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Production and characterization of activated carbon from *Leucaena* plant wastes for removal of some toxic metal ions from waste solutions

E.A. Abdel-Galil[a,*], H.E. Rizk[a], A.Z. Mostafa[b]

[a] *Atomic Energy Authority, Hot Labs. Centre, P. No. 13759, Cairo, Egypt, Tel. +20 1159895618; Fax: +20 244620784; email: ezzat_20010@yahoo.com (E.A. Abdel-Galil), Tel. +20 1094037730; Fax: +20 244620784; email: ahmhoda@gmail.com (H.E. Rizk)*
[b] *Atomic Energy Authority, Nuclear Research Center, P. No. 13759, Cairo, Egypt, Tel. +20 1114448460; Fax: +20 244620784; email: mostafa_zhran@yahoo.com*

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ABSTRACT

The use of chemically activated biomass from *Leucaena* as an economic agricultural waste was investigated for the removal of Cu(II) and Pb(II) ions. The structural morphology and composition of the studied activated carbon were evaluated by scanning electron microscope (SEM), XRD, FTIR, X-ray fluorescence, and CHNS elemental analyses. SEM and FTIR analyses indicated that a lot of cavities and functional groups, such as carboxyl and amino groups, were present on the external surface of activated carbon. Effects of various parameters such as contact time, pH, temperature, and adsorbent dose on the adsorption percentage of Cu(II) and Pb(II) have been investigated. The data indicated the proportional dependence of the adsorption of these metals on both pH of the solution and the amount of adsorbent up to 0.05 g. On the basis of distribution studies, the linear relations between $\log K_d$ and pH were observed for Cu^{2+} and Pb^{2+} ions with slopes 0.53 and 1.20, respectively, with the selectivity order $Pb^{2+} > Cu^{2+}$. Thermodynamic parameters, ΔH°, ΔS°, and ΔG° were calculated and indicated an endothermic and spontaneous process. The values of breakthrough capacity were calculated and found to be equal to 4.92 and 15.09 mg/g for Cu^{2+} and Pb^{2+}, respectively.

Keywords: *Leucaena* plant wastes; Activated carbon; Heavy toxic metals; Distribution studies; Thermodynamic parameters; Separation

1. Introduction

Water pollution is one of the most significant environmental problems. The most common toxic heavy metal are Cr, Se, Al, As, Cd, Cu, Pb, and Hg. These heavy metals reach the human body through drinking and skin absorption [1].

Researchers were interested to find cheaper adsorbents with high adsorption efficiency relative to these costly wastewater treatment methods such as chemical precipitation, ion-exchange, electroflotation, membrane separation, reverse osmosis, electrodialysis, solvent extraction, etc. [2]. According to Bailey et al. [3], an adsorbent can be considered as cheap, especially if it is abundant in nature. Biological materials are one of these adsorbents that are available in large quantities from agricultural operations [4]. Different agricultural byproducts such as *nut shells*, *wood*, *bone*, *peat*, and *coconut shells*, were processed into activated carbons [5–14] and biomass, such as *Aspergillus tereus* [15] *Rhizopus arrhizus* [16], were reported as an important

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*Corresponding author.

adsorbent for the removal of heavy metals, radionuclides, and organics from industrial wastewater.

Leucaena belonging to *Leguminacae*, is a giant, dense, and quick growing tree, cultivated in the tropical dry regions including Pakistan, Egypt, etc., used for forage [17–19], medicinally it has been studied on tumor cells [20], as anti-fertility agent [21], and it is also used in the treatment of parasitic diseases [22], it has fungicidal properties [23] and normalize the soil acidity, salinity. *Leucaena* seeds increase the level of provitamin in chicken [24], and its foliage is a good source of dietary nutrients, serving as an animal feed and poultry diet [25,26], and it is also used as human food [26].

Leucaena adsorbent has a good efficiency, fast kinetics, as well as easily handing with small amount of secondary sludge. Different processes are used for the preparation of activated carbon, the so-called physical and chemical activation. Chemical activation is a well-known method for preparing activated carbons, which has been the object of great study in the last years, as it presents several advantages compared to physical activation. An important advantage of chemical activation is that the process allows us to obtain very high surface area activated carbons [27–30].

In this work, laboratory studies to produce activated carbon from *Leucaena* by chemical activation are presented. The prepared activated carbon was characterized using different analytical techniques such as chemical stability, scanning electron microscope (SEM), DTA, and TGA, XRD analysis, and FTIR spectra. It is essential to study the thermodynamics parameters (ΔG°, ΔS°, and ΔH°) for the adsorption of Cu^{2+} and Pb^{2+} on *Leucaena* activated carbon, equilibrium distribution coefficients of metal ions on the prepared activated carbon were determined to explore the removal efficiency of the studied cations.

2. Experimental

2.1. Preparation of activated carbon from Leucaena

Leucaena agricultural waste byproducts were collected from a farm of soil & water research department, nuclear research center, atomic energy authority, Inshass, Egypt. The dry *Leucaena* agricultural waste byproducts were washed with tap water several times, then washed with distilled water to remove earthy impurities. Then, it was dried in an air oven at 50 ± 5℃ for 8 h.

Leucaena agricultural waste byproducts were treated chemically by mixing with 1.0 M KOH in the ratio of 1:10 (*Leucaena*: KOH, w/v) at room temperature. The mixture was allowed to stand for 24 h, and then the excess solution was decanted off. Treated *Leucaena* was repeatedly washed with distilled water until the base was undetected in the filtrate and then dried at 105 ± 5℃ until its weight attained a constant value, followed by grinding and sieving to ~0.168 mm. The product was washed sufficiently with 4 M HCl in the ratio of 1:10 (*Leucaena*: HCl, w/v) at room temperature for 3 h, and washed with distilled water until the pH of the supernatant was above 4.0 to remove the residual KOH, and then the wet product was dried in the laboratory at room temperature until the constant weight. The dried material was activated by burning it in a muffle furnace at 800℃ for 30 min. The pyrolyzed sample was preserved in desiccators and then stored in airtight plastic bottles. No other physical and chemical treatments were performed prior to batch sorption experiments.

2.2. Physical and chemical characteristics of the adsorbent

Particle size was determined using sieves of different particle size. Packed and apparent densities were determined by a tamping procedure using a 10 mL graduated glass cylinder. The sorbents were analyzed for their BET-specific surface area (calculated using the BET standard method). The XRD spectra of the powdered samples were obtained using a Shimadzu X-ray diffractometer obtained from Shimadzu Kyoto "Japan", model XD-Dl, with a nickel filter and a Cu Kα-X-radiation tube ($\lambda = 1.5418$ Å), in a diffraction angle (2θ) range of 4–90˚. SEM image of the particles was identified using Jeol SEM of JSM-6510A Model, Japan, operating with beams of primary electrons ranging from 5 to 30 keV. The chemical composition of the studied sorbent was performed by X-ray fluorescence (XRF) of solid samples with Philips XRF detector, Holland, while, the chemical composition of the organic part was performed by the Flash EA Analyzer, Italy (Elemental analysis, C, H, and N concentrations). The IR spectra of the prepared activated carbon were measured by the KBr disk method by mixing the solid with potassium bromide in the ratio 1:4 and ground to a very fine powder. A transparent disk was formed in a moisture-free atmosphere. The IR spectra were recorded using a Shimadzu infrared spectrometer (BOMEM-FTIR) obtained from Shimadzu Kyoto "Japan", in the range 400–4,000 cm^{-1}. Measurements of differential thermal and thermogravimetric (TG) analyses were carried out using a Shimadzu DTG-60 thermal analyzer obtained from Shimadzu Kyoto "Japan". The sample was measured for ambient temperature of up to 1,000℃ in N_2 atmosphere, with the heating rate of 10 deg/min and using alumina powder as a reference material.

