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Removal of Pb^{2+} and Zn^{2+} from the aqueous solutions by activated carbon prepared from *Dates stone*

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ABSTRACT

The low-cost activated carbon prepared from *Date stone*, an agricultural solid waste by-product, were prepared by chemical activation with sulphuric acid for the removal of lead and zinc from aqueous solutions has been studied as a function of pH, contact time, metal concentrations and adsorbent concentrations. Adsorption equilibrium was reached after an equilibration time of 60 min and adsorption kinetics data were tested using Lagergren pseudo-first-order and pseudo-second order, the studies showed the adsorption process followed pseudo-second-order rate model. The maximum removal of Pb^{2+} and Zn^{2+} is observed at pH 6.0 (94.4%) and 7.0 (93.2%) respectively at initial concentration 20 mg/L. The isotherm equilibrium data were well fitted by the Langmuir and Freundlich models. The adsorption capacity (q_{max}) calculated from the Langmuir isotherm was 19.64 mg Pb^{2+}/g and 10.41 mg Zn^{2+}/g at an initial pH of 6.0 at 20 ± 2°C.

Keywords: Lead and zinc removal; Adsorption; Isotherm; Activated carbon; *Date stone*

1. Introduction

The wastewater from many industrial activities contains metal ions such as Pb, Cd, Zn, Cu, etc these toxic heavy metal ions get introduced to the aquatic streams by means of various industrial activities viz. mining, refining ores, fertilizer industries, tanneries, batteries, paper industries, pesticides etc. and can seriously affect plants and animals, causing a large number of afflictions [1–4]. Metals of interest were Zn and Pb. They were chosen based on their industrial applications and potential pollution impact on the environment. Lead is ubiquitous in the environment and is hazardous at high levels. It is a general metabolic poison and enzyme inhibitor [5], causes toxicity to the neuronal system, and affects the function of brain cells [6]. Zinc is a toxic element. Among the main symptoms of zinc toxicity, irritability, muscular stiffness, loss of appetite and nausea are to be mentioned [7]. Because of the above factors, there is a necessity to remove these metals from wastewater in order to prevent contamination of natural water bodies by effluents containing toxic metals.

Many methods have been proposed for their removals from wastewaters include ion exchange, solvent extraction, reverse osmosis, precipitation and adsorption [8–10]. These methods do not seem to be economically feasible because of relative high costs, particularly when used for the removal of heavy metals at low concentrations (<100 mg/L) [11]. Furthermore, most of these methods generate toxic sludge [12], the disposal of which is an additional burden on the technoeconomic feasibility of treatment procedures. Activated carbon is one of the most widely employed adsorbents. Its industrial usage can be found in the treatment process for flue gas and volatile solvents, etc. Activated carbon

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production from agricultural waste has two advantages. First, waste material is converted to useful, value-added adsorbents. Disposal of agricultural by-products has become a major, costly waste disposal problem. Second, produced activated carbons are used for removing organic chemicals and metals from wastewater. A wide variety of materials such as rice husk [13], modified cellulosic materials [14], fly ash [15], wheat brean [16], modified bark [17], sawdust [13] and pine bark [18], are being used as low-cost alternatives to expensive adsorbents. Most of the activated carbons are produced by a two-stage process carbonization followed by activation. The first step is to enrich the carbon content and to create an initial porosity and the activation process helps in enhancing the pore structure. Basically, the activation is two different processes for the preparation of activated carbon: physical activation and chemical activation. In fact, there are two important advantages of chemical activation in comparison to physical activation. One is the lower temperature in 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. Among the numerous dehydrating agents, sulphuric acid in particular is the widely used chemical agent in the preparation of activated carbon.

Date is a Mediterranean tall-size tree that may reach up to 25–30 m tall. The fruit matures in autumn. The aim of this work was first to prepare activated carbons using a *Dates stone*. Next, to assess the ability of low-cost activated carbon prepared from *Date stone* to remove Pb^{2+} and Zn^{2+} from aqueous solution. The effect of the solution pH, contact time, initial adsorbate concentration and adsorbent doses on the removal of lead and zinc was studied. The adsorption capacity of adsorbent was investigated using batch experiments data obtained were evaluated and fitted using various isotherm models including Langmuir and Freundlich; and kinetic models such as the pseudo-first-order, and pseudo-second-order, have been put forward to describe or predict the adsorption isotherms and kinetics, respectively.

