorbent dose

Different amounts of activated carbon varying from 0.05 to 0.30 g/100 mL of solution with 30 mg/L concentration of lead are used to optimize the required amount of adsorbent under prescribed conditions for maximum uptake. It is elaborated in Fig. 3 that maximum uptake capacity from the solutions with 30

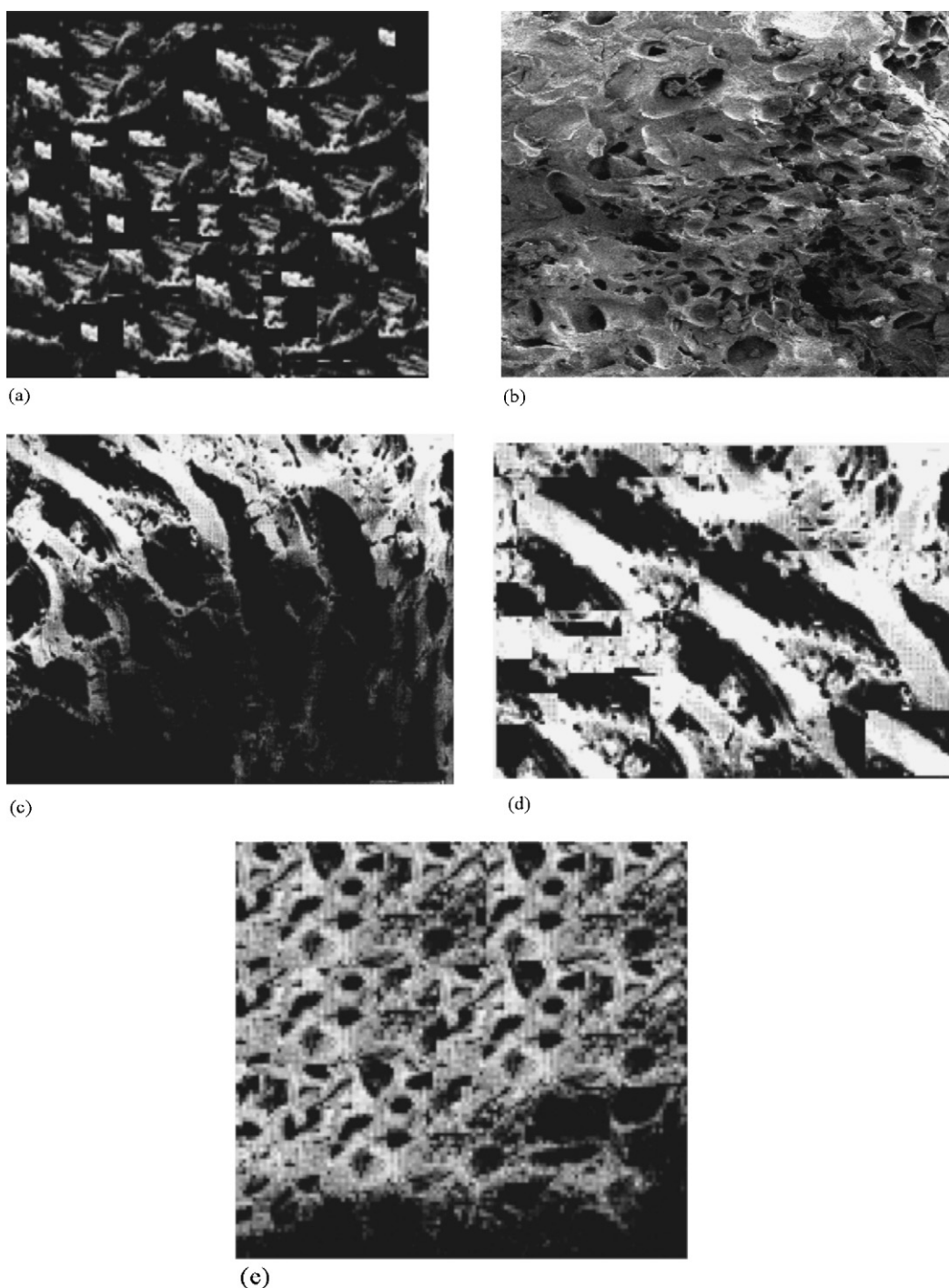


Fig. 1. SEM images of unmodified and chemically modified adsorbents. (a) SEM micrograph of steam activated *Moringa* carbon surface showing skeletal structure of activated surface. (b) SEM micrograph of steam activated *Moringa* carbon surface modified by hydrochloric acid. (c) SEM micrograph of steam activated *Moringa* carbon surface modified by sulfuric acid. (d) SEM micrograph of steam activated *Moringa* carbon surface modified by phosphoric acid. (e) SEM micrograph of steam activated *Moringa* carbon surface modified by CTAB.

