



Study of the Adsorption of Heavy Metal (Pb) at batch conditions in Aqueous Solution onto Apricot Stone as low cost Adsorbent.

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Abstract. In the present study, batch experiments were carried out to elucidate the potential of Apricot stone activated carbon ASAC to remove Pb^{2+} ions from aqueous solution. ASAC was characterized by Bruanauer, Emmett and Teller surface area $S = 80.08$ (m^2/g), Fourier transform infrared spectroscopy and scanning electron microscopy. The Effects of various process parameters such as initial pH (2-14), adsorbent dose (5-45 g/L) initial metal ion concentration (20–0 mg/L), contact time (0-90 min), Agitation speed (100-700 rpm) and temperature (298-323k) were investigated in their respective range and their optimum conditions were ascertained. The Adsorption kinetics was analyzed by the pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion kinetic models. It was found that the adsorption of the metal ions followed pseudo-second-order kinetic model. The Adsorption isotherms were modeled with Langmuir, Freundlich, Temkin, Hasley and Harkins models and their isotherm constants were calculated. The Freundlich model fits the data with a monolayer adsorption capacity of 166.813 mg/g at pH 8. The thermodynamic parameters such as the Gibb's free energy, enthalpy and entropy were calculated to predict the nature of adsorption process. The calculated thermodynamic parameters showed that the adsorption of Pb^{2+} ions on ASAC is endothermic ($\Delta H^0 = 121.38$ KJ/mol) and not spontaneous ($\Delta G^0 > 0$) in nature.

Keywords: Apricot stone, Heavy metal, Isotherm, Removal, Thermodynamic, Equilibrium, Modeling.

1. Introduction

The effects of heavy metals like lead, mercury, copper, zinc and cadmium on the human health have been extensively studied and well documented. Excessive ingestion of such metals can cause accumulative poisoning, cancer, nervous system damage, etc [1, 2]. We are interested by lead which is ubiquitous in the environment and hazardous at high level [3]. It is a general metabolic poison and enzyme inhibitor [4] and can accumulate in bones, brain, kidney and muscles. Long-term drinking water containing lead causes serious disorders, like anemia, kidney disease and mental retardation. Effluents contaminated by heavy metals are commonly produced from many industrials processes and the residues in contaminated habitats may accumulate in microorganisms, aquatic flora and fauna,

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which in turn, enter into the human body through the food chain, thus resulting in health problems [5, 6]. So its removal from aqueous medium is necessary because of frequent appearance of this metal in wastewaters from industrial activities. Lead is a common industrial metal that has become widespread in air, water and soil. Lead is widely used in the storage batteries, gasoline additives and other chemicals, ammunition (shot and bullets), solder, and other uses and the world production exceeds 3 million tons per year. The presence of heavy metals in the aquatic environment has been of great concern for the scientists and engineers because of their increased discharge, toxic nature, and other adverse effects on receiving waters. In this respect, the excessive utilization of lead has dramatically raised its concentration in blood. In order to insure a better quality of life and protect the environment, removing lead from industrial wastes is of vital importance. Unlike organic compounds, lead is non-biodegradable and, therefore, must be removed from water [7]. In this regard, various methods have been developed and the adsorption with activated carbon is a simple and common used technique. Increasingly stringent standard on the quality of drinking water has stimulated a growing effort for exploiting new efficient adsorbents. Among various treatment, the adsorption onto activated carbon is one of the most effective and reliable physicochemical methods [8]. However, commercially available activated carbons are usually derived from coal or wood, and therefore are relatively expensive [9]. Hence, there is a need to produce low cost and effective carbons that can be applied for the water depollution [10]. A wide variety of inexpensive materials, have been exploited for the lead removal from aqueous medium, including kaolinite [11] and bentonite [12]. Many investigations [13] showed that apricot stone activated carbon (ASAC) is a promising material for the elimination of metals by adsorption. It was also reported that the adsorption process was strongly influenced by the pH and contact time. This research is centered on gaining more information to understand the chemical and physical phenomena associated with the binding of lead to apricot stone activated. Agricultural by-products exist in large amounts and about 20.000 tonnes of apricot stones per year are produced in Algeria [14], which represents consequently a solid pollutant to the environment. Over the past, these by-products were used as fuel in rural areas but currently the preparation of activated carbon is considerably encouraged. Apricot stone is a cheap precursor for activated carbon source. Therefore, it is important to evaluate its performance as adsorbent. The apricot production in Algeria is increasing sharply and this has prompted us to think of recycling apricot kernels for the development of activated carbons that will be used for the elimination of both organic and mineral pollutants, the physical and chemical activations mode are somewhat different from those of previous works, which influences porosity and specific surface. In addition the origin of the apricot stone and the atmospheric climate at harvest time is an important parameter that influences the chemical composition. This work has been undertaken in the field of the environment to evaluate the application potential of activated carbon prepared from apricot stone as a low-cost adsorbent for the removal of toxic pollutants. The wastewater has long been a major environmental problem all over the world and is further aggravated by rapid industrialization, population growth and unskilled use of natural water resources. The advantages of the adsorption reside in the simplicity of the operation, low cost compared to other separation methods and no sludge [15], the adsorption is also an efficient and economic processes. Therefore, this study deals with the adsorption ability of ASAC for the removal of lead from synthetic aqueous solutions. The influence of the operating parameters such as initial Pb^{2+} concentration, pH, temperature, adsorbent dose, particle size and contact time on ASAC is explored.