2.3. Batch technique

The adsorption of Cu^{2+} and Pb^{2+} ions by the synthesized activated carbon was carried out using a batch technique, where 0.05 g of carbon was contacted with 5 mL of a 50 mg/L of the above mentioned metal ions solution at a V/m ratio of 100 mL/g. The experiments were conducted in mono element system. The liquid/solid ratio (v/m) in all adsorption measurements was kept constant, whereas otherwise parameters were specified. In all cases, the pH of the solution was adjusted using a few drops of 12 M hydrochloric acid and was measured before and after equilibration using a pH meter of the bench, model 601A, USA. The mixture was placed overnight (time within an equilibrium was attained) in a shaker thermostat adjusted at 25 ± 1℃; agitating rate, 400 rpm. After equilibrium, the solutions were separated by centrifugation. The percentage adsorption (U%) of metal ions by solid phase was deduced as in Eq. (1). The concentration of the metal ions was measured (using atomic absorption spectrophotometer). All tests were repeated for three times and the total experimental error was found to be about ±3%.

$$U\ (\%) = \frac{A_o - A_f}{A_o} \times 100 \tag{1}$$

$$K_d\ (\text{mL/g}) = \frac{[A_o - A_f]}{A_f} \times V/m \tag{2}$$

where K_d is the distribution coefficient, A_o and A_f are the concentrations of the ions in solution before and after equilibration (mg/L), respectively, V is the solution volume (mL), and m is the adsorbent mass (g).

2.4. Separation factor

The separation factor may be considered as the relative tendency of two ions to be adsorbed on an exchanger from solutions of equal concentration. It is used as a measure of the possibility of chromatographic separation and is also expressed as the ratio of the distribution coefficients of the elements to be separated as:

$$\text{Separation factor } (\alpha^{A/B}) = K_{dA}/K_{dB}$$

where K_{dA} and K_{dB} are the distribution coefficients for the two competing species A and B in the ion-exchange system.

2.5. Continuous flow experiment

Chromatographic column breakthrough investigations were conducted in a multi element system, as follows; 0.3 g of the activated carbon of particle size 0.168 mm was packed in a glass column (0.5 cm diameter and 5 cm height) to give a bed height of 1.1 cm^3 volume. 150 mL of the desired neutral solutions (pH 4.65) containing 100 mg/L of metal chloride [$M\ (Cl)_x$, where $M = Cu^{2+}$ and Pb^{2+}] were passed through the column beds at a flow rate of 0.75 mL/min, this volume is sufficient to make all the active sites in the surface of the studied sorbent completely saturated with Pb^{2+} and Cu^{2+} ions; equal fractions were collected, about 10 mL in each fraction, and the concentrations were continuously measured using atomic absorption spectrophotometer.

3. Results and discussion

3.1. Characterization of material

The physicochemical characterization and chemical composition of the studied activated carbon are shown in Tables 1 and 2.

The solubility experiments show that the studied sorbent has reasonably good chemical stability (Table 1). As the results indicate that the material is resistant to HNO_3 and HCl media, the chemical stability of the studied activated carbon is very high as compared to other activated carbons [31–33].

The IR spectrum of the chemical activated biomaterial is shown in Fig. 1, from which, the broad mixed stretching vibration adsorption band of amino and hydroxyl groups could be seen at 3,442–3,750 cm^{-1} [34]. The peak at 3,419 cm^{-1} represents the stretching

Table 1
Characteristics of the *Leucaena* activated carbon

Parameter	Value
Moisture content (%)	9.88
Bulk density (g/mL)	0.236
Apparent density (g/mL)	0.148
Ash content (%)	2.26
pH	5.78
Surface area (m^2/g)	245
Particle size (mm)	0.168–0.750
Solubility in water (%)	0.10
Solubility in 0.5 M HCl (%)	0.25
Solubility in 5 M HCl (%)	0.88
Solubility in 0.5 M HNO_3 (%)	0.3
Solubility in 5 M HNO_3 (%)	0.98

Table 2
Chemical composition of the *Leucaena* activated carbon

Component	Concentration (%)
C	52
H	2.2
N	3.9
S	2.22
Cl	1.68
Al_2O_3	6.7
SiO_2	7.8
CaO	15.38
Na_2O	1.2
Fe_2O_3	1.33
K_2O	0.82
P_2O_5	0.66
MgO	0.78
Others	1.07

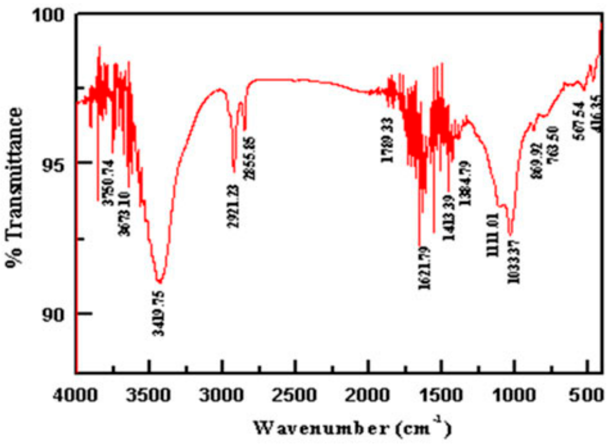

Fig. 1. IR spectrum of *Leucaena* activated carbon.

vibrations of the surface hydroxyl group Si–OH as well as the –OH stretching vibrations of carboxylic [34–36]. The bands around 2,855 and 2,920 cm^{-1} are due to asymmetric and symmetric C–H stretching vibrations in aliphatic –CH, $–CH_2$, $–CH_3$ [37]. There was an obvious characteristic stretching vibration absorption band of carboxyl groups at 1,750 cm^{-1} [37]. The band at 1,620 cm^{-1}, can be attributed to the bending vibrations of adsorbed water [36]. The peak at 1,413 cm^{-1} is due to the deformation vibration of hydroxyl groups (may be due to Si, Al, and/or Ca-OH deformation vibration) [38,39]. The peak at 1,384 cm^{-1} represents the COO^- symmetric stretching vibrations as well as the C–N stretching vibrations [34]. The peak at 1,250.40 cm^{-1} represents the symmetric SO_3 stretching vibrations [34]. The 1,111 cm^{-1} peak corresponds to C–O stretching vibration and O–H bending modes of alcoholic, phenolic, and/or carboxylic groups [37]. The peak at 1,033 cm^{-1} is due to the presence Si–O stretching bond [40]. The band at 869 cm^{-1} is the characteristic of out-of-plane deformation vibration of C–H in aromatic structure [41]. The peak at 763 cm^{-1} is considered to be the bonding between C and Si, or the overlapping of the Si–O and Si–OH [42–44]. The bands at 567 and 465 cm^{-1} are assigned to Si–O–Al and Si–O–Si bending vibrations, respectively [45]. The bands between 416 and 465 cm^{-1} are associated with metal oxygen bonds **(**may be due to Ca–O**)** [46,47]. The FTIR spectrum gives the indication of the polyfunctional nature of the biosorbent.

