Alkali Activated Cedar Wood as an Efficient Adsorbent for Pb$^{2+}$ Removal from Aqueous Solutions: Optimization, Kinetic and Thermodynamic Study

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Abstract
In the present study, activated carbon prepared from cedar wood was synthesized, via NaOH activation, and optimized to be used as the adsorbent for Pb$^{2+}$ removal from aqueous solutions in a batch process mode. The physicochemical properties of the synthesized adsorbent were examined by SEM, FTIR and BET analysis. In order to determine the optimum operational conditions, the effects of different parameters including pH, adsorbent dosage, contact time, temperature, and initial Pb$^{2+}$ concentration on the adsorptive performance of synthesized samples were also investigated. According to the obtained results, the highest Pb$^{2+}$ ion adsorption capacity (971.9 mg/g) took place at the optimum operational condition of pH=4, adsorbent dosage of 0.025 g/L, contact time of 60 minutes, 300 ppm of Pb$^{2+}$ and 30 ºC. The results showed that among Langmuir, Freundlich, and Temkin isotherms, the obtained data were fitted the best with the Freundlich model. Additionally, the process of Pb$^{2+}$ adsorption was consistent with the pseudo-second order kinetics model, indicating that the rate-determining step is the surface adsorption that involves chemisorption. Finally, according to the calculated thermodynamic parameters, i.e., $\Delta H^o$, $\Delta S^o$ & $\Delta G^o$, Pb$^{2+}$ adsorption on activated cedar wood can be considered as an exothermic and spontaneous process.

Keywords: Cedar wood; Adsorption isotherm; Activated carbon; Pb$^{2+}$ removal.

1. Introduction
Lack of water resources is considered as one of the most important threats to human societies and sustainable development because of economic and population growth [1]. Water shortage problem may be the most important and complicated problem in the dry and semi-arid regions of the world. Throughout history, policymakers in these areas have been trying to solve the problem of water scarcity in different ways. Water pollution is one of the important environmental problems which can be caused by heavy metals. The heavy metals produced by human activities such as industrial, mining operations, and also population increase and urbanization are non-
biodegradable in nature, even at low concentrations [2, 3]. Among different heavy metal ions, Pb\(^{2+}\) is one of the most major heavy metals which is commonly useful in many industries like battery manufacturing, smelting, paints, and paper industries [4-6]. However, Pb\(^{2+}\) may cause many damages to human health like anemia, irritability, dizziness and renal sickness [7], due to its toxicity, accumulation in food and persistence in nature [8]. It can cause severe harms to human organs like kidney, liver, brain, etc. World Health Organization has determined the allowable concentration of Pb\(^{2+}\) (0.05 mg/L) in drinking water. There are lots of methods for removing Pb\(^{2+}\) ions from aqueous solutions such as chemical precipitation/coagulation, membrane technology, electrolytic reduction, ion exchange and adsorption that had been investigated by the time [9, 10]. However, high operational cost, unaffordable on large-scale metals and being ineffective at higher concentrations make most of these methods inefficient. Adsorptive processes have been considered as one of the most common approaches in energy and environment industries because of its easy operation and low cost [11-14]. Various low-cost materials such as biomass, moss, fly ash, natural materials like clay and zeolite, clinoptilolite, and synthetic resins have been tested as adsorbent material for heavy metals removal from water samples [14-22]. Among all, activated carbons are considered the most suitable materials for heavy metal removal from wastewater [23-32].

In the current study, the activated carbon from cedar wood has been synthesized to be used as the adsorbent in Pb\(^{2+}\) removal from water samples. The synthesis parameters including impregnation ratio (NaOH/precursor), activation temperature, and activation time has been optimized. Also, the effect of operational parameters such as contact time, pH, temperature and adsorbent dosage on the adsorption capacity of the optimized adsorbent was studied. In order to describe the adsorption mechanism, Langmuir, Freundlich, and Temkin isotherms were examined and the kinetic data were modeled by adsorption kinetic models (pseudo-first-order, pseudo-second-order, and intraparticle diffusion models).

2. Materials and methods

2.1. Preparation of the adsorbent

Cedar wood was collected from Khuzestan province, Iran. The samples were completely crushed and sieved to the mesh size of 150 (less than 0.1 mm in diameter), washed with distilled water and then dried in an oven at 50 °C, for 2 h. Next, the carbonization process was carried out in a tube furnace under a nitrogen atmosphere at 500 °C, for 2 h and a heating rate of 20 °C/min. After that, the sample was mixed with NaOH/Char ratio of 2:1 and stirred for 2 h. The resulted sample dried in an oven at 80 °C for 12 h. Then, the treated mixture was heated up to 575 °C for 90 min with a heating rate of 20 °C/min. All heating steps were carried out under a nitrogen stream. In order to remove the impurities, the sample was washed in 1 M HCl aqueous solution and then neutralized with distilled water. In order to optimize the synthesis conditions, the same process as above was repeated at different conditions.

