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Batch sorption of Pb(II) ions from aqueous solutions using activated carbon prepared from date stones: equilibrium, kinetic, and thermodynamic studies

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ABSTRACT

The sorption of Pb(II) ions onto activated carbon prepared from Tunisian date stones was studied in a batch process. The effects of the main parameters, such as contact time, initial concentration of Pb(II), solution pH, and temperature were studied. The kinetic data were analyzed by applying pseudo-first-order, pseudo-second-order, and Weber-Morris diffusion models. The applicability of Langmuir and Freundlich adsorption isotherms was evaluated to better understand the adsorption process. The results revealed that the equilibrium data were perfectly represented using a Langmuir isotherm. The maximum monolayer adsorption capacity was found to be 38.46 mg/g at 20°C, pH 6, contact time 120 min, and 0.5 g activated carbon. The kinetic data followed closely the pseudo-second-order model. The application of an intraparticle diffusion model revealed that the adsorption mechanism of Pb(II) is a rather complex process and that diffusion is involved in the overall rate of the adsorption process, but it is not the only rate-controlling step. Thermodynamic studies revealed the spontaneous and endothermic nature of the adsorption process. Results from this study suggest that activated carbon produced from date stones residue is an effective adsorbent for the removal of lead from aqueous solutions.

Keywords: Activated carbon; Batch sorption; Lead; kinetic; Isotherms

1. Introduction

In recent years, there has been growing concern over the environmental problem of the disposal of industrial waste containing substances that are toxic in nature, generated from both primary and secondary metal industries. Heavy metals, such as lead (Pb), released into the subsurface pose a threat to human health and the surrounding environment [1]. Lead is ubiquitous in the environment and is hazardous at high levels. The toxicity and deleterious effects of lead are well documented [2,3]. It causes severe poisoning

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in the kidneys, reproductive system, liver, brain, and central nervous system.

The treatment of heavy metals bearing effluents has been studied by several methods, such as reduction precipitation, ion exchange, electrochemical reduction, evaporation, reverse osmosis, adsorption and direct precipitation [4,5]. Most of these methods require high capital cost and recurring expenses, such as chemicals, which are not suitable for small-scale industries.

The process of adsorption is by far the most versatile and widely used technique for metal ions removal [6–10]. However, the preparation and regeneration of carbon adsorbents are fairly expensive, which hampers their application. Hence, a considerable amount of interest has recently been focused on the production of activated carbons from low-cost wastes for the removal of heavy metals from wastewater [11–22].

In the present work, an activated carbon prepared from Tunisian date stones, an agro-food waste predominantly produced in the Mediterranean countries, was prepared by chemical activation with phosphoric acid and was used for the removal of lead ions from dilute aqueous solutions. The equilibrium and kinetics data of the adsorption process were analyzed to study the adsorption characteristics and the mechanism of adsorption.

2. Materials and methods

2.1. Preparation of the activated carbon

In the present study, date stones were used as raw material to produce activated carbon via chemical activation using phosphoric acid (analytical grade) as a dehydrating agent. The preparation of the activated carbon was conducted as follows: 40 g of the crushed (Ø < 1.5 mm) and dried precursor was mixed with a H_3PO_4 solution with a concentration of 60% H_3PO_4 in weight. The impregnation ratio, defined by the weight ratio of impregnant (H_3PO_4) to precursor, was 1.75. The impregnation was conducted in a stirred Pyrex reactor equipped with a reflux condenser. Stirring was used to ensure the acid had access to the interior of the date stones cake particles. The temperature and the duration of the reaction were 104℃ and 2 h, respectively. Agitation and heating were ensured using a heating magnetic stirrer with connected temperature regulator probe made of Teflon. The pyrolysis of the impregnated material was conducted in a cylindrical stainless steel reactor, inserted into a tubular regulated furnace under continuous nitrogen flow (0.5 l/min). The pyrolysis temperature and pyrolysis time were maintained at 450℃ and 2 h, respectively. After cooling down to room temperature under the same flow of nitrogen, the obtained activated carbon was thoroughly washed with hot distilled water until it reached neutral pH. The sample was then dried at 105℃ overnight, ground (to a granulometry ranging between 100 and 160 μm) and finally kept in a hermetic bottle for subsequent use.

More details of the preparation of the activated carbon and optimization of various synthesis conditions as well as their effect on the properties of the prepared adsorbent have been discussed in a previous study [23]; thus, they are beyond the scope of this paper. Nevertheless, some of its characteristics are shown herein for data interpretation purposes.

2.2. Characterization of the prepared activated carbon

Specific surface area of the prepared activated carbon, which will be used later for the lead sorption, was evaluated through N_2 adsorption at 77 K, using an Autosorb1-Quantachrome instrument. The BET (Brunauer–Emmet and Teller) model was applied to fit nitrogen adsorption isotherm and evaluate the surface area (S_{BET}) of the sorbent.

A morphological and elemental composition study of the prepared activated carbon was done with scanning electron microscopy (SEM, Philips XL30) equipped with an energy dispersive X-ray analysis (Philips EDAX 9100).

The FTIR spectra of samples were recorded with an FTIR spectrophotometer SHIMATZU 470 FT-IR model, using the potassium bromide (KBr) pellet method. Oven-dried solid samples of pure activated carbon and lead ions adsorbed activated carbon were thoroughly mixed with KBr in the ratio of 1:100 (weight ratio of sample to KBr). The spectra were recorded by 64 scan with 4 cm^{-1} resolution in the fingerprint spectral region of 4,000–400 cm^{-1}.

The pH of zero point of charge (pH_{zpc}) was determined by adding a known amount of adsorbent (0.1 g) to a series of bottles that contained 50 ml of deionized water. Before adding the adsorbent, the pH of the solutions was adjusted to be in the range 1.0–9.0 by the addition of either 0.1 M HNO_3 or 0.1 M NaOH. These bottles were then rotated for one hour in a shaker, and pH values were measured at the end of the test. The pH of the suspensions is 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 [24].