2. Experimental

2.1 Materials and methods

Analytical grade reagents are used in all experiments. Apricot stones obtained from Boumerdes region (30 km east Algiers), are air-dried, crushed and screened to obtain two fractions with geometrical mean sizes ranging from 63 μ m to 2mm. 100 g of the selected fraction are impregnated with concentrated H₃PO₄ (85 %) and air-dried. Then it is activated in a hot air oven at 250°C (4 h). The carbonized material is washed with distilled water to remove the free acid until the pH reached 6.8 and dried at 105 °C. The clean biomass is mechanically ground and sifted to get powders of different particle sizes: < 63 μ m to 2mm.

2.2 Determination of zero point charge pH (zpc)

The zero point charge pH_(zpc) of ASAC, i.e the pH for which the surface charge is zero, is determined using a procedure similar to that described elsewhere [16]. 20 mL of KNO₃ solutions (0.01 M) are placed in closed conical flasks; the pH of each solution is adjusted between 2 and 14 by adding HCl or NaOH solution. Then, 0.1 g of ASAC is added and the final pH is measured after 24 h under agitation at room temperature. The pH_(zpc) is the final pH versus initial pH crosses the line at final pH = initial pH.

2.3 Batch mode adsorption studies

The effects of the experimental parameters such as, the initial Pb²⁺ concentration (20-80 mg/L), pH (2-14), adsorbent dose (5-45 g/L) and temperature (298-323 K) on the adsorptive removal of Pb²⁺ is studied in batch mode for a specific period of contact time (0-90 min). The stock solution is prepared by dissolving the accurate amount of PbSO₄.7H₂O (99 %, Merck) in distilled water and other solutions are prepared by dilution. pH is adjusted with HCl (0.1) or NaOH (0.1 M). For the kinetic studies, desired quantity of ASAC is contacted with 20 mL of Pb²⁺ solutions in Erlenmeyer flasks. The flasks are then placed on a rotary shaker at 250 rpm and the samples are taken at regular time intervals and centrifuged (3000 rpm, 10 min). The Pb²⁺ content in the supernatant is determined using Flamme Atomic Absorption Spectrometry (FAAS, model Perkin Elmer 2380). The amount of Pb²⁺ adsorbed on activated carbon q_t (mg/g) is calculated by using the following equation Eq.1:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad \text{Eq.1}$$

