

57 (2016) 24487–24497 November



Removal of Pb(II) from its aqueous solution by activated carbon derived from Balam Khira (*Kigelia Africana*)

Kaman Singh^{*,1}, Manisha Gautam, Bhuwan Chandra, Ajay Kumar

Advanced Center of Surface Chemistry, Department of Applied Chemistry, School for Physical Sciences, Babasaheb Bhimrao Ambedkar University (A Central University), Lucknow 226 025, India, Tel. +91 9415409189; email: drkamansingh@yahoo.com (K. Singh), Tel. +91 9580905946; email: manisha10486@gmail.com (M. Gautam), Tel. +91 9411773266; email: drbhuwanchandra@gmail.com (B. Chandra), Tel. +91 9125526558; email: ajayamuchem@gmail.com (A. Kumar)

Received 19 October 2015; Accepted 7 January 2016

ABSTRACT

A low cost activated carbon derived from the fruit of Kigelia Africana (KA) was characterized by using Powder X-ray diffraction, Fourier transform infrared spectroscopy, and Brunauer-Emmett-Teller techniques for effective removal of Pb(II) from its aqueous solution. The derived activated carbon from Kigelia Africana (CKA) had micro porous and meso porous pore size distribution with high surface area (799 $m^2 g^{-1}$) and high carbon content (79.42%). The batch mode experiments are carried out to investigate the effect of process parameters such as solution concentration, pH, temperature, contact time, CKA amount on adsorption. The maximum adsorption was found at pH 5.0 (97% for 2.5 g/l CKA in 50 mg/l Pb(II) initial concentration). The Langmuir, Freundlich, and Temkin models were modeled to evaluate the equilibrium adsorption data, and the results describe the best representation of the Langmuir isotherm model with adsorption capacity 79.87 mg/g $(R^2 = 0.99)$ at 30°C. Thermodynamic study demonstrates spontaneous and endothermic nature of the adsorption. Kinetic studies were examined using different kinetic models (Lagergren first-order and pseudo-second-order) and found pseudo-second-order kinetic data are well fitted for adsorption process. It is observed that adsorption of Pb(II) ions followed Lagergren-second-order kinetics. These results suggest that the synthesized CKA is a promising adsorbent for the removal of Pb(II) ions from wastewater.

Keywords: Low cost activated carbon (CKA); Pb(II); Isotherm models; Lagergren-first-order; Pseudo-second-order

1. Introduction

Lead is the one of such highly toxic element that is found both naturally and as introduced contaminant

*Corresponding author.

in the environment. In recent times, Pb has been introduced into natural water from a variety of sources such as acid battery manufacturing, metal plating and finishing, ammunition manufacturing, tetraethyl lead (TEL) manufacturing, and ceramic and glass industries [1]. Lead poisoning in humans causes severe damage

¹Surface Science Laboratory, Faculty of Science, Department of Chemistry, University of Lucknow-226 007, India.

^{1944-3994/1944-3986 © 2016} Balaban Desalination Publications. All rights reserved.

to the kidney, nervous system, reproductive system, liver, and brain and causes sickness or death. Severe exposure to lead has been associated with sterility, abortion, stillbirths, and neonatal deaths. The permissible limit for Pb(II) in wastewater as given by the Environmental Protection Agency (EPA) is 0.05 mg/ dm³ [2]. The presence of excess lead in drinking water causes diseases such as anemia, encephalopathy, and hepatitis. Lead ions have an affinity for ligands containing thiol and phosphatic groups and they inhibit the biosynthesis of heme, causing damage both to the kidney and liver; this behavior of lead is similar to that of calcium. However, Pb can remain immobilized for years, and hence it is difficult to detect the metabolic disorders it causes [3].

There are various methods developed to remove the heavy metals from the aqueous solutions and wastewater. Traditionally, the most widely applied methods for heavy metal removal from wastewater are chemical and electrochemical precipitation, cationic and anionic ion-exchange resins, ion-flotation, evaporation, membrane filtration, reverse osmosis, adsorption, etc. However, adsorption technique has been widely employed in the purification of wastewater. Adsorption is surface phenomenon in which collection or accumulation of substance on the surface of the solid or liquid takes place. It is a physicochemical process in which dissolved molecules are attached to the surface of an adsorbent by physical or chemical forces. Adsorption technology is currently used extensively for the removal of organic and inorganic micro pollutants from aqueous solutions [4]. Taking these criteria into consideration, the search for a low-cost and easily available adsorbent has led many investigators to seek more economic and efficient techniques using natural and vegetal adsorbents [5-10].

