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Removal of lead(II) from water using activated carbon developed from jujube stones, a low-cost sorbent

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ABSTRACT

The preparation of activated carbon from jujube stones with H₂SO₄ activation and its ability to remove lead from aqueous solutions were reported in this study. The surface structure of the activated carbon was characterized by various physico-chemical methods. Sorption studies were carried out by varying the initial metal ion and the pH: the amount of sorbed Pb(II) ions increased with increasing pH and initial Pb(II) ions concentration. The removal of lead ions was rapid and the kinetic of sorption can be well described by pseudo-second order modelling. The Langmuir model conveniently fits the data of isotherm experiments and the monolayer sorption capacity of Pb(II) ions was determined as 71.43 mg/g at pH 6.0 and 25°C. These results showed that activated carbon prepared from jujube stones could be considered for application as a potential sorbent for the removal of lead from wastewaters.

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Chemical activation; jujube stones; lead; sorption isotherms; sorption kinetics

Introduction

Pollution of water with metallic elements has attracted much attention because it can be the main cause of harm to living organisms. Among other metals, lead is a toxic species present in wastewaters generated by various industries such as metal plating, metal finishing, battery manufacturing and electronic industries.^[1] Lead poisoning causes damage to liver and kidney and reduction in haemoglobin formation, mental retardation, infertility and abnormalities in pregnant women. Due to the hazardous nature of lead(II), it directly or indirectly may cause anaemia, headache, chills, diarrhoea and poisoning, leading to the dysfunction of kidneys, reproductive system, liver, brain and central nervous system.^[2] A recent study established the relationship between lead exposure, increased blood pressure and angiotensinogen expression.^[3] Moreover, lead poisoning has been from a long time evidenced for people living near a Pb/Zn mine site;^[4] due to the current project of the Amizour-Bejaia mining site (eastern Algeria), one of the most valuable natural reserves for Pb and Zn ores in the whole of Algeria,^[5] we are of course interested in any method for Pb removal from such mining wastewaters.

Physical and chemical processes have been extensively studied to remove metallic pollutants from wastewaters when present at high concentrations. Some of these processes are adsorption, coagulation, flotation, biosorption, chemical precipitation, ultra-filtration and electrochemical methods.

Removal of potentially toxic metals from wastewater by sorption process is very common. Although activated carbon is a preferred sorbent,^[6] its application is often restricted due to its high cost. Within a 'sustainable development' framework, it is interesting to select some wastes from agricultural processes in order to treat polluted wastewaters and/or soils.^[7–9] While several researchers have adopted various low-cost sorbents, there is still a need to develop activated carbon from cheaper and readily available materials, which can be effective and economical. Activated carbon production from agricultural waste has two advantages. First, disposal of agricultural by-products has become a major, costly waste disposal problem but they can be converted to useful, value-added sorbents. Second, these produced activated carbons can be used for removing organic chemicals and metals from wastewaters. Basically, there are two different processes

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for the preparation of activated carbon: physical activation and chemical activation. Compared with physical activation, chemical activation has two important advantages: one is the lower temperature at which the process is accomplished; the other is that the global yield of the chemical activation tends to be greater since burn-off char is not required. Thus, there is a growing demand to find low-cost and efficient, locally available sorbents^[10] for the sorption of, for example, lead(II), with among others activated carbon prepared by date stones,^[11,12] apricot stones^[13] or olive stones,^[14] but also with several other solids such as pine bark,^[15] wheat bran,^[16] tobacco stems,^[17] sago waste,^[18] grape stalks,^[19] (chest)nut shells,^[20,21] rice husk,^[22] coir pith^[23] and many others.

The aim of this study was to investigate the application of an activated carbon prepared from the jujube stones for the removal of lead(II) from aqueous solutions. The tree *Ziziphus jujuba* Mill. (*Rhamnaceae*) is widely distributed in deciduous forests of central Algeria. The produced activated carbon will be characterized by N₂ adsorption (for BET surface area measurement), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). In this work, kinetics and isotherms data were presented for this sorption system and modelled; the influence of pH on metal sorption was also studied and discussed on the basis of speciation diagrams.

Materials and methods

All reactants were of analytical grade and used without further purification.