and 45 mg/L lead and maximum uptake of lead was found to be, 79.43 and 73.5% with adsorbent 2 g/L for 30 and 45 mg/L concentrations, respectively. This decrease in metal uptake capacity with increase in dose of activated carbon and initial metal concentration may be due to the formation of clusters of carbon particles resulting in decreased surface area, when amount is increased from a particular value and limitations of available

sites for higher concentrations, respectively. At same adsorbent dose and contact time, there is drop in percentage removal with higher initial concentration because lower initial metal concentrations, sufficient adsorption sites are available for the sorption of metals ions. However, at higher concentrations the numbers of metal ions are relatively higher as compared to availability of adsorption sites. Hence, the percent removal of heavy metals

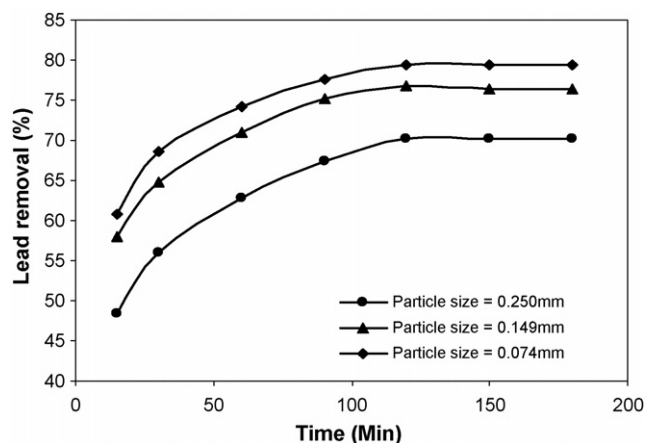


Fig. 2. Effect of particle size on lead removal.

depends on the initial metal concentration and decreases with increase in initial metal concentration. The difference in percentage removal of different metal ions at the same initial metal ions concentration, adsorbent dose and contact time may also be attributed to the difference in their chemical affinities and ion exchange capacity with respect to the chemical functional group on the surface of the adsorbent but for the same metal ion availability of adsorption sites dominates.

### 3.4. Effect of pH

Digital pH meter was used to measure the pH of aqueous suspensions of all the carbon adsorbents. It is reported in Fig. 4 that percentage adsorption increased with pH of the solution and reached to a maximum value, 79.3% at  $\text{pH } 5.8 \pm 0.5$  which is also in agreement with the results reported by Feng et al. [3] that the percentage removal of Pb(II) from aqueous solution is additional at this pH. In alkaline medium lead is liable to be hydrolyzed and precipitated instead of adsorption. pH of the solutions was adjusted with a difference of 0.5 from 1 to 10 and the removal efficiency was measured. In the region

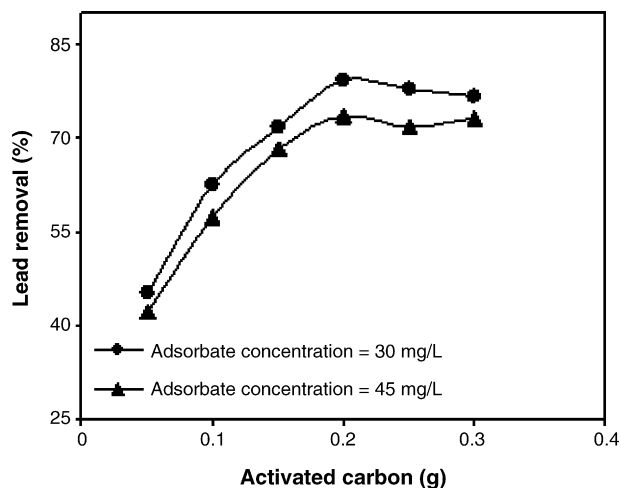


Fig. 3. Effect of initial metal concentration and adsorbent dose on lead removal.

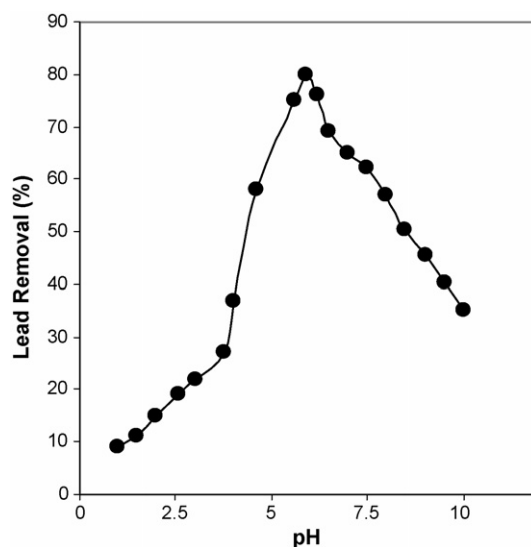


Fig. 4. Effect of pH on lead removal.

having  $\text{pH} > 5.5$  desorption of lead, from the adsorbents, using ethylene diamine acetic acid (EDTA) was done in order to distinguish the percentage removal of lead by adsorption and precipitation.