The objective of the present work was to evaluate the analytical potential of CKA (Activated Carbon from Kigellia Africana) for an effective removal of Pb (II) from its aqueous solutions. The physical and chemical properties of the CKA were evaluated and the effect of process parameters such as solution concentration, pH, temperature, contact time, CKA amount on adsorption was studied. Adsorption equilibrium and kinetic have been studied under the opticonditions. mum adsorption The Langmuir, Freundlich, and Temkin isotherms were applied to evaluate the adsorption properties in the batch mode experiments. In addition, the pseudo-first-order and pseudo-second-order kinetic models were also applied to examine the uptake kinetics of Pb(II) in the adsorption process.

2. Materials and methods

2.1. Biosorbent characterization

2.1.1. SEM analysis

The particle morphologies of the CKA were studied using scanning electron microscope of JEOL (JSM 6490 LV). Samples were mounted on aluminum stab with the help of double-sided tape. Mounted stabs were coated with gold palladium prior to analysis using a Polaron sputter coater.

2.1.2. Infrared spectroscopy (FTIR)

The CKA (2 mg) was mixed with 200 mg of KBr and then pelleted. The FT-IR spectra of the pellets were recorded using a Fourier Transform Infra-Red Spectrometer (FTIR) Thermo Scientific (Nicole 6700).

2.1.3. X-ray diffraction

Crystallographic parameters of the activated carbon produced by optimum preparation condition were obtained from X-ray diffraction (XRD) studies. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Miniflex II desk top X-ray diffractometer at 30 kV and 15 mA using CuK radiation.

2.1.4. BET surface area

The surface area and pore characteristics of the derived adsorbent CKA was determined from nitrogen adsorption/desorption isotherms at 77 K (boiling point of nitrogen gas at 1 atm pressure) using a surface area analyzer (BELSORP-max, Japan).

2.1.5. Point of zero charge for adsorbent

The PZC characteristic of CKA was determined by solid addition method using 0.1 M KCl and 0.002 M citrimide solutions. KCl and citrimide solution (40 ml) was taken in 100 ml stoppered conical flask. The initial pH values of the solutions were adjusted between 2.0 and 12.0 by adding either 0.1 N HCl or 0.1 N NaOH. The total volume of the solution in each flask was adjusted exactly to 50 ml by adding the KCl and citrimide solution. The initial pH of the solution was then accurately noted. The CKA (0.5 gm) was added to each flask. The suspensions were shaken and allowed to equilibrate for two days with intermittent shaking. The final pH values of the supernatant liquid were noted. The difference between the initial and final pH values ($\Delta pH = pH_i - pH_f$) were plotted

against the initial pH value. The point of intersection of the resulting curve at which change in pH is zero gives the PZC.

2.2. Reagent and solutions

All reagents used were AR-grade chemicals. Stock solutions (1,000 mg/l) of the test solution were made by dissolving required amount of Pb(NO₃)₂ in double distilled water. The pH of the test solutions was adjusted using dilute HCl (0.1 N) and NaOH (0.1 N). The CKA was derived from an inexpensive, abundantly available, and eco-friendly vegetal source of Balam Khira (*Kigelia Africana*).

2.3. Preparation of the activated carbon from Kigelia Africana

The fruit of Kigelia Africana (Hindi name Balam Khira) obtained from the local area of Lucknow, Uttar Pradesh (India) was used as a precursor for activated carbon employing ZnCl₂ activation method. The raw material was first washed with distilled water to remove any water soluble impurities and ashes on the surface and then dried at 65°C to remove the moisture and other volatile impurities. The precursor was then crushed in a pestle and motor and sieved to desired particle size. The chemical activation of the powdered precursor was done with ZnCl₂ at a ratio of 2:1 (activating agent/precursor) over 24 h at 60°C for activation, followed by carbonization at 550°C in a muffle furnace for 1 h in presence of nitrogen (flow rate of 150 ml/min STP). After cooling, the produced material was washed with 0.5 N HCl, hot water and finally cold distilled water to remove residual organic and mineral matters. It was then dried at 110 C for 12 h and sieved to the desired particle size by standard sieves. The product derived so was referred to as CKA.