Preparation of activated carbon

Jujube stones used in this study as a source of activated carbon were collected from Bouira, Algeria. The fruits were harvested between September and December; washed stones were roughly crushed and their seeds were discarded. Hundred grams of the selected fraction was impregnated with 98% concentrated H₂SO₄, and then was activated in a hot air oven at 600°C for 2 h. The carbonized material was washed with distilled water to remove the free acid and thereafter soaked in 0.01 M NaOH solution to remove any remaining acid. Then it was washed with distilled water until the pH of the activated carbon suspension reached 7.0, and dried at 60°C. Finally, the material (hereafter named JSAC) was sieved to < 100 μm size and stored in a desiccator for further use.

Characterization of the solid

This activated carbon was characterized by various physicochemical methods. True density of JSAC was

measured using the pycnometric method, with methanol as solvent. The ash content was determined in a platinum crucible heated at 700°C for 3 h. To determine the specific surface area and pore structure of raw material and activated carbon, the nitrogen adsorption-desorption isotherms at 77 K were measured by an automated gas adsorption analyser ASAP2000 (Micromeritics, Norcross, GA) with ± 5% accuracy. SEM analysis of samples was performed using a Philips SEM-505 scanning electron microscope, operated at 300 kV/SE and 50° inclination. The X-ray diffraction (XRD) analysis of the samples was carried out via a Powder X-ray Diffractometer (Bruker AXS) in the 2θ angle ranging from 2° to 65° employing a 0.025° step. FTIR spectra were obtained using a Spectrum GX spectroscope (Perkin-Elmer, Norwalk, CT) at a 4 cm⁻¹ resolution; undiluted activated carbons, in the powdered form, were scanned and recorded between 4000 and 400 cm⁻¹.

The Boehm titrations method^[24,25] was applied in order to determine the surface functional groups containing oxygen. The main principle of this method is that oxygen groups on carbon surfaces have different acidities and can be neutralized by bases of different strengths. The solid JSAC was dried at 100°C for 2 h. Then, 0.5 g samples were added to PVC bottles containing 30 mL of the following 0.1 M solutions: NaOH, Na₂CO₃, NaHCO₃ and HCl. The mixtures were shaken for 48 h, filtered and back-titrated using 0.1 M hydrochloric acid with phenolphthalein as the indicator. The number of acidic sites was calculated assuming that NaOH neutralizes carboxylic, phenolic and lactonic groups; Na₂CO₃ neutralizes carboxylic and lactonic groups, while NaHCO₃ neutralizes carboxylic groups only. The number of surface basic sites was determined from the back-titration of the HCl aliquot using NaOH.^[26]

The pH of the point of zero charge (pH_{pzc}) was determined by the immersion technique.^[27] A known amount of solid JSAC (0.1 g) was added to a series of bottles containing 50 mL of deionized water whose pH was previously adjusted to be in the range of 1.0–9.0 by the addition of either 0.1 M HNO₃ or 0.1 M NaOH. These bottles were then rotated for 1 h in a shaker and pH values were measured at the end of the test. The pH of the suspensions is then represented as a function of the initial pH of the solutions: the curve obtained theoretically crosses the bisector of axes at the point of zero charge.

The cation exchange capacity (CEC) of JSAC was determined by using 0.2 g of solid with 30 mL of 0.1 M NaOH in a sealed PVC bottle. After 72 h of agitation, 20 mL of the filtrate was pipetted out from the filtrated suspension and pHmetrically titrated using 0.1 M HCl. The amount of NaOH consumed was converted to CEC using the following relationship:

$$CEC = \frac{(N_1 - N_2) \times V}{m} \quad (1)$$

where N_1 and N_2 are the normality of the NaOH solution before and after equilibrium, respectively, V is the volume of NaOH taken in the flask, and m is the mass of activated carbon used.

Both iodine number and methylene blue number for JSAC were determined according to classical methods, as described elsewhere.^[28]

A pH meter (Jenway 3010) equipped with a combined glass electrode SENTIX 92, was standardized using buffer solutions of pH values 3.4, 6.0 and 9.0, and used to measure the pH of all solutions.

Stock solution of Pb(II) (1000 mg/L) was prepared by dissolving the analytical reagent-grade lead nitrate (Plasma Pure Standard Solutions, Leeman Labs) in deionized water. This stock solution was further diluted to the required concentrations before use. The concentrations of Pb in all solutions were measured with a Shimadzu AA6500 atomic absorption spectrometer (AAS).

