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# Design of surface functionalization of waste material originated charcoals by an optimized chemical carbonization for the purpose of heavy metal removal from industrial waste waters

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## ABSTRACT

A high capacity activated charcoal was produced from waste material specifically from Lapsi (*Choerospondias axillaris*) seeds using an optimized chemical method. The chemical carbonization and the subsequent chemical activation were designed to optimize the heavy metal adsorption capacity of the prepared charcoal. The charcoals were characterized by the rate constant of the sorption, by the adsorption capacities, and by the determination of the quality and quantity of functional groups. According to the experimental results the kinetics of the sorption process was found to be pseudo-second order. The rate constants depended on the quality of metal ions as well as on the preparation method of charcoals. The sorption isotherms were experimentally studied at various pHs and the results could be modeled by the Langmuir equation. The pseudo-second-order rate constant and the monolayer adsorption capacities were considerably higher than the literary data. Based on the obtained results a new mechanism was suggested which demonstrates that heavy metal ions form complexes with the surface carboxylic and lactone groups in the midst of hydrogen ion development. The transformation of coordinative bonds to ionic ones was completed by drying process. The dried charcoal had a cation-exchange character therefore the sorption and desorption process showed a hysteresis loop.

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## 1. Introduction

Rapid industrialization especially in developing countries, leads to an increased disposal of heavy metals into the environment [1,2]. The toxic heavy metals (e.g. lead, cadmium, mercury, and nickel) entering the food chain through contamination of natural waters, could be toxic and carcinogenic even at very low concentrations and as a consequence they generated a serious risk for the environment as well as for the human health [1]. Various chemical and physical treatments have been developed (e.g. oxidation, reduction, precipitation, electrolytic recovery, solvent extraction, membrane separation, ion exchange and adsorption) for the removal of heavy metal ions from water bodies [1]. Among these the adsorption was considered to be the least expensive and very effective separation technique for the removal of metal ions being present at low concentrations in industrial waste waters [e.g. 1–6].

The locally available low-cost adsorbents were preferred for industrial applications by the use of various agricultural, industrial, natural and biological waste materials. These waste products were utilized

with or without chemical and physical pretreatment [e.g. 1–8]. The carbonization process completed with various chemical activation methods was a widely applied technique to increase the adsorption capacity of these materials [e.g. 9–14].

The characterization of the activated carbon could be performed by various techniques, among these the most useful ones gave information about the quality and quantity of surface functional groups, e.g. Fourier Transform-Infrared Spectroscopy (FT-IR) [5,9–15] and chemical titration [16,17].

In order to study the adsorption properties usually the sorption isotherms were taken at different conditions (pH, ionic strength etc.) and additionally the sorption kinetics used to be investigated. The sorption isotherms modeled by various mathematical equations (Langmuir, Freundlich etc.) gave information about the maximum sorption capacity and the mechanism of the adsorption. The most important data for industrial utilization were the maximum sorption capacity, the optimal pH and the sorption rate constant.

Lapsi (*Choerospondias axillaris*) seed is an agricultural waste product generated in plenty of tons in the Indian subcontinent. The main purpose of this work was to develop a cheap chemical process easily adaptable in developing countries for the carbonization and activation of Lapsi seed (and other waste products). It was also important that by the elaborated chemical procedure one could design the number of

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surface functional groups to obtain a charcoal having optimal heavy metal adsorption capacity. Another goal was the comparative study of the sorption properties of the produced activated charcoals and the suggestion of a bonding mechanism. After physical carbonization of Lapsi seeds the charcoal was applied for the removal of Cd(II) [18] and after its chemical carbonization the charcoal was used for the removal of Cr(VI) by Varga et al. [19] successfully. In this paper the sorption of lead (as a representative of main-group heavy metals) and nickel (as a representative of transition elements) was investigated at various pHs in aqueous solutions.

## 2. Experimental

### 2.1. Preparation of charcoals

All chemicals used for the experiments (sulfuric acid, nitric acid, hydrochloric acid, sodium hydroxide, lead nitrate, nickel sulfate etc.) were of analytical grade. High purity water was used to prepare any solution.

#### 2.1.1. Preparation of charcoal labeled C-1

The crushed Lapsi seed (particle size <0.5 mm) was mixed with concentrated sulfuric acid (98% m/m) in various weight ratios for the carbonization and activation. Finally 1:2–2.5 ratios were chosen for the preparation of charcoal used for the sorption experiments. The black slurry was heated in a drying oven for 24 h at 150 °C. The resulted material was washed several times by distilled water during continuous stirring. The washing continued until the conductivity of the solution reached a value less than 10  $\mu\text{S cm}^{-1}$ . The washed charcoal was dried in a drying oven at 110 °C then ground and sieved using a 100  $\mu\text{m}$  sieve.

#### 2.1.2. Preparation of charcoal labeled C-2

In another experiment, the Lapsi seed powder was mixed with concentrated sulfuric acid in the optimal ratio found in the course of C-1 preparation. After 10 min reaction time concentrated nitric acid (65% m/m) was added in various ratios of sulfuric acid/nitric acid and the ratios were optimized. Finally the ratio of 1:0.5 was chosen for further treatment. The mixture was placed in a drying oven for 24 h at 150 °C and the procedure continued the same way as described in the case of preparation of C-1.

#### 2.1.3. Preparation of charcoal labeled C-3

A portion of whole Lapsi seeds was carbonized at 900 °C for 2 h under  $\text{N}_2$  atmosphere in a vacuum-argon tube-furnace. The product was ground in a grinding mill and the chemical activation and washing were made as in the case of charcoal C-2.