2. Materials and methods

2.1. Preparation of solutions

The heavy metal ions tested in this study included Pb^{2+} and Zn^{2+}. Synthetic stock solutions of heavy metals at 1000 mg/L concentrations were prepared by dissolving a required quantity of $Pb(NO_3)_2$ and $ZnCl_2$ for Pb^{2+} and Zn^{2+}, respectively. Diluted metal ion solutions were prepared as required by further dilution with distilled water. Analytical grades of HCl and NaOH (Merck) solutions were used for pH adjustment.

2.2. Preparation of activated carbon

Date stone was used in this study a source of activated carbon, collected from Ourgla, Algeria. It was harvested between September and December. The *Date stone* were washed with distilled water, dried at 105°C and crushed in a mortar. Sulfuric acid as a chemical reagent added during the activation process help produce more effective adsorbent. The activation procedure was accomplished as: *Date stone* was impregnated with 50% H_2SO_4 then this mixture of H_2SO_4 and untreated *Date stone* was heated at 200°C for 2 h and then filtered and the resulting chemical loaded *Date stone* was placed in a furnace and heated (10°C min^{-1}) to the final carbonization temperature of 650°C for 30 min [19]. In all experiments, the heating rate was kept constant. After cooling, the activated carbon was washed to get it acid free and its pH was checked. The carbonized adsorbents were dried and rewashed many times until its pH reaches 4. After this the activated carbon was deacidified by use of water and ammonical solution in later stages. Deacidification was done in following manner. After 20–25 times washing carbon was treated with liquid aqueous ammonia solution in such a fashion that it does not affect the surface properties. Then activated carbon was dried to 60°C [19]. The carbonized material was sieved to <125 μm size and used for adsorption experiments. The specific surface area of the activated carbon was measured by N_2 gas adsorption at −196°C (COULTER-SA3100). BET equation was used to calculate the specific surface area. The physical characteristics of the adsorbent are given in Table 1.

2.3. Adsorption experiments

Equilibrium batch adsorption studies were carried out by exposing the activated carbon from *Date stone* to aqueous solutions of lead and zinc of different concentrations in 100 mL. Erlenmeyer flasks at 20 ± 2°C. A 0.5 g of activated carbons were added to 100 mL of solution. This amount of activated carbon and solution assured that an equilibrium condition was reached. Experiments were carried out at initial pH values ranging from 2 to 8.4. The initial pH of the solution was adjusted to the desired value either by 0.1 M HNO_3 acid or 0.1 M NaOH solution.

Table 1
Main characteristic of the adsorbent.

Parameters	DSAC
BET surface area (m^2 g^{-1})	307.8
Iodine number (mg g^{-1})	202
Methylene blue number (mg g^{-1})	76
Bulk density	0.74
Acidic surface functional groups (mmol g^{-1})	0.72

The flasks were placed in a constant temperature shaker bath for 10 h to ensure that equilibrium was reached. Following the exposure of activated carbons to lead or zinc ion, the samples were collected for analysis. The solutions were filtered through slow filter paper (Whatman No. 42), and the supernatants were determined by a Shimadzu AA6500, atomic absorption spectrometer (AAS) with lead/zinc hallow cathode lamp and air acetylene flame.

Isotherm studies were recorded by varying the initial concentrations of heavy metal solutions from 10 to 100 mg/L for lead and zinc. The amount of metal ion sorbed by activated carbon (*qe*) in the sorption system was calculated using the mass balance:

$$qe = \frac{(C0 - Ce) \times V}{m} \, . \tag{1}$$

Eq. (1) where *qe* (mg g^{-1}) is the equilibrium adsorption capacity, *C*0 and *Ce* are the initial and equilibrium concentrations (mg/L) of lead and zinc ions in solution, *V* (l) is the volume aliquot adsorbate, and *m* (g) is the weight of the adsorbent.