2.4. Experimental adsorption

2.4.1. Batch studies

The adsorption equilibrium was probed by batch technique in 250 ml conical flasks contacting the CKA (1.0 g/L) with 100 ml of lead solutions of known concentrations (25–1,000 mg/L), shaking at 120 rpm for 2 h at room temperature (30 °C), followed by filtration (0.45 μ m) and subsequent analysis of residual Pb(II) concentration in the filtrate (AAS on flame mode by lead-hollow cathode lamp and wavelength 283.0 nm). The effect of adsorbent dose, adsorbate concentration,

temperature, pH, and contact time was investigated. For determining the effect of pH on Pb(II) adsorption, initial pH of solutions were adjusted to the desired value (2.0–7.0) using 0.1 N HCl or 0.1 N NaOH. The amount of Pb(II) adsorbed by the adsorbent at equilibrium was calculated as follows:

$$q_{\rm e} = \frac{(C_0 - C_{\rm e})V}{m} \tag{1}$$

where C_0 and C_e are initial and equilibrium concentrations (mg l⁻¹) Pb(II) in the solution, *V* the volume (l), *m* the weight (g) of the adsorbent, and q_e is the amount Pb(II) adsorbed by the adsorbent at equilibrium (mg g⁻¹).

3. Results and discussions

3.1. Biosorbent characterization

The SEM images shown in Fig. 1 clearly demonstrate the porosity and surface texture of new adsorbent material.

The CKA was found to contain following elemental compositions Table 1.

Fourier transform infrared (FT-IR) spectroscopy provides evidence for the presence of specific functional groups on the surface of carbon material. Several characteristics bands were observed in the FT-IR spectrum shown in Fig. 2. Each of the bands has been assigned to specific functional group reported in literature. The details of band assignments to functional groups are shown in Table 2.

In IR spectra of activated carbon after deposition of Pb(II) some new peaks are also observed due to increased sharpness of surface of activated carbon. The surface of carbon becomes smooth and sharp with some broad peaks converted into multiple peaks and assigned at 1,214.9, 1,004.9, and 795.5 cm⁻¹.

The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) was measured by means of standard BET equation applied in the relative pressure range of 0.05–0.10. The BET analysis reveals that the CKA had a surface area 799.91 m² g⁻¹, which was primarily contributed by micropores. The average pore diameter of CKA was found to be 4.72 nm, which is an indicative of its micropores character as defined by IUPAC (International Union of Pure & Applied Chemistry) Table 3.

PXRD spectrum shown in Fig. 3 illustrates that the treated carbon derived from KA fruit under optimum preparation condition is crystalline in structure. There are three broad peaks centered on 2θ value of 24° , 42° ,



Fig. 1. SEM images of CKA at different magnifications.

Table 1 Elemental composition of CKA

Elements	Percentage (%)		
C	79.42		
0	18.57		
K	0.01		
Na	0.02		
Mg	0.91		
Ca	1.07		



Fig. 2. FT-IR spectrum of activated carbon derived from CKA.

and 83° are visible in the PXRD spectrum. Two broad diffraction peaks centered around 2θ values of 24° and 42° are attributed to the reflections from the (0 0 2) and (1 0) diffraction peaks of carbon material. These reflections are compulsory for activated carbon and indicate better layer alignment with an increased regularity in crystal structures. The presence of broad peak around

 $2\theta = 83^{\circ}$ is not clearly described. These results and description are also explained by Prahas et al. [18] and Yang et al. [19].

The surface potential of the adsorbent may be influenced by the pH value [20] of the coexisting liquid bulk phase. The pH value, at which the surface charge is zero, is called the point of zero charge (PZC). The surface will be positively charged at pH < pH_{PZC} and negatively charged at pH > pH_{PZC}. Since pH_{PZC} of the CKA was found to be about 6.6, at any pH < pH_{ZPC}, the surface of CKA will be positively charged and at pH > pH_{ZPC}, the surface will be negative.

