

## Removal of lead(II) ions from aqueous solutions by adsorption onto pine cone activated carbon

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### ABSTRACT

Activated carbon prepared from the cones of the European Black pine was used as adsorbent for the removal of lead(II) ions from aqueous solutions. The effect of pH, initial concentration of lead(II) ions, contact time, and adsorbent dosage on the adsorption was studied in a batch process mode. Equilibrium data were analyzed by the Langmuir, Freundlich and Temkin isotherm model. Langmuir isotherm provided the best fit to the equilibrium data with maximum adsorption capacity of 27.53 mg/g. The kinetic data were found to follow closely the pseudo-second-order model. The microstructures of the activated carbon before and after adsorption of lead(II) ions were observed by scanning electron microscope. Textural analysis was employed in order to determine specific surface area and pore size distribution of the prepared activated carbon. Surface structure was characterized by using Fourier transform infrared spectroscopy and Boehm titration.

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### 1. Introduction

Lead is recognized as a longstanding environment contaminant. It can be found in wastewater generated by various industries such as acid battery, ceramic and glass manufacturing, metal plating and finishing, printing, tanning, and production of lead additives for gasoline.

The efforts on reducing lead concentration in the effluent wastewaters are motivated by the toxic effects of lead on the aquatic world and the risk of contamination of water resources designated for human consumption. Current USEPA drinking water standard for lead is 0.015 mg/l [1]. Acute lead poisoning in humans causes severe damage to the kidneys, liver, brain, and nervous system while a long term exposure may induce sterility, abortion, and neonatal death [2]. The removal of such a harmful ingredient from the water bodies became unavoidable. The most widely used techniques to remove lead from wastewater include ion exchange, chemical coprecipitation, reverse osmosis, evaporation, membrane filtration and adsorption [3]. Adsorption onto activated carbon was found to be a promising technique as it enables the removal of trace amounts of lead from solutions [4]. Activated carbon is a porous adsorbent with a high surface area, a great adsorption capacity and an effective regeneration. Carboxylic, carbonylic, lactonic, phenolic, aldehydic, and other organic functional groups are located at the edges of hexagonal carbon layer planes and are responsible for surface reactivity of activated carbon [5]. Ionization

of these functional groups in solution is pH dependant and leads to a build-up of a charged interface between the solid surface and the bulk of the solution [6]. The type and quantity of surface functional groups are influenced by the preparation method and by the sort of the precursor [7].

Commercial activated carbons are mostly prepared from coal, wood, peat and coconut shells [8]. However, the demand for novel and more efficient adsorbents initiated a research on low-cost, locally available and renewable materials as potential alternative precursors in activated carbon production. For this purpose, many materials such as: fruit stones [9], pyrolyzed coffee residues [10], pine bark [11], nutshells [12], and olive stones [13] were studied.

European Black pine (*Pinus nigra* Arn.) is a widespread conifer in Southern and Eastern Europe, occurring in a wide range of environmental conditions [14]. It grows up to 50 m, has dark green needles and 5–10 cm long cones with rounded scales. Large quantities of cones are produced annually throughout the world, especially in pine plantations grown for the pulp and paper industry [15]. Cones are mostly composed of lignin and resins that contain a variety of organic compounds [16]. The preparation of activated carbon from the cones of European Black pine was hardly studied and reported in the literature.

The objective of this research is to investigate the lead removal efficiency of pine cone activated carbon (PCAC) by adsorption from aqueous media. The effects of contact time, initial concentration of lead(II) ions, pH and adsorbent dosage were examined. In addition to this, structural characterization of the prepared adsorbent was performed in order to provide relations of its structure and adsorption capacity of lead(II) ions.

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## 2. Materials and methods

### 2.1. Adsorbent preparation

Powdered activated carbon was derived by thermal–chemical process from the ground pine cones collected from Cair Park in Nis, Serbia. Thirty grams of the milled cones was passed through 20 mesh sieve and impregnated with 85 wt.%  $H_3PO_4$  in the weight ratio of 1:3. The mixture was placed in a programmable muffle furnace with inert atmosphere of nitrogen and heated in two phases. The first phase included heating with the rate of 6 °C/min up to 170 °C and 60 min retention at this temperature. In the second phase temperature rose by 8 °C/min up to 500 °C where held for the next 60 min. After gradual cooling down to room temperature, the final product was repeatedly washed at the Buchner funnel with hot distilled water until the washings showed pH > 5. The washed carbon was oven-dried at 110 °C for 24 h and finally stored in a desiccator for later use.