The lead and zinc percent removal (%) was calculated using the following equation:

$$\text{Removal (\%)} = \frac{(C0 - Ce)}{C0} 100 \, . \tag{2}$$

3. Results and discussions

3.1. Effect of pH

The effect of pH on the sorption capacity can be attributed to the chemical form of heavy metals in the solution at a specific pH, i.e. pure ionic metal form or hydroxyl-metal form. At low pH, the metals ions are present in the form of M^{2+} and $M(OH)^+$. This lead to an effective competition between H^+ and H_3O^+. Aqueous speciation of lead and zinc as a function of pH was studied at 30 and 10 mg L^{-1} of the respective metal in the nitrate form using the computer program Visual MINTEQ, Version 2.30. Below pH 8.0, Pb occurs predominantly as Pb^{2+} and $Pb(OH)^+$. Besides Pb^{2+} and $Pb(OH)^+$, a nitrate species $PbNO^{+3}$ is also present in a significant amount up to pH 6.5, after which its concentration starts decreasing. Small amounts of other Pb species ($Pb(NO_3)_2$(aq), $Pb_4(OH)_4^{4+}$, and $Pb_2(OH)^{3+}$) also occur in solution, but their concentration does not significantly change over the entire pH range. Zinc occurs predominantly as Zn^{2+}. The concentration of Zn^{2+} starts to decrease after pH ≈ 7.5 in both the systems. Other Zn species ($ZnNO^{+3}$, $Zn(NO_3)_2$(aq), $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$, and $Zn_2(OH)^{3+}$) occur at negligible concentrations under the solution conditions of our experiments.

In addition, due to different functional groups on the biosorbent surface, which become active sites for the metal biding at a specific pH, the effect of pH on sorption can vary substantially. In order to establish the effect of pH on the sorption of Pb^{2+} and Zn^{2+} ions, the batch equilibrium studies at different pH values were carried out in the range of 2–8 for the two metals (Fig. 1) shows that the maximum uptake of lead by activate carbon from aqueous solution was observed at pH 6.0 and the maximum uptake of zinc ions occurred at a pH 7.0. Several researchers [20–22] also noted a similar phenomenon with other biosorbents; maximum uptake at pH close to 6.0. This means that at higher H^+ concentration, the biosorbent surface becomes more positively charged, thus, reducing the attraction between adsorbent and metal ions. In contrast as the pH increases, more negatively charged surface become available, thus, facilitating greater metal uptake [23]. At a higher pH, the lead and zinc ions precipitated as their hydroxides which decreased the rate of adsorption and subsequently the percent removal of metal ions.

3.2. Effect of contact time

The removal of lead and zinc ions increases with time and attains saturation in about 60 min. Basically, the removal of sorbate is rapid, but it gradually decreases with time until it reaches equilibrium. Figs. 2 and 3 represents the percent removal of Pb^{2+} and Zn^{2+} ions versus the contact time for the initial concentration and by using the optimum pH value which was obtained for the two heavy metals. The main plot in Figs. 2 and 3 shows that at temperature of 20 ± 2°C, the lead and zinc removal rate could generally divided into two steps. A rapid initial uptake of heavy metal ions is observed at the period of

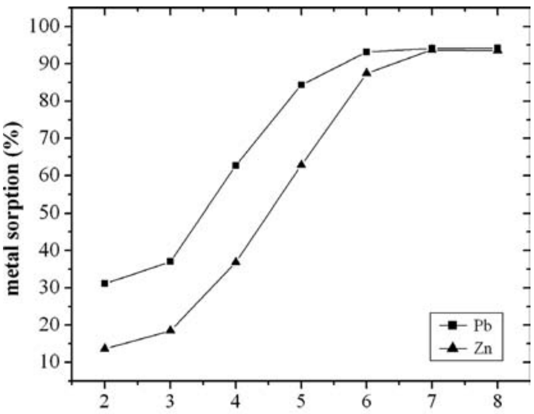

Fig. 1. Effect of pH on removal of lead and zinc from aqueous solution by activated carbon from *Dates stone* at T = 20°C, S/L = 0.5/100 mL.