Sorption kinetic study

The kinetic experiments were performed at $25.0 \pm 0.5^\circ\text{C}$ in batch reactors placed on a shaker (Benchmark Orbi-Shaker). First, 0.5 g of JSAC was introduced in 100 mL of deionized water. After the introduction of the metal ions, samples were collected at suitable time intervals, filtered through a 0.45 μm cellulose acetate membrane filter and then analysed for lead with AAS.

Batch sorption experiments

A known weight of activated carbon is left in contact with 100 mL of Pb(II) solution (10, 20, 30, 50, 70, 90 mg/L) during 2 h; then the optimal weight of JSAC can be selected. In order to select the optimum initial concentration, a range of Pb(II) concentrations (10–90 mg/L), adjusted to pH 6.0, was used; 0.5 g sample of JSAC was added to each 100 mL volume of solution and agitated for 140 min at 25°C . Aliquot samples (10.0 mL) were withdrawn at suitable time intervals and the filtrate analysed by AAS.

During the study of pH effect, the sorbent dosage, rotation speed, solution temperature and initial lead concentration were fixed at 0.5 g, 140 rpm, 25°C and 50 mg/L, respectively.

For isotherm studies, the initial solution pH was adjusted to 6.0 with HNO_3 . Small-volume liquid samples are withdrawn after 140 min (an optimum contact time, as determined from the previous kinetics experiments) and immediately filtered to remove JSAC particles. The

amount of Pb(II) sorbed at equilibrium was calculated using the following relationship:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where q_e (mg/g) is the equilibrium sorption capacity of lead sorbed per gram of JSAC, C_0 and C_e are the initial and equilibrium lead concentrations (mg/L), respectively; V is the volume of the solution (L); and m is the weight of the JSAC (g). The sorption percentage at equilibrium (% removal) of metal ions from aqueous solution is calculated as follows:

$$\text{Removal Percentage} = \frac{(C_0 - C_e)}{C_e} \times 100 \quad (3)$$

Data treatment

Each experiment or analysis was duplicated; in all the figures, the size of symbols includes the standard deviation from experimental data (3–5%). The unknown constants in the model equations for kinetics and isotherm studies are obtained using non-linear least-squares (NLLS) data processing by the Origin 8.0 software at the 95% confidence level.

Results and discussion

Characterization of the activated carbon from jujube stones

Jujube, also known as ‘Chinese date’, is the fruit of *Ziziphus jujuba* Mill. (*Rhamnaceae*). This is a drupe, varying in size from a cherry to a plum, with a thin edible skin surrounding a flesh of sweet flavour. Its single hard stone contains two seeds. From our previous studies with other fruit stones^[12,13] we applied the chemical activation method for the preparation of activated carbon. After several essays with varying temperature and/or H_2SO_4 concentration (detailed data not shown), we selected the following conditions: 600°C and 98% H_2SO_4 for the preparation of JSAC.

The FTIR technique is useful for an identification of the functional groups of the JSAC solid.^[29,30] The FTIR spectrum reveals (Fig. 1) the bands appearing at 4000 and 3500 cm^{-1} corresponding to the OH groups of the phenol function. The peak at 3388 cm^{-1} indicates the presence of the OH group, which can probably be attributed to adsorbed water on the carbon surface. The peak at 2918 cm^{-1} was assigned to C-H interaction with the surface of the carbon. The spectra also displayed bands at 1586 cm^{-1} corresponding to the C=C vibration in aromatic rings, and a peak at 1230 cm^{-1} could be assigned to the stretching of C-O in esters, ethers or phenol groups. The

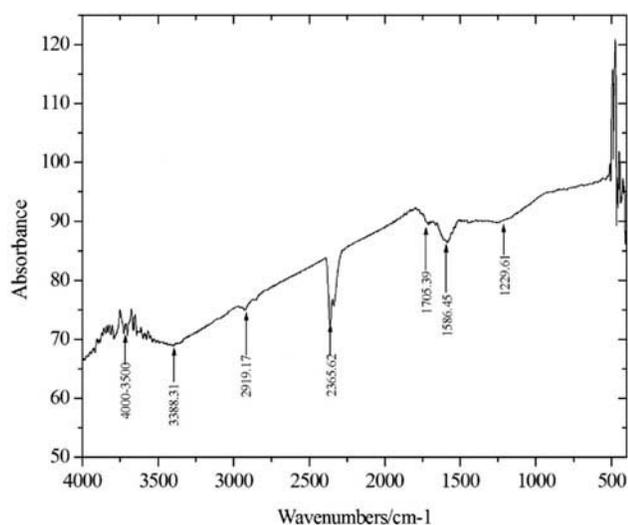


Figure 1. FT-IR spectrum of activated carbon derived from jujube stones.