### 3.5. Effect of chemical modification

It is presented in Fig. 5 that the uptake capacities of the adsorbents towards lead are 98.89, 96.58, 91.80, 88.63 and 79.43% by CTAB,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ , HCl and untreated carbon adsorbents, respectively. All the used chemicals have revealed prominent effect regarding the efficacy of activated carbon from *M. oleifera* in the removal of Pb(II), however, the maximum adsorption capacity was shown by CTAB-treated activated carbon adsorbent. Monser and Adhoum [12] have also reported that by applying the tetrabutyl ammonium iodide (TBA) or sodium diethyl dithiocarbamate (SDDC) onto an activated carbon, a substantial improvement in Cu(II), Zn(II) and Cr(VI) removal capacity can

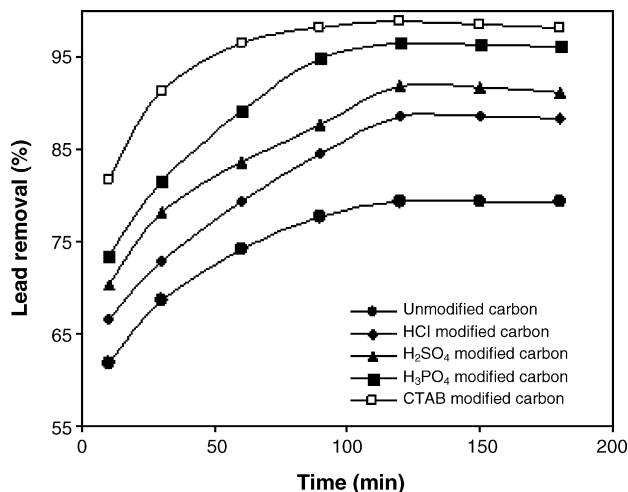


Fig. 5. Effect of chemical modification on lead removal.

be achieved. Moreover, activated carbon from coconut shells, coal dust, husk and pods of *M. oleifera* is an H-type activated carbon (which adsorbs  $H^+$  ions). Numerous studies on H-type activated carbon state that pH of the solution increases as they adsorb more and more  $H^+$  ions. The removal efficiency for heavy metals is supposed to increase from 10 to 95% in the equilibrium pH values ranging from 2.3 to 7. Modification of activated carbon with HCl, HF and  $HNO_3$  introduce oxygen surface complexes that alter the surface chemistry and can change the surface area and porosity of the original samples [18–20]. The ability of surfactant to accelerate the removal efficiency of toxic, noble and rare metals can be ascribed to wettability alterations and/or micellar solubilization [13]. Moreover, carbon surface have both negative (anionic) and positive (cationic) functional groups to attract free ions in solution or suspension. Apart from wetting and solubilization surfactants are also capable to produce the electrostatic charge on surface of activated carbon and in turn creating more available active sites for adsorption. That may be the reason for carbon adsorbents modified by CTAB to increase the removal of Pb(II) as compared to the acidic treatment. Moreover, in case of CTAB-modified carbon sorption of lead is rapid, indicating maximum penetration of adsorbate in less time, due to easy transport of the metal ions to mesopores and micropores.

### 3.6. Adsorption kinetics

The prediction of kinetics is necessary for the design of sorption systems. Chemical kinetics explain how fast the rate of chemical reaction occurs and also on the factors affecting the reaction rate. The nature of sorption process depends on physico-chemical characteristics of the adsorbent and system conditions like temperature, pressure, etc. as well. Measurement of sorption rate constants is an important physico-chemical parameter to evaluate the basic qualities of a good sorbent such as time required for a sorbent to remove particular metals/compounds, efficacy of the sorbents, etc. [21–23]. In batch adsorption processes the adsorbate molecules diffuse into the interior of the porous adsorbent. It was investigated that the adsorption of lead ions from aqueous solution is a linear phase within a time period about 120 min. This behavior can be attributed to the utilization of available adsorbing sites on the surface of adsorbent. After this phase, sorption of lead was almost ignorable. This might be attributed to extremely slow diffusion of the metal ions from the surface film into the micropores which are the least accessible sites for adsorption [11]. In order to observe the sorption process of lead ions, on unmodified and chemically modified adsorbents, four kinetic models were implemented, including Bangham, pseudo-first, second-order and intra-particle diffusion.