3.2. Effect of process parameters on Pb(II) adsorption

3.2.1. Effect of pH

The effect of pH on adsorption of Pb(II) on to CKA is shown in Fig. 4. The pH of the solution has a significant role on the removal of heavy metals, since it determines the surface charge of the adsorbent, the degree of ionization, and speciation of the adsorbate. In order to establish the effect of pH on adsorption of Pb(II) on to the CKA, equilibrium studies at different pH values were carried out in the range of 1-7 at 50 and 100 mg/l, respectively. The maximum percent removal of Pb(II) ions on to CKA was observed at pH 4.5-5.0. Above and below this pH, extent of adsorption of Pb(II) onto CKA was found to be quite low. Above pH 7.0, Pb(II) starts precipitating as Pb(OH)₂ and hence studies in this range are not conducted. The ion exchange mechanism between H⁺ ions at the CKA surface and metal ions may follow two reactions [21].

$$2(S-COH) + M^{2+} \rightarrow (S-CO)2M + 2H^{+}$$

Frequency (cm ⁻¹)	Bond	Functional group	Refs.
3,035.5	=C-H stretching	Alkenes	[11]
2,879.2	-C-H stretching	Alkane	[12–14]
2,774.1	H–C=O, C–H stretch	Aldehyde	[14]
1,607.6	-C=C stretching	Olfinics	[13]
1,500.1	-C=C stretching	Aromatic compound	[15,16]
1,053.6	–C–O stretching	Acids, Alcohols, Phenols, Ethers, Esters	[13]
680.5	-С=С-С, С-Н	Alkene	[17]

Table 3 Surface parameters of activated carbon derived from CKA

Table 2

$(V_{\rm m})$ $(\rm cm^3 g^1)$	$(S_{\rm BET})$	$(V_{\rm T})$	d _{avg}	R _p
	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(nm)	(nm)
183.78	799.91	0.9443	4.72	1.21



Fig. 3. PXRD spectra of activated carbon derived from (Balam Khira) Kigelia Africana.

 $S-COH + MOH^+ \rightarrow S-COMOH + H^+$

where S is the adsorbent surface. The Pb(II) speciation diagram indicates that in the highest sorption range, the dominant species of adsorption are Pb²⁺ and PbOH⁺ [22]. In acidic solution, the surface being positively charged, the adsorption of Pb²⁺ and Pb(OH)⁺ species are not favored. Because electrostatic attraction between positively charged adsorbent surfaces and positively charged metal ion surfaces is not possible, it



Fig. 4. Plots illustrating the effect of pH on adsorption (%) of Pb(II) onto CKA (1 g/l, 30° C).

seems that some non electrostatic forces are also involved in adsorption process.

3.2.2. Effect of initial Pb(II) concentration

The adsorption capacity of the CKA obtained from experimental data at different initial concentration of Pb(II) are shown in Fig. 5 As observed from result, the adsorption percentage of the adsorbent decreased with increasing adsorbate concentration . The CKA amount was fixed 1.0 g and equilibrated for 2 h, 30°C (120 rpm) at the initial Pb(II) concentration was increase from 25 to 150 mg/l.

3.2.3. Effect of adsorbent dose

The effect of adsorbent dosage on the percentage removal of Pb(II) at pH 5.0 has been shown in Fig. 6. The CKA amount was varied from 0.5 to 3 g and equilibrated for 2 h, 30°C (120 rpm) at 50 and 100 mg/l Pb (II) initial concentration, respectively. It can be seen from the figure that initially the percentage removal increases very sharply with the increase in adsorbent



Fig. 5. Plots illustrating the effect of initial Pb(II) concentration on adsorption (%) (CKA 1 g/l, 30°C, pH 5.0).

dosage but beyond a certain value (2.5-3.0 g/l), the percentage removal reaches almost a constant value. This trend is expected because as the adsorbent dose increases the number adsorbent particles increases and thus more Pb(II) is attached to its surface.

3.3. Adsorption equilibrium

Several equilibrium isotherm equations were applied to optimize of an adsorption system for the adsorption of Pb(II) onto the CKA. The Freundlich isotherm [23] is employed by assuming a heterogeneous surface with a non uniform distribution of heat of adsorption over the surface which may be written as:

$$q_{\rm e} = K_{\rm F} \, C_{\rm e}^{\frac{1}{n}} \tag{2a}$$

The above equation can be linearized as:



Fig. 6. Plots illustrating the effect of adsorbent dose on adsorption(%) of Pb(II) (Conc. 50, 100 mg/l, 30 °C, pH 5).

$$\ln q_{\rm e} = \ln K_{\rm F} + \frac{1}{n} \ln C_{\rm e} \tag{2b}$$

where $q_e (mg/g)$ is the amount of solute adsorbed per unit weight of adsorbent, $C_e (mg/l)$ is the equilibrium concentration of solute, $K_F (mg/g)$ is the Freundlich constant which indicate the relative adsorption capacity of the adsorbent, and 1/n is the constant indicate the intensity of adsorption.