### 2.2. Characterization of charcoals

The specific surface area of the three charcoals was determined by volumetric method after degassing. The evaluation was made by BET equation. In the case of some selected charcoals, the surface morphology was recorded by a scanning electron microscope (SEM) (Type: AMRAY 1830) at an accelerating voltage of 20 kV. The SEM photographs were taken at different magnifications (between 50 and 500 times). The carbon and nitrogen content of the raw material and the charcoals was determined after oven drying at a temperature of 105 °C (multi N/C 2100 S, Analytik Jena, Germany).

The acidic surface functional groups were measured using Boehm titration [16] after modification of the method described in [17] (applying Automatic Titrator 388 Titrand, Metrohm AG, Switzerland). For the determination 0.1 g portions of charcoals were weighed by analytical balance and were mixed with 20 mL standard solutions of 0.05 M NaOH (resulting sample-1),  $\text{Na}_2\text{CO}_3$  (resulting sample-2) and  $\text{NaHCO}_3$  (resulting sample-3) respectively. The solutions were shaken for 24 h by means of a shaking machine (Orbital Shaker

OS-20, Biotech, Praha) at 250 rpm. Then the slurries were filtered through cartridges filled with glass-fiber filter using Visiprep DL Vacuum Manifold (Supelco, Bellefonte, PA, USA). 3–3 mL of filtered sample-1, sample-2 and sample-3 was taken for further procedure. Sample-1 was titrated directly by 0.05 M HCl. 10 mL and 5 mL 0.05 M HCl were added to sample-2 and sample-3, respectively before back titration by 0.05 M NaOH. The evaluation was done by Tiamo software (Version 1.3, Metrohm AG, Switzerland). All titrations were repeated three times.

Internal reflection IR spectra of the three types of charcoals were recorded by a Perkin-Elmer 1605 FT-IR spectrometer and a horizontal ATR cell. The spectrometer was equipped with a lithium tantalate detector. The sample was laid flatly and evenly on a 45° trapezoidal ZnSe crystal (ATR plate) and an increasing pressure was applied directly on the sample powder. Spectra were acquired at 2  $\text{cm}^{-1}$  resolution and 64 scans were averaged to reduce noise.

### 2.3. Sorption kinetics and equilibrium

The equilibrium measurements were performed at room-temperature (25 °C) by weighing 0.05 g charcoal by analytical accuracy for each experiment. Different aliquots of nickel-sulfate and lead-nitrate solutions were added. The initial concentrations for nickel and lead were varied from 30 to 1000  $\text{mg L}^{-1}$ . The pH of the solutions was adjusted to 2, 3, 4, 5 and 6 (only in the case of Ni) by 0.1, 1.0, 5.0  $\text{mol L}^{-1}$  HCl or NaOH after adding the charcoal into the solution. The mixtures were shaken for 3 h by a shaking machine at 250 rpm. After the reaction time the slurries were filtered through cartridges filled with glass-fiber filter using vacuum manifold. The pH of the filtered solutions was measured again, and the samples were stored in closed glass vessels at 4 °C until analysis. All series of measurements were executed using three parallels at every pH. The amount of adsorbed ions was calculated on the basis of atomic absorption spectrophotometric (AAS1N equipped with 10 cm slit burner, Zeiss, Germany) determination of residual Ni and Pb concentrations of the solutions. A stoichiometric air-acetylene flame was used for the determination of Pb concentration and the absorbance was measured at the wavelength of 283.3 nm. Absorbance of Ni was measured at 232.0 nm in a slightly oxidative air-acetylene flame.

Concentration of adsorbed lead and nickel was measured directly in loaded charcoal samples by X-ray fluorescence spectrometry (MiniPal2, Panalytical, The Netherlands). Potassium chromate was used as an internal standard for XRF measurements.

In further experiments only charcoal C-1 and charcoal C-2 were applied. During the desorption experiments 0.5 g charcoal C-1 and charcoal C-2 were weighed and added into 250–250 mL distilled water containing  $3 \times 10^3$  ppm nickel at pH=6 and  $10^4$  ppm lead at pH=5. The solutions were shaken for 3 h than filtered the same way as before. The metal-ion saturated charcoals were dried at room temperature and  $3 \times 0.05$  g were weighed from the charcoal samples by analytical accuracy and were added into 25 mL distilled water. The pH of the mixtures was varied in the range of 2–6. After this step the samples were treated the same way as it was done during the sorption experiments.

To follow the sorption kinetics 0.25 g charcoal was weighed by analytical accuracy, and was added promptly into 250 mL solution of 200 ppm lead of which pH was adjusted to pH=4 using some drops of 0.1 M NaOH. For the investigation of sorption kinetics of nickel the same amount of charcoal was applied but the 250 mL solution contained 100 ppm nickel and the pH was shifted up to 5 before adding the carbon. The temperature was kept at 25 °C using water bath and the mixture was intensively stirred by a magnetic stirrer. 5 mL samples were taken by Finn-pipette at first in every 30; 60 and later in every 120 s in the case of lead and nickel respectively. The samples were filtered immediately after their withdrawal in the same way as in the case of the sorption experiments. The filtered

samples were collected in glass tubes then closed and stored at 4 °C until analysis. The pH of the charcoal-heavy metal mixtures was checked continuously by a pH-sensitive glass electrode. The complete procedure was repeated twice.

### 3. Results and discussion

#### 3.1. Characterization of charcoals