The results illustrated in Fig. 2 show the FTIR spectra of the unloaded chemical activated biomaterial, Pb(II)-loaded, and Cu(II)-loaded chemical activated biomaterial. These results represent the information about the functional groups on the surface of the cell wall of the biomass material and the possible interaction between the metals and these functional groups. It could be observed that the intensity and broad of the peaks at 3,750, 3,419, 1,111, and 1,033 cm^{-1} are changed after loading of Pb(II) and Cu (II). These significant changes in the intensity and broad of these peaks after loading of Pb(II) and Cu(II) indicate that the functional groups (amino, hydroxyl, and C–O) were involved in the adsorption of Pb(II) and Cu(II) on the surface of activated carbon and thus confirmed that the adsorption is chemical adsorption.

The X-ray diffraction patterns of *Leucaena* activated carbon are presented in Fig. 3, from which, it can be deduced that calcium aluminum silicate hydrate ($Ca–Al_2Si_4O_{12}·2H_2O$), calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$), and carbon are the main phases present in the sorbent. The peaks, at incidence angles

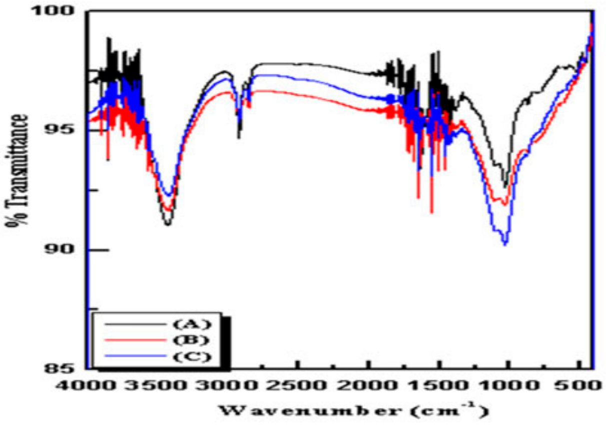

Fig. 2. IR spectrum of (A) unloaded chemical activated biomaterial, (B) Pb(II)-loaded chemical activated biomaterial, and (C) Cu(II)-loaded chemical activated biomaterial.

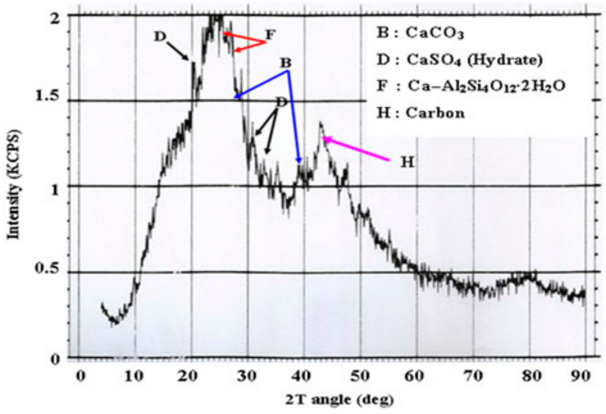

Fig. 3. XRD diagrams of *Leucaena* activated carbon (as-prepared).

29.50˚ and 39.10˚ 2θ, indicate the presence of ($CaCO_3$) [48], as it is known that $CaCO_3$ minerals are usually present in most ground and surface soils [49]. The peaks, at 20.50˚, 30.70˚, and 32.90˚ 2θ, are due to the presence of ($CaSO_4$) [48], The peaks, at 25.10˚ and 26.90˚ 2θ, indicate the presence of silica group which corresponds to ($Ca–Al_2Si_4O_{12}·2H_2O$) [48,50,51]. The peak at incidence angles (2θ) of 44.30 corresponds to carbon [50,51]. These results are confirmed with the data obtained from the elemental and FTIR analyses.

The TGA–DTA data curve of *Leucaena* activated carbon given in Fig. 4 shows that as the biomass sorbent was heated from room temperature to 100˚C, the moisture was vaporized out [34], and the total mass loss has reached 9.88%. A little degradation occurred at 437˚C, the total mass loss was about 1.29%. It might be possible that the free radical mechanism occurred to eliminate water and to produce the volatile gasses up to that temperature [34]. 87.03% of rapid weight loss occurred between 437 and 762˚C, and this may be due to the decomposition of hemicellulose components [34]. From 762 to 1,000˚C, the weight of the biomass sorbent became constant.

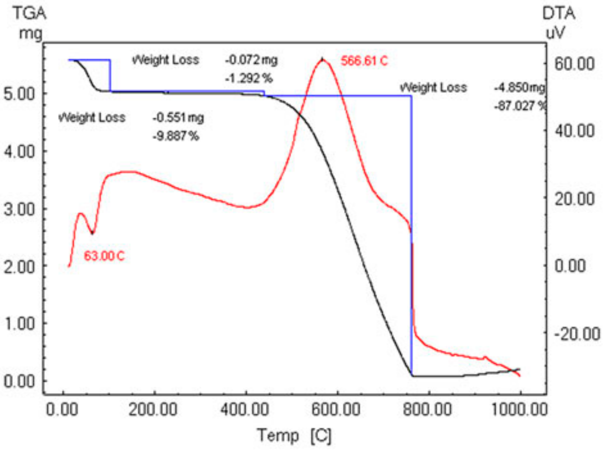

Fig. 4. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of *Leucaena* activated carbon (as-prepared).

Fig. 5 displays the SEM micrographs for particles of the *Leucaena* activated carbon prepared at three magnifications (1.0, 2.0, and 5k×). It can be seen from Fig. 4, that the external surface of activated carbon is full of cavities.

3.2. Adsorption dynamics

3.2.1. Effect of contact time

Equilibrium time is one of the most important operational parameters for an economical wastewater treatment process. Fig. 6 depicts Pb(II) and Cu(II) removal efficiencies as a function of contact time, from which, it is shown that increase in contact time increased removal efficiency until equilibrium adsorption was established. Equilibrium adsorptions were established within 120 min in which Pb(II) and Cu(II) removal efficiencies were 97 and 50%, respectively. Therefore, 120 min shaking time was selected for all further studies.