2.2. Characterization of the adsorbent
The morphology of the adsorbent surface was studied using a scanning electron microscope (SEM, JSM – 6700 F model, made in Japan) analysis. In order to identify the surface functional groups, Fourier transform infrared spectroscopy (FTIR) analysis was conducted. Also, BET surface area, pore diameters, and pore size distribution according to BET MP-method were estimated using N₂ adsorption/desorption at the boiling point of nitrogen. For this purpose, a TriStar II 3020 instrument (Micromeritics Co. USA) was used.

2.3. Determination of point of zero charge (pH\text{pzc})

The point at which the electrical charge density on an adsorbent surface is zero is called the isoelectric point (pH\text{pzc}). It is important to specify this point in order to determine the adsorbing-surface properties, in the way that increasing pH resulted in an increased negative surface charge; therefore, positive ions can easily adsorb and conversely [33]. This experiment was conducted to find out the best range of pH for the adsorption process. At First, 20 mL of 0.01 M NaCl solution was set on pH value (pH\text{H}) of 2, 0.01 g of absorbent was added, remained intact for 72 h and then the final pH value (pH\text{f}) of the solution was measured by a pH meter (HI8915 HANNA – made in USA). This test was repeated for different pH values from 3 to 11. By plotting pH\text{f} - pH\text{i} versus pH\text{i}, the cross point of the curve with the horizontal Axe, represents the pH\text{pzc} of activated carbon samples.

2.4. Effect of operational conditions

To examine the effect of operational parameters (i.e. pH, temperature, and adsorbent dosage) on the performance of activated carbon, 100 mL of Pb(NO₃)₂ solution (100 ppm) was poured in 500 mL beaker and the pH adjusted at a certain value. Then 0.025 g of adsorbent powder was added to the solution under vigorous stirring and at a controlled temperature. After equilibrium time, the adsorbent was filtered and separated from the solution. Then 5 mL of each sample were tested to determine the concentration of Pb²⁺ by atomic adsorption apparatus.

2.5. Adsorption studies

The adsorption capacity of activated carbon samples and the removal efficiency of the Pb²⁺, were calculated using the Equations 1 and 2, respectively.

\[
q_e = \frac{c_0 - c_e}{m} \times V
\]

\[
\%\text{Removal efficiency} = \frac{C_0 - C_e}{C_0} \times 100
\]

Here, \(C_0\) and \(C_e\) are the initial and equilibrium concentration of Pb²⁺ (mg/L) respectively, \(V\) is solution volume (L) and \(m\) is the adsorbent mass (g).

The adsorption kinetics of Pb²⁺ were assessed using the adsorption models of pseudo-first-order, pseudo-second-order, and intraparticle diffusion. Furthermore, different adsorption isotherm models including Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich were used to
describe the adsorption equilibrium. Thermodynamic parameters of Pb\(^{2+}\) adsorption were calculated using Van’t Hoff equation.

3. Results and Discussions

3.1. Textural characterization of the adsorbent

Scanning electron microscope (SEM) is often used to examine the morphological features and adsorbent pore shapes [34]. The morphology and structure of synthesized sample after adsorption of Pb\(^{2+}\) ions is shown in Fig. 1. SEM image revealed a highly porous structure of the adsorbent. The Porosity and Surface area characteristics of the adsorbent were estimated by BET method (see Table 1). The BET surface area and micropore area were found to be 2125 and 1989 m\(^2\)/g respectively. The N\(_2\) adsorption/desorption isotherms and the pore size distribution diagram of the sample is shown in Figs. 2a and 2b. The lack of hysteresis in N\(_2\) adsorption/desorption isotherms suggest that the synthesized adsorbent has a microporous structure, which is also along with pore size distribution observed in fig. 2b. According to table 1, more than 85% of total pore volume belongs to pores with diameter lower than 2nm, strongly confirms the results in figure 2. Besides physical properties such as the surface area and pore shape parameters, some chemical specifications such as surface functional groups affect adsorption capabilities of activated carbon. FTIR spectra (Fig. 3) demonstrates the functional groups responsible for heavy metal ions (Pb\(^{2+}\)) adsorption on the nanostructured activated carbon. A peak around 1631 cm\(^{-1}\) can be ascribed to C=C and C=O stretching vibrations of anhydride, lactonic or carboxyl groups [35-39]. An adsorption band located at 3471 cm\(^{-1}\) is assigned to O-H stretching vibration of hydrogen-bonded hydroxyl groups or adsorbed water [40-42]. The band at 1385 cm\(^{-1}\) can be attributed to C-H bending vibration of alkanes. These data prove the presence of some oxygen-containing groups on the surface which may act as the adsorption sites on the surface of activated carbons interacting with Pb\(^{2+}\) ions.