#### 3.6.1. Bangham's equation

The rate constants,  $K_r$  for the sorption of lead were calculated using the simplest form of Bangham equation [24]:

$$dQ/dt = Q_t/mt \quad (2)$$

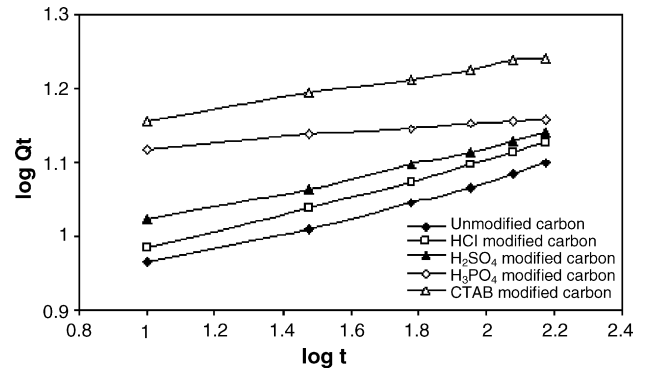


Fig. 6. Bangham's model for the adsorption kinetics of lead ions by carbon adsorbents.

The integral form of the equation can be written as:

$$Q_t = K_r t^{1/m} \quad (3)$$

Assessment of the rate constants is possible by simple linear transformation of the equation:

$$\log Q_t = \log K_r + (1/m) \log t \quad (4)$$

As can be observed from Fig. 6, the linearity of the obtained plots indicate the applicability of the  $(1/m)$ th order kinetics for the system under observation. The adsorption rate constants were calculated from the intercepts and slopes of the straight lines and are reported in Table 2. Rate constant for the adsorption of lead ions onto CTAB-modified carbon is higher, followed by  $H_3PO_4$ -modified carbon indicating that these chemical modifications are much more suitable as compared to the chemical modifications by hydrochloric and sulfuric acids.

#### 3.6.2. Pseudo-first-order model

The pseudo-first-order equation can be written as:

$$dq_t/dt = k_f(q_e - q_t) \quad (5)$$

where  $q_t$  (mg/g) is the amount of adsorbate absorbed at time  $t$ ,  $q_e$  (mg/g) the adsorption capacity in equilibrium,  $k_f$  ( $\text{min}^{-1}$ ) the rate constant for pseudo-first-order model and  $t$  (min) is the time. After definite integration by applying the initial conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$ , the equation becomes [25]:

$$\log(q_e - q_t) = \log q_e - k_f t/2.303 \quad (6)$$

Adsorption rate constants ( $k_f$ ) and adsorption capacity ( $q_e$ ) for the adsorption of lead ions by unmodified and chemically modified adsorbents were calculated from the slope and intercept of the plots of  $\log(q_e - q_t)$  against  $t$  (Fig. 7) and are reported in Table 2. The obtained values indicate that the adsorption rates and adsorption capacity of modified adsorbents are increased. Particularly the efficacy of CTAB-modified adsorbent is enhanced as the surfactant increases the possibility of adsorption in different available active sites.

Table 2  
Kinetics for the adsorption of lead ions by carbon adsorbents

Bangham's constants	$\log K_r$	$K_r$ (mg/g min)	$1/m$	Correlation coefficient, $R^2$
Unmodified carbon	0.086	1.218	0.126	0.994
HCl-modified carbon	0.868	7.372	0.099	0.994
H <sub>2</sub> SO <sub>4</sub> -modified carbon	0.922	8.364	0.099	0.997
H <sub>3</sub> PO <sub>4</sub> -modified carbon	1.084	12.134	0.035	0.995
CTAB-modified carbon	1.087	12.218	0.071	0.997
Pseudo-first-order constants	$k_f$ (min <sup>-1</sup> )	$q_e$ (mg/g)	Correlation coefficient, $R^2$	
Unmodified carbon	0.0035	10.212	0.784	
HCl-modified carbon	0.0046	12.008	0.794	
H <sub>2</sub> SO <sub>4</sub> -modified carbon	0.0048	13.934	0.802	
H <sub>3</sub> PO <sub>4</sub> -modified carbon	0.0053	15.801	0.860	
CTAB-modified carbon	0.0058	19.204	0.997	
Pseudo-second-order constants	$h$ (mg/g min)	$k_s$ (g/mg min)	$q_e$ (mg/g)	Correlation coefficient, $R^2$
Unmodified carbon	5.131	0.0085	24.57	0.999
HCl-modified carbon	3.989	0.0052	27.70	0.998
H <sub>2</sub> SO <sub>4</sub> -modified carbon	4.868	0.0060	28.49	0.998
H <sub>3</sub> PO <sub>4</sub> -modified carbon	5.243	0.0062	29.08	0.999
CTAB-modified carbon	7.550	0.0087	29.46	0.999
Intra-particle diffusion constants	$k_{id}$ (mg/g min)	$C$ , thickness of boundary layer	Correlation coefficient, $R^2$	
Unmodified carbon	0.6699	16.385	0.857	
HCl-modified carbon	0.8826	16.529	0.935	
H <sub>2</sub> SO <sub>4</sub> -modified carbon	0.8194	18.197	0.902	
H <sub>3</sub> PO <sub>4</sub> -modified carbon	0.9044	18.874	0.882	
CTAB-modified carbon	0.6699	22.111	0.891	