2.3. Chemicals

Aqueous solutions containing lead (Pb^{2+}) at various concentrations were prepared from nitrate lead salt ($Pb(NO_3)_2$). The initial pH of the solutions was adjusted by adding either nitric acid or sodium hydroxide.

Measurements of the initial pH of lead ion solutions were carried out using a laboratory pH-meter (model pH 540 GLP) equipped with a combined glass electrode (SENTIX 41). A preliminary calibration is systematically carried out using suitable buffer solutions.

A Hitachi Z-6100 model Atomic Absorption Spectrometer operating with an air-acetylene flame was employed to measure metal ion concentrations.

2.4. Batch adsorption studies

Batch-mode adsorption studies were carried out on the prepared activated carbon using a 250-ml stoppered Erlenmeyer flask containing 200 ml test solution of 10, 20, 30, 40, 50, 70, and 100 mg/l of initial concentration. About 0.5 g of the adsorbent was then added. The solution pH was adjusted to the desired value by adding HCl or NaOH. Then, the flasks were shaken in a temperature-controlled shaker for a prescribed time to attain the equilibrium. The contents of the flask were then filtered and the Pb(II) concentrations were determined using flame atomic absorption spectrometry (Hitachi Z-6100 model). The instrument calibration was periodically checked by using standard metal solutions for every 15 readings. Blank solutions were treated similarly (without adsorbent) and the concentration at the end of each operation was taken as the initial one. The effects of various operating parameters, contact time (5–480 min), solution pH (2–8), initial Pb(II) concentration (10–100 mg/l), and temperatures (283, 293, and 313 K) were studied. All of the investigations were conducted in triplicate to avoid discrepancies in the experimental results. The adsorption capacity was determined by calculating the mass balance equation for the adsorbent:

$$q = \frac{(C_i - C_e)V}{W} \tag{1}$$

where q is the adsorption capacity (mg/g), V is the volume of the metal ion solution (L), C_0 and C_e represent initial and equilibrium concentrations, respectively; (mg/l) of lead, and W is the weight of the adsorbent (g).

2.5. Batch desorption studies

After the adsorption experiment, the lead ion loaded carbon (initial concentration was 100 mg/l) was separated and stirred with 200 ml of HCl of various strengths ranging from 0.01 to 0.3 M and was analyzed as before.

3. Results and discussion

3.1. Characterization of the prepared active carbon

The knowledge of the characteristics of the activated carbon is necessary to contribute to the comprehension of many phenomena, like adsorption, desorption, or others. Table 1 represents some of the most important characteristics.

The textural characteristics (specific surface area and porous volume) indicate that the prepared activated carbon can be used as potential adsorbent.

The microstructure of the raw date stones and the resulting activated carbon are shown in Fig. 1. Comparison of the precursor morphology (Fig. 1(a)) with that of the derived carbon (Fig. 1(b)) attests substantial changes occa-sioned by phosphoric acid activation. The sorbent surface exhibits a clear porous structure and a predominately microporous character which is responsible of the high developed surface area of this material.

The results of analysis of the activated carbon (Table 1) showed that the essential of the carbonized or activated matter is the carbon. The high percentage of this element (91.3%) represents well a traditional structure of carbon [25]. This interprets a good pyrolysis of the raw material or date stones. A small percentage of phosphorous atom (1.4%) was also reported in EDX results.

FTIR spectra were recorded before and after the adsorption of Pb(II) separately as presented in Fig. 2.

Table 1
Physical characteristics and elemental composition of the prepared activated carbon

Parameter	Value
Specific surface area (m^2/g)	826
Total pore volume (cm^3/g)	0.46
Average pore diameter (nm)	2.25
pH_{zpc}	3.34
Particle size (μm)	100–160
Carbon (%)	91.3
Oxygen (%)	7.1
Phosphor (%)	1.4

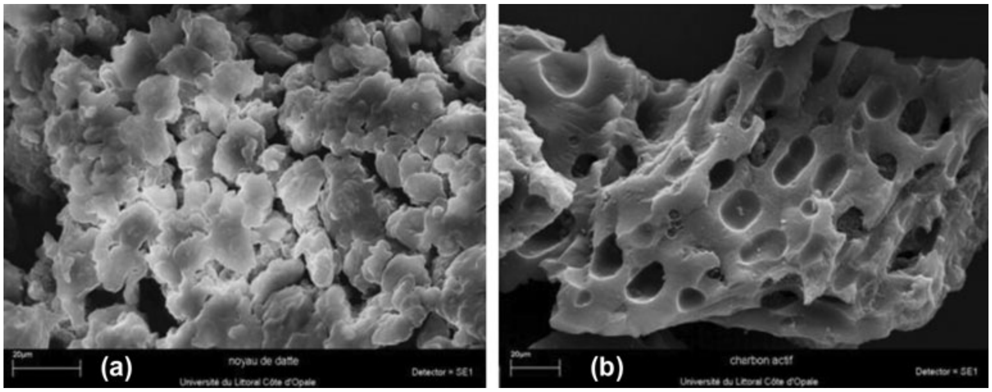

Fig. 1. SEM micrograph of (a) the raw date stones residue and (b) the prepared activated carbon.

The FTIR spectrums of the activated carbon pre- and post-adsorption condition provide information of the chemical structure and surface functional groups changes on adsorption of lead. The spectra of pure activated carbon (Fig. 2(a)) have distinguished peaks at 2,921.6 cm^{-1} (due to asymmetric C–H stretching of methylene groups in aliphatic compounds or fragments) and 2,851 cm^{-1} (symmetric C–H vibration of methylene groups in aliphatic compounds or fragments), but after adsorption of Pb(II), these peaks were almost extinct (Fig. 2(b)). Activated carbon has no peak at 2,358.06 cm^{-1} (characteristic to multiple bonding between the atoms), but after Pb(II) adsorption, a new peak generated at this frequency. These changes in the functional group frequency are probably due to the metal ion interaction with the electron rich sites in the activated carbon, which causes the shift of peak from 2,921.6 and 2,851 cm^{-1} to 2,358.06 cm^{-1} [26]. These two are the significant changes in the backbone chemical structure and functional groups of the activated carbon after lead adsorption.