3.2. The effect of synthesis parameters

3.2.1. Impregnation ratio

The ratio of the chemical activation agent, i.e. NaOH, to the carbonized material (impregnation ratio) has a profound influence on the final structure of activated carbons. Fig. 4 shows changes in adsorption capacity with different impregnation ratios. The results revealed that the adsorption capacity increases continuously with the increasing NaOH/Char ratio, till reaching a maximum at the impregnation ratio of 4:1. Nevertheless, above this ratio, the adsorption ratio declines slightly, due possibly to the pores widening and the reduction in the specific surface area [27]. Also, at the ratios lower than the maximum, the adsorption capacity is not high enough due to the lack of porosity [43].

3.2.2. Activation temperature

Figure 5 shows the effect of activation temperature on the Pb\(^{2+}\) adsorption capacity of the synthesized activated carbons. As it can be seen here, the highest adsorption capacity happens at
650 °C. In fact, such a high carbonization temperature causes a large amount of non-carbonaceous species to be eliminated from the solid structure from cellulosic source, i.e. walnut shell powder. This can deeply improve the porosity and final sorption capacity [44]. While at temperatures higher than the optimum (i.e. 650 °C), the rate of oxidation reactions between surface carbon atoms and NaOH are too high, which may cause micro-pores to be converted into meso/macro-pores with a smaller surface area and lower adsorption capacity [45]. At lower temperatures, the adsorption capacity is not abundant due to the slow rate of oxidation reactions.

3.2.3. Activation time
During synthesis procedure, the activation time (t_{act}) is an important parameter affecting final adsorption capacity of activated carbons. Fig. 6 represents the effect of activation time on the performance of activated carbons in Pb^{2+} removal from water samples. According to the results presented here, the adsorption capacity reached 454 mg/g at the optimum tact of 60 min. So, according to the results in fig. 6, it seems that the activated carbon synthesized at t_{act} = 1h, T_{act}= 650K, and impregnation ratio of 4:1 shows better performance in Pb^{2+} removal from water, comparing to the samples synthesized at other conditions. However, the final performance of the adsorbents is still deeply dependent on the operational conditions in which the Pb^{2+} ion is adsorbed.

3.3. The effect of operational conditions
3.3.1. Determination of point of zero charge (pH_{pzc})
The results of the pH_{pzc} experiment are presented in fig. 7a. According to the pH_{f}-pH_{i} values reported in this figure, the pH_{pzc} is likely to be at pH 4, which is very close to the pH_{pzc} reported by Hafshejani et al. on carbonized cedar leaf, i.e. 3.76 [39]. At pH higher than pH_{pzc} = 4 the surface of the synthesized activated carbon is negatively charged, which is preferable for adsorption of metal cations, i.e. Pb^{2+}, than anionic species [46, 47]. While, the condition is more favorable for adsorption of anionic groups at pH values lower than pH_{pzc}, where the surface of the adsorbent is covered by positively charged species.

3.3.2. Effect of pH
The pH of the solution is one of the most critical factors in adsorption processes because it could affect the solubility of metal ions, the degree of ionization of ion species during the reaction, the electrostatic bonding of ions to the relevant functional groups and the number of metal ions on the functional groups of the adsorbent surface [33, 48]. Fig. 7(b) shows the effect of pH on the adsorption of Pb^{2+} by the adsorbent. Results demonstrate that at the range of pHs lower than 3, the adsorption capacity is low due to the high concentrations of hydronium ions that compete with Pb^{2+} ions to adsorb onto adsorbent surface. The adsorption capacity intensively increases with increasing pH from 3 to 4. Although the Pb^{2+} removal increases at pH higher than 5, it seems that the higher removal performance is due to formation of precipitation of metal complexes at higher pH values rather than adsorption of Pb^{2+} ions. In fact, the adsorption of Pb^{2+}
decreases at high pH values, due to the increase in the concentration of hydroxyl ions and the formation of the complex with the Pb$^{2+}$ ions in the solution. As a result, in the range of pH values higher than 5, there is a strong possibility of precipitation [48]. Hence, the pH value of 4 is selected as the optimal point due to the reduction of positive surface charges and the increase in the negative charge density of the adsorbent [49].