### 3.6.3. Pseudo-second-order model

The pseudo-second-order model can be presented in the following form [26,27]:

$$dq_t/dt = k_s(q_e - q_t)^2 \quad (7)$$

where  $k_s$  is the rate constant of pseudo-second-order model (g/mg min). Definite integration of Eq. (7) for boundary conditions  $q_t = 0$  when  $t = 0$  and  $q_t = q_t$  at  $t = t$ , the following form of

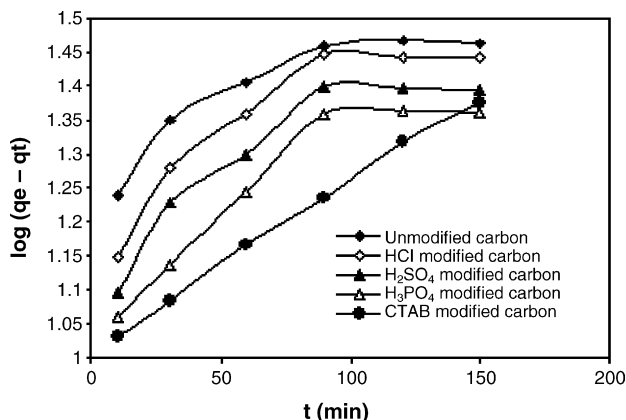


Fig. 7. Pseudo-first-order kinetics for the removal of lead ions by carbon adsorbents.

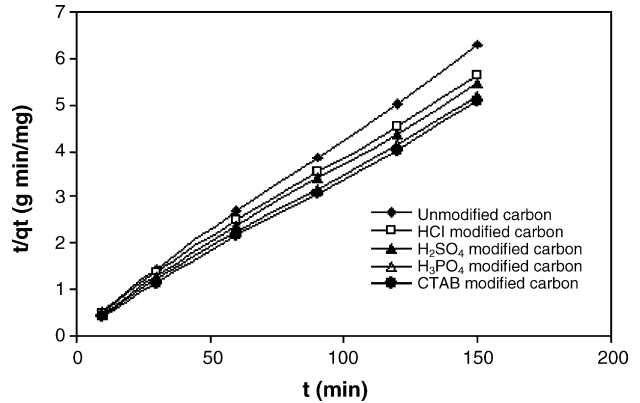


Fig. 8. Pseudo-second-order kinetics for the removal of lead ions by carbon adsorbents.

equation can be obtained:

$$t/q_t = 1/(k_s q_e^2) + (1/q_e)t \quad (8)$$

The initial sorption rate constant,  $h$  (mg/g min), at  $t = 0$  can be defined as [27]:

$$h = k_s q_e^2 \quad (9)$$

The initial sorption rate ( $h$ ), the equilibrium adsorption capacity ( $q_e$ ) and the pseudo-order rate constants  $k_s$  were obtained from the slope and intercept of the plots of  $t/q_t$  against  $t$  for various adsorbents (Fig. 8) and are reported in Table 2. Since the calculated correlation coefficients are consistent and closer to unity for pseudo-second-order kinetics model than the pseudo-first-order kinetic model, therefore, the adsorption kinetics could well be explained and approximated more favorably by pseudo-second-order kinetic model for unmodified and modified carbon adsorbents, respectively.