The Langmuir equilibrium isotherm [24] is based on the fact that the adsorption occurs at specific homogenous site within the surface of adsorbent and monolayer sorption onto a surface with a finite number of identical sites assuming that there are no interactions between adsorbed molecules on the surface, may be written as:

$$q_{\rm e} = \frac{q_{\rm m} K_{\rm L} C_{\rm e}}{1 + K_{\rm L} C_{\rm e}} \tag{3a}$$

Which can be linearlized as:

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{K_{\rm L} q_{\rm m}} + \frac{C_{\rm e}}{q_{\rm m}} \tag{3b}$$

where $q_e (mg/g)$ is the amount of solute adsorbed per unit weight of adsorbent, $C_e (mg/l)$ is the equilibrium concentration of solute, q_m is the monolayer adsorption capacity (mg/g) and is a constant, and K_L is a constant related to the free energy of sorption $(K_L\alpha e^{-\Delta G/RT})$. It is the reciprocal of the concentration at which the adsorbent is half-saturated. Using plot of experimental data as C_e/q_e vs. $1/q_m$, values of the constants were evaluated.

The Temkin isotherm [25] is given as:

$$q_{\rm e} = \frac{RT}{b} \ln(K_{\rm T} C_{\rm e}) \tag{4a}$$

Which can be linearized as:

$$q_{\rm e} = B_1 \ln K_{\rm T} + B_1 \ln C_{\rm e} \tag{4b}$$

where $B_1 = RT/b$, *b* is the Temkin energy constant (J mol⁻¹). The factor K_T in this isotherm explicitly takes into account the interactions between adsorbing species and the adsorbent. A plot of q_e vs. ln C_e enables the determination of the isotherm constants *b*, B_1 , and K_T from the slope and intercept, respectively (Table 4 and Figs. 7–9).

 Table 4

 Adsorption characteristics' of Pb(II) on to CKA

S. no.	Adsorption isotherm	Isotherm parameters		R^2	
1	Freundlich	$K_{\rm F}$	8.82	0.96	
		п	2.11		
2	Langmuir	$K_{\rm L}$	0.051	0.99	
	-	$q_{\rm m}$	79.87		
3	Temkin	\dot{B}_1	41.64	0.98	
		$K_{\rm T}$	2.13		



Fig. 7. Freundlich adsorption isotherm of Pb(II) on to CKA at 30 $^\circ\!\!\mathrm{C}.$



Fig. 8. Langmuir adsorption isotherm of Pb(II) onto CKA at 30 $^\circ\!\mathrm{C}.$

Table 5 also presents the comparison of surface area and adsorption capacity of CKA for Pb(II) ion with that of various biosorbents. The adsorption capacity of CKA for Pb(II) ion was found to be comparable and moderately higher than those of many corresponding biosorbents in literature.



Fig. 9. Temkin adsorption isotherm of Pb(II) on to CKA at 30 °C.

3.4. *Kinetics of adsorption*

Adsorption kinetics was studied by monitoring the progress of the adsorption process at different time intervals. Fig. 5 clearly demonstrates that the amount of adsorption was found to increase up to 90 min. and finally attained a constant value up to 150 min for 25, 50, 100, and 150 mg/l initial Pb(II) concentration, respectively. Several kinetic models were tested with observed experimental results in order to describe the mechanism of adsorption process. The results of the two models are represented in Figs. 10 and 11. The kinetic parameters of each model are tabulated in Table 6.

3.4.1. Lagergren first order Kinetics

The Lagergeren first-order rate expression [28] is written as:

$$\log(q_{\rm e} - q_t) = \log q_{\rm e} - \frac{k_{\rm ad}}{2.303}t$$
(5)

where q_t and q_{eq} are the amount adsorbed at time t and at equilibrium, t is time K_{ad} is rate constant for adsorption. A $\log(q_e - q_t)$ vs. time plots give a straight line, (Fig. 10.) K_1 was calculated from the slope at temperature 30°C and data are presented in Table 6.