Table 1. Physical properties of activated carbon derived from jujube stones.

Parameter	Value
Yield (%) ^a	52.1
CEC (10 ⁻² mol/kg)	2.84
Ash (%)	3.32
Density (g/mL)	1.41
pH _{pzc}	4.68
S _{BET} (m ² /g)	418
Mesoporous volume (mL/g)	0.52
Mesoporous area (m ² /g)	138.47
Microporous volume (mL/g)	0.21
Acidic surface functional groups (mmol/g)	3.12
Carboxylic	1.78
Lactonic	0.94
Phenolic	0.52
Basic surface functional groups (mmol/g)	1.23
Methylene blue number (mg/g)	98.4
Iodine number (mg/g)	103

^aPercentage of final activated carbon obtained from the initial amount of raw jujube stones

bands appearing at 2366 and 1705 cm⁻¹ are assigned to the C=O stretching vibrations in ketones or carbonyl groups. Thus, the FTIR results indicated that JSAC presents different functional groups such as hydroxyl, carboxyl and carbonyl, which may be potential sorption sites for lead(II) species.

These data are in accordance with the results from Boehm titrations (Table 1) showing that most of the acidic functional groups are carboxylic, followed by lactone and phenol groups. The total number of surface basic sites was calculated to be 1.23 mmol/g and is smaller than the total number of acidic surface sites (3.12 mmol/g).

The SEM image of JSAC is shown in Fig. 2. The surface morphology appeared to have a fluffy, irregular porous texture with a large, accessible surface area that can favour sorption. The availability of pores and

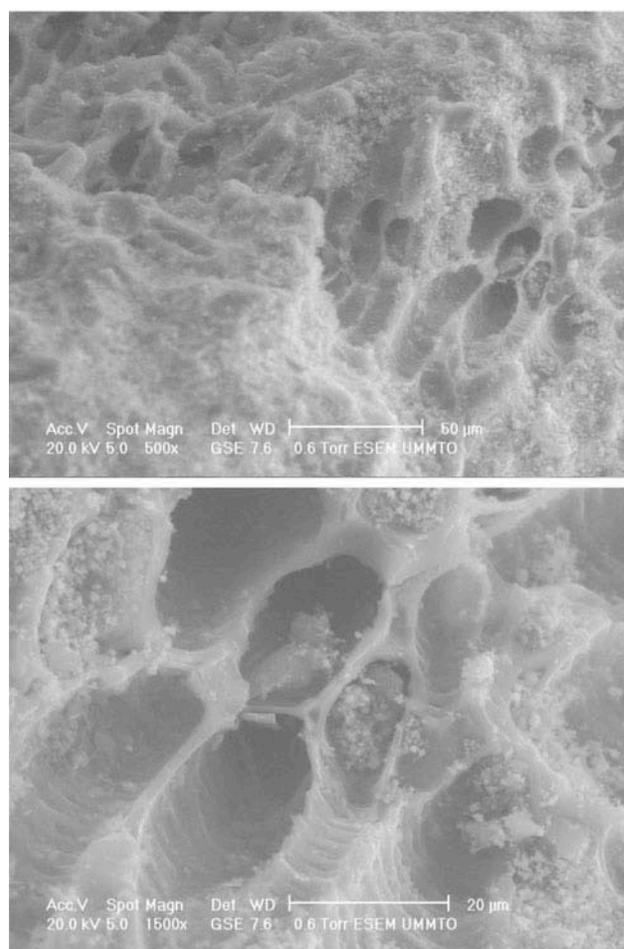


Figure 2. SEM photographs of the activated carbon (a) 20 kV, ×500; (b) 20 kV, ×1500.

internal surface, which is a requisite for a potential sorbent, is clearly displayed in this SEM picture.