3.2. Effect of contact time on Pb (II) adsorption

To establish an appropriate contact time between the activated carbon developed from date stones and metallic ion solution, sorption capacity of Pb(II) was measured as a function of time and concentration (Fig. 3). The results indicate that the removal of Pb(II) shows a time- and concentration-dependent character. The uptake of Pb(II) is fast at the initial stages of the contact period, and thereafter, it becomes slower near the equilibrium. This is obvious by the fact that a large number of vacant surface sites are available for sorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute ions on the solid and the bulk phases. It is also observed that the amount of Pb(II) uptake per unit weight of activated carbon (mg/g) increases with increasing the metal ion concentration. The necessary time to reach the equilibrium is about 2 h. The found equilibrium time is comparable to others reported in the literature [27,28].

3.3. Effect of initial pH on Pb(II) removal

The effect of the solution pH on the adsorption of Pb (II) ions on activated carbon prepared from date stones was examined under the following conditions: an initial lead concentration (30–100 mg/L), 0.50 g of adsorbent, $T = 20^\circ C$, and constant contact time 120 min. The initial solution pH range was adjusted between 2 and 8. This pH range is chosen in order to avoid metal solid hydroxide precipitation. No attempt was made to maintain a constant pH of the solution in the adsorption progress. The experimental results are shown in Fig. 4. We note that the uptake is quite

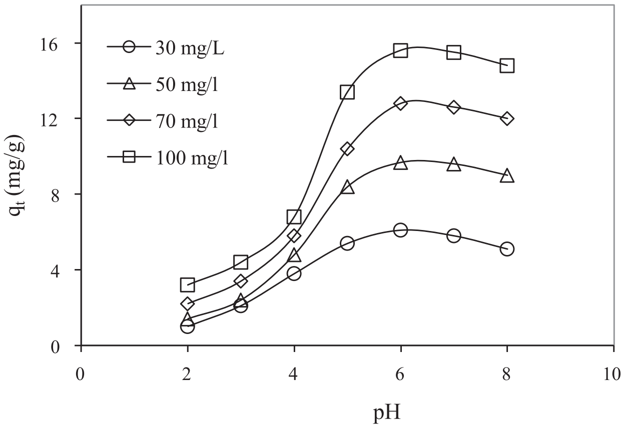

Fig. 4. Effect of solution pH on adsorption of Pb(II) on the prepared activated carbon.

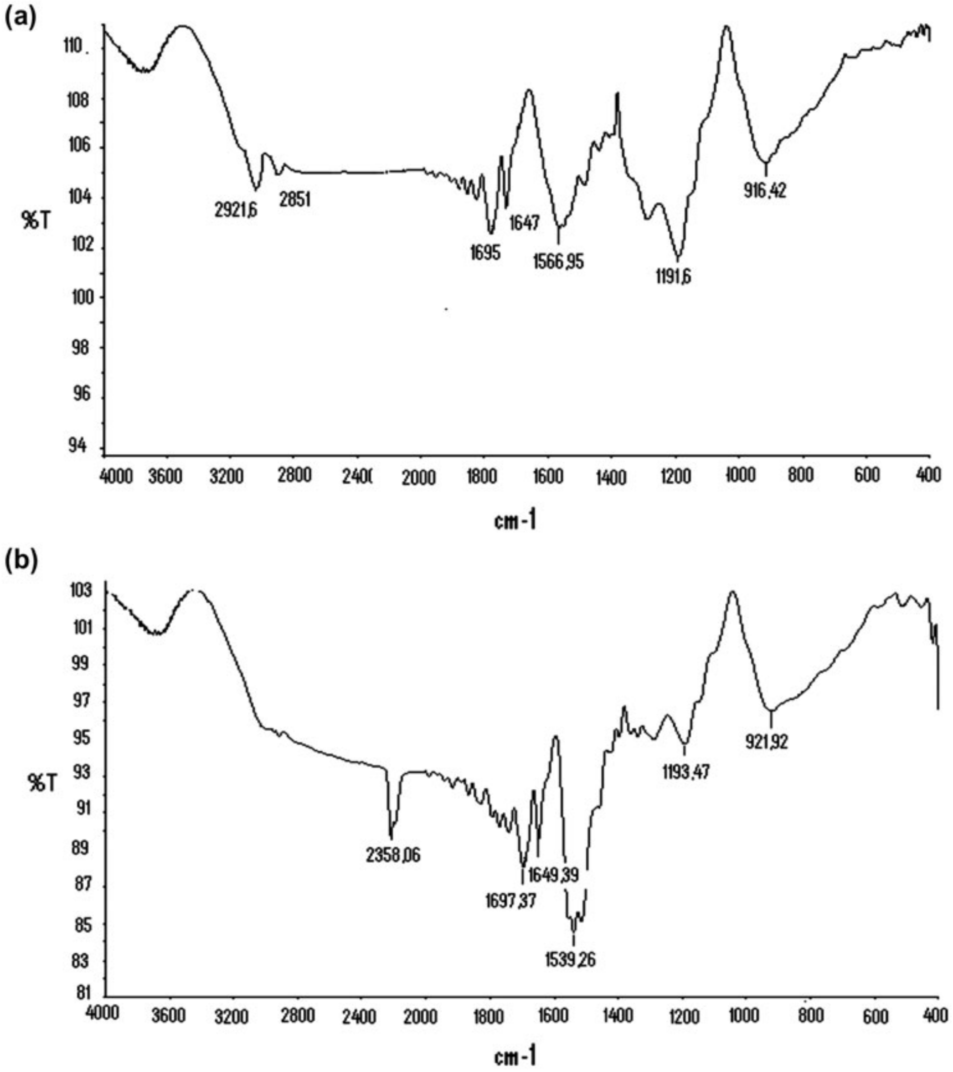

Fig. 2. FTIR spectrum of the prepared activated carbon (a) before and (b) after adsorption of lead ions.