Where C₀ is the initial Pb²⁺ concentration and C_e the Pb²⁺ concentrations (mg/L) at any time, V the volume of solution (L) and m the mass of the activated carbon (g). Due to the inherent bias resulting from the linearization of the isotherm and kinetic model, the non-linear regression (Root Mean Square Error, RMSE) evaluated Eq.2 is used as criterion for the quality of fitting [16].

$$\text{RMSE} = \sqrt{\frac{1}{N-2} \cdot \sum_{i=1}^N (q_{e,\text{exp}} - q_{e,\text{cal}})^2} \quad \text{Eq.2}$$

Where, $q_{e(\text{exp})}$ (mg/g) is the experimental value of uptake, $q_{e(\text{cal})}$ the calculated value of uptake using a model (mg/g), and N the number of observations in the experiment (the number of data points). The Sum of Error Squares (SSE) is widely used in the literature to test the validity of each model that has been used. The SSE is given by equation Eq.3 [17]:

$$SSE = \frac{1}{N} \sum_{i=1}^N (q_{e,\text{exp}} - q_{e,\text{cal}})^2 \quad \text{Eq.3}$$

The chi-square statistic is given by Eq.4.

$$X^2 = \sum_{i=1}^N \frac{(q_{e,\text{exp}} - q_{e,\text{cal}})^2}{q_{e,\text{cal}}} \quad \text{Eq.4}$$

If the data from the model are similar to the experimental ones, X^2 is small. Conversely, if they are different, X^2 becomes large. The small the RMSE and X^2 values, the better the curve fitting [18].

3. Results and Discussion

The physical and chemical properties of ASAC and the elementary analysis are summarized in **Table 1** and the optimization study of operating conditions such as Effect of ASAC size, pH, stirring speed, adsorbent dose were used the determined the adsorption isotherm.

The adsorption capacity of Pb^{2+} increases over time and reaches a maximum after 20 min of contact time and thereafter, tends toward a constant value indicating that no more Pb^{2+} ions are further removed from the solution. The equilibrium times averages 40 min but for practical reasons the adsorption experiments are run up to 60 min. With raising the initial Pb^{2+} concentration (C_0) from 20 to 80 mg/L, the amount of Pb^{2+} adsorbed increases from 3.83 to 20.95 mg/g (**Fig.1**). The Pb^{2+} ions are adsorbed initially on the external surface area of ASAC which makes the adsorption rate easy and fast. When the external surface is saturated, the Pb^{2+} ions entered into the pores and absorb on the internal surface of the particles and such phenomenon takes relatively longer contact time. Similar behaviour was reported in the literature [19]. This may be attributed to an increase of the driving force due to the concentration gradient with increasing C_0 in order to overcome the mass transfer resistance of Pb^{2+} ions between the aqueous and solid phases. Therefore, a higher initial Pb^{2+} concentration C_0 increases the adsorption capacity.

Table 1: Physical and chemical properties of the ASAC

	C : 48.45	H : 6.03	N : 0.44	O : 45.08
pH _{zpc}	7.06			
Surface area (m ² /g)	88.05			
Average pore diameter (Å)	176.3			
Average pore volume (mL/g)	0.264			
Conductivity (μS/cm)	112			
Humidity (%)	1.48			
The rate of ash (%)	1.68			
The percentage of organic matter (%)	98.32			