### 3.6.4. Intra-particle diffusion study

An empirically functional relationship, common to the most adsorption processes, is that the uptake varies almost proportionally with  $t^{1/2}$ , the Weber-Morris plot, rather than with the contact time,  $t$  [28]:

$$q_t = k_{id}t^{1/2} + C \quad (10)$$

where  $k_{id}$  is the intra-particle diffusion rate constant. According to Eq. (10), a plot of  $q_t$  versus  $t^{1/2}$  should be a straight line with a slope  $k_{id}$  and intercept  $C$  when adsorption mechanism follows the intra-particle diffusion process. Values of intercept give an idea about the thickness of boundary layer, i.e., the larger the intercept the greater will be the boundary layer effect [29]. In Fig. 9, plot of mass of lead ions adsorbed per unit mass of adsorbent,  $q_t$  versus  $t^{1/2}$  is presented. The deviation of straight lines from the origin can be attributed to the difference in rate of mass transfer in the initial and final stages of adsorption [27,30]. The values of  $k_{id}$  as obtained from the slopes of straight lines are listed in Table 2. Higher values of  $k_{id}$  for acid modified carbon adsorbents indicate that intra-particle diffusion can be significantly enhanced through the chemical modification of adsorbents. But no change was observed as far as the surfactant modified carbon

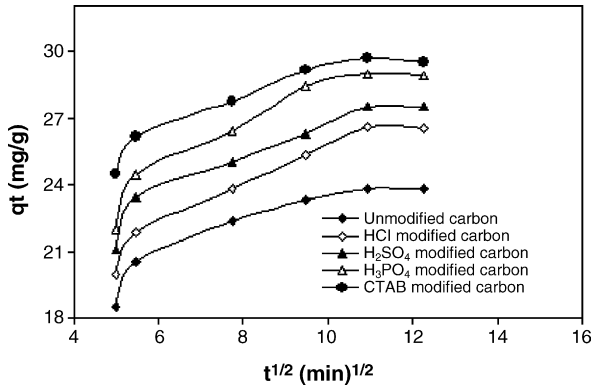


Fig. 9. Weber and Morris intra-particle diffusion plots for the removal of lead ions by carbon adsorbents.

adsorbent is concerned which is an indication of the fact that due to increased wetting and surface area instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface occurs. Thickness of boundary layer,  $C$ , for CTAB-treated adsorbent is having greater value, i.e., 22.111, whereas it was 16.385 for the unmodified carbon adsorbent. Moreover, intra-particle-diffusion is responsible to consumes more time due to very slow diffusion of the adsorbates from the surface film into

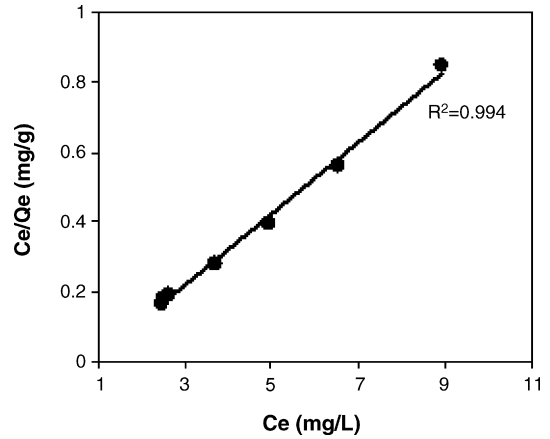


Fig. 12. Langmuir isotherm for H<sub>2</sub>SO<sub>4</sub>-modified carbon.

the micropores, which are the least accessible sites of adsorption and later on creates interference in the regeneration of the adsorbents. Surfactant's modification can be a better alternative for the prompt removal, of hazardous substances, and proper regeneration of the adsorbents for future applications.

### 3.7. Adsorption isotherms

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The Langmuir and Freundlich isotherms are the equations most frequently used to represent the data on adsorption from solution. Langmuir and Freundlich isotherms are represented by the following equations [3]:

$$C_e/Q_e = C_e/Q_0 + K_L/Q_0 \quad (11)$$

$$\log Q_e = \log K + (1/n) \log C_e \quad (12)$$

### 3.8. Langmuir isotherms

Langmuir isotherms are presented in Figs. 10–14, which are plots of  $C_e/Q_e$  versus  $C_e$ . Straight lines were obtained, with  $R^2$  values 0.9959, 0.9941, 0.9949, 0.9952 and 0.9981 for unmodified, HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and CTAB-modified adsorbents,