### 2.2. Adsorbent characterization

The BET surface area measurement of PCAC sample was made by nitrogen adsorption at –196 °C using Sorptomatic 1990 (Thermo Fisher Scientific, USA). Before the measurement, the carbon sample was outgassed under a reduced atmosphere for 4 h at room temperature, then 8 h at 110 °C and then 12 h at 200 °C. Cumulative pore volume and area for mesopores were calculated using Barret–Joyner–Halenda method. The Dubinin–Radushkevich equation was applied to obtain micropore volume. The results of the textural study are given in Table 1.

The surface micrographs of PCAC samples before and after the adsorption were taken by using a scanning electron microscope JSM 5300 (JEOL, Japan). The instrument was operated at 30 kW. Prior to the analysis, the samples were dried at 110 °C for 4 h. A thin layer of gold was coated on the samples for charges dissipation.

The Boehm titration method was applied to determine the surface functional groups containing oxygen. The main principle of this method is that oxygen groups on carbon surfaces have different acidities and can be neutralized by bases of different strength. Prior to the analysis, carbon was dried in oven at 110 °C for 3 h. Then, 0.5 g samples were added to PVC bottles containing 30 ml of the following 0.1 M solutions: NaOH,  $Na_2CO_3$ ,  $NaHCO_3$ , and HCl. The bottles were sealed and shaken for 48 h to reach equilibrium. Then, the suspensions were filtered and 20 ml of the filtrates were pipetted to 100 ml

Erlenmeyer flasks and the excess base or acid was back titrated with 0.1 M standard solutions of HCl or NaOH, respectively. The number of acidic sites was calculated assuming that NaOH neutralizes carboxylic, phenolic, and lactonic groups,  $Na_2CO_3$  neutralizes carboxylic and lactonic groups, while  $NaHCO_3$  neutralizes carboxylic groups only. The number of the surface basic sites was determined from the retitration of the HCl aliquot using NaOH [17].

Organic functional groups present on PCAC surface were determined by the FTIR spectroscopy. The KBr pastille method was used for the carbon sample preparation. Dry and fine pulverized carbon weighting 1 mg was mixed with 150 mg of KBr, stored at 80 °C for 6 h, and then pressed at 200 MPa to obtain a transparent pellet. The reference measurement was performed with pure KBr. The FTIR spectrum was recorded on a BOMEM MB-100 FTIR spectrometer (Hartmann & Braun, Canada) equipped with a standard DTGS/KBr detector in the range of 4000–400  $cm^{-1}$  with a resolution of 2  $cm^{-1}$ . The spectrometer was purged with dry  $N_2$ .

Cation exchange capacity (CEC) refers to the quantity of negative charges existing on the adsorbent surface that could exchange cations. CEC determination was done by contacting 0.2 g of PCAC with 30 ml of 0.1 M NaOH in the sealed PVC bottle for 72 h. After this time, suspension was filtered and 20 ml of the filtrate was pipetted out and pH-metrically titrated using 0.1 M HCl. Calculated differences in  $Na^+$  quantity are used to express CEC value (mmol/g).

Suspension pH ( $pH_{SUS}$ ) relates with the overall acidity of the adsorbent. In the present study, 0.3 g of PCAC was suspended into 30 ml of deionized water and equilibrated for 24 h. The resulting pH was denoted as  $pH_{SUS}$ . The ash and moisture content analysis of PCAC followed ASTM D 2866-94 and ASTM D 2867-04, respectively. Gay–Lussac pycnometer was used for density determination. All of the obtained results are given in Table 1.

## 3. Experimental

The adsorption experiments were carried out by contacting precisely weighted samples of PCAC with 50 ml of lead(II) solutions in the sealed 100 ml Erlenmeyer flasks. The suspensions were magnetically stirred at 120 rpm at room temperature (25 °C). After the specified time, suspensions were filtered through filter paper Whatman 44. Concentrations of lead(II) ions in the filtrates were determined by ICP-OES spectrometer iCAP 6000 (Thermo Electron Corporation, USA) at 261.42 nm.