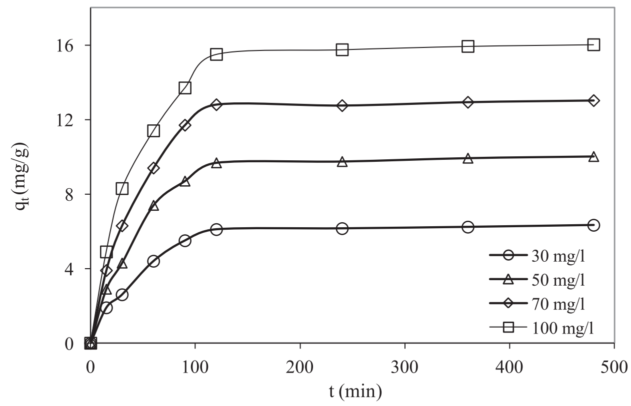

Fig. 3. Kinetic study for Pb(II) adsorption on the prepared activated carbon at different concentrations.

low at lesser pH. However, with the increase in pH, a significant enhancement in adsorption is recorded. At low pH (below pH_{zpc}), the activated carbon surface has positive charge, so the smaller adsorption values can be attributed to electrostatic repulsion that takes place between the same charge of the cation and the activated carbon. In addition, in high acidic medium, there would be competition between H^+ and Pb^{2+} for adsorption at the ion-exchangeable sites of carbon, leading to a low removal of metal ion. With increasing pH (beyond pH_{zpc}), negative charge density on the surface increases due to the successive deprotonation of positive charged groups and unprotonated carboxylic groups on the surface of activated carbon, and also low H^+ ion concentration. As a result, electrostatic attraction between the negatively charged sites of the adsorbent and the positively charged cation rise. The amount adsorbed of Pb(II) increase significantly with increasing the pH from 3 to 6, reaches a maximum, and then decreases from pH 6 to 8. The decrease in adsorption of Pb(II) observed at higher pH ($\text{pH} > 6$) is due to the formation of soluble hydroxyl complexes.

The removal efficiencies of lead ions is affected by the initial lead ions concentration with the removal decreasing as the concentration increases at constant pH. This can be explained as follows: at low lead/carbon ratio, the lead ions adsorption involves the high energy sites, as the lead/carbon ratio increases, the higher energy sites are saturated and adsorption begins on the lower energy sites, resulting in a decrease of adsorption efficiencies [29]. Similar findings have been reported by other researchers working on removal of Pb (II) ions from aqueous solution by activated carbon [30–32]. With respect to the abovementioned information, subsequent studies were conducted at pH 6.

3.4. Modeling of adsorption isotherm

Analysis of equilibrium data is important for developing an equation that can be used to design and optimize an operating procedure [33]. To quantify the adsorption capacity of the prepared activated carbon for the removal of Pb(II) ions from aqueous solution, two isotherm models were applied to the experimental data: Langmuir and Freundlich isotherm equations.

The Langmuir model assumes that adsorption occurs at specific homogeneous sites on the adsorbent and can be successfully applied to monolayer adsorption processes. It can be expressed by the following equation [34]:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \tag{2}$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of lead sorbed at equilibrium, b is the sorption constant (L/mg) (at a given temperature) related to energy of sorption, and q_0 is the maximum sorption capacity (mg/g). q_0 and b are determined from the slope and intercept of the plot. The essential feature of the Langmuir isotherm can be expressed in terms of dimensionless separation parameter R_L, which is indicative of the isotherm shape that predicts whether an adsorption system is favourable or unfavourable.

R_L is defined as [35]:

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

where R_L is a dimensionless separation factor, C_0 is the initial metal ions concentration, and b is Langmuir constant. The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The values of R_L were found in the range of 0.38–0.47, confirming the favorable adsorption process for all systems.

The Freundlich model is applicable for non ideal sorption on heterogeneous surfaces and multilayer adsorption processes. According to the Freundlich model [36]:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{4}$$

where K_f and n are Freundlich constants, indicating the adsorption capacity and the adsorption intensity,

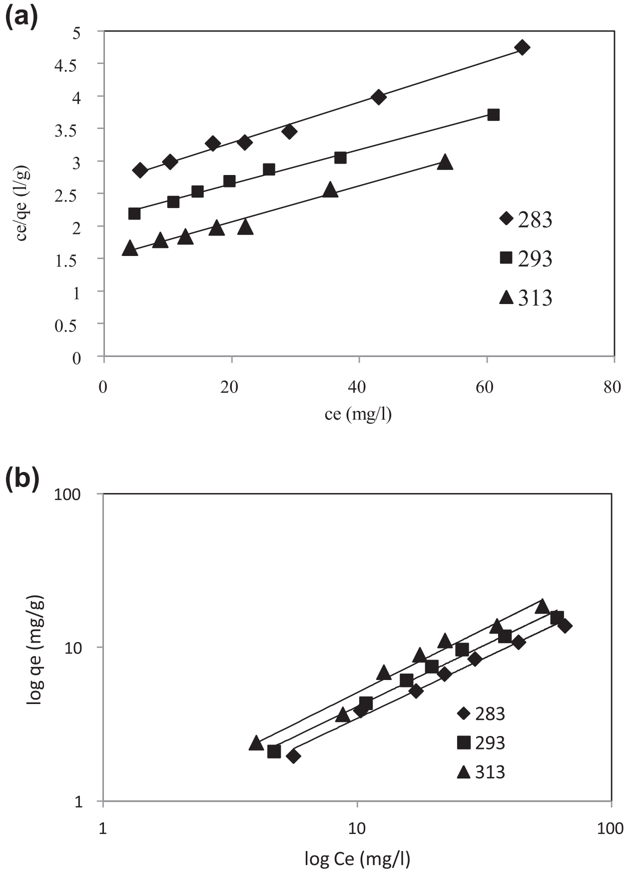

Fig. 5. Linearizations according to Langmuir (a) and Freundlich (b) isotherms for Pb(II) adsorption onto the prepared activated carbon at different temperatures.