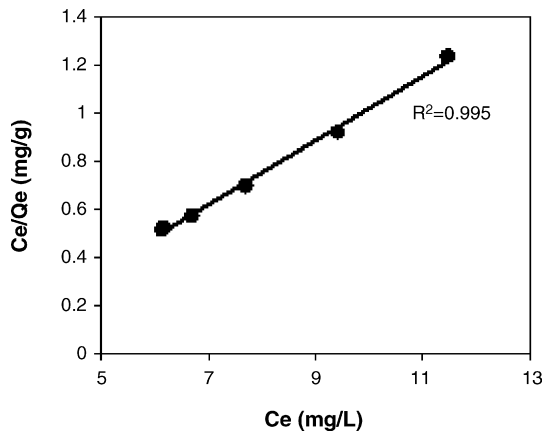


Fig. 10. Langmuir isotherm for unmodified carbon

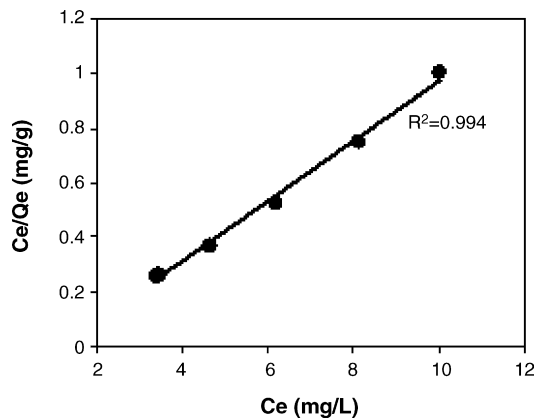


Fig. 11. Langmuir isotherm for HCl-modified carbon.

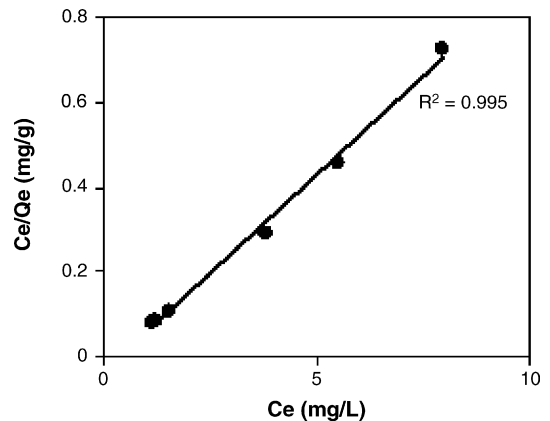


Fig. 13. Langmuir isotherm for H<sub>3</sub>PO<sub>4</sub>-modified carbon.



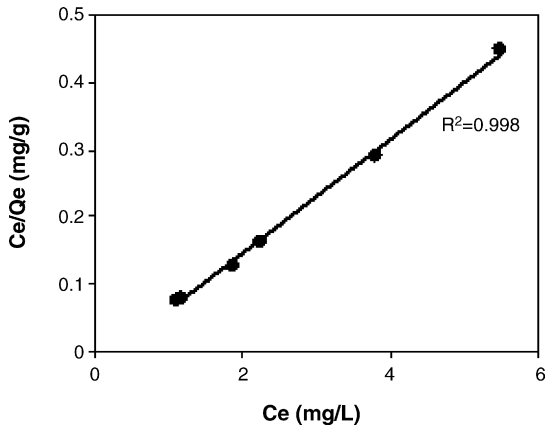


Fig. 14. Langmuir isotherm for CTAB-modified carbon.

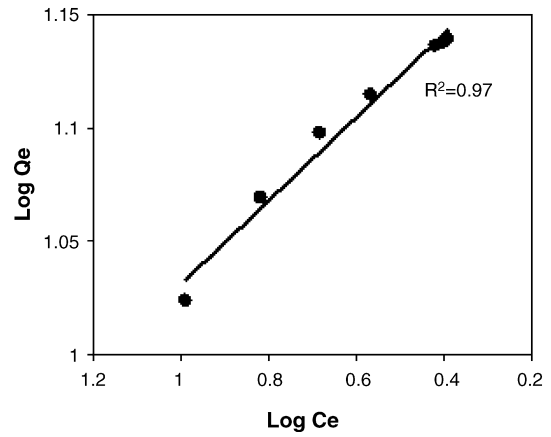


Fig. 17. Freundlich isotherm for H<sub>2</sub>SO<sub>4</sub>-modified carbon.

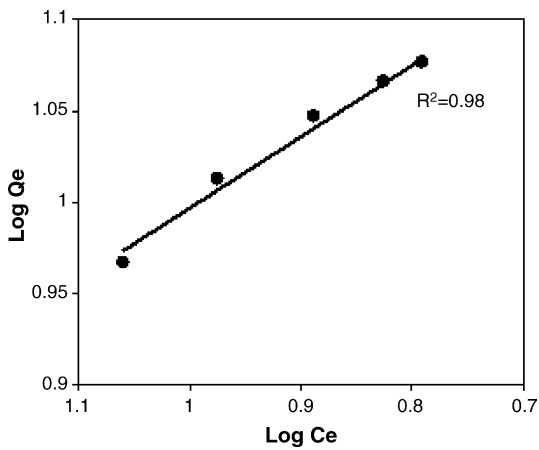


Fig. 15. Freundlich isotherm for unmodified carbon.