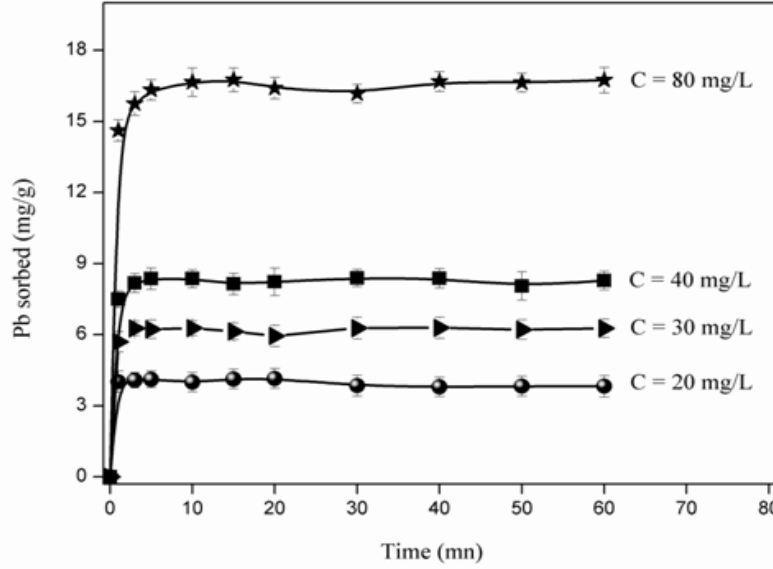


Figure 1: Effect of initial concentration on the adsorption of Pb^{2+} by ASAC (pH: 8, particle size: [315-800] μm , adsorbent dose: 5 g/L, stirring speed: 250 rpm, contact time: 60 mn and temperature: 298 K).

3.1 Adsorption Isotherms

The shape of the isotherms is the first experimental tool to diagnose the nature of a specific adsorption. The isotherms are generally classified in four main groups: L, S, H, and C shapes according to Giles et al [20]. In our case the isotherm of Pb^{2+} on ASAC displays an L shape (**Fig.2**). The initial part of the L curve indicates a small interaction between Pb^{2+} and adsorption sites at low concentrations but when the concentration C_0 in the liquid phase increases, the adsorption occurs more readily. Such behaviour is due to a synergistic effect with the adsorbed Pb^{2+} , facilitating the uptake of additional ions as a result of attractive interactions adsorbate-adsorbate.

Four models have been tested for the adsorption equilibrium: Langmuir, Freundlich, Temkin (resp. eqs. 5,6 and 7) are used in the present study and their applicability is compared. The linear forms are represented by the following equations:

$$\frac{1}{q_e} = \frac{1}{q_{max}} - \frac{1}{q_{max} \cdot K_L \cdot C_e} \quad \text{Eq.5}$$

Where C_e is the equilibrium concentration (mg/L), q_{max} the monolayer adsorption capacity (mg/g) and K_L the Langmuir constant related to the free adsorption energy (L/mg)

$$\ln q_e = \ln K_F + \frac{1}{n} \cdot \ln C_e \quad \text{Eq.6}$$

K_F is a constant indicative of the adsorption capacity (L/g) and n an empirical constant related to the adsorption driving force.

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e = B \ln A + B \ln C_e \quad \text{Eq.7}$$

C_e is the equilibrium concentration (mg/L), A_T and b are the Temkin constants, R the universal gas constant and q (mg/g) the Langmuir adsorption capacity.. The theoretical parameters of adsorption isotherms along with the regression coefficients, RMSE, SSE and X^2 are listed in **Table 2**. The small the RMSE and X^2 values, the better the curve fitting.