Table 2
Isotherm parameters for the sorption of Pb(II) on the prepared activated carbon

Isotherms	Parameter	Value		
		Temperature (K)		
		283	293	313
Langmuir isotherm	q_0 (mg/g)	32.25	38.46	39.37
	b (L/mg)	0.011	0.012	0.016
	R^2	0.99	0.99	0.98
Freundlich isotherm	K_f (L/g)	0.56	0.65	0.75
	n	1.27	1.25	1.20
	R^2	0.98	0.98	0.97

respectively. K_f and n are, respectively, determined from the intercept and slope of plotting ln q_e vs. ln C_e.

The linearizations according to Langmuir and Freundlich model are plotted in Fig. 5 and the calculated constants (K_f and n) are tabulated in Table 2. Compared with Freundlich, Langmuir adsorption isotherm provides better fitting in terms of R^2 (0.99).

The adsorption capacity of the prepared activated carbon calculated by Langmuir model at 283, 293, and 313 K is estimated to be 32.25, 38.46, and 39.37 mg Pb (II)/g activated carbon, respectively. An increase in the temperature could enhance the adsorption progress, thereby resulting in an increase in the amount of Pb (II) adsorbed.

In order to compare the adsorption capacities of Pb(II) on the prepared activated carbon, the adsorption capacities of various adsorbents derived from agriculture residues are given in Table 3. Before comparison of adsorption capacities, it should be mentioned that it is impossible to direct comparison, since adsorption capacity of adsorbents depends on lots of parameters, such as surface area, pore structure, functional groups of activated carbon, and experimental condition [42,43]. It seems that the adsorption capacity of the prepared activated carbon is comparable as qualitatively and it has also greater removal efficiency than some adsorbents which are given in Table 3. The result shows that the prepared activated carbon as attractive candidates for Pb(II) ions removal from aqueous solutions.

3.5. Sorption kinetic study

In order to study the kinetic of Pb(II) adsorption by prepared activated carbon, pseudo-first-order [44], pseudo-second-order [45], and intraparticle diffusion [46] kinetic models were tested.

The pseudo-first-order equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{5}$$

The pseudo-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \tag{6}$$

The intraparticle diffusion model:

$$q_t = K_d t^{0.5} + C \tag{7}$$

where q_e and q_t refer to the amount of solute (mg/g) adsorbed at equilibrium and at any time t (min), respectively, k_1 is the equilibrium rate constant of

Table 3
Adsorption capacities (mg/g) of lead (II) by various adsorbents

Adsorbent	Q_0 (mg/g)	Reference
Date stones activated carbon	38.46	Present study
Amanita rubescens biomass	38.4	[37]
Coffee residue activated carbon	63	[38]
Apricot stone activated carbon	21.38	[31]
Sawdust	3.19	[39]
Hazelnut husk activated carbon	13.5	[40]
Coconut shell activated carbon	26.5	[28]
Crushed concrete fines	37	[41]

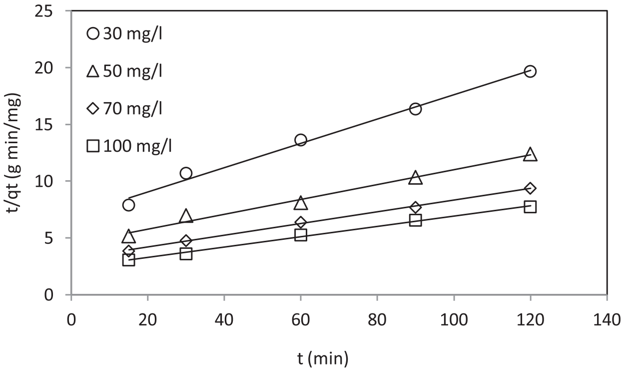

Fig. 6. The pseudo-second order adsorption kinetics for Pb (II) adsorption on the prepared activated carbon.

pseudo-first-order sorption(1/min), k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/mg min), k_d is the intraparticle rate constant (mg/gmin$^{0.5}$), and C is the intercept.

The kinetic model studies were carried out for the adsorption of Pb(II) onto the prepared activated carbon. Results show that the first-order equation does not apply well throughout the whole range of contact times (data not shown). The insufficiency of the first-order model to fit the kinetic data could possibly be due to a boundary layer controlling the beginning of the sorption process [47]. This is also consistent with most cases reported in literature.

The kinetic data were also analyzed by applying the pseudo-second-order model to the experimental data (Fig. 6). The calculated kinetic parameters at various initial concentrations are given in Table 4. It can be seen from the table that the pseudo-second-order kinetic model has the highest correlation coefficient ($R^2 > 0.99$). Similar kinetic results have also been reported for the adsorption of Pb(II) on activated carbon developed from Apricot stone [38].

In order to understand the adsorption mechanism of Pb(II) on the prepared activated carbon, intraparticle diffusion model was also studied.

The intraparticle diffusion plots show multilinearity in the process (Fig. 7), indicating that three steps are operational. The first stage can be attributed to the diffusion of adsorbate through the solution to the external surface of the adsorbent or the boundary surface diffusion of the sorbate molecules. The second stage describes the gradual sorption, where intraparticle diffusion is rate limiting, and the third stage is attributed to the final equilibrium due to extremely low sorbate concentration left in solution and the reduction of interior active sites.

The linear portion of the curves does not pass the origin and the latter stage of metal ions adsorption does not follow Webber–Morris equation. It may be concluded that Pb(II) adsorption control with not only the intraparticle diffusion but also the surface adsorption. The obtained results agree with those found by Nadeem et al. [48] for the adsorption of Pb(II) onto modified carbon adsorbents. The Values of intercept (Table 4) gave an idea about the thickness of boundary layer, i.e. the larger the intercept the greater will be the boundary layer effect [49].