In order to investigate kinetics, suspensions consisting of 0.1 g of PCAC and 50 ml of 100 mg/l lead(II) solutions were stirred from 5 to 100 min.

For the adsorption isotherm studies, 0.1 g of PCAC samples was stirred with lead(II) solutions of different concentrations (50, 75, 100, 125, 150, 175 and 200 mg/l) until equilibrium was attained. On the basis of kinetic study, 60 min time was taken as the time enough to reach the equilibrium state.

With the goal to examine the influence of solution pH on the mechanism and the capacity of the adsorption, 0.1 g of PCAC was stirred for 60 min with 100 mg/l lead(II) solutions at pH values ranging from 3 to 10.

For the assessment of adsorbent dosage on adsorption, 100 mg/l lead(II) solutions were stirred for 60 min with different amounts of carbon (0.5, 1.0, 1.5, 2.0, and 2.5 mg/l).

In all the cases, the adsorption capacity,  $q$  (mg/g), was calculated by:

$$q = \frac{(C_0 - C)V}{W} \quad (1)$$

where  $C_0$  is the initial concentration of lead(II) ions,  $V$  is the volume of the solution,  $W$  is the mass of activated carbon and  $C$  is the residual concentration of lead(II) ions at equilibrium or any time  $t$ , which

**Table 1**  
Characteristics of pine cone activated carbon.

Parameter	Value
Yield (%)	55.7
$pH_{PZC}$	3.06
$pH_{SUS}$	3.51
CEC (mmol/g)	2.259
Ash (%)	6.35
Moisture (%)	2.87
Density (g/ml)	1.58
<i>Textural properties</i>	
$S_{BET}$ ( $m^2/g$ )	1094.1
Mesopore volume (ml/g)	0.701
Mesopore area ( $m^2/g$ )	481.65
Micropore volume (ml/g)	0.395
<i>Surface functional groups (mmol/g)</i>	
Acidic groups	2.958
Carboxylic	1.742
Lactonic	0.723
Phenolic	0.493
Basic groups	1.357

defines  $q_e$  or  $q_t$ , respectively. The experimental data were fitted to the kinetic and isotherm theoretical models. The best-fit model indicates the most probable adsorption mechanism.

## 4. Results and discussion

### 4.1. SEM

The SEM micrographs of PCAC samples before and after adsorption of lead(II) ions are given in Fig. 1a and b, respectively. SEM enables a direct observation of any surface microstructure changes in the samples that would have occurred due to the adsorption of lead(II) ions. Some slight differences at the micrographs are noticeable. The number and shape of cracks and attached fine particles over the carbon surface clearly differ before and after adsorption. Minor decrease in the size of the particles after adsorption is apparent. However, the effect that would cause vast changes in the pore structure of PCAC during adsorption is not present in this case.

### 4.2. Boehm titration

Table 1 summarizes the results of Boehm titration and shows that most of acidic functional groups are carboxylic, followed by lactonic and phenolic. The total number of the surface basic sites was calculated to be 1.357 mmol/g and is smaller than the total number of the acidic surface sites. This is in agreement with  $\text{pH}_{\text{SUS}}$ , which is

also acidic. Predominately acidic character of PCAC is most probably influenced by the method of carbon activation, which includes  $\text{H}_3\text{PO}_4$  as the activating agent.

### 4.3. FTIR

The FTIR spectrum of PCAC is illustrated in Fig. 2. A wide absorption band at  $3200\text{--}3600\text{ cm}^{-1}$  with a maximum at about  $3411\text{ cm}^{-1}$  is assigned to O–H stretching vibrations of hydrogen-bonded hydroxyl groups. A peak around  $1685\text{ cm}^{-1}$  can be ascribed to C=O stretching vibrations of ketones, aldehydes, lactones or carboxyl groups. This peak probably suffers minor overlapping with C=C aromatic ring stretching vibration which is usually found at  $1580\text{ cm}^{-1}$ . Aliphatic C–H stretching vibration is found as a very weak peak at  $2851\text{ cm}^{-1}$  while asymmetric vibration of  $\text{CH}_2$  group appears at  $2922\text{ cm}^{-1}$ . The strong band around  $1200\text{ cm}^{-1}$  with a shoulder around  $1080\text{ cm}^{-1}$  may originate from phosphoric compounds developed due to  $\text{H}_3\text{PO}_4$  activation. According to this, the peak at  $1173\text{ cm}^{-1}$  is attributed to the stretching vibrations of hydrogen-bonded P=O, stretching vibrations of O–C in P–O–C linkage, and P=OOH. The shoulder at  $1072\text{ cm}^{-1}$  can be ascribed to ionized linkage  $\text{P}^+\text{--O}^-$  in acid phosphate esters and to symmetrical vibration in a chain of P–O–P [18].