3.4.2. Pseudo-second-order kinetic

The pseudo-second-order kinetic equation [28] is given as:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = K_2 \left(q_\mathrm{e} - q_t\right)^2 \tag{6a}$$

Comparison of adsorption capacity (mg/g) of CKA for Pb(II) with that of different biosorbents

Low cost biosorbentsSurface area (m^2/g) Adsorption capacit	ty $q_{\rm m}$ (mg/g) pH	Refs.
Papaya seed carbon – 68.4	5.0	[26]
Peat 8.54 79.68	-	[27]
Tamarind wood treated with Zncl ₂ 1,322 43.85	6.0	[28]
Cucumber peel – 28	5.0	[29]
Coconut shell 0.52 24.24	5.0	[30]
Moringa oleifera husk Unmodified 725.0 79.43	8.0	[31]
<i>M. oleifera</i> husk modified with HCl 746.3 88.63	5.8	[31]
<i>M. oleifera</i> husk modified with H_2SO_4 769.8 91.8	5.4	[31]
CKA 799.9 79.87	5.0	[Present work]



Fig. 10. Lagergren first-order plots for the adsorption of Pb (II) on to CKA (pH 5.0, CKA 1 g/l, and 30 $^{\circ}$ C).



Fig. 11. Pseudo-second-order plots for the adsorption of Pb (II) on to CKA (pH 5.0, CKA 1 g/l, and 30° C).

The integration of the equation leads to:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{e2}^2} + \frac{1}{q_{e2}}t$$
(6b)

where K_2 is the rate constant (g mg⁻¹ min⁻¹).

The slope and intercept of the plot between t/q_t vs. time gives the value of q_e and K_2 , respectively (Fig. 11) and data are shown in Table 6.

From Table 6 it is found that the first-order kinetic equation, the values of q_e are not in the agreement with the experimental (q_{exp}) values. However, the pseudo-second-order kinetic equation represent the adsorption data well satisfactorily with $R^2 = 0.99$ that are obtained from linear regression methods. Such representative plots are shown in Figs. 10 and 11, respectively.

3.5. Thermodynamics of adsorption

The temperature range used in this study was 20–60°C. The values of equilibrium constants (K_c) at 20, 30, 40, 50, and 60°C, Pb(II) initial concentration (50 mg/l) and CKA amount (1 g/l) at pH 5.0 were calculated using the following relation [32]:

$$K_{\rm c} = \frac{C_{\rm Ac}}{C_{\rm e}} \tag{7}$$

where C_{Ac} and C_{e} are the equilibrium concentrations (mg/l) of Pb(II) on the adsorbent and in solution, respectively.

$$\Delta G^{\circ} = -RT \log K_{\rm c} \tag{8}$$

where *T* is the absolute temperature, *R* gas constant, and ΔG° is the standard free energy change. The values of enthalpy change (ΔH°) and entropy change (ΔS°) were calculated using the following relation:

$$\log K_{\rm c} = \frac{\Delta S^{\circ}}{2.303 R} - \frac{\Delta H^{\circ}}{2.303 RT} \tag{9}$$

Table 5

Pb(II) concentration (mg/l)	$K_1 (\min^{-1})$		$q_{\rm e}~({\rm mg}/{\rm g})$	R^2
Lagergren first-order kinetics				
25	0.050		177.82	0.93
50	0.059		309.02	0.91
100	0.056		119.11	0.93
150	0.049		111.13	0.98
Pseudo-second-order kinetics				
Pb(II) concentration (mg /l)	$K_2 ({\rm gm}{\rm min}^{-1})$	$q_{\rm exp} ({\rm mg/g})$	$q_{\rm e} ({\rm mg/g})$	R^2
25	5.1×10^{-4}	75.21	90.68	0.99
50	$4.2 imes 10^{-4}$	71.30	85.54	0.99
100	$5.6 imes 10^{-4}$	56.07	67.11	0.99
150	$5.5 imes 10^{-4}$	42.22	53.13	0.99

Table 6 Kinetics parameters for adsorption of Pb(II) at different initial concentration on to CKA



Fig. 12. vant's Hoff plot for Pb(II) on to CKA.

 ΔS° and ΔH° were calculated from the slope and intercept of linear plot of log $K_{\rm c}$ vs. 1/T. The vant's Hoff plot for Pb(II) on CKA is shown in Fig. 12. The thermodynamic data are given in Table 7.

The endothermic nature of the adsorption was confirmed by the thermodynamic parameters as shown in Table 7. Apparent enthalpy of adsorption ΔH° also confirms the endothermic nature of the adsorption process.