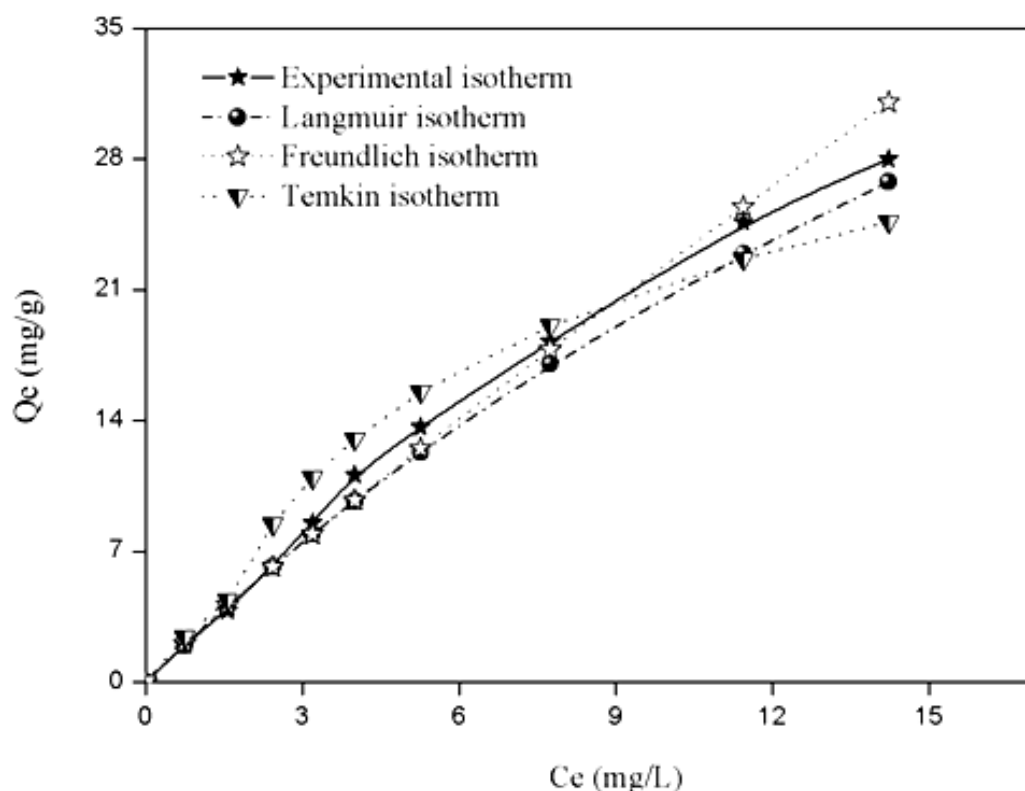


Figure 2: Adsorption isotherm of lead by ASAC. (pH : 8, particle size : [315-800] μm , adsorbent dose : 5 g/L, stirring speed : 250 rpm, contact time : 40 mn and temperature : 298 K).

The favourable nature of adsorption can be expressed in terms of dimension less separation factor of equilibrium parameter is defined by equation Eq.8 [21]:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad \text{Eq.8}$$

The R_L value indicates the type of isotherm: ($R_L = 0$): irreversible, ($0 < R_L < 1$): favourable, ($R_L = 1$): linear,

($R_L > 1$): unfavourable. In this study, R_L lies between 0.383 to 0.756 over the C_0 range (20-80 mg/L). R_L is less than 1, confirming that the Pb^{2+} adsorption on ASAC is favoured in both cases with the successful applicability of Langmuir isotherm.

Table 2: Sorption isotherm coefficients of Langmuir, Freundlich, Temkin and Harkins, Hasley models.

Model	Langmuir	Freundlich	Temkin	Hasley	Harkins
	$Q_{\max} = 166.813 \text{ mg/g}$ $K_L = 0.01612 \text{ L/mg}$	$1/n = 0.91345$ $K_F = 2.7456 \text{ mg/g}$	$B_T = 9.17196$ $\Delta Q = 45.054 \text{ kJ/mol}$ $A_T = 1.033$	$n = -0.916$ $K_H = 0.3037 \text{ mg/g}$	$A = 14.49$ $B = 1.94$
R^2	0.9973	0.9908	0.9079	0.95236	0.5728
RMSE	3.0032	2.8135	3.4907	766.35	125.01
SSE	9.0191	7.9160	18.1849	587307.6	15627.5
χ^2	0.1011	0.1026	0.2072	11.64	69.97

3.2 Adsorption kinetics

The kinetic study is important for the adsorption process because not only it describes the uptake rate of adsorbate, but controls the residual time of the whole process. Two kinetic models namely the, pseudo first order and pseudo second-order are selected in this study to describe the adsorption process.