### 4.4. Adsorption kinetics

A kinetic study of adsorption is necessary as it provides the information about the adsorption mechanism, which is crucial for the practicality of the process. In our case, four different kinetic models were applied in order to establish which of them shows the best fit with experimentally obtained data.

The pseudo-first-order kinetic model is frequently used in kinetic studies [19]. It is expressed by the following equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where  $k_1$  (g/mg min) is the rate constant of pseudo-first-order adsorption, which is obtained from the slopes of the linear plots of  $\ln(q_e - q_t)$  versus  $t$  (Fig. 3a).

The pseudo-second-order kinetic model may be expressed by the equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where  $k_2$  (g/mg min) is the equilibrium rate constant for the pseudo-second-order adsorption and can be obtained from the plot of  $t/q_t$  against  $t$  (Fig. 3b) [20].

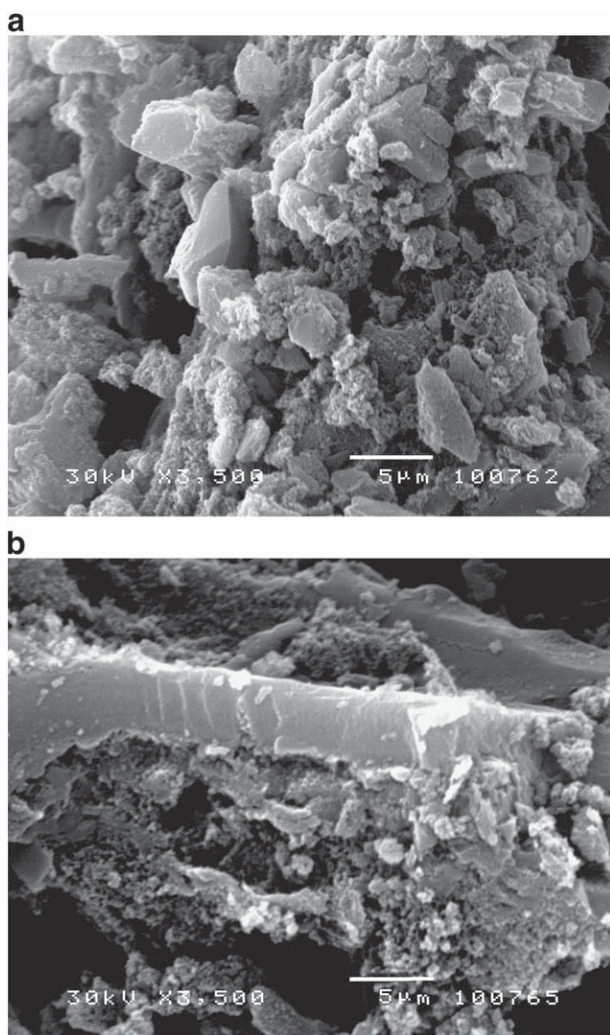


Fig. 1. SEM micrographs of the carbon particles (a) before (b) after lead(II) adsorption.

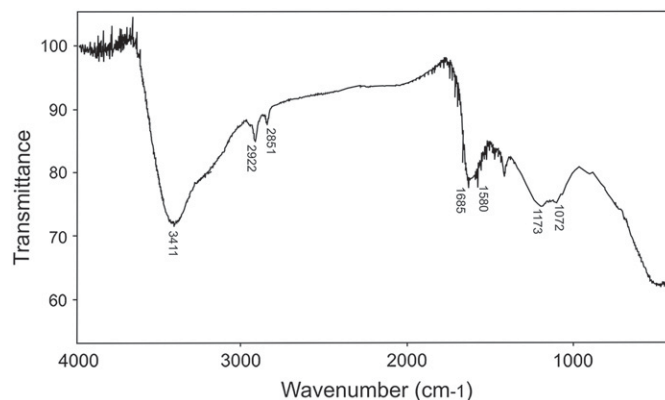


Fig. 2. FTIR spectrum of PCAC.