3.2.2. Effect of solution pH

The effect of pH on the adsorption of Pb(II) and Cu(II) is presented in Fig. 7. The pH of the aqueous solutions is an important operational parameter in the adsorption process because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent, and the degree of ionization of the adsorbate during the reaction [52,53]. Thus, the role of hydrogen ion concentration was examined on the Pb(II) and Cu(II) removal efficiencies. The percentage adsorption increases with increasing the pH of the solution for the studied metal ions, at lower pH range, the ion mobility of Pb^{2+} and Cu^{2+} ions decreased by increasing hydrogen ion concentration. The decrease in the ions mobility may be explained by an increase in the frictional forces exerted on the ions due to the change in the nature of hydrogen bonds in water [54]. As the proton concentration increases, the following water cluster ions are formed H_3O^+, $H_5O_2^+$, $H_7O_3^+$, $H_9O_4^+$, modifying the structure of water, and, thus the ion–water interaction [54]. Also, the sorbent takes up the H^+ ions from the solution, hence, the surface becomes positively charged, which eventually restricts the uptake of Pb^{2+}

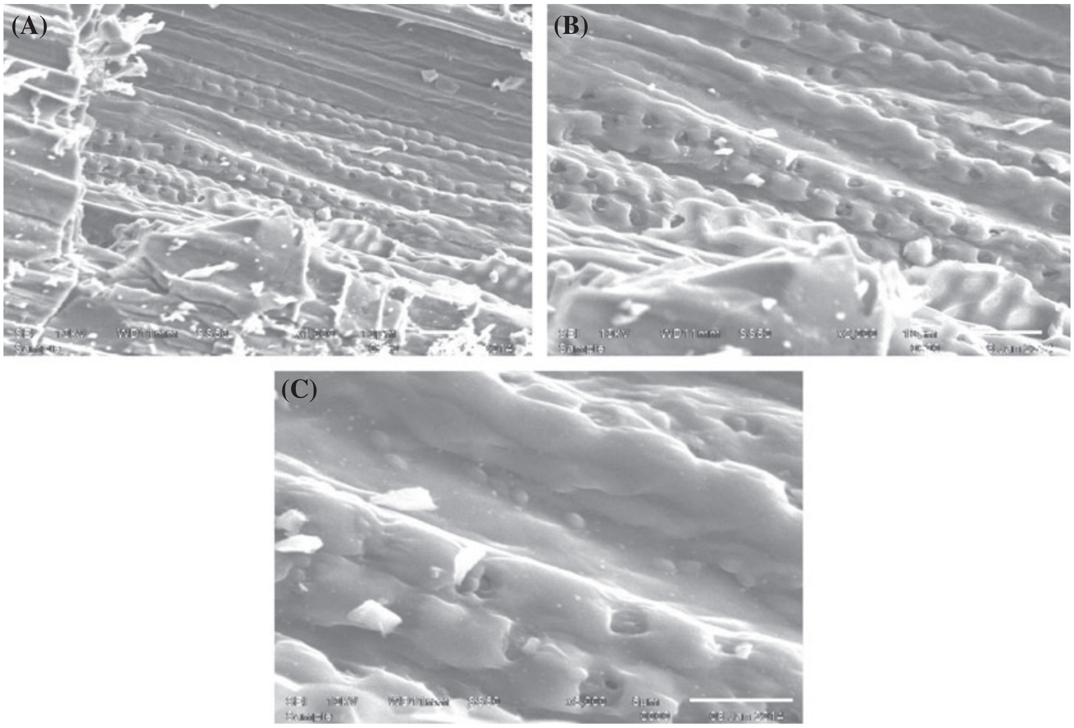

Fig. 5. SEM analysis of *Leucaena* activated carbon sample: (A) Magnitude of 1,000×, (B) magnitude of 2,000×, and (C) magnitude of 5,000×.

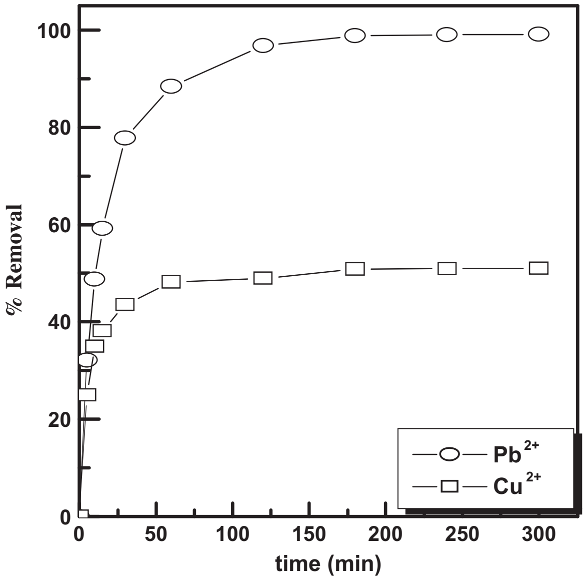

Fig. 6. Effect of contact time on the removal of Cu^{2+} and Pb^{2+} by activated carbon at agitating rate, 400 rpm; temperature, 25 ± 1℃; *dp* = 0.168 mm; initial metal concentration, 50 mg/L.

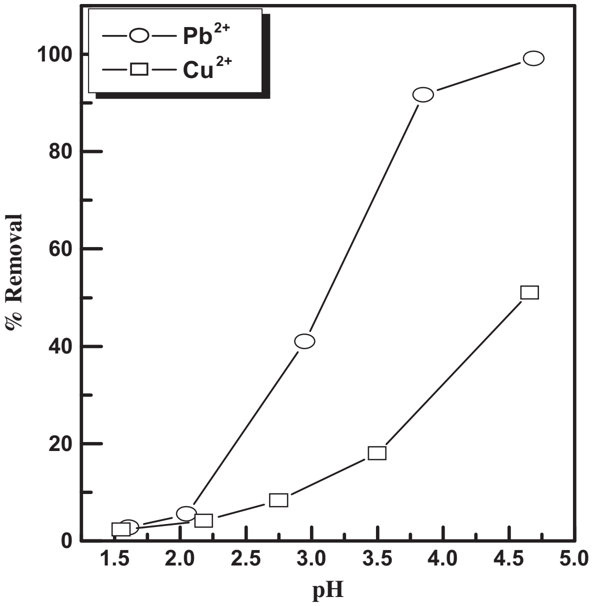

Fig. 7. Effect of pH on the removal of Cu^{2+} and Pb^{2+} by activated carbon at agitating rate, 400 rpm; temperature, 25 ± 1℃; *dp* = 0.168 mm; initial metal concentration, 50 mg/L.

and Cu^{2+} ions [54]. Upon increasing the pH, the percentage adsorption increased substantially. This increase was considered to be due to hydrolytic adsorption of ions [54].

3.2.3. Effect of carbon dose

From the results in Fig. 8, increasing doses of the adsorbents increased Pb(II) and Cu(II) removal efficiencies. This is expected because more binding sites for ions are available at higher doses of adsorbents [53]. The removal efficiencies stay nearly constant for both metal ions with no significant increase above 0.05 g. Hence, the optimum dose from *Leucaena* activated carbon samples was found to be 0.05 g/5 mL (i.e. 10 g per liter of Pb(II) and Cu(II) solutions).