3.3.3. Equilibrium time
The equilibrium contact time is the time required for the adsorption process to reach the equilibrium. To determine the equilibrium time for Pb$^{2+}$ adsorption process, the adsorption capacity was measured during the time (Fig. 8). According to the results, the equilibrium time is estimated 60 min, when the adsorption data become steady during the time. In fig. 8, the adsorption capacity of the adsorbent is found to increase sharply with the contact time during the first 30 minutes, just before the adsorption capacity leveled off at its highest amount. Then, the rate of adsorption declines gradually till the equilibrium to be reached. The fast adsorption rate at the beginning of the experiment may be explained by the large difference between the chemical potential of the vacant active sites on the surface and that in the bulk of the solution. This leads to a high driving force for mass transfer, from the bulk to the surface, increasing the absorption rate at the beginning [50, 51].

3.3.4. Determination of optimum amount of adsorbent
Adsorbent dosage is crucial for estimating of the amount of adsorbent required for complete removal of a certain amount of metal ions from the solution [52]. In order to obtain the optimum adsorbent dosage of synthesized activated carbons, the adsorption capacities of Pb$^{2+}$ at different dosages of adsorbent is depicted in fig. 9. The Experiments were performed at different adsorbent concentrations from 0.025 to 0.1 g and the initial Pb$^{2+}$ concentration of 100 mg/L. All data were recorded at 25 °C, and the optimum pH of 5.

The results in Fig. 9 revealed that the maximum adsorption is related to the lowest initial amount of adsorbent with no optimum point, i.e. 0.025 g. According to the results, it is found that the adsorption capacity decreased with increasing the adsorbent dose. It seems normal that adsorption capacity increases with increasing adsorbent dosage as more adsorption sites are available. However, the reasons that are usually presented to explain the negative effect of increasing the adsorbent dose is that when the amount of activated carbon in the solution increases, activated carbon beads begin to accumulate and form large clusters, which It reduces the available contact surface, resulting in a decrease in the amount of adsorbed ion [53].

3.3.5. Effect of temperature
Temperature is an environmental parameter that significantly affects the adsorption capacity of heavy metals. Fig. 10, represents the adsorption capacity of Pb$^{2+}$ at different temperatures. According to the results reported here, the adsorption capacity declined from 362.9 mg/g to 234.0 mg/g when the temperature increased from 30 to 50 °C, indicating that the adsorption of
Pb\(^{2+}\) on the synthesized activated carbon is an exothermic process. Therefore, lowering the temperature over the adsorption process of lead is thermodynamically desirable. In fact, the physical bonds between adsorbed species and surface active sites might weaken at higher temperatures leads to lower adsorption capacity [33, 54, 55].

3.3.6. Effect of initial concentration of metal ion

Fig. 11 shows the adsorption capacity of Pb\(^{2+}\) ions as a function of initial concentration of adsorbate. According to this figure, Pb\(^{2+}\) heavy metal uptake rises from 28.13 to 971.96 mg/g by increasing the initial concentration of Pb\(^{2+}\) ions from 25 to 300 mg/L. This can be attributed to the fact that a higher initial metal ion concentration not only provides a noticeable driving force to overcome the mass transfer resistance of the Pb\(^{2+}\) ions between the bulk and solid surface but also increases the number of collisions between metal ions and adsorbent, which enhances the adsorption capacity overall [56].

3.4. Kinetics and equilibrium studies

3.4.1. Adsorption Kinetics

In order to determine the kinetic parameters of adsorption, different adsorption isotherms i.e. pseudo-first-order model (Equation 3), pseudo-second-order model (Equation 4) and intraparticle diffusion model (Equation 5) were examined. The related equations are shown as follows [55, 57]:

\[
\log \left( q_e - q_t \right) = \log \left( q_e \right) - \frac{k_1}{2.303} t \\
\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \\
q_t = k_id t^{1/2} + C
\]

Where, \(q_t\) (mg/g) and \(q_e\) (mg/g) are the adsorption capacity of activated carbon at arbitrary time, \(t\) (min) and at equilibrium time respectively. \(k_1\) (1/min), \(k_2\) (g/mg min) and \(k_id\) (mg/g min\(^{1/2}\)) are the adsorption rate constants of pseudo-first-order equation, pseudo-second-order equation, and intra-particle diffusion equation, correspondingly. \(C\) (mg/g) is intra-particle diffusion constant i.e. intercept of the line.