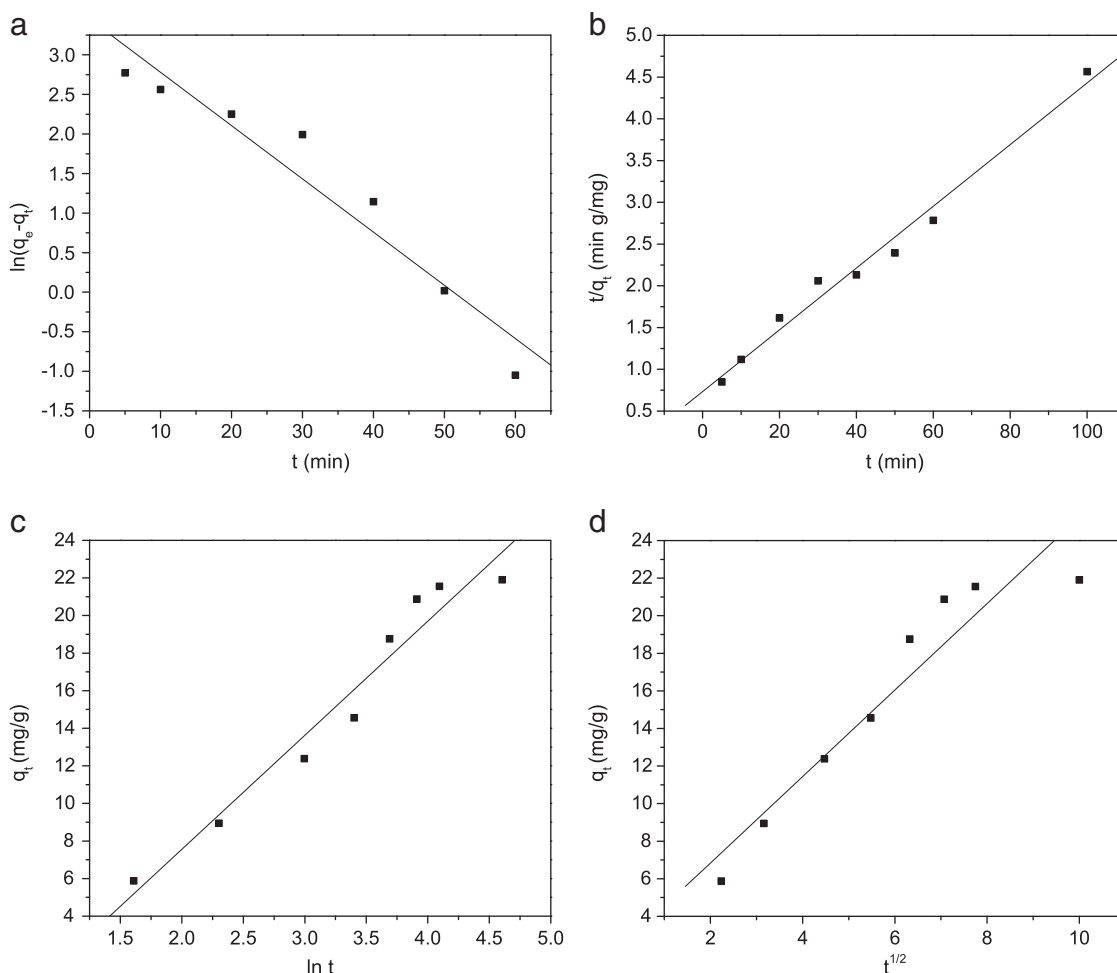


Fig. 3. Kinetic models for adsorption of lead(II) onto PCAC: (a) Pseudo-first-order model (b) Pseudo-second-order model (c) Elovich model (d) Intraparticle diffusion model.

The Elovich model describes a number of reaction mechanisms including bulk and surface diffusion and the activation and deactivation of catalytic surfaces [21]. It is represented as:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (4)$$

where  $\alpha$  (mg/g min) and  $\beta$  (g/mg) are the constants of the adsorption and are determined from a plot depicted in Fig. 3c.