3.6. Effect of temperature and thermodynamic parameters

Temperature has a pronounced effect on the adsorption capacity of activated carbon. It was found that the Pb(II) adsorption uptake increases with increasing solution temperature from 10 to 40°C, indicating that the adsorption is an endothermic process. The increase in the adsorption may be a result of

Table 4
Kinetic parameters for Pb(II) sorption on the prepared activated carbon

Kinetic models		Parameter	Pb (II) (mg/l)			
			30	50	70	100
Pseudo-first-order		K_1 (g/mg min)	0.02	0.02	0.016	0.02
		R^2	0.98	0.98	0.97	0.98
Pseudo-second-order		K_2 (g/mg min)	0.0016	0.00094	0.00086	0.00085
		R^2	0.99	0.98	0.99	0.99
Intraparticle diffusion model	The first phase	Kd_1 (mg/g min$^{0.5}$)	0.58	0.99	1.28	1.46
		$R_1{}^2$	0.95	0.98	0.99	0.98
		C_1	0.74	0.88	0.80	0.22
	The second phase	Kd_2 (mg/g min$^{0.5}$)	0.02	0.032	0.021	0.048
		$R_2{}^2$	0.94	0.95	0.70	0.98
		C_2	5.85	9.28	12.5	14.9

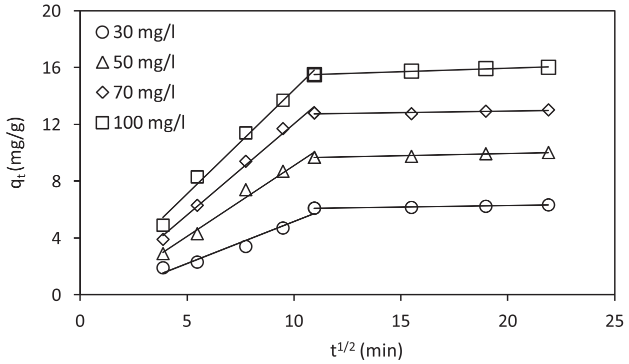

Fig. 7. Plots of intraparticle diffusion for adsorption of Pb (II).

increase in the mobility of the metal ions with increasing temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface [50].

Thermodynamic parameters, such as free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) for the sorption of Pb(II) on activated carbon was determined using the following equations [51,52]:

$$\Delta G^\circ = -RT\ln b \tag{8}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{9}$$

where ΔG° is the change in free energy (kJ/mol), ΔH° the change in enthalpy (kJ/mol), ΔS° the change in entropy (J/molK), T the absolute temperature K, R the gas constant (8.314×10^{-3}), and b is the equilibrium constant of sorption. From Eqs. (8) and (9), it can be rewritten as:

$$\ln b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{10}$$

The enthalpy and entropy changes can be, respectively, determined from the slope and intercept of the plot ln b against $1/T$.

Van't Hoff plot of Pb(II) ions adsorption onto prepared activated carbon is depicted in Fig. 8. The calculated thermodynamic parameters are summarized in Table 5.

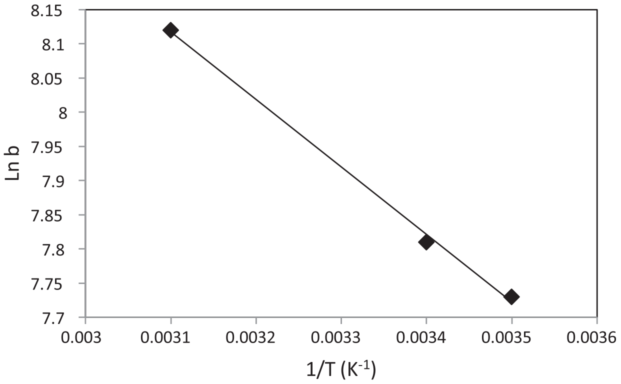

Fig. 8. van't Hoff plots of Pb(II) adsorption on the prepared activated carbon.

The positive value of ΔS° indicates that there is an increase in the randomness at the solid/solution interface during the adsorption of Pb(II) on the activated carbon [53]. This positive value may be explained as follows: during the adsorption of the metal ions, the adsorbate species displace the adsorbed solvent molecules to gain more translational entropy than was lost by the adsorbate, thus allowing randomness in the system. The positive value of ΔH° showed that the sorption process was endothermic in nature. The decrease in the ΔG° values shows the feasibility of adsorption as temperature is increased [54].

3.7. Desorption studies

Desorption of lead using HCl by disruption of coordination of metal ions and subsequent release from the activated carbon surface into the desorption medium was studied. The effect of HCl concentration on the desorption of Pb(II) is represented in Fig. 9. The results show that with increase in concentration of HCl, the desorption also increased but remained constant with 0.15 M HCl. The effectiveness of HCl solution is due to a combination of H^+ attack, which promotes displacement, and conversion of Pb(II) species into chloro-complex formation. Quantitative

Table 5
Thermodynamic parameters of Pb(II) sorption on the prepared activated carbon

Temperature (K)	ΔG° (kcal/mol)	ΔH° (kcal/mol)	ΔS° (cal/mol K)
283	−4.33	1.95	22.13
293	−4.53	1.95	22.13
313	−5.03	1.95	22.13

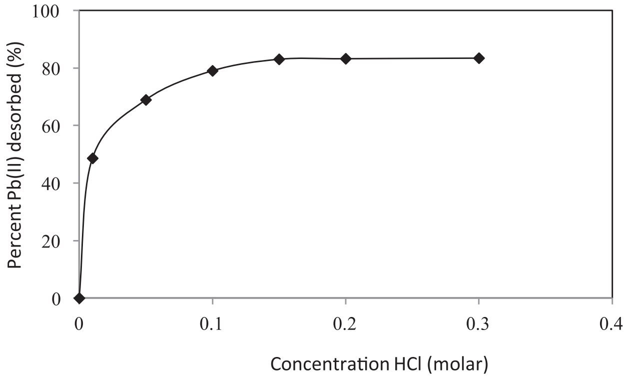

Fig. 9. Effect of HCl concentration on Pb(II) desorption.

desorption clearly indicates that the mechanism of adsorption is ion exchange. The adsorption results observed are in agreement with those previously reported for other activated carbon [29,55].