From BET measurements, the specific surface area and porous volumes were determined (Table 1). They confirmed the SEM information concerning the presence of pores with adequate dimension and surface for sorption of ions or molecules. Because BET measurements are time-consuming and expensive, similar data are often obtained from the sorption of iodine and methylene blue, and useful correlations were recently established^[31]; our experimental data for iodine number and methylene blue number (Table 1) confirmed the information gained from both SEM and BET.

Figure 3 illustrates the XRD pattern of JSAC prepared with an activation temperature of 600°C. The activated carbon exhibited peaks at around $2\theta = 27^\circ$, corresponding to the highly organized layer structure of graphite, with an interlayer distance of 0.34 nm along the (002) orientation.^[32] Simultaneously there are noise signals corresponding to the AC powder, revealing a predominantly amorphous structure of JSAC. This result can be

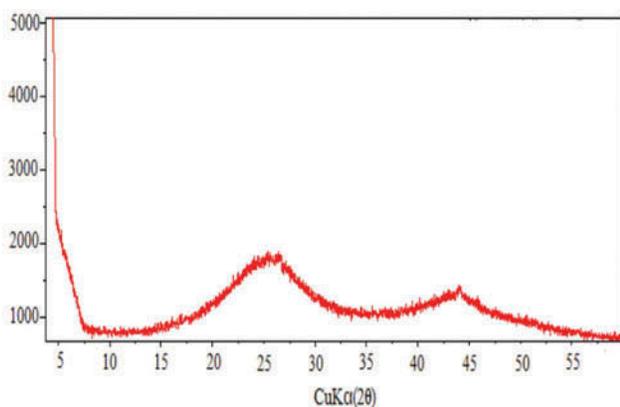


Figure 3. X-ray diffraction of activated carbon derived from jujube stones.

explained by the fact that the pyrolytic reaction of organic compounds consists of breaking of chemical bonds with temperature and condensing further into active compounds.^[33] These compounds form typical graphitic layers and stacks of planes during carbonization.^[32] The influence of the nature and amount of lignocellulosic components in the initial agricultural by-product (stones or seeds) has been previously discussed.^[34]

Effect of pH on Pb(II) sorption

The pH is an important parameter affecting metal sorption onto a sorbent: this is due to the fact that H^+ ions themselves are strongly competing with the sorbate. Effect of pH was studied here by varying the initial pH of the solution from 2 to 10 by the addition of 0.1 M NaOH or 0.1 M HNO_3 . The results indicate (Fig. 4a) that the maximum amount of lead fixed by JSAC is obtained at pH 6. At lower pH values, there is an excessive protonation of the carbon surface, resulting in a decrease in the sorption of Pb(II) ions. The uptake of Pb(II) increases with increasing the pH from 2 to 6 and reaches a plateau for $pH > 6$. This increase in metal removal as pH increases can be explained on the basis of a decrease in competition between protons (H^+) and positively charged metallic species at the surface sites. Because the pH of point of zero charge is 4.68 (Table 1), JSAC surface is negatively charged at $pH > pH_{pzc}$ and the coulombic interactions are favoured. The decrease in sorption efficiency at higher pH (> 6.0) was due to the formation of soluble hydroxylated complexes of lead(II) ions and their competition with the active sites; as a result, the retention would decrease again.

Indeed, we modelled aqueous speciation of lead(II) as a function of pH (for the nitrate salt) using the computer program Visual-MINTEQ.^[35] Below pH 8.0, Pb(II) predominantly occurs as Pb^{2+} and $Pb(OH)^+$