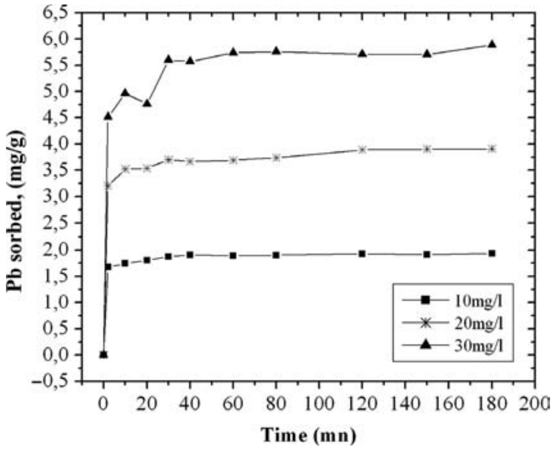

Fig. 2. Effect of contact time for the adsorption of lead ions onto activated carbon from *Dates stone* at T = 20°C, pH = 6, S/L = 0.5g/100 mL.

less than 10 min. This may primarily be ascribed to a rapid attachment of lead and zinc ions to the surfaces of the activated carbon. After this period of time, the adsorption rate becomes slower, which is probably due to the diffusion of the heavy metal ions into the pores of the sorbent [24].

3.4. *Effect of adsorbent concentrations*

The results of the experiments with varying adsorbent concentrations are presented in Fig. 4. With increase in the adsorbent concentration, from 0.2 to 10.0 g dm^{-3}, the amount of adsorbed Pb^{2+} removal increases from 41.8% to 92.5% and from 24.8% to 84.1% for Zn^{2+}. This increase is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent, i.e. with increasing adsorbent dosage more surface area is available for the adsorption due to increase in active sites on the adsorbent and its availability for adsorption, making easier penetration of ions to the adsorption sites and that increasing this number had also no effect after equilibrium was reached.

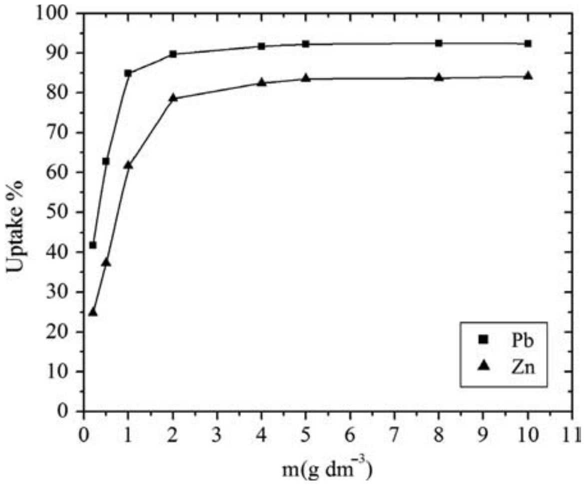

Fig. 4. Effect of adsorbent concentration for the adsorption of lead and zinc ions onto activated carbon from *Date stone* at 20°C, *C*0 = 30 mg/L, pH = 6.

3.5. *Effect of initial metal ion concentration*

The metal uptake mechanism is particularly dependent on the initial heavy metal concentration: at low concentrations, metals are adsorbed by specific sites, while with increasing metal concentrations the specific sites are saturated and the exchange sites are filled [25]. Fig. 5 shows the effect of metal concentration on the percent removal of lead and zinc ions. It is clear that

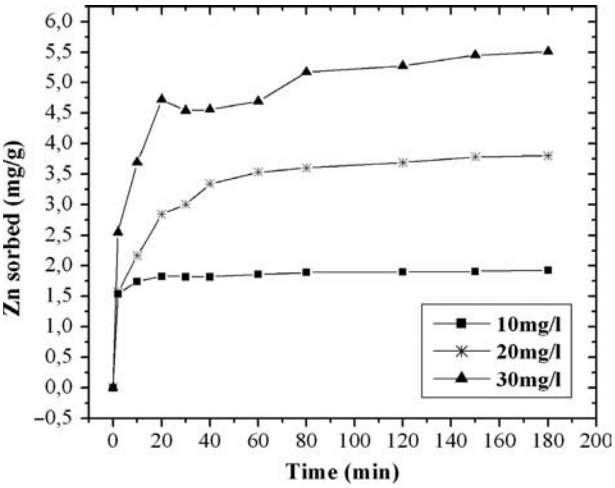

Fig. 3. Effect of contact time for the adsorption of zinc ions onto activated carbon from *Dates stone* at T = 20°C, pH = 7, S/L = 0.5g/100 mL.