3.2.4. Distribution and selectivity studies

The distribution coefficient (K_d) of Cu^{2+} and Pb^{2+} ions on the activated carbon was determined at different pH values.

$$\log K_d = \text{Constant} + n\,\text{pH} \tag{3}$$

When log K_d values are plotted against log [H^+], a straight line having slope—*n* should be obtained. Fig. 9 and Table 3 showed the pH dependency of K_d values of Cu^{2+} and Pb^{2+} ions. It was found that the distribution coefficient was increased by increasing the pH of the solution for the studied metal ions. The linear relations between log K_d and pH were observed for Cu^{2+} and Pb^{2+} ions with slopes (0.53 and 1.20), respectively. These slopes were not equal to the valence of the metal ions sorbed, which proved the non ideality of the exchange reaction. This variation may be due to the prominence of a mechanism other than ion exchange, like precipitation, surface adsorption, or simultaneous adsorption of anions.

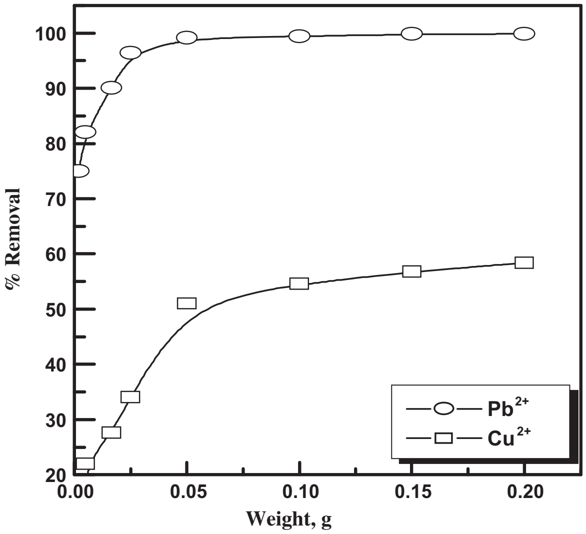

Fig. 8. Effect of adsorbent dosage on removal of Cu^{2+} and Pb^{2+}, agitating rate, 400 rpm; temperature, 25 ± 1˚C; *dp* = 0.168 mm; initial metal concentration, 50 mg/L.

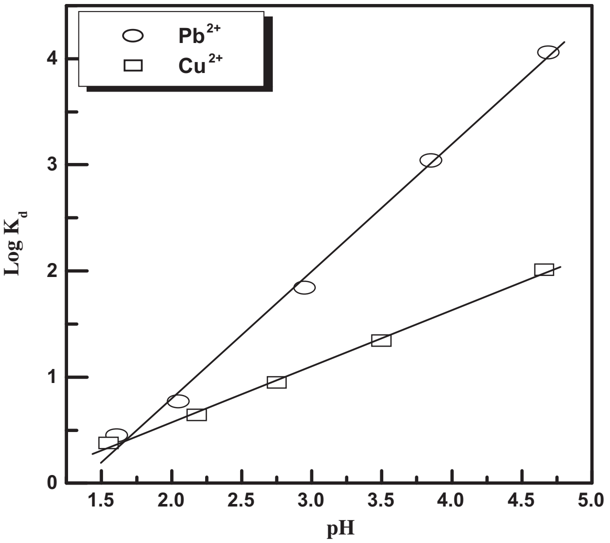

Fig. 9. log K_d of Cu^{2+} and Pb^{2+} ions as a function of pH on the activated carbon at agitating rate, 400 rpm; temperature, 25 ± 1˚C; *dp* = 0.168 mm; initial metal concentration, 50 mg/L.

Table 3
K_d values and separation factors $\alpha^{Pb/Cu}$ (in parentheses) of Cu^{2+} and Pb^{2+} ions on the activated carbon as a function of pH at agitating rate, 400 rpm; temperature, 25 ± 1˚C; initial metal concentration, 50 mg/L

	K_d (mL/g)	
pH	Pb^{2+}	Cu^{2+}
1.5	2.51	2.39 (1.05)
2.5	26.30	6.76 (3.89)
3.5	398.11	21.87 (18.2)
4.5	6,309.57	79.43 (79.43)

The selectivity order of the investigated cations on the activated carbon in the same conditions has the following sequence; $Pb^{2+} > Cu^{2+}$.

This sequence is in accordance with the hydrated ionic radii and the hydration energy of the exchanged

Table 4
K_d values of the adsorbed ions on the activated carbon at 25 ± 1˚C

Exchanging ions	pH of the metal solutions	K_d (mL/g)	Ionic radii (Å)	Hydration energy
Pb^{2+}	4.50	6,309.57	1.20	1,480
Cu^{2+}		79.43	0.72	2,100

ions, the ions with smaller hydrated ionic radii and hydration energy are easily exchanged and moves faster than that the ion with greater ionic radii (Table 4) [55–57].

The K_d values and separation factors ($\alpha = K_{dA}/K_{dB}$, where A and B are any neighboring pair ions) of Cu^{2+} and Pb^{2+} ions at different pH on the activated carbon samples are summarized in Table 3, it is clear that the separation factors between Pb^{2+} and Cu^{2+} metal ions are large on the studied activated carbon. From the above studies, some selective separation is feasible. Separation of Pb^{2+}–Cu^{2+} may be taken on the activated carbon at pH 2.50, 3.50, and 4.50. From these results, the studied activated carbon can be used for the recovery of Cu^{2+} and Pb^{2+} ions from waste streams.

3.2.5. Adsorption modeling

The values of thermodynamic parameters are relevant for the practical application of adsorption process [58,59]. Isotherm data related to adsorption of Cu^{2+} and Pb^{2+} ions onto the activated carbon at various temperatures were analyzed to obtain the values of thermodynamic parameters according to the Van′t Hoff relation;

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{4}$$

where ΔS° (J/mol K) is the entropy change, ΔH° (kJ/mol) is the enthalpy change, R (8.314 J/mol K) is the gas constant, and T (˚K) is the absolute temperature.

It was found that the distribution coefficient (K_d) of Cu^{2+} and Pb^{2+} ions onto the activated carbon increased with increasing the temperature from 298 to 338˚K (i.e. the distribution coefficient decreased with increasing $1/T$). This trend can be attributed to acceleration of some originally slow adsorption steps and creation of some new active sites on the adsorbent surfaces [55,57,60]. From the slopes and intercepts of these straight lines represented in Fig. 10, the enthalpy change (ΔH°) and entropy change (ΔS°) were evaluated and summarized in Table 5.