The pseudo first order equation is given by [22]:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} \cdot t \quad \text{Eq.9}$$

While the pseudo second order model [23] is given by:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \cdot t \quad \text{Eq.10}$$

Where q_t (mg/g) is the amount of Pb^{2+} adsorbed on ASAC at the time t (min). K_1 (min^{-1}) and K_2 ($\text{g/mg} \cdot \text{min}$) are the pseudo-first order and pseudo-second order kinetics constants respectively. The rate constants, predict the uptakes and the corresponding correlation coefficients for ASAC summarized in **Table 3**.

Table 3: Pseudo-first order and pseudo-second order kinetic model constants for the adsorption of Pb^{2+} ions onto ASAC

Pseudo-second order kinetic					Pseudo-first order kinetic		
Co	$q_{e,\text{exp}}$	$q_{e,\text{cal}}$	K_2	R^2	$q_{e,\text{cal}}$	K_1	R^2
(mg/L)	(mg/g)	(mg/g)	(g/mgmin)		(mg/g)	(mn^{-1})	
30	6.250	6.27	1.499	0.999	0.583	0.139	0.950
40	8.300	8.33	2.996	0.999	0.731	0.312	0.884
80	16.39	16.72	0.299	0.999	1.184	0.117	0.829
100	20.01	20.92	0.524	0.999	1.045	0.096	0.897

For the pseudo-first-order kinetic, the experimental data deviate from linearity, as evidenced from the low values of q_e and C_0 . Therefore, the pseudo-first order model is inapplicable for the present system. By contrast, the correlation coefficient and $q_{e,cal}$ determined from the pseudo-second order kinetic model are in good agreement with the experimental data (**Fig.3**). The applicability of the pseudo-second-order kinetic model suggests that the adsorption Pb^{2+} onto ASAC is based on chemical reaction (chemisorption), involving an exchange of electrons between adsorbent and adsorbate. In the chemisorptions, the metal ions are attached to the adsorbent surface by chemical bond and tend to find sites that maximize their coordination number with the surface.

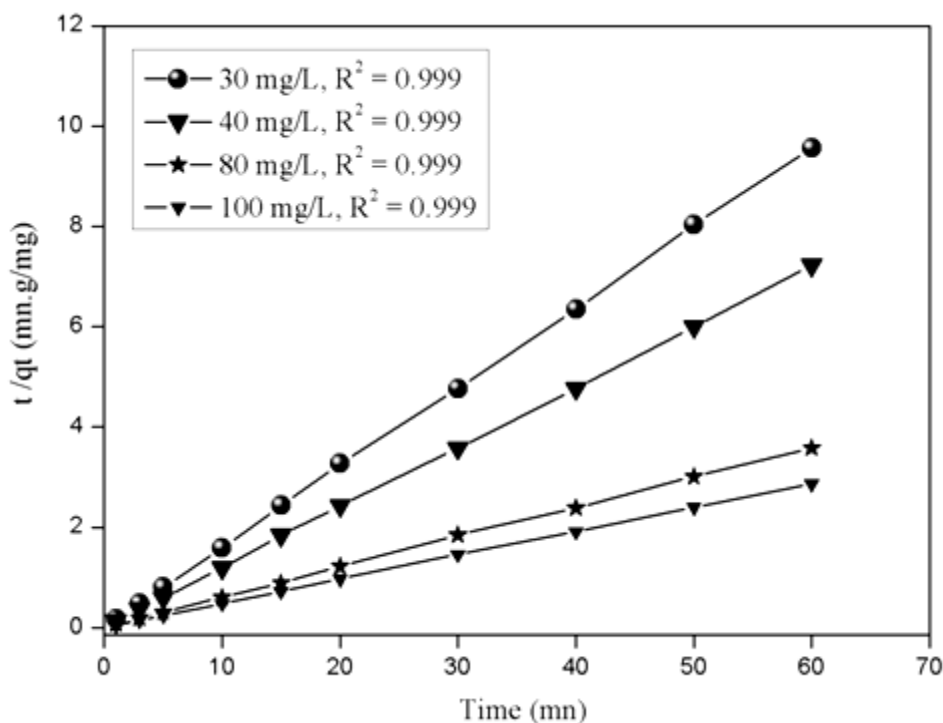
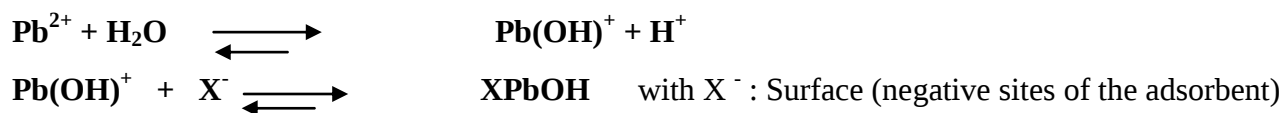
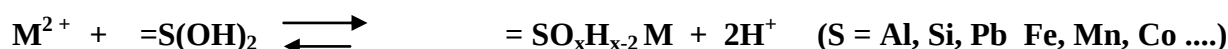