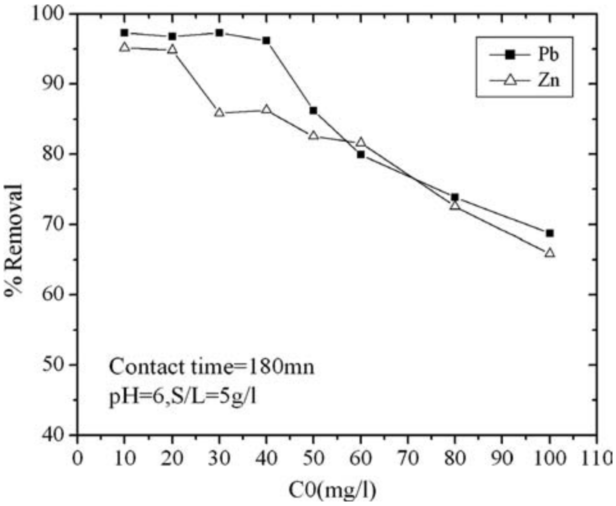

Fig. 5. Effect of initial metal concentration on the adsorption of heavy metals onto activated carbon from *Date stone* at 20°C.

with increasing initial concentrations, the percent metal removal decreases.

3.6. Kinetic models

In order to investigate the mechanism of adsorption, two kinetic models were considered as follows. Lagergren proposed a pseudo-first-order kinetic model. The integral form of the model is

$$\ln(qe - qt) = \ln qe - K_{pf}t. \quad (3)$$

Table 2
Kinetic parameters for the adsorption of Pb^{2+} and Zn^{2+} ions onto activated carbon by *Date stone* at various initial concentrations.

Metals	C_0(mg/L)	First-order kinetic model		Second-order kinetic model	
		K_{pf} (L min^{-1})	R^2	K_{ps} (g mg^{-1} min^{-1})	R^2
Pb^{2+}	10	0.021	0.716	0.515	0.999
	20	0.026	0.923	0.116	0.999
	30	0.013	0.574	0.079	0.998
Zn^{2+}	10	0.016	0.877	0.823	0.997
	20	0.028	0.963	1.796	0.999
	30	0.012	0.874	1.321	0.995

R^2 = correlation coefficient.

Eq. (3),where q_t is the amount adsorbed (mg/g) at time *t* (min), *qe* is the amount adsorbed (mg/g) at equilibrium, and K_{pf} is the equilibrium rate constant of pseudo-first-order adsorption (l min^{-1}). The straight line of the plot of $\ln(qe - qt)$ versus time (Figs. 6 and 7) suggest the applicability of the Lagergren equation for the present system [26]. The values of K_{pf} were determined from the slope of the plots and are given in Table 2. Recently, Ho and Mc Kay [27] have reported that most of the sorption systems followed a second-order kinetic model which can be expressed as

$$\frac{t}{q_t} = \frac{1}{K_{ps}q_e^2} + \frac{1}{q_e}t \, . \quad (4)$$

Eq. (4), where K_{ps} is the pseudo-second order rate constant of adsorption. The plots of t/q_t versus *t* curves (Figs. 8 and 9) were used to determine the rate constants and correlation coefficients. Table 2 shows the pseudo-second-order rate constants and correlation coefficients for removal of lead and zinc from aqueous solutions.

The calculated correlation coefficients are less than 0.963 for the first-order kinetic model, whereas the values of the correlation coefficient are greater than 0.995 for the pseudo-second-order kinetic model; therefore, the adsorption kinetics could be well explained and approximated

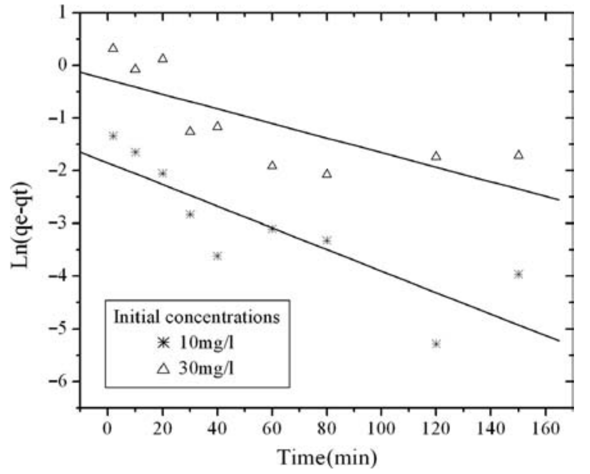

Fig. 6. Kinetics of lead removal according to the Lagergren model at initial lead.