The diagrams for each kinetic model were plotted (Fig. 12) and the results were tabulated in Table 2. By comparing the linear correlation coefficient \((R^2)\) and normal standard deviation \((\Delta\delta^2)\) of applied models, the pseudo-second-order model, with \(R^2>0.90\), and the minimum standard deviation shows the best fit with empirical data. This is in a good compliance with what reported in the literature for adsorption of Pb\(^{2+}\) on different adsorbent [3, 32, 38, 39]. The pseudo-second-order model assumes: a) monolayer adsorption, b) the same adsorption energy for each adsorbent and independent of surface coverage, c) adsorption occurs only at localized sites and does not involve any interactions between adsorbed pollutants, and d) The rate of adsorption is almost negligible compared to the initial adsorption rate [55]. The consistency of the pseudo-second-
order model with experimental data in this study indicates that the rate-determining step is the surface adsorption that involves chemisorption [58].

3.4.2. Adsorption isotherms
Equilibrium relationships between the amount of Pb\textsuperscript{2+} ions adsorbed on the samples and its concentration remained in the solution at a constant temperature can be described by adsorption isotherms. In this study, three extensively equilibrium adsorption isotherms, the Langmuir, Freundlich, and Temkin model were used to analyze the experimental equilibrium data obtained for the adsorption of Pb\textsuperscript{2+} ions onto the adsorbent (Fig. 13). Also, the parameters of each model have been summarized in Table 3.

The linear form of theoretical Langmuir isotherm is given as (Equation 6):

\[
\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m}
\]

where \(q_m\) (mg/g) is the monolayer adsorption capacity, and \(K_L\) is Langmuir equilibrium constant (1/mg). Both are calculated by plotting \(1/q_e\) versus \(1/C_e\) (Fig. 13a). To evaluate the Langmuir isotherm, a separation factor (\(R_L\)) (Equation 7) is defined as follow:

\[
R_L = \frac{1}{1 + K_L C_0}
\]

Where \(C_0\) is the highest initial solute concentration. The nature of the adsorption process is indicated by the value of the separation factor, i.e. the process can be irreversible (\(R_L=0\)), unfavorable (\(R_L>0\)), favorable (0< \(R_L<1\)) or linear (\(R_L=1\)) [59]. Considering the value of \(R_L=0.021\) shown in Table 3, confirms the favorable adsorption of Pb\textsuperscript{2+} ions on the prepared samples.

The empirical Freundlich isotherm assumes the non-ideal sorption on heterogeneous surfaces [60] and its linear form equation (Equation 8) is expressed as below:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

where \(K_F\) (g\textsuperscript{-1}) is Freundlich constant and \(1/n\) is the heterogeneity factor and both of them are determined by plotting \(\ln(q_e)\) against \(\ln(C_e)\) (Fig. 13b). As the value of heterogeneity factor is below unity (1/n=0.281), the adsorption process type is inferred as chemisorption [61].

Temkin and Pyzhev represented the following equation (Equation 9) which presumes that heat of adsorption of the molecules in the layer would decline linearly with coverage due to the adsorbate/adsorbent interactions and ignoring very low and very large values of concentration:

\[
q_e = BlnA_T + BlnC_e \quad ; \quad B = \frac{RT}{b}
\]

Where \(A_T\) and \(B\) are the Temkin constants.

By comparing the linear correlation coefficient (\(R^2\)) of the summarized data in Table 3, it seems that the Freundlich isotherm model provides the best fit with the empirical data for the adsorption of Pb\textsuperscript{2+} ions (\(R^2=0.998\)).
3.4.3. Determination of thermodynamic parameters

The thermodynamic parameters, i.e., standard free energy ($\Delta G^\circ$), standard enthalpy change ($\Delta H^\circ$), and standard entropy change ($\Delta S^\circ$) can describe the nature of adsorption. The standard enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) were calculated from the following Van’t Hoff equation (Equation 10):

$$\ln \left( \frac{q_e}{C_e} \right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$ (10)

Where $R$ is the universal gas constant, and $T$ is temperature in Kelvin. The Van’t Hoff plot of Pb$^{2+}$ ions adsorption onto the synthesized adsorbent is represented in Fig. 14. The Gibbs free energy was obtained from the equation below (Equation 11):

$$\Delta G^\circ = \Delta H^\circ + \Delta S^\circ$$ (11)

The calculated thermodynamic parameters are listed in Table 4. The negative enthalpy ($\Delta H^\circ$) value of -119.72 (kJ mol$^{-1}$) indicates that the interactions between Pb$^{2+}$ ions and the adsorbent are exothermic. The entropy was found negative too, suggesting that the Pb$^{2+}$ ions adsorption is a reversible process. Also, the negative values of Gibbs free energy indicate the favorable thermodynamics and spontaneous nature of the process. The increase in $\Delta G^\circ$ values from -90.64 to -83.44 (kJ mol$^{-1}$) with the temperature suggests the feasibility of the Pb$^{2+}$ removal at lower temperatures, preferable for industrial applications.