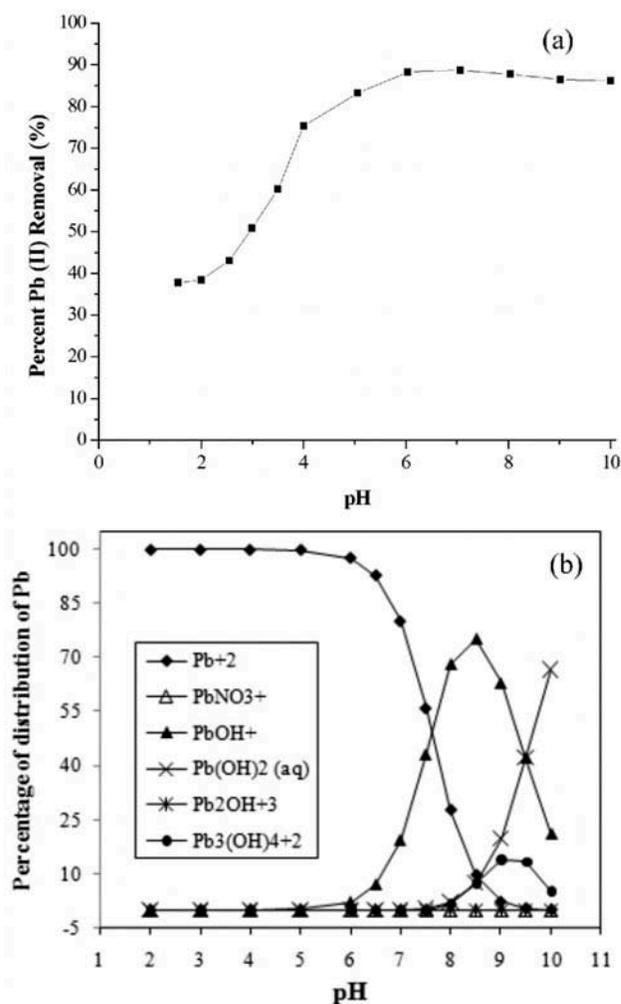


Figure 4. (a) Effect of initial pH on the removal percentage of lead solution (initial concentration 50 mg/L, contact time 140 min, and sorbent dose 0.5 g/100 mL). (b) Pb(II) speciation at 30 mg/L from Visual-MINTEQ modelling.

(Fig. 4b). Besides these two cationic species, $Pb(OH)_2(aq)$ is also present in a significant amount up to pH 6.0. Very low amounts (less than 10^{-7} mol/L) of other Pb(II) species like $PbNO_3^+$, $Pb_4(OH)_4^{4+}$ and $Pb_2(OH)_3^+$ also occur in solution, but their concentrations do not significantly change over the entire pH range.

Effect of contact time

Figure 5 shows that the Pb(II) sorption approaches to plateau smoothly and continuously, suggesting the monolayer coverage of Pb(II) on the outer surface of the JSAC. During the initial first 10 min, the sorption of Pb(II) is fast due to available vacant surface sites. After this time (*i.e.* 10 min), the sorption sites become unavailable and the remaining free surface sites are difficult to be occupied due to the repulsive forces between the solute molecules on the solid and bulk phases.

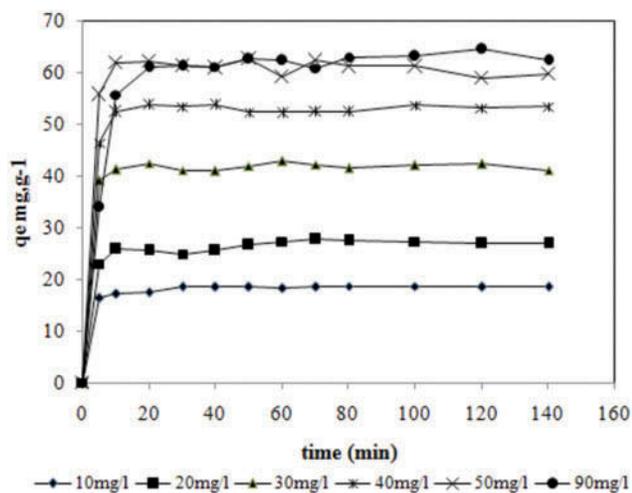


Figure 5. Effect of contact time and initial concentration of Pb(II) on the sorption of lead by activated carbon from jujube stones (pH 6.0, sorbent dose 0.5 g/100mL, rotation speed 140 rpm, and $T = 25^{\circ}\text{C}$).

Effect of initial concentration

A series of lead sorption experiments (with initial concentration 10–90 mg/L) display a direct linear relationship between the metal uptake and initial concentration of the metal ions present in the solution up to the limiting initial concentration at 50 mg/L (Fig. 5). This value was therefore selected for the other experiments.