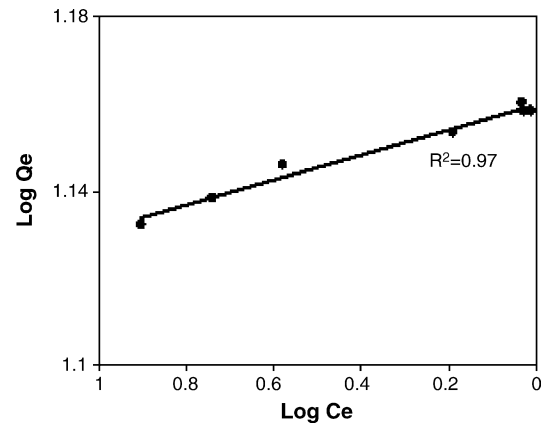


Fig. 18. Freundlich isotherm for H<sub>3</sub>PO<sub>4</sub>-modified carbon.

respectively, which is an indication of the applicability of the Langmuir isotherm for the system under observation.

### 3.9. Freundlich isotherms

Freundlich isotherms are presented in Figs. 15–19, the  $\log Q_e$  is plotted against  $\log C_e$ . Straight lines with  $R^2$  values 0.9877,

0.969, 0.9796, 0.9755 and 0.9969 for unmodified, HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and CTAB-modified adsorbents, respectively, slope  $1/n$  and intercept  $\log k_f$  were obtained. This indicates the satisfaction of the Freundlich isotherm model for the adsorption of lead ions.

In the present investigation the obtained data was analyzed for both the Freundlich and Langmuir isotherms. Comparatively the obtained  $R^2$  values are more satisfactory for Langmuir isotherm.

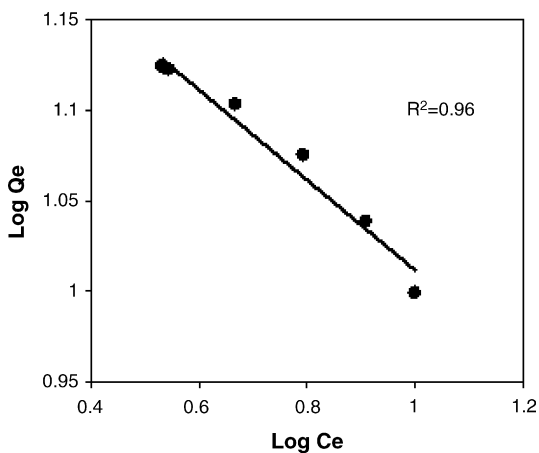


Fig. 16. Freundlich isotherm for HCl-modified carbon.

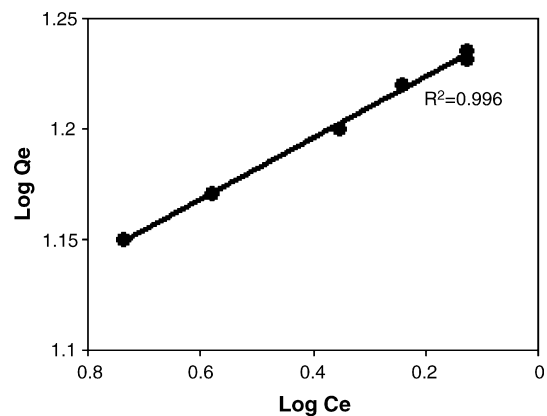


Fig. 19. Freundlich isotherm for CTAB-modified carbon.

The basic assumption of Langmuir adsorption isotherm is based on monolayer coverage of the adsorbate on the surface of adsorbent [25,27,31] which is an indication of the fact that the sorption of lead on to the investigated sorbents generates mono layer formation.

#### 4. Conclusions

This study investigated the sorption of lead from aqueous solution using indigenously prepared and chemically modified adsorbents. The adsorption was found to be strongly dependent on pH, adsorbate, adsorbent dose and contact time. It can be concluded that single step steam pyrolysis is an easy and economical method for the conversion of agricultural waste from *M. oleifera* into good quality microporous activated carbon. Adsorption capacity of the activated carbon can be further increased by chemical modification. Surfactant modified adsorbents can be more efficient for the removal of toxic metals and hazardous materials from industrial effluents. Pseudo-second-order equation can be applied to calculate the adsorption rate constants. Equilibrium adsorption of lead ions by activated carbon from *M. oleifera* follows typical adsorption isotherms and fits both Langmuir and Freundlich isotherms but Langmuir isotherm is found to be more favorable than Freundlich. Moreover, surfactants are also very useful in chromatographic separations of the tedious compounds. Their use in the chemical modification of adsorbents can lead to the selective separation and recovery of noble metals as well.

#### Acknowledgements

The authors (M. Nadeem and S.A. Shahid) are grateful to University of Agriculture Faisalabad (UAF) for granting the leave to pursue higher studies.

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