Intraparticle diffusion model is defined by the following equation:

$$q_t = k_i t^{1/2} \quad (5)$$

where  $k_i$  (g/mg min) is the constant of the adsorption and is determined from a plot  $q_t$  versus  $t^{1/2}$  (Fig. 3d) [22].

All kinetic data for the adsorption of lead(II) ions onto PCAC, calculated from the related plots, are summarized in Table 2. The validity of the exploited models is verified by the correlation coefficient,  $r^2$ . Comparison of the  $r^2$  values for different models suggests that the pseudo-second-order kinetic model fits best since its highest value ( $r^2 = 0.9914$ ). Pseudo-second-order kinetic model implies that the predominant process here is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent. Chemisorption is usually restricted to just one layer of molecules on the surface, although it may be followed by additional layers of physically adsorbed molecules [23].

#### 4.5. Adsorption isotherms

The adsorption isotherm indicates how molecules of adsorbate are partitioned between the adsorbent and liquid phase at equilibrium as a function of adsorbate concentration. In this study, the equilibrium data obtained for the adsorption of lead(II) ions onto PCAC were analyzed by considering the Langmuir, Freundlich and Temkin isotherm model.

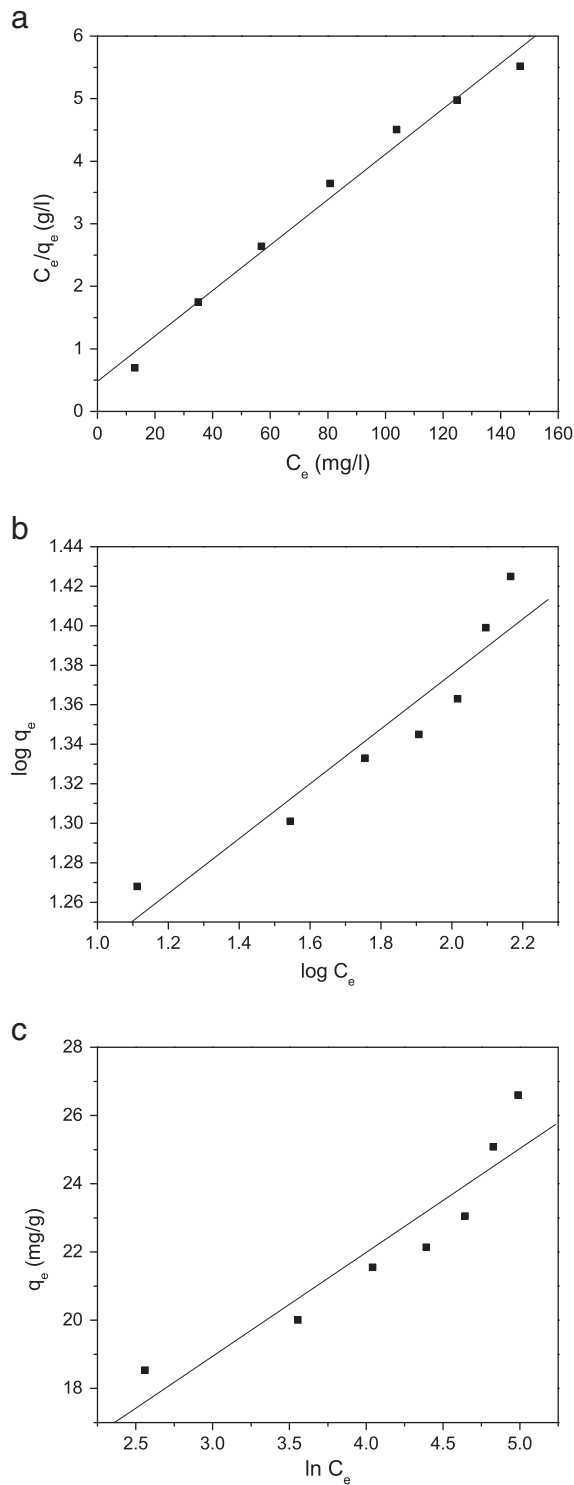
The linear form of Langmuir isotherm equation is given as:

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

Table 2  
Kinetic model parameters for adsorption of lead(II) onto PCAC.