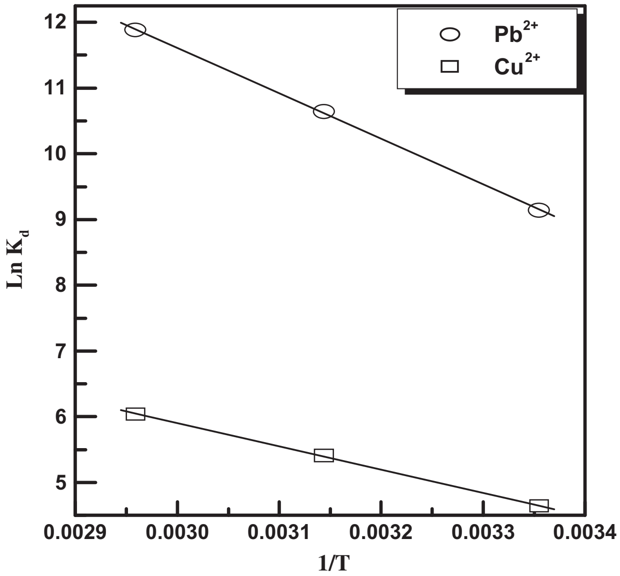

Fig. 10. Van′t Hoff plot of the adsorption of Cu^{2+} and Pb^{2+} ions by activated carbon.

The positive values of (ΔH°) indicate the endothermic nature of the adsorption process [55–57], while the positive values of ΔS° for Cu^{2+} and Pb^{2+} indicate the increased randomness at the solid–solution interface during the adsorption of these cations by the activated carbon.

The free energy change of specific adsorption (ΔG° kJ/mol) was calculated using the relation;

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5}$$

and

$$\Delta G^\circ = -RT \ln K_d \tag{6}$$

The negative values of the free energy change (ΔG°), (Table 5), for the investigated metal ions indicate that the adsorption process is spontaneous, which means the preferable adsorption of these cations on the activated carbon as compared to H^+ ion.

Table 5
Thermodynamic parameters for adsorption of Cu^{2+} and Pb^{2+} ions by activated carbon

Metal ions	Temp. (°K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol/K)
Cu^{2+}	298	−11.50	29.41	137.28
	318	−14.30		137.48
	338	−16.97		137.24
Pb^{2+}	298	−22.64	57.56	269.14
	318	−28.13		269.46
	338	−33.38		269.06

3.3. Fixed-bed experiment

Investigations were conducted to explore suitable conditions for quantitative loading and adsorption of Cu^{2+} and Pb^{2+} ions in neutral media (pH 4.65) by chromatographic column procedures at room temperature (25 ± 1°C). As far as the breakthrough capacity of the column is concerned, Fig. 11 shows curves for Cu^{2+} and Pb^{2+} ions (100 mg/L for each) from the activated carbon column in the feed solutions. Each breakthrough curve reflects the percent concentrations of the respective metal ion in the effluent to the feed solution (C/C_o %) vs. effluent volume (V mL) as shown in Fig. 11.

The values of breakthrough capacity under the conditions of the experiment can be easily estimated from Fig. 11 and was calculated and found to be 4.92 and 15.09 mg/g for Cu^{2+} and Pb^{2+}, respectively according to the equation;

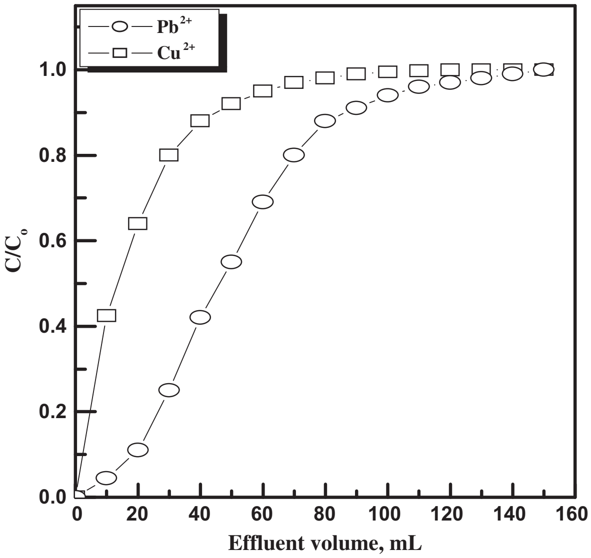

Fig. 11. Break-through curves of Cu^{+2} and Pb^{2+} ions uptake by activated carbon in pH 4.65; temperature, 25 ± 1°C; dp = 0.168 mm; initial metal concentration, 100 mg/L.

Table 6
Comparison of capacity values of Pb^{2+} and Cu^{2+} ions for various adsorbent

Adsorbent	Capacity (mg/g) Pb^{2+}	Cu^{2+}	Refs.
Leucaena activated carbon[a]	15.09	4.92	
Rice husk	120.48	31.85	[61]
Sawdust (Oak tree)	–	3.60	[62]
Peanut husk	29.14	10.15	[63]
Cassava tuber bark waste	–	90.9	[64]
Banana pith	–	13.46	[65]
Imperata cylindrica leaf powder	13.50	–	[66]
Carrot residues	–	32.74	[67]
Bagasse fly ash	2.50	–	[68]
Groundnut shells	–	7.60	[69]

[a] The material under study.

$$\text{Breakthrough capacity} = V_{(50\%)} \times \frac{C_o}{m}\ (\text{mg/g}) \qquad (7)$$

where $V_{(50\%)}$ is the effluent volume at 50% breakthrough (mL), C_o is the concentration of feed solution (mg/L), and m is the amount of the column bed in (g).

It is of interest to compare the values of capacity obtained for Pb^{2+} and Cu^{2+} ions on *Leucaena* activated carbon with that previously reported using other adsorbent as shown in Table 6.

4. Conclusions

The aim of this work was to explore the possible use of *Leucaena* plant wastes, which are agricultural wastes, as sorbents for the removal of Cu(II) and Pb (II) from aqueous solutions. The produced activated carbon was characterized using recent analytical techniques and shows high chemical stability in different acid media. The percentage removal of Cu^{2+} and Pb^{2+} ions was found to depend on contact time, pH, adsorbent dosage, and temperature. The selectivity order of the investigated cations on the activated carbon was found to; $Pb^{2+} > Cu^{2+}$. The breakthrough capacity for Cu^{2+} and Pb^{2+} was investigated and found to be 4.92 and 15.09 mg/g, respectively. The temperature dependence and thermodynamic results indicate an endothermic and spontaneous process.

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References

[1] Inamuddin, M. LuqmanIon, Ion Exchange Technology II, Springer, Dordrecht, Heidelberg, New York, London, 2012.

[2] C. Namasivayam, K. Ranganathan, Removal of Pb(II), Cd(II) and Ni(II) and mixture of metal ions by adsorption onto waste Fe(III)/Cr(III) hydroxide and fixed bed studies, Environ. Technol. 16 (1995) 851–860.

[3] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.

[4] J.R. Deans, B.G. Dixon, Uptake of Pb^{2+} and Cu^{2+} by novel biopolymers, Water Res. 26(4) (1992) 469–472.

[5] R.R. Bansode, J.N. Losso, W.E. Marshall, R.M. Rao, R.J. Portier, *Pecan shell* based granular activated carbon for treatment of chemical oxygen demand (COD) in municipal wastewater, Bioresour. Technol. 94 (2004) 129–135.

[6] C. Ng, J.N. Losso, W.E. Marshall, R.M. Rao, Physical and chemical properties of selected agricultural by products based activated carbons and their ability to adsorb geosim, Bioresour. Technol. 84 (2000) 177–185.