Figure 3: Pseudo second order kinetic for the adsorption of Pb^{2+} onto ASAC (pH : 8, particle size : [315-800] μm , adsorbent dose : 5 g/L, stirring speed : 250 rpm, temperature : 298 K and contact time : 40 mn).

The mechanism of the adsorption reaction of metals has been proposed to interpret the phenomenon [24].



Other mechanisms for fixing M^{2+} can be superimposed. Thus, the hydrophilic sites on the surface can, by protons exchange mechanism, form surface complexes [25].



Similarly, with increasing the adsorbent dose and adsorbate concentration the precipitation of $\text{Pb}(\text{OH})_2$ can also occur [26].

3.3 Effect of temperature

The adsorption capacity of ASAC increases with raising temperature over the range (298-323 K), above, the vaporization becomes increasing problem. The insights of the adsorption mechanism can be determined from the thermodynamic parameters: the free energy (ΔG°), the enthalpy (ΔH°) and the entropy (ΔS°). The thermodynamic equilibrium constant (K) was determined by Khan and Singh [27] by plotting $\ln(q_e/C_e)$ versus q_e and extrapolating to zero q_e . Thermodynamic parameters are determined from the following equations.

$$\Delta G^\circ = -RT \ln K \quad \text{Eq.11}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad \text{Eq.12}$$

Where, K is the equilibrium constant, C_e (mg/L) the concentration at equilibrium, T the absolute temperature (K). The plot of $\ln K$ versus $1/T$ is linear (Fig.4).