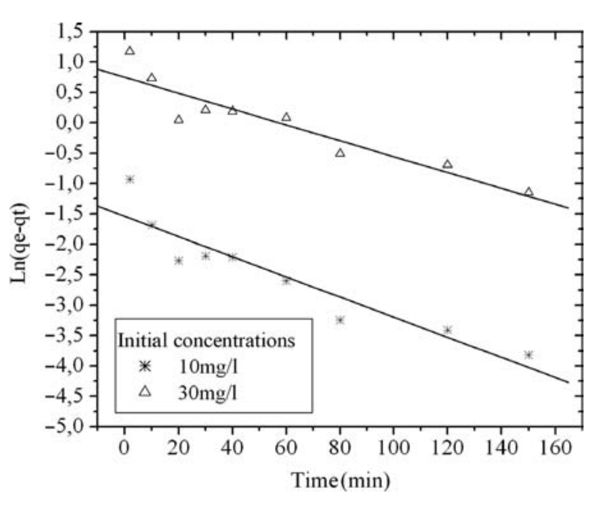

Fig. 7. Kinetics of zinc removal according to the Lagergren model at initial zinc.

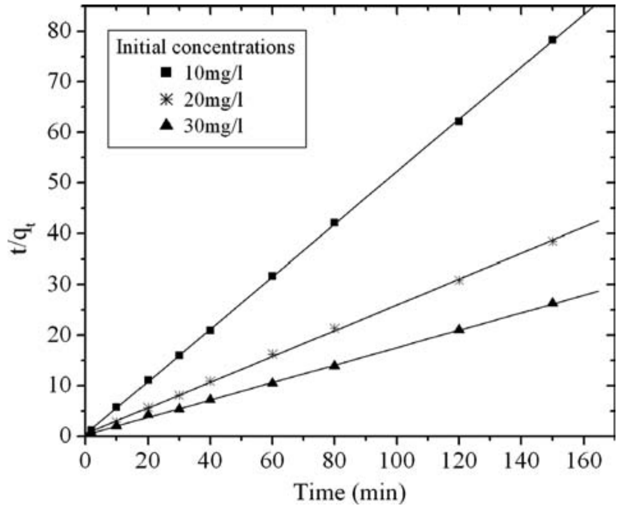

Fig. 8. Kinetics of lead removal according to pseudo-second-order model at initial lead concentration of 10, 20, and 30 mg/L.; pH = 6; S/L = 0.5g/100 mL.

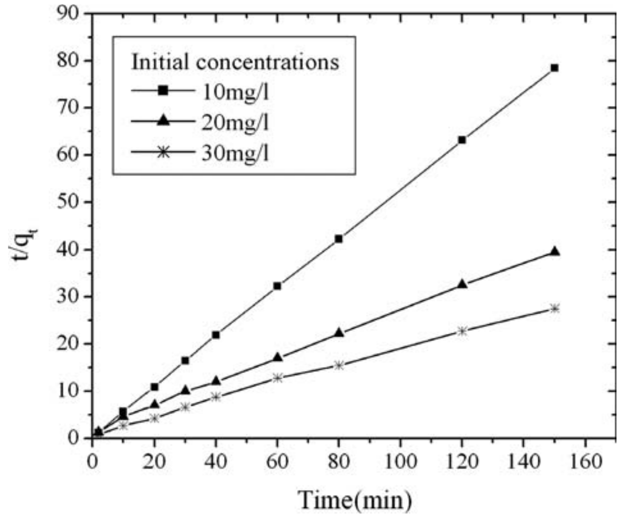

Fig. 9. Kinetics of zinc removal according to pseudo-second-order model at initial zinc concentration of 10, 20, and 30 mg/L; pH = 6; S/L = 0.5 g/100 mL.

more favorably by the pseudo-second-order kinetic model for the activated carbon from *Date stone*. Hence, the pseudo-second-order equation is useful for the kinetic studies in the present investigation.