[7] F.E. Okieimen, E.U. Okundia, D.E. Ogbeifun, Sorption of cadmium and lead ions on modified groundnut (*Arachis hypogea*) husks, J. Chem. Technol. Biotechnol. 51 (1991) 97–103.

[8] O. Fadil, S. Mohd Razman, A. Rahmalan, Metal removal by modified *oil palm shell*. Environ. Technol., vol. 93 UTM, Kuala Lumpur, 1993.

[9] B. Girgis, L. Khalil, T. Tawfik, Activated carbon from *sugar cane bagasse* by carbonization in the presence of inorganic acids, J. Chem. Technol. Biotechnol. 61(1) (1994) 87–92.

[10] M. Tam, M. Antal, Preparation of activated carbons from Macadamia *nut shell* and *coconut shell* by air oxidation, Ind. Eng. Chem. Res. 38 (1999) 5268–5276.

[11] M. Ahmedna, M.M. Johns, S.J. Clarke, W.E. Marshall, R.M. Rao, Potential of agricultural by product based activated carbons for use in raw sugar decolorization, J. Sci. Food Agric. 75 (1997) 117–124.

[12] C.A. Toles, W.E. Marshall, M.M. Johns, Phosphoric acid activation of nutshells for metals and organic remediation: process optimization, J. Chem. Technol. Biotechnol. 72 (1998) 255–263.

[13] C. Ng, J.N. Losso, W.E. Marshall, R.M. Rao, Freundlich adsorption isotherms of agricultural by products based powered activated carbons in a geosmin-water system, Bioresour. Technol. 85 (2000) 131–135.

[14] S.A. Dastgheib, D.A. Rockstraw, *Pecan shell* activated carbon: synthesis, characterization and application for the removal of copper from aqueous solution, Carbon 39 (2001) 1849–1855.

[15] M.S. Azab, P.J. Peterson, The removal of Cd from wastewater by the use of biological sorbent, Water Sci. Technol. 21 (1989) 1705–1706.

[16] B. Preetha, T. Viruthagiri, Biosorption of zinc(II) by *Rhizopus arrhizus*; equilibrium and kinetic modeling, African J. Biotechnol. 4 (2005) 506–508.

[17] F.R. Rushkin, Leucaena: Promising Forage and Tree Crops for the Tropics, second ed., National Research Council, National Academy Press, Washington, DC, 1984.

[18] D.W. Catchpoole, Blair Gal, Forage tree legumes. III. Release of nitrogen from leaf, feces and urine derived from *Leucaena* and *Gliricidia* leaf, Aust. J. Agric. Res. 41 (1990) 539–547.

[19] J.P.F. D'Mello, D. Thomas, Animal feed, in: F.R. Rusbkin (Ed.), *Leucaena*: Promising Forage and Tree Crops for the Tropics, National Academy of Sciences, Washington, DC, 1977, pp. 30–32.

[20] S. Itzhaki, P.R. Abdulla, Effect of numosine on RNA synthesis in Ehrlich ascites-tumour cells, Biochem. Soc. Trans. 10 (1982) 176.

[21] J.H.G. Holmes, J.D. Humphrey, E.A. Walton, J.D. O'Shea, Cataracts, goitre and infertility in cattle grazed on an exclusive diet of *Leucaena* leucocephala, Aust. Vet. J. 57 (1981) 257–261.

[22] R.B. Monzon, Traditional medicine in the treatment of parasitic diseases in the Philippines, South East Asian J. Trop. Med. Public Health 26(3) (1995) 421–428.

[23] A.N. Shukla, P.C. Sharma, S.K. Sheel, Effects of fungicidal seed dressing and other treatments on the germination and growth of subabul (*Leucaena* leucocephala) (Lam) de Wit, Indian J. Forest 13 (1990) 97–104.

[24] S.T. Chou, E. Ross, Comparative vitamin K activity of dehydrated *alfalfa* and *Leucaena* leucocephala meal, Poultry Sci. 44 (1965) 972–974.

[25] J.P.F. D'Mello, D.E. Taplin, *Leucaena* leucocephala in poultry diets for the tropics, World Rev. Anim. Prod. 24 (1978) 41–47.

[26] M.M. Labadan, Effects of various treatments and additives on the feeding value of *Ipil ipil* leaf meal in poultry, Philipp Agric. 53 (1969) 392–401.

[27] M.A. Lillo-Ródenas, D. Cazorla-Amorós, A. Linares-Solano, Behaviour of activated carbons with different pore size distributions and surface oxygen groups for benzene and toluene adsorption at low concentrations, Carbon 43 (2005) 1758–1767.

[28] D. Lozano-Castello, M.A. Lillo-Rodenas, D. Cazorla-Amoros, A. LinaresSolono, Preparation of activated carbons from *Spanish Anthracite* I. Activation by KOH, Carbon 39 (2001) 741–749.

[29] M.A. Lillo-Ródenas, D. Cazorla-Amorós, A. Linares-Solano, Understanding chemical reactions between carbons and NaOH and KOH: An insight into the chemical activation mechanism, Carbon 41 (2003) 267–275.

[30] M.A. Lillo-Ródenas, J. Juan-Juan, D. Cazorla-Amorós, A. Linares-Solano, About reactions occurring during chemical activation with hydroxides, Carbon 42 (2004) 1371–1375.

[31] M. Kobya, E. Demirbas, E. Senturk, M. Ince, Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from *apricot stone*, Bioresour. Technol. 96 (2005) 1518–1521.

[32] R. Sivaraj, V. rajendran, G.S. Gunalan, Preparation and characterization of activated carbons from *Parthenium* biomass by physical and chemical activation techniques, E-J. Chem. 7(4) (2010) 1314–1319.

[33] O.S. Amuda, I.A. Amoo, Y. Hung, Radioactive element removal from contaminated groundwater by agricultural waste-based activated carbon, Int. J. Water Resour. Arid Environ. 1(1) (2011) 71–82.

[34] W. Hassan, U. Farooq, M. Ahmad, M. Athar, M. Ain Khan, Potential biosorbent, *Haloxylon recurvum plant stems*, for the removal of methylene blue dye Arabian, Sep. Purif. Technol. (in press), doi: 10.1016/j.arabjc.2013.05.002.

[35] Y.F. El-Aryan, H. El-Said, E.A. Abdel-Galil, Synthesis and characterization of polyaniline–titanium tungstophosphate; its analytical applications for sorption of Cs^+, Co^{2+}, and Eu^{3+} from waste solutions, Radiochemistry 56(6) (2014) 614–621.

[36] C.N.R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York, NY, 1963, p. 355.

[37] B.K. Pradhan, N.K. Sandle, Effect of different oxidizing agent treatments on the surface properties of activated carbons, Carbon 37(8) (1999) 1323–1332.

[38] S.A. Nabi, M. Naushad, Inamuddin, Synthesis and characterization of a new inorganic cation-exchanger-Zr(IV) tungstomolybdate: Analytical applications for metal content determination in real sample and synthetic mixture, J. Hazard. Mater. 142 (2007) 404–411.