Effect of sorbent dosage

The results of the experiments with varying sorbent concentrations are presented in Fig. 6. An increase in the JSAC concentration from 0.5 to 10 g/L involves an increased removal of Pb(II) ions from 7.16% to 99.95% (when $C_0 = 50$ mg/L). Of course, when the sorbent dosage increases, more surface area and more active sites become available for the sorption, thus making easier the penetration of ions into the sorption sites. The optimum dosage of JSAC for sorption of Pb(II) ions is found to be 5.0 g/L. All active sites on the sorbent surface are then occupied and a further increase in sorbent dosage does not provide a higher uptake of lead(II) ions.

Kinetic modelling

It is now well known that sorption kinetic data can be mainly described by a pseudo-second order equation^[36]; this is why we only analysed our results for Pb(II) onto JSAC with this model.

The pseudo-second order kinetic model is expressed as

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

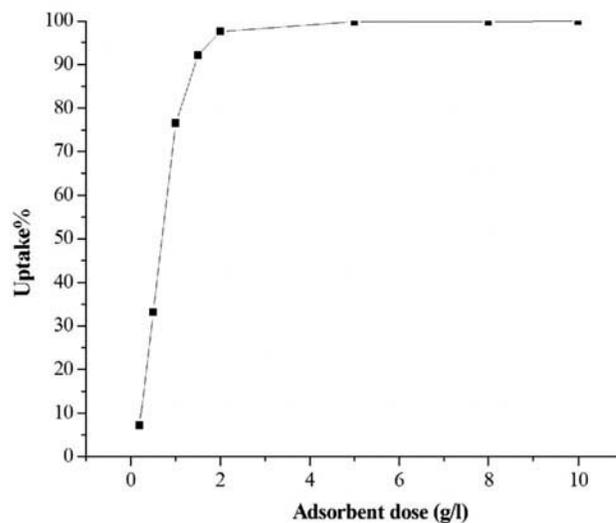


Figure 6. Effect of sorbent concentration for the sorption of lead onto activated carbon from jujube stones at 25°C ($C_0 = 50$ mg/L, pH = 6.0, contact time = 140 min).

where k_2 (in (g/mg)/min) is the rate constant of second order sorption. Eq. (4) can be integrated to

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (5)$$

Data treatment with NLLS allowed one to determine the rate constants and correlation coefficients (Table 2). They showed that the pseudo-second order model, an indication of a chemisorption mechanism, correctly fits the experimental data.

Sorption isotherms modelling

Equilibrium studies that give the capacity of the sorbent and the relationship between sorbent and sorbate concentrations (Fig. 7) are here described by the Langmuir isotherm model,^[37] which assumes a maximum in the sorption of the target species, and is defined as follows:

$$q_e = \frac{q_{\max} K_L C_e}{(1 + K_L C_e)} \quad (6)$$

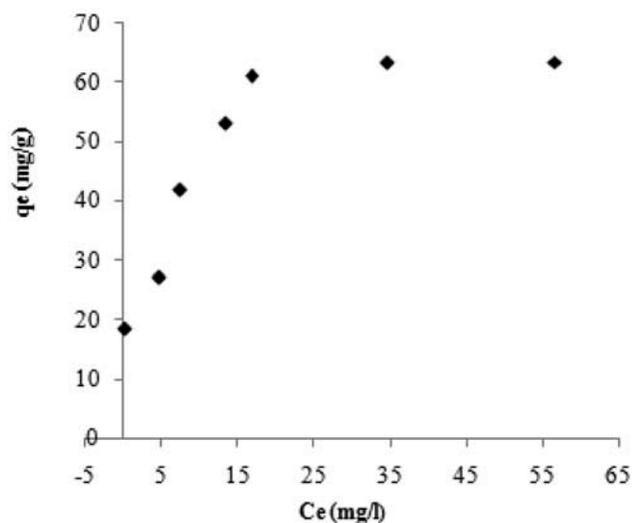
where q_{\max} is the sorption capacity (mg/g), or monolayer capacity, and K_L the Langmuir constant (L/mg) related to the free energy of sorption. These parameters were obtained using NLLS data processing.

The essential feature of the Langmuir isotherm can be expressed in terms of the dimensionless separation parameter R_L , which is indicative of the isotherm shape and that predicts whether a sorption system is favourable ($0 < R_L < 1$) or unfavourable ($R_L > 1$). R_L is defined as^[38]

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (7)$$

Table 2. Pseudo-second-order kinetic parameters for the sorption of Pb(II) ions onto activated carbon from jujube stones at various initial concentrations.