Kinetic model	Parameter	Value
Pseudo-first-order	$k_1$ (g/mg min)	-0.0673
	$r^2$	0.9641
Pseudo-second-order	$k_2$ (g/mg min)	0.0018
	$r^2$	0.9914
Elovich model	$\alpha$ (mg/g min)	2.8508
	$\beta$ (g/mg)	0.1647
	$r^2$	0.9768
Intraparticle diffusion model	$k_i$ (g/mg min)	2.3019
	$r^2$	0.9501





**Fig. 4.** Adsorption isotherm models for lead(II) adsorption onto PCAC: (a) Langmuir (b) Freundlich (c) Temkin.

where  $K_L$  is Langmuir equilibrium constant (l/mg), and  $q_{max}$  (mg/g) is the monolayer adsorption capacity. Both are determined from a plot  $C_e/q_e$  versus  $C_e$  (Fig. 4a). Langmuir isotherm is frequently evaluated by a separation factor,  $R_L$ , which is defined as follows:

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

where  $C_0$  in this case is the highest initial solute concentration. The value of separation factor indicates the type of the isotherm and the nature of the adsorption process. Considering the  $R_L$  value, adsorption can be unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ) [24]. In our case, the  $R_L$  value was found to be 0.00657 and confirmed that prepared activated carbon shows favorable adsorption for lead(II) ions.

Freundlich isotherm is purely empirical and it best describes the adsorption on heterogeneous surfaces [25]. Freundlich isotherm equation is shown below in its linear form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

where  $K_F$  (l/g) is Freundlich constant and  $n$  is Freundlich exponent. These parameters are determined from a plot  $\log q_e$  versus  $\log C_e$  (Fig. 4b).

Temkin isotherm is represented by the linear equation as follows:

$$q_e = B \ln K_t + B \ln C_e \quad (9)$$

where  $K_t$  (l/mg) is the equilibrium binding constant corresponding to the maximum binding energy and constant  $B = RT/b$  represents the heat of adsorption, while  $R$  is the universal gas constant,  $T$  is the absolute temperature in Kelvin and  $1/b$  indicates the adsorption potential of the adsorbent. Both  $K_t$  and  $B$  can be determined from a plot  $q_e$  versus  $C_e$  (Fig. 4c) [26].

The isotherm parameters for the adsorption of lead(II) ions onto PCAC are given in Table 3. Langmuir adsorption model provides the best fit with experimentally obtained data ( $r^2 = 0.9926$ ). Adsorbents that exhibit the Langmuir isotherm behavior are supposed to contain fixed individual sites, each of which equally adsorbs only one molecule, forming thus a monolayer with the thickness of a molecule. Monolayer adsorption capacities for adsorption of lead(II) ions onto PCAC and other activated carbons derived from organic precursors are compared in Table 4.

#### 4.6. Effect of pH

Generally, the pH of a solution is recognized as a very influential parameter that governs the adsorption process. It was established that pH affects the surface charge of the adsorbent. In the present study, an increase in the solution pH led to an increase in  $q_e$  for the adsorption of lead(II) ions, especially at pH values greater than 5 (Fig. 5). According to the Pourbaix diagram of lead, lead(II) ion precipitates as  $Pb(OH)_2$  at pH values greater than 6.7. Although this range (pH = 7, 8, 9, 10) was investigated for removal of lead(II) ions, no uptake could be ascribed to the adsorption onto PCAC within this range. However, at pH values lower than 6.7, removal of lead(II) ions by adsorption onto PCAC is probable. Great differences in  $q_e$  values at pH 5 and 6 could be explained by the competitive effect. Namely,  $H^+$  and lead(II) cations compete for the negative adsorption sites on the carbon surface. In

**Table 3**

Equilibrium model parameters for adsorption of lead(II) onto PCAC.

Equilibrium model	Parameter	Value
Langmuir isotherm	$K_L$ (l/mg)	2.0817
	$q_{max}$ (mg/g)	27.53
	$R_L$	0.00657
	$r^2$	0.9926
Freundlich isotherm	$K_F$ (l/g)	12.527
	$n$	7.2015
	$r^2$	0.9482
Temkin isotherm	$A$	9.8217
	$B$ (l/g)	3.0413
	$r^2$	0.9295

**Table 4**

Results for adsorption of lead(II) ions by activated carbons obtained from various plants, agricultural and wood based materials.