3.7. Adsorption isotherms

In order to successfully represent the equilibrium adsorptive behavior, it is important to have a satisfactory description of the equation state between the two phases composing the adsorption system. Several isotherm equations are available and two important isotherms are chosen in this study, which are namely the Langmuir and Freundlich isotherms:

Langmuir isotherms. The linear form of the Langmuir isotherm equation [28], which assumes a maximum in the sorption of the target element, is defined as follows:

$$\frac{1}{q_e} = \left(\frac{1}{q_{\max}}\right) + \left(\frac{1}{q_{\max} K_l}\right)\frac{1}{Ce} \cdot \qquad (5)$$

Eq. (5), where q_{max} is the adsorption capacity (mg g^{-1}), or monolayer capacity, and K_l, the Langmuir constant (L mg^{-1}) related to the free energy of adsorption.

Freundlich isotherms. This model represents an ideal situation, which does not include the possible saturation of the sorption sites. The linear form of the Freundlich isotherm equation [29] is defined as follows:

$$\ln qe = \ln K_f + 1/n \ln Ce. \qquad (6)$$

Eq. (6), where the intercept ln K_f is a measure of adsorbent capacity, and the slope $1/n$ is the sorption intensity. The effect of isotherm shape has been used [30] with a view to predict whether an adsorption system is favorable or unfavorable. 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 [30]:

Table 3
Different values of R^L at different concentrations of lead and zinc.

Metals	Concentrations (mg/L)	R_L
Pb^{2+}	10	0.2004
	20	0.1113
	30	0.0771
Zn^{2+}	10	0.1101
	20	0.0582
	30	0.0396

$$R_L = 1/(1 + K_l C_0). \qquad (7)$$

Eq. (7), where K_l is the Langmuir constant. The R_L values for the adsorption of lead and zinc on different initial concentrations (10, 20 and 30 mg/L) are listed in Table 3. The R_L values between 0 and 1 show (Table 3) that the adsorption is favorable [31].

The linearized Langmuir and Freundlich isotherms of lead and zinc are shown in Figs. 10–11. The estimated model parameters with correlation coefficient (R^2) for the different models are shown in Table 4. From the values of R^2 summarized in Table 4 it may be concluded that both equations fit reasonably well the experimental data, although the equation Freundlich provides a better fit than the Langmuir one.

The calculated adsorption capacities for lead and zinc were 19.64 and 10.41 mg g^{-1}, respectively. Freundlich

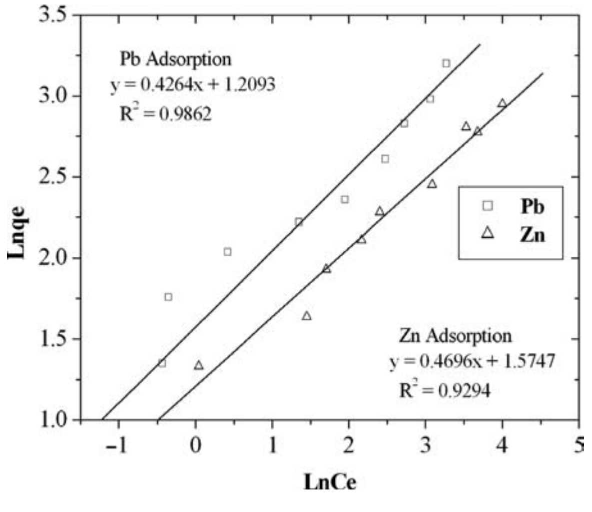

Fig. 10. Langmuir isotherms plot for lead and zinc adsorption onto activate carbon from *Datte stone*; T = 20 ± 2°C, S/L = 0.5 g/100 mL, pH = 6.0.