C_0 (mg/L)	k_2 ((g/mg)/min)	R^2
10	0.09	0.9999
20	0.04	0.9992
40	0.05	0.9998
70	0.02	0.9999
90	0.01	0.9999

**Figure 7.** Isotherm data for Pb(II) sorption onto activated carbon obtained from jujube stones (pH = 6.0, sorbent dose 0.5 g/100mL, contact time = 140 min and T = 25°C).

where K_L is the Langmuir constant (L/mg) and C_0 the initial Pb(II) concentration (mg/L). Table 3 shows that $0.039 \leq R_L \leq 0.270$, a result indicating favourable sorption.

The monolayer sorption capacity according to the Langmuir isotherm model was found to be $q_{max} = 71.43$ mg/g at 25°C and the Langmuir constant is $K_L = 0.27$ L/mg ($R^2 = 0.988$). The fact that the Langmuir isotherm fits the experimental data well may be due to the homogeneous distribution of active sites on the JSAC surface in accordance with the Langmuir sorption model assumptions.

A comparison between the sorption capacities of JSAC and several other sorbents under similar conditions is presented in Table 4. The value of q_{max} in the present study is larger than those in most of the previous works. Hence, it can be concluded that jujube stones waste could be applied as an effective low-cost sorbent for the removal of Pb(II) from aqueous solutions. The observed differences between some of the selected activated carbons can be traced to the nature of the lignocellulosic components of these various kinds of fruit stones (apricot, date, olive) and their initial texture.^[34]

Table 3. Different values of the dimensionless parameter R_L for various Pb(II) concentrations.

Concentrations (mg/L)	R_L
10	0.270
20	0.157
30	0.109
50	0.068
70	0.050
90	0.039

Table 4. Comparison of maximal capacity of JSAC with other low-cost sorbents from biowastes (rounded values).

Sorbent	q_{max} (mg/g)	References
Cocoa shells	6	[39]
Tobacco stems	6	[17]
Crushed olive stones	9	[40]
Corn straw	15	[41]
Modified soda lignin	20	[42]
Date stones AC	20	[12]
Apricot stones AC	21	[13]
Coconut shell AC	22	[6]
Pine cone AC	28	[43]
Coir pith AC	46	[23]
Sago waste	47	[18]
Peanut shells AC	47 to 153 (a)	[44]
Rice husk AC	49 to 262 (a)	[22]
Grape stalks	50	[19]
Tea waste	65	[45]
Wheat bran	69	[16]
Jujube stones AC	71	Present study
Peat	122	[46,47]
Chestnut shells AC	139	[21]
Olive stones AC	148	[14]
Saw dust AC	200	[10]
Bagasse AC	227	[10]
Date pits AC	227	[11]
Sargassum algae non-living biomass	238 or 285 (b)	[48]
Pith AC	250	[10]
Euphorbia rigida biomass AC	280	[49]

(a) Dependent of the activation method

(b) Dependent of species

Conclusions

The use of low-cost sorbents constitutes a real challenge for developing countries, in order to protect their water resources and environment. Jujube stone can be used as a suitable raw material with H_2SO_4 activation in order to prepare the corresponding activated carbon solid. From the kinetics studies it is observed that the sorption of Pb (II) is very rapid in the initial stage and decreases while approaching a steady state. The results of this research revealed that the sorption process is strongly dependent on pH of the solution, in accordance with changes in the surface charges of the solid and in Pb(II) speciation in the aqueous solution. The kinetics of Pb(II) sorption followed the pseudo-second order rate relationship, and the Langmuir model is appropriate to describe lead sorption isotherm at fixed pH 6.0. The JSAC could be an economical alternative for the commercially available activated carbon in the removal of toxic metals such as lead from aqueous solutions

A question remains: what can be the future of the spent JSAC when loaded with the lead extracted from a polluted wastewater? Although the study of the corresponding engineering process is of course out of the present work, we can suggest burning off this new waste in a dedicated plant, in order to recover secondary smelting lead metal, thanks to the presence of carbon as a reducing reactant. Indeed, a recent study^[50] showed that Pb remains within ashes after combustion in a flow reactor of a sample of olive tree pruning loaded with 2.3% Pb(II) by sorption.

Disclosure statement

No potential conflict of interest was reported by the authors.

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