Activated carbon source	pH	t (°C)	Adsorbent dosage (g/l)	Adsorbent capacity (mg/g)
Soybean hulls [27]	5.0	23	10.0	39.37
Apricot stone [28]	6.5	25	2.0	22.85
Pine cones	5.2	25	2.0	27.53
Coconut shell [29]	5.6	25	2.0	76.66
Date pits [30]	5.2	25	4.0	30.7
Peanut husks [31]	6.0	20	0.6	113.96
Palm shell [32]	3.0	27	5.0	95.2
Mature pods of <i>M. oleifera</i> containing seeds [33]	5.8	30	2.0	19.2

In addition to this, adsorbent surface is positively charged due to already adsorbed  $H^+$ . Raising the pH decreases positive charge of the adsorbent surface and enhances the adsorption of lead(II) ions.

#### 4.7. Effect of adsorbent dosage

The results of the experiments with varying adsorbent concentrations are presented in Fig. 6. Increase in the adsorbent concentration, from 0.5 to 2.5 mg/l, increases removal of lead(II) ions from 23.95% to 43.72%. It is obvious that the removal of lead(II) ions is not increased considerably when adsorbent concentrations are higher than 2.0 mg/l. Thus, optimum dosage of PCAC for adsorption of lead(II) ions is found to be 2.0 mg/l. All active sites on the adsorbent surface are then occupied and increase in adsorbent dosage do not provide higher uptake of lead (II) ions.

## 5. Conclusion

Activated carbon obtained from cones of European Black pine was employed as an adsorbent for removal of lead(II) ions from aqueous solution. This study revealed that the adsorption process fit well with the Langmuir isotherm and pseudo-second-order kinetic model. The monolayer adsorption capacity,  $q_{max}$ , calculated from Langmuir model is 27.53 mg/g. Optimum adsorbent dosage was established to be 2.0 mg/l. Removal of lead(II) ions was pH dependent and better in basic medium, though, at pH values higher than 6.7 it is ascribed to lead precipitation. The analysis of the carbon surface structure indicated that carboxylic groups are the most abundant from all oxygen containing functional groups. SEM micrographs did not show any significant changes in the carbon morphology caused by lead adsorption. It may be concluded from the above presented results that activated carbon from pine cones can be considered as a potential

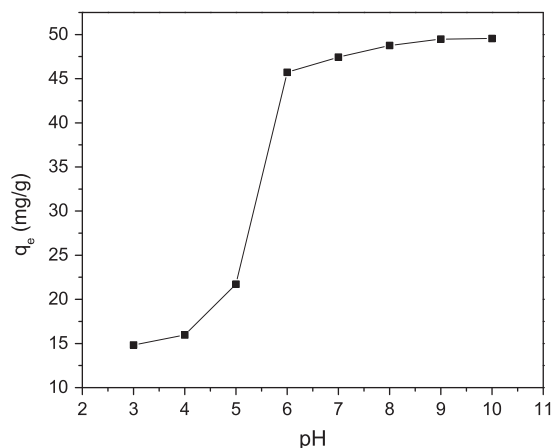


Fig. 5. Effect of pH on the adsorption of lead(II) onto PCAC.

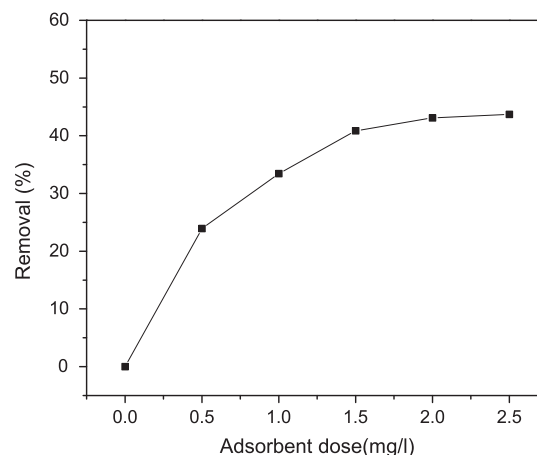


Fig. 6. Effect of adsorbent dosage on lead(II) removal.

adsorbent used for the elimination of lead(II) ions from wastewater since it is a low-cost and locally available adsorbent.

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