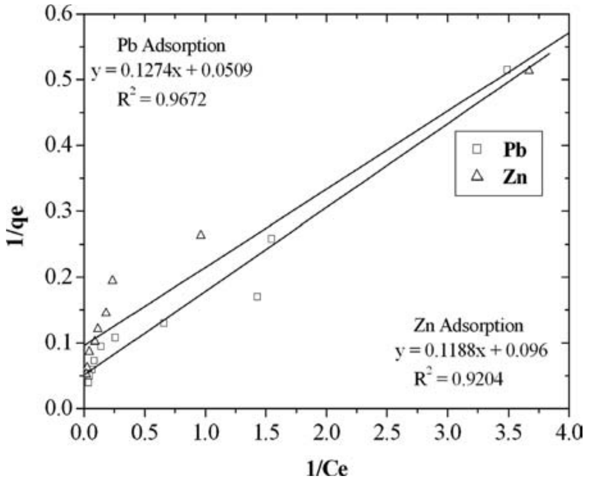

Fig. 11. Freundlich plots for the adsorption of Pb^{2+} and Zn^{2+} onto activate carbon from *Date stone*, T = 20 ± 2°C, S/L = 0.5 g/100 mL, pH = 6.0.

Table 4
Freundlich and Langmuir constants.

Metals	Freundlich constants			Langmuir constants		
	K_f	$1/n$	R^2	q_{max}(mg g^{-1})	K_l	R^2
Pb^{2+}	4.83	0.4696	0.9294	19.64	0.399	0.9672
Zn^{2+}	3.35	0.4264	0.9862	10.41	0.808	0.9204

Table 5
Maximum sorption capacities for Zn and Pb sorption to different biosorbents.

Biosorbents	Pb^{2+} (mg g^{-1})	Zn^{2+} (mg g^{-1})	Reference
Zoogloea ramigera	10.4	–	[32]
Aspergillus flavus	13.5	–	[33]
Sawdust	3.19	–	[34]
Coir	18.9	8.6	[35]
Barley straw	–	5.3	[36]
Coniferous bark	–	7.4	[37]
Bone powder	55.3	–	[38]
Fly ash	–	46.6	[39]
Date stone	19.64	10.41	This study

model is characterized by $1/n$ the hetrerogeneity factor; hence, it is applicable to sorption on hetrogenous surfaces, i.e., surface with non-energetically equivalent sites. The values of $1/n$ between $0.1<1/n<1.0$ represent good adsorption of metal onto the sorbent [31]. The other Freundlich constant K_F indicates the adsorption capacity of the adsorbent and the values of K_F at equilibrium, thus for an equilibrium concentration of 1 mg/L of Pb^{2+} and Zn^{2+}, one gram of sorbent can remove 4.83 and 3.35 mg of Pb^{2+} and Zn^{2+} respectively at 20 ±2°C.

Table 5 present the comparison of sorption capacity (q_{max}) of DSAC for Pb^{2+} and Zn^{2+} ions with that of various Adsorbents reported in literature [32–37]. The sorption capacity of DSAC for Pb^{2+} and Zn^{2+} is higher than that of the majority of other Adsorbents mentioned.

4. Conclusion

The following conclusion can be drawn based on investigation of Pb^{2+} and Zn^{2+} removal by activate carbon derived from *Date stone.*

1. Activated carbon prepared from chemically treated *Dates stone* appears to be an effective adsorbent for the removal of lead and zinc ions from aqueous solutions.
2. The amount (expressed as a percent) of adsorbed lead and zinc ions are dependent on its initial concentrations, the amount of adsorbent, time contact and pH of the metals solution, the optimum pH was 6.0 for Pb^{2+} and 7.0 for Zn^{2+}.
3. The adsorption kinetics indicates that the equilibrium time is, in all cases, below 60 min. The results show that the pseudo-second-order mechanism is predominant and that chemisorption might be the rate-limiting step that controls the adsorption process.
4. The adsorption isotherm of lead and zinc conformed to equation better Freundlich than Langmuir equation. The maximal adsorption capacity (q_{max}) of lead and zinc on *Date stone* was calculated as 19.64 mg g^{-1} and 10.41 mg g^{-1} respectively. *Date stone* showed a stronger affinity to lead than to zinc.

It may be concluded from above results that activated carbon from *Date stone* can be used for the elimination of heavy metal pollution from wastewater since it is a low-cost, abundant and locally available adsorbent.

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