4. Conclusions

The synthesized CKA produced from Kigelia Africana fruit seems to have great potential to remove Pb(II) from wastewater. The various equilibrium models such as Freundlich, Langmuir, and Temkin were tested to describe the equilibrium adsorption. However, Langmuir isotherm was found most suitable as representative of the equilibrium adsorption data. The kinetic modeling of the Pb(II) adsorption onto CKA indicates that adsorption process is pseudo-secondorder with the R^2 0.99. Different thermodynamic calculations indicate that the sorption process is feasible, spontaneous, endothermic, and positive value of ΔS suggests the increased randomness. The adsorption properties of studied system depend on several factors such as surface area of adsorbent and solution condition such as pH and adsorbate concentration. The waste material used for the preparation of CKA is widely available and inexpensive hence it is expandable for industrial purpose.

Table 7 Thermodynamics parameters at different temperatures for the adsorption of Pb(II) onto CKA

, I		1 1		
Temperature (°C)	K _c	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹)
20	2.95	-2.63		
30	3.78	-3.32		
40	4.99	-4.16	12.36	0.0518
50	5.58	-4.59		
60	5.14	-4.53		

24496

Acknowledgments

The authors express their great thanks for the support of USIC, Babasaheb Bhimrao Ambedkar University (A Central University), India for FT-IR and SEM analysis. The Financial support to one author (MG) from UGC-JRF (17-1/2006 SA-1) is gratefully acknowledged.

References

- J. Goel, K. Kadirvelu, C. Rajagopal, V.K. Garg, Removal of lead (II) from aqueous solution by adsorption on carbon aerogel using a response surface methodological approach, Ind. Eng. Chem. Res. 44 (2005) 1987–1994.
- [2] Guidelines for Drinking Water Quality, World Health Organization Geneva, Switzerland, third ed., 2008.
- [3] M. Sekar, V. Sakthi, S. Rengaraj, Kinetics and equilibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell, J. Colloid Interface Sci. 279 (2004) 307–313.
- [4] G. Raj, Advanced Physical Chemistry, Goel Publication House, Meerut, thirty-fourth ed., 2008.
- [5] L. Das, P. Kolar, J.J. Classen, J.A. Osborne, Adsorbents from pine wood via K₂CO₃-assisted low temperature carbonization for adsorption of p-cresol, Ind. Crops Prod. 45 (2013) 215–222.
- [6] M. Kilic, E.A. Varol, A.E. Pütün, Adsorptive removal of phenol from aqueous solutions on activated carbon prepared from tobacco residues: Equilibrium, kinetics and thermodynamics, J. Hazard. Mater. 189 (2011) 397–403.
- [7] D. Kalderis, D. Koutoulakis, P. Paraskeva, E. Diamadopoulos, E. Otal, J. Valle, Adsorption of polluting substances on activated carbons prepared from rice husk and sugarcane bagasse, Chem. Eng. J. 144 (2008) 42–50.
- [8] D. Mohan, K.P. Singh, V.K. Singh, Wastewater treatment using low cost activated carbons derived from agricultural byproducts—A case study, J. Hazard. Mater. 152 (2008) 1045–1053.
- [9] M. Achak, A. Hafidi, N. Ouazzani, S. Sayadi, L. Mandi, Low cost biosorbent "banana peel" for the removal of phenolic compounds from olive mill wastewater: Kinetic and equilibrium studies, J. Hazard. Mater. 166 (2009) 117–125.
- [10] S. Mubarik, A. Saeed, Z. Mehmood, M. Iqbal, Phenol adsorption by charred sawdust of sheesham (Indian rosewood; *Dalbergia sissoo*) from single, binary and ternary contaminated solutions, J. Taiwan Inst. Chem. Eng. 43 (2012) 926–933.
- [11] M. Mastalerz, R.M. Bustin, Application of reflectance micro-Fourier transform infrared spectrometry in studying coal macerals: Comparison with other Fourier transform infrared techniques, Fuel 74 (1995) 536– 542.
- [12] A.M. Puziy, O.I. Poddubnaya, A. Martínez-Alonso, F. Suárez-García, J.M.D. Tascón, Synthetic carbons activated with phosphoric acid III. Carbons prepared in air, Carbon 41 (2003) 1181–1191.