4. Conclusion

The adsorption of Pb(II) ions using activated carbon prepared from date stones was investigated. The equilibrium, kinetics, and thermodynamics aspects of the adsorption were then evaluated. In the equilibrium study, results obtained indicate that the adsorption equilibrium data were fitted well by the Langmuir isotherm model in the studied concentration range. Maximum adsorption capacity calculated from the Langmuir isotherm is equal to 38.46 mg/g at an initial pH of 6. Time-based investigations revealed that that the pseudo-second-order model provides better correlation of the sorption data than the pseudo-first-order model.

Based on the obtained results it appears that the activated carbon prepared from Tunisian date stones constitutes a good adsorbent for removing Pb(II) ions from aqueous systems for environmental protection purpose.

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References

[1] M. Fan, T. Boonfueng, Y. Xu, L. Axe, T.A. Tyson, Modeling Pb sorption to microporous amorphous oxides as discrete particles and coatings, J. Colloid. Interface Sci. 281 (2005) 39–48.

[2] M.M. Ahammed, M. Chaudhuri, Sand-based filtration/adsorption media, J. Wat. SRT Aqua. 45 (1996) 67–71.

[3] S. Bhattacharjee, S. Chakrabarty, S. Maity, S. Kar, P. Thankur, G. Bhattacharyya, Removal of lead from contaminated water bodies using sea nodule as an adsorbent, Water Res. 37 (2003) 3954–3966.

[4] H.Y. Xu, L. Yang, P. Wang, Y. Liu, M. Peng, Kinetic research on the sorption of aqueous lead by synthetic carbonate hydroxyapatite, J. Environ. Manage. 86 (2008) 319–328.

[5] 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.

[6] B. Sen Gupta, M. Curran, H. Shameem, T.K. Ghosh, Adsorption characteristics of Cu and Ni on Irish peat moss, J. Environ. Manage. 90 (2009) 954–960.

[7] M.R. Panuccio, A. Sorgona, M. Rizzo, G. Cacco, Cadmium adsorption on vermiculite, zeolite and pumice: Batch experimental studies, J. Environ. Manage. 90 (2009) 364–374.

[8] C. Volzone, L. Beatriz Garrido, Use of modified hydroxy-aluminum bentonites for chromium(III) removal from solutions, J. Environ. Manage. 88 (2008) 1640–1648.

[9] R. Salim, M. Al-Subu, E. Dawod, Efficiency of removal of cadmium from aqueous solutions by plant leaves and the effects of interaction of combinations of leaves on their removal efficiency, J. Environ. Manage. 87 (2008) 521–532.

[10] M.F. Sawalha, J.R. Peralta-Videa, B. Sanchez-Salcido, J.L. Gardea-Torresdey, Sorption of hazardous metals from single and multi-element solutions by saltbush biomass in batch and continuous mode: Interference of calcium and magnesium in batch mode, J. Environ. Manage. 90 (2009) 1213–1218.

[11] M.C. Basso, A.L. Cukierman, Arundo donax-based activated carbons for aqueous-phase adsorption of volatile organic compounds, Ind. Eng. Chem. Res. 44 (2005) 2091–2100.

[12] V. Fierro, V. Torné-Fernández, A. Celzard, Kraft lignin as a precursor for microporous activated carbons prepared by impregnation with orthophosphoric acid: Synthesis and textural characterization, Microporous Mesoporous Mater. 92 (2006) 243–250.

[13] A. Klijanienko, E. Lorenc-Grabowska, G. Gryglewicz, Development of mesoporosity during phosphoric acid activation of wood in steam atmosphere, Bioresource. Technol. 99 (2008) 7208–7214.

[14] H. Lata, V.K. Garg, R.K. Gupta, Sequestration of nickel from aqueous solution onto activated carbon prepared from Parthenium hysterophorus L, J. Harad. Mater. 157 (2008) 503–509.

[15] J.V. Nabais, P. Carrott, M.M.L. Ribeiro Carrott, V. Luz, A.L. Ortiz, Influence of preparation conditions in the textural and chemical properties of activated carbons from a novel biomass precursor: The coffee endocarp, Bioresource. Technol. 99 (2008) 7224–7231.

[16] P. Patnukao, P. Pavasant, Activated carbon from *Eucalyptus camaldulensis* Dehn bark using phosphoric acid activation, Bioresource. Technol. 99 (2008) 8540–8543.

[17] C.K. Singh, J.N. Sahu, K.K. Mahalik, C.R. Mohanty, B. Raj Mohan, B.C. Meikap, Studies on the removal of Pb(II) from wastewater by activated carbon developed from Tamarind wood activated with sulphuric acid, J. Hazard. Mater. 153 (2008) 221–228.

[18] F. Sousa, A. Oliveira, J. Ribeiro, M. Rosa, D. Keukeleire, R.F. Nascimento, Green coconut shells applied as adsorbent for removal of toxic metal ions using fixed-bed column technology, J. Environ. Manage. 91 (2010) 1634–1640.

[19] R. Zein, R. Suhaili, F. Earnestly, Indrawati, E. Munaf, Removal of Pb(II), Cd(II) and Co(II) from aqueous solution using *Garcinia mangostana* L fruit shell, J. Hazard. Mater. 181 (2010) 52–56.

[20] L. Wang, Application of activated carbon derived from 'waste' bamboo culms for the adsorption of azo disperse dye: Kinetic equilibrium and thermodynamic studies, J. Environ Manage. 102 (2012) 79–87.