4. Conclusion

In the current survey, activated carbon obtained from cedar tree was synthesized using NaOH to be applied as a new and efficient adsorbent for Pb$^{2+}$ heavy metal ions. In order to study morphology, surface species, and the micropore structure of the synthesized activated carbon SEM, FTIR, and BET analysis have been conducted. The effect of different parameters such as pH, temperature, equilibrium time, and initial concentration of Pb$^{2+}$ ions on final adsorption capacity were also investigated. The maximum adsorption of Pb$^{2+}$ was 971.9 mg/g which has been achieved at optimum condition of the pH=5, contact time of 60 minutes, adsorbent dosage of 0.025 g/L, temperature of 30 °C, and metal ion concentration of 300 ppm. Among Langmuir, Freundlich, and Temkin isotherm models, the experimental data were fitted the best with the Freundlich model. The process of Pb$^{2+}$ ions adsorption was well simulated with the pseudo-second-order kinetics model, indicating that chemical adsorption is the dominant mechanism of adsorption. The negative thermodynamic parameters ($\Delta H^\circ$, $\Delta S^\circ$ & $\Delta G^\circ$) confirmed that Pb$^{2+}$ adsorption is an exothermic and spontaneous process. According to the results reported here, the nanostructured activated carbon from cedar wood can be considered as a promising adsorbent for Pb$^{2+}$ ions and other heavy metals from aqueous solutions.

References


Biographies

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**Figure Captions:**

**Fig. 1** SEM photographs of the synthesized activated carbon at different resolutions

**Fig. 2** (a) N$_2$ adsorption/desorption isotherms, and (b) Pore size distribution diagram of the synthesized activated carbon.

**Fig. 3** FTIR spectrum of the synthesized activated carbon

**Fig. 4** The effect of impregnation ratio on the adsorption capacity of Pb$^{2+}$ on the synthesized activated carbons. The samples were prepared at Activation temperature = 900°C and Activation time 90 min. the adsorption measurements were conducted at Adsorbent Dosage= 0.001 g$_{adsorbent}$/100 ml, Pb$^{2+}$ concentration= 100 ppm, Temperature= 20°C.

**Fig. 5** The effect of activation temperature on the adsorption capacity of Pb$^{2+}$ on the synthesized activated carbons. The samples were prepared at Activation time 90 min and Impregnation Ratio of 4:1. The adsorption measurements were conducted at Adsorbent Dosage= 0.001 g$_{adsorbent}$/100ml, Pb$^{2+}$ concentration= 100 ppm, Temperature= 20°C.

**Fig. 6** The effect of activation time on the adsorption capacity of Pb$^{2+}$ on the synthesized activated carbons The samples were prepared at Activation Temperature of 650°C and Impregnation Ratio of 4:1. The adsorption measurements were conducted at Adsorbent Dosage= 0.001 g$_{adsorbent}$/100ml, Pb$^{2+}$ concentration= 100 ppm, Temperature= 20°C.

**Fig. 7** (a) pH$_{pzc}$ of the activated carbon derived from cedar wood and, (b) The effect of pH on the adsorption capacity of Pb$^{2+}$ on the synthesized samples (Adsorbent Dosage= 0.1 g$_{adsorbent}$/100ml, pH=2; 3; 4; 5, Pb$^{2+}$ concentration= 100 ppm, Temperature = 20°C).

**Fig. 8** The effect of contact time on the adsorption capacity of Pb$^{2+}$ on the synthesized activated carbons (Adsorbent Dosage= 0.025 g$_{adsorbent}$/100ml, pH=4, Pb$^{2+}$ concentration= 100 ppm, Temperature = 20°C).

**Fig. 9** The effect of adsorbent dosage on the adsorption capacity of Pb$^{2+}$ on the synthesized activated carbons (Adsorbent Dosage= 0.025; 0.05; 0.075; 0.1, g$_{adsorbent}$/100ml, pH=4, Pb$^{2+}$ concentration= 100 ppm, Temperature = 20°C).

**Fig. 10** The effect of temperature on the adsorption capacity of Pb$^{2+}$ on the synthesized activated carbons (Adsorbent Dosage= 0.025 g$_{adsorbent}$/100ml, pH=4, Pb$^{2+}$ concentration= 100 ppm, Temperature= 30; 40; 50°C ).

**Fig. 11** The effect of initial concentration of Pb$^{2+}$ ion on the adsorption capacity of Pb$^{2+}$ on the synthesized activated carbons (Adsorbent Dosage= 0.025 g$_{adsorbent}$/100ml, pH=4, Pb$^{2+}$ concentration= 25; 50; 100; 200; 300 ppm, Temperature=30°C).