- [13] A.M. Puziy, O.I. Poddubnaya, A.M. Alonso, F.S. Garcia, J.M.D. Tascón, Surface chemistry of phosphoruscontaining carbons of lignocellulosic origin, Carbon 43 (2005) 2857–2868.
- [14] Ö. Gerçel, A. Özcan, A.S. Özcan, H.F. Gerçel, Preparation of activated carbon from a renewable bio-plant of *Euphorbia rigida* by H₂SO₄ activation and its adsorption behavior in aqueous solutions, Appl. Surf. Sci. 253 (2007) 4843–4852.
- [15] D.J. Pasto, C.R. Johnson, Organic Structure Determination, Prentice-Hall, Englewood Cliffs, New Jersey, 1969, pp. 375–378.
- [16] T.H. Liou, Development of mesoporous structure and high adsorption capacity of biomass-based activated carbon by phosphoric acid and zinc chloride activation, Chem. Eng. J. 158 (2010) 129–142.
- [17] S. Biniak, G. Szymański, J. Siedlewski, A. Świątkowski, The characterization of activated carbons with oxygen and nitrogen surface groups, Carbon 35 (1997) 1799– 1810.
- [18] D. Prahas, Y. Kartika, N. Indraswati, S. Ismadji, Activated carbon from jackfruit peel waste by H_3PO_4 chemical activation: Pore structure and surface chemistry characterization, Chem. Eng. J. 140 (2008) 32–42.
- [19] T. Yang, A.C. Lua, Textural and chemical properties of zinc chloride activated carbons prepared from pistachio-nut shells, Mater. Chem. Phys. 100 (2006) 438–444.
- [20] K. Singh, R. Bharose, S.K. Verma, V.K. Singh, Potential of powdered activated mustard cake for decolorising raw sugar, J. Sci. Food Agri. 93 (2012) 157–165.
- [21] A. Shukla, Y.H. Zhang, P. Dubey, J.L. Margrave, S.S. Shukla, The role of sawdust in the removal of unwanted materials from water, J. Hazard. Mater. 95 (2002) 137–152.
- [22] C. Raji, K.P. Shubha, T.S. Aniurudhan, Use of chemically modified sawdust in the removal of Pb(II) ions from aqueous media, Indian J. Environ. Health 39 (1997) 230–238.
- [23] H. Freundlich, Ueber die adsorption in loesungen, J. Phys. Chem. 57 (1907) 385–470.
- [24] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.
- [25] D. Mohan, K.P. Singh, S. Sinha, D. Gosh, Removal of pyridine derivatives from aqueous solution by activated carbons developed from agricultural waste materials, Carbon 43 (2005) 1680–1693.
- [26] D.K. Singh, S.K. Yadav, S. Sinha, Removal of lead (II) from aqueous solution using papaya seed carbon: Characteristics and kinetics study, Int. J. Chem. Environ. Eng. 4 (2013) 127–136.
- [27] R. Balasubramanian, S.V. Perumal, K. Vijayaraghavan, Equilibrium isotherm studies for the multicomponent adsorption of lead, zinc, and cadmium onto indonesian peat, Ind. Eng. Chem. Res. 48 (2009) 2093–2099.
- [28] J. Acharya, J.N. Sahu, C.R. Mohanty, B.C. Meikap, Removal of lead(II) from wastewater by activated carbon developed from Tamarind wood by zinc chloride activation, Chem. Eng. J. 149 (2009) 249–262.
- [29] R. Pandey, N.G. Ansari, R.L. Prasad, R.C. Murthy, Pb (II) Removal from aqueous solution by *Cucumissativus* (Cucumber) peel: Kinetic, equilibrium and thermodynamic study, Amari. J. Environ. Prot. 2 (2014) 51–58.

- [30] B. Singha, S.K. Das, Removal of Pb(II) ions from aqueous solution and industrial effluent using natural biosorbents, Environ. Sci. Pollut. Res. 19 (2012) 2212–2226.
- [31] M. Nadeem, A. Mahmood, S.A. Shahid, S.S. Shah, A.M. Khalid, G. McKay, Sorption of lead from aque-

ous solution by chemically modified carbon adsorbents, J. Hazard. Mater. 138 (2006) 604-613.

[32] C. Namasivayam, K. Ranganathan, Removal of Cd(II) from wastewater by adsorption on "waste" Fe(III)Cr (III) hydroxide, Water Res. 29 (1995) 1737–1744.