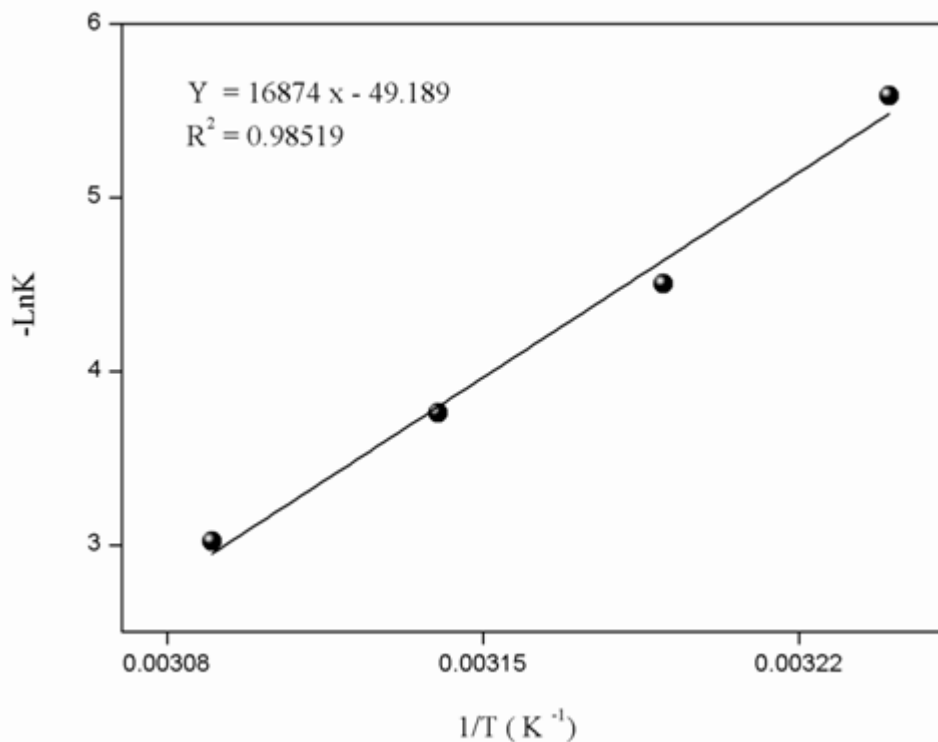


Figure 4: Thermodynamic parameters, enthalpy and entropy for the adsorption of Pb^{2+} ions onto ASAC.

The values of ΔH° and ΔS° are obtained from the slope and intercept of the Van't Hoff equation Eq.15 while the free enthalpy ΔG° at various temperatures are reported in **Table 4**.

Table 4: Equilibrium constant and thermodynamic parameters for the adsorption of Pb^{2+} ion onto ASAC
 particle size : ([315-800] μm , adsorbent dosage :5 g/L, stirring speed : 250 rpm, contact time : 40 mn, initial concentration : Co : 80 mg/L and pH : 8)

T	Ce	qe	Kc	-LnKc	1/T	ΔG°	ΔH°	ΔS°
(K)	(mg/L)	(mg/g)			(K^{-1})	kJ/mol	kJ/mol	kJ/mol K
308	0.1107	16.776	0.0014	5.208	0.00324	13.888		
313	0.8783	16.610	0.0111	4.501	0.00319	12.143		
318	1.5720	16.410	0.0233	3.759	0.00314	10.398	121.38	0.349
323	2.1013	16.170	0.0269	3.022	0.00309	8.6530		

The positive ΔG° indicates a not spontaneous process. The positive values of ΔH° and ΔS° show that the Pb^{2+} adsorption on ASAC is endothermic with an increased randomness at the solid solution interface

4. Conclusions

The present study has shown that the activated carbon prepared from apricot stone can be employed as effective and low cost adsorbent for the removal of Pb^{2+} in aqueous solution. Increasing the initial concentration and pH led to an improved adsorption capacity of ASAC. The Freundlich model provides the best fit of the equilibrium data with a maximum adsorption capacity of 166.813 mg/g at pH $\sim$ 8. The positive thermodynamic parameters indicate that the Pb^{2+} adsorption onto ASAC is endothermic and not spontaneous. The Pb^{2+} uptake follows the pseudo-second-order kinetic model, which relies on the assumption that the chemisorption is the rate-limiting step. The enthalpy (ΔH° , 40 kJ/mol) clearly indicates that Pb^{2+} is strongly attached to the adsorbent surface by forming chemical bond and tends to find sites that maximize their coordination number with the surface. The results of the present investigation showed that ASAC is a potentially useful adsorbent for the adsorption of heavy metals, an issue of environmental concern and the natural abundance of this food waste can provide an adsorption medium which contributes to the wastewater treatment. The comparison of the adsorption capacity of the prepared adsorbent with other adsorbents shows its attractive properties from industrial and economic interests.

Acetic acid has been found effective for the regeneration of adsorbent. It has been noted during the experiments in the laboratory in batch mode that the adsorbent regenerated after several washings showed a decrease the adsorption capacity by $\sim$ 30 % and can be used again efficiently for subsequent use.

The study in tiny batch gave rise to encouraging results, and we wish to achieve the adsorption tests in column mode under the conditions applicable for the treatment of industrial effluents.

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