**Fig. 12** Kinetic models for adsorption of Pb$^{2+}$ on the synthesized activated carbons: (a) Pseudo-first-order model (b) Pseudo-second-order model (c) Intra-particle diffusion model
Fig. 13 Adsorption isotherm models for adsorption of Pb$^{2+}$ on the synthesized activated carbons: (a) Langmuir (b) Freundlich (c) Temkin

Fig. 14 The Van’t Hoff plot of Pb$^{2+}$ adsorption on the synthesized activated carbon.

Table Captions:
Table 1 Characteristics of the synthesized activated carbon.
Table 2 Parameters of kinetic models for the adsorption of Pb$^{2+}$ on the synthesized activated carbon
Table 3 Parameters of isotherm models used for the adsorption of Pb$^{2+}$ of the synthesized activated carbon
Table 4 Thermodynamics parameters of Pb$^{2+}$ adsorption of the synthesized activated carbon
Fig. 1 SEM photographs of the synthesized activated carbon at different resolutions
Fig. 2 (a) $\text{N}_2$ adsorption/desorption isotherms, and (b) Pore size distribution diagram of the synthesized activated carbon.
Fig. 3 FTIR spectrum of the synthesized activated carbon
Fig. 4 The effect of impregnation ratio on the adsorption capacity of Pb\textsuperscript{2+} on the synthesized activated carbons. The samples were prepared at Activation temperature = 900°C and Activation time 90 min. the adsorption measurements were conducted at Adsorbent Dosage= 0.001 g\textsubscript{adsorbent}/100 ml, Pb\textsuperscript{2+} concentration= 100 ppm, Temperature= 20°C.
Fig. 5 The effect of activation temperature on the adsorption capacity of Pb$^{2+}$ on the synthesized activated carbons. The samples were prepared at Activation time 90 min and Impregnation Ratio of 4:1. The adsorption measurements were conducted at Adsorbent Dosage= 0.001 g$_{\text{adsorbent}}$/100ml, Pb$^{2+}$ concentration= 100 ppm, Temperature= 20°C.
Fig. 6 The effect of activation time on the adsorption capacity of Pb$^{2+}$ on the synthesized activated carbons. The samples were prepared at Activation Temperature of 650°C and Impregnation Ratio of 4:1. The adsorption measurements were conducted at Adsorbent Dosage = 0.001 g$_{adsorbent}$/100ml, Pb$^{2+}$ concentration = 100 ppm, Temperature = 20°C.
Fig. 7 (a) $pH_{pzc}$ of the activated carbon derived from cedar wood and, (b) The effect of pH on the adsorption capacity of Pb$^{2+}$ on the synthesized samples (Adsorbent Dosage= 0.1 g$_{adsorbent}$/100ml, pH=2; 3; 4; 5, Pb$^{2+}$ concentration= 100 ppm, Temperature = 20°C).
Fig. 8 The effect of contact time on the adsorption capacity of Pb$^{2+}$ on the synthesized activated carbons (Adsorbent Dosage= 0.025 g$_{adsorbent}$/100ml, pH=4, Pb$^{2+}$ concentration= 100 ppm, Temperature = 20°C).
Fig. 9 The effect of adsorbent dosage on the adsorption capacity of Pb$^{2+}$ on the synthesized activated carbons (Adsorbent Dosage= 0.025; 0.05; 0.075; 0.1, g$_{\text{adsorbent}}$/100ml, pH=4, Pb$^{2+}$ concentration= 100 ppm, Temperature = 20°C).
Fig. 10 The effect of temperature on the adsorption capacity of Pb\(^{2+}\) on the synthesized activated carbons (Adsorbent Dosage= 0.025 g\(_{\text{adsorbent}}/100\text{ml}, \text{pH}=4, \text{Pb}\(^{2+}\) concentration= 100 ppm, Temperature= 30; 40; 50°C ).
Fig. 11 The effect of initial concentration of Pb\(^{2+}\) ion on the adsorption capacity of Pb\(^{2+}\) on the synthesized activated carbons (Adsorbent Dosage= 0.025 g\(_{\text{adsorbent}}\)/100ml, pH=4, Pb\(^{2+}\) concentration= 25; 50; 100; 200; 300 ppm, Temperature=30\(^{\circ}\)C).
Fig. 12 Kinetic models for adsorption of Pb\(^{2+}\) on the synthesized activated carbons: (a) Pseudo-first-order model (b) Pseudo-second-order model (c) Intra-particle diffusion model
Fig. 13 Adsorption isotherm models for adsorption of Pb\(^{2+}\) on the synthesized activated carbons: (a) Langmuir (b) Freundlich (c) Temkin
Fig. 14 The Van’t Hoff plot of Pb$^{2+}$ adsorption on the synthesized activated carbon.
Table 1 Characteristics of the synthesized activated carbon.