[21] Z.A. AL-Othman, R. Ali, Mu. Naushad, Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: Adsorption kinetics, equilibrium and thermodynamic studies, Chem. Eng. J. 184 (2012) 238–247.
[22] T. Depci, Comparison of activated carbon and iron impregnated activated carbon derived from Golbası lignite to remove cyanide from water, Chem. Eng. J. 182 (2012) 467–478.
[23] F. Bouhamed, Z. Elouear, J. Bouzid, Adsorptive removal of copper(II) from aqueous solutions on activated carbon prepared from Tunisian date stones: Equilibrium kinetics and thermodynamics, J. Taiwan Inst. Chem. Eng. 43 (2012) 741–749.
[24] J. Bouzid, Z. Elouear, M. Ksibi, M. Feki, A. Montiel, A study on removal characteristics of copper from aqueous solution by sewage sludge and pomace ashes, J. Hazard. Mater. 152 (2008) 838–845.
[25] S. Hazourli, M. Ziati, A. Hazourli, Characterization of activated carbon prepared from lignocellulosic natural residue: Example of date stones, Phys. Procedia. 2 (2009) 1039–1043.
[26] G.C. Panda, S.K. Das, T.S. Bandopadhyay, A.K. Guha, Adsorption of nickel on husk of *Lathyrus sativus*: Behavior and binding mechanism, Colloids. Surf. B 57 (2007) 135–142.
[27] O.F. Olorundare, R.W.M. Krause, J.O. Okonkwo, B.B. Mamba, Potential application of activated carbon from maize tassel for the removal of heavy metals in water, Phys. Chem. Earth 50 (2012) 104–110.
[28] 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.
[29] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from coirpith, Sep. Purif. Technol. 24 (2001) 497–505.
[30] G.E. Jean, G.M. Bancroft, Heavy metal adsorption by sulphide mineral surfaces, Geochim. Cosmochim. Acta 50 (1986) 1455–1463.
[31] L. Mouni, D. Merabet, A. Bouzaza, L. Belkhiri, Adsorption of Pb(II) from aqueous solutions using activated carbon developed from apricot stone, Desalination 276 (2011) 148–153.
[32] M. Momčilović, M. Purenović, A. Bojić, A. Zarubica, M. Ranđelović, Removal of lead(II) ions from aqueous solutions by adsorption onto pine cone activated carbon, Desalination 276 (2011) 53–59.
[33] H. Parab, S. Joshi, N. Shenoy, A. Lali, U.S. Sarma, M. Sudersanan, Determination of kinetic and equilibrium of Co (II) Cr(III) and Ni(II) onto coir pith, Process Biochem. 41 (2006) 609–618.
[34] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.
[35] T.W. Weber, R.K. Chakraborty, Pore and solid diffusion models for fixed bed adsorbents, J. Am. Inst. Chem. Eng. 20 (1974) 228–238.
[36] H.M.F. Freundlich, Uber die adsorption in losungen, Z. Phys. Chem. 57 (1906) 385–470.
[37] A. Sarı, M. TuzenKinetic, Equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass, J. Hazard. Mater. 164 (2009) 1004–1011.
[38] F. Boudrahem, F. Aissani-Benissad, H. Aït-Amar, Batch Sorption dynamics and equilibrium for the removal of lead ions from aqueous phase using activated carbon developed from coffee residue activated with zinc chloride, J. Environ Manage. 90 (2009) 3031–3039.
[39] B. Yu, Y. Zhang, A. Shukla, S.S. Shukla, K.L. Dorris, The removal of heavy metals from aqueous solutions by sawdust adsorption removal of lead and comparison of its adsorption with copper, J. Hazard Mater B 84 (2001) 83–94.
[40] M. Imamoglu, O. Tekir, Removal of copper(II) and lead(II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husk, Desalination 228 (2008) 108–113.
[41] N.J. Coleman, W.E. Lee, I.J. Slipper, Interactions of aqueous Cu^{2+}, Zn^{2+} and Pb^{2+} ions with crushed concrete fines, J. Hazard. Mater. 121(1–3) (2005) 203–213.
[42] F. Boudrahem, A. Soualah, F. Aissani-Benissad, Pb(II) and Cd(II) removal from aqueous solutions using activated carbon developed from coffee residue activated with phosphoric acid and zinc chloride, J. Chem. Eng. Data 56 (2011) 1946–1955.
[43] M.A. Ferro-Garcia, J. Rivera-Ultrilla, J. Ropdriquez-Gordillio, I. Bautista-Tolego, Adsorption of zinc cadmium and copper on activated carbons obtained from agricultural by-products, Carbon 26 (1988) 363–373.
[44] P.E.P. Barrett, L.G. Joyner, P.P. Halenda, The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms, J. Am. Chem. Soc. 73 (1951) 373–380.
[45] Y.S. Ho, G. Mckay, Pseduo-second-order model for sorption process, Process.Biochem. 34 (1999) 451–465.
[46] W.J. Weber, J.R. Moris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. ASCE Civil Eng. 89 (1963) 31–39.
[47] E.L. Cochrane, S. Lu, S.W. Gibb, I. Villaescusa, A comparison of low-cost biosorbents and commercial sorbents for the removal of copper from aqueous media, J. Hazard. Mater. B137 (2006) 198–206.
[48] M. Nadeem, A. Mahmood, S.A. Shahid, S.S. Shah, A.M. Khalid, G. McKay, Sorption of lead from aqueous solution by chemically modified carbon adsorbents, J. Hazard. Mater. 138 (2006) 604–613.
[49] K. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbonsa comparative study, Dyes Pigm. 51 (2001) 25–40.
[50] B.H. Hameed, A.A. Ahmad, N. Aziz, Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash, Chem. Eng. J. 133 (2007) 195–203.
[51] H. Ucun, Y.K. Bayhan, Y. Kaya, Kinetic and thermodynamic studies of the biosorption of Cr(VI) by *Pinus sylvestris* Linn, J. Hazard. Mater. 153 (2008) 52–59.
[52] A. Sarı, M. Tuzen, O.D. Uluozlu, M. Soylak, Biosorption of Pb(II) and Ni(II) from aqueous solution by lichen (*Cladonia furcata*) biomass, Biochem. Eng. J. 37 (2007) 151–158.
[53] A. Aziz, M.S. Ouali, E. El Hadj, L.C.H. De Menorval, M. Lindheimer, Chemically modified olive stone: A low-cost sorbent for heavy metals and basic dyes removal, J. Hazard. Mater. 163 (2009) 441–447.
[54] M. Kilic, E. Apaydin-Varol, E. Ays, E. Putun, 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.
[55] L.H. Huang, Y.Y. Sun, T. Yang, L. Li, Adsorption behavior of Ni (II) on lotus stalks derived active carbon by phosphoric acid activation, Desalination 268 (2011) 12–19.