[39] I.M. El-Naggar, E.S. Zakaria, I.M. Ali, M. Khalil, M.F. El-Shahat, Kinetic modeling analysis for the removal of cesium ions from aqueous solutions using polyaniline titanotungstate, Arabian J. Chem. 5 (2012) 109–119.

[40] Y.S. Al-Degs, M.I. El-Barghouthi, A.A. Issa, M.A. Khraisheh, G.M. Walker, Sorption of Zn(II), Pb (II), and Co(II) using natural sorbents: Equilibrium and kinetic studies, Water Res. 40 (2006) 2645–2658.

[41] C. Moreno-Castilla, M.V. López-Ramón, F. Carrasco-Marín, Changes in surface chemistry of activated carbons by wet oxidation, Carbon 38(14) (2000) 1995–2001.

[42] D.M. Ibrahim, S.A. El-Hemaly, F.M. Abdel-Kerim, Study of *rice-husk* ash silica by infrared spectroscopy, Thermochim. Acta 37(3) (1980) 307–314.

[43] B.K. Padhi, C. Patnaik, Development of Si_2N_2O, Si_3N_4 and SiC ceramic materials using rice husk, Ceram. Int. 21 (1995) 213–220.

[44] B. Stuart, Modern Infrared Spectroscopy, John Willy & Sons, New York, NY, 1996.

[45] J. Madejová, FTIR techniques in clay mineral studies, Vib. Spectro. 31 (2003) 1–10.

[46] S.A. Nabi, Z.M. Siddiqi, Preparation, properties, and analytical applications of crystalline tin(IV) tungstoselenate, Bull. Chem. Soc. Jpn. 58 (1985) 724–730.

[47] J.P. Rawat, A.A. Ansari, Synthesis and ion exchange properties of sodium stannosilicate: A silver selective inorganic ion exchanger, Bull. Chem. Soc. Jpn. 63 (1990) 1521–1525.

[48] K.T. Lee, S. Bhatia, A. Mohamed, Preparation and characterization of sorbents prepared from ash (waste material) for sulfur dioxide (SO2) removal, J. Mater. Cycles Waste Manage. 7 (2005) 16–23.

[49] C.C. Fuller, J.A. Davis, Processes and kinetics of Cd^{2+} sorption by a calcareous aquifer sand, Geochim. Cosmochim. Acta 51 (1987) 1491–1502.

[50] R.V. Krishnarao, J. Subrahmanyam, T.J. Kumar, Studies on the formation of black particles in *rice husk* silica ash, J. Eur. Ceram. Soc. 21 (2001) 99–104.

[51] M.G.A. Vieira, A.F. Almeida Neto, M.G. Silva, C.C. Nóbrega, A.A. Melo Filho, Characterization and use of in *natura* and *calcined rice husks* for biosorption of heavy metals ions from aqueous effluents, Braz. J. Chem. Eng. 29(3) (2012) 619–634.

[52] S.M. Nomanbhay, K. Palanisamy, Removal of heavy metal from industrial wastewater using *chitosan* coated oil palm shell charcoal, Electron. J. Biotechnol. 8(1) (2005) 43–53.

[53] O.S. Amuda, A.A. Giwa, I.A. Bello, Removal of heavy metal from industrial wastewater using modified activated *coconut shell* carbon, Biochem. Eng. J. 36 (2007) 174–181.

[54] H. Moloukhia, Use of animal charcoal prepared from the Bivalve Chaelatura (Chaelatura) Companyoi in treatment of waste solution containing cesium and strontium ions, J. Rad. Res. Appl. Sci. 3(2) (2010) 343–356.

[55] I.M. El-Naggar, E.A. Mowafy, E.A. Abdel-Galil, M.F. El-Shahat, Synthesis, characterization and ion-exchange properties of a novel 'organic–inorganic' hybrid cation-exchanger: polyacrylamide Sn(IV) molybdophosphate, Global J. Phys. Chem. 1(1) (2010) 91–106.

[56] I.M. El-Naggar, E.S. Zakaria, W.M. El-Kenany, M.F. El-Shahat, Synthesis and equilibrium studies of titanium vanadate and its use in the removal of some hazardous elements, Radiochemistry 56(1) (2014) 86–91.

[57] I.M. El-Naggar, K.A. Hebash, E.S. Sheneshen, E.A. Abdel-Galil, Preparation, characterization and ion-exchange properties of a new 'organic–inorganic' composite cation exchanger polyaniline silicotitanate: Its applications for treatment of hazardous metal ions from waste solutions, Inorg. Chem. Indian J. 9(1) (2014) 1–14.

[58] V. Singh, S. Pandey, S.K. Singh, R. Sanghi, Removal of cadmium from aqueous solutions by adsorption using poly(acrylamide) modified guar gum–silica nanocomposites, Sep. Purif. Technol. 67 (2009) 251–261.

[59] A. Özcan, E.M. Öncü, A.S. Özcan, Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural *sepiolite*, Colloids Surf., A 277 (2006) 90–97.

[60] A. Clark, Theory of Adsorption and Catalysis, Academic Press, New York, NY, 1970.

[61] K.K. Wong, C.K. Lee, K.S. Low, M.J. Haron, Removal of Cu and Pb from electroplating wastewater using tartaric acid modified *rice husk*, Process Biochem. 39 (2003) 437–445.

[62] M.E. Argun, S. Dursun, C. Ozdemir, M. Karatas, Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics, J. Hazard. Mater. 141 (2007) 77–85.

[63] Q. Li, J. Zhai, W. Zhang, M. Wang, J. Zhou, Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by *sawdust* and modified *peanut husk*, J. Hazard. Mater. B 141 (2006) 163–167.

[64] M. Horsfall Jr., A.A. Abia, A.I. Spiff, Kinetic studies on the adsorption of Cd^{2+}, Cu^{2+} and Zn^{2+} ions from aqueous solutions by cassava (*Manihot sculenta Cranz*) tuber bark waste, Bioresour. Technol. 97 (2006) 283–291.

[65] K.S. Low, C.K. Lee, A.C. Leo, Removal of metals from electroplating wastes using *banana pith*, Bioresource Technology 51 (1995) 227–231.

[66] M.A.K. Hanafiah, S.C. Ibrahim, M.Z.A. Yahya, Equilibrium adsorption study of lead ions onto sodium hydroxide modified *Lalang* (*Imperata cylindrica*) leaf powder, J. Appl. Sci. Res. 2 (2006) 1169–1174.

[67] B. Nasernejad, T.E. Zadeh, B.B. Pour, M.E. Bygi, A. Zamani, Camparison for biosorption modeling of heavy metals (Cr(III), Cu(II), Zn(II)) adsorption from wastewater by carrot residues, Process Biochem. 40 (2005) 1319–1322.

[68] V.K. Gupta, I. Ali, Removal of lead and chromium from wastewater using *bagasse fly ash*—A sugar industry waste, J. Colloid Interface Sci. 271 (2004) 321–328.

[69] S.R. Shukla, R.S. Pai, Adsorption of Cu(II), Ni(II) and Zn(II) on dye loaded *groundnut shells* and *sawdust*, Sep. Purif. Technol. 43 (2005) 1–8.