<table>
<thead>
<tr>
<th>$S_{BET}$ (m² g⁻¹)</th>
<th>Micropore area (m² g⁻¹)</th>
<th>External surface area (m² g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
<th>Micropore volume (cm³ g⁻¹)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2125</td>
<td>1989</td>
<td>136.8</td>
<td>0.91</td>
<td>0.78</td>
<td>1.71</td>
</tr>
</tbody>
</table>

*AC=Activated Carbon
Table 2 Parameters of kinetic models for the adsorption of Pb\(^{2+}\) on the synthesized activated carbon

<table>
<thead>
<tr>
<th>Pseudo-first-order model</th>
<th>C (mg L(^{-1}))</th>
<th>K(_1) (min(^{-1}))</th>
<th>q(_e) (mg g(^{-1}))</th>
<th>%Δδ(^2)</th>
<th>R(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.0237</td>
<td>1.177</td>
<td>212</td>
<td>0.1651</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.0356</td>
<td>4.859</td>
<td>247</td>
<td>0.826</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.0642</td>
<td>13.029</td>
<td>339</td>
<td>0.8688</td>
<td></td>
</tr>
</tbody>
</table>

**K\(_1\):** The Model Adsorption Rate Constant  
**δ\(^2\):** and normal standard deviation  
**q\(_e\):** The adsorption capacity at equilibrium  
**R\(^2\):** The linear correlation coefficient (R\(^2\))

<table>
<thead>
<tr>
<th>Pseudo-second-order model</th>
<th>C (mg L(^{-1}))</th>
<th>K(_2) (g mg(^{-1}) min(^{-0.5}))</th>
<th>q(_e) (mg g(^{-1}))</th>
<th>%Δδ(^2)</th>
<th>R(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.01971</td>
<td>80.6</td>
<td>0.034</td>
<td>0.999</td>
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<tr>
<td>50</td>
<td>0.00145</td>
<td>163.9</td>
<td>7.09</td>
<td>0.999</td>
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</tr>
<tr>
<td>100</td>
<td>0.000089</td>
<td>454.5</td>
<td>40</td>
<td>0.928</td>
<td></td>
</tr>
</tbody>
</table>

**K\(_2\):** The Model Adsorption Rate Constant  
**δ\(^2\):** and normal standard deviation  
**q\(_e\):** The adsorption capacity at equilibrium  
**R\(^2\):** The linear correlation coefficient (R\(^2\))

<table>
<thead>
<tr>
<th>Intraparticle diffusion model</th>
<th>C (mg L(^{-1}))</th>
<th>K(_{id}) (g mg(^{-1}) min(^{-0.5}))</th>
<th>C(_{id}) (mg g(^{-1}))</th>
<th>%Δδ(^2)</th>
<th>R(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.222</td>
<td>77.78</td>
<td>2.3</td>
<td>0.2696</td>
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<tr>
<td>50</td>
<td>4.625</td>
<td>113.03</td>
<td>13.3</td>
<td>0.6399</td>
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<tr>
<td>100</td>
<td>27.47</td>
<td>101.89</td>
<td>59</td>
<td>0.5726</td>
<td></td>
</tr>
</tbody>
</table>

**K\(_{id}\):** The Model Adsorption Rate Constant  
**δ\(^2\):** and normal standard deviation  
**C\(_{id}\):** intra-particle diffusion constant  
**R\(^2\):** The linear correlation coefficient (R\(^2\))
Table 3 Parameters of isotherm models used for the adsorption of Pb\(^{2+}\) of the synthesized activated carbon

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_L) (L mg(^{-1}))</td>
<td>7.197</td>
<td>K(_f) (L mg(^{-1}))</td>
<td>1.305</td>
</tr>
<tr>
<td>(q_m) (mg g(^{-1}))</td>
<td>18.08</td>
<td>n</td>
<td>3.563</td>
</tr>
<tr>
<td>(R_L)</td>
<td>0.021</td>
<td>1/n</td>
<td>0.281</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.6617</td>
<td>R(^2)</td>
<td>0.998</td>
</tr>
</tbody>
</table>
Table 4 Thermodynamics parameters of Pb$^{2+}$ adsorption of the synthesized activated carbon

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (kJ mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>-90.64</td>
<td>-199.72</td>
<td>-0.36</td>
</tr>
<tr>
<td>313</td>
<td>-87.04</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>323</td>
<td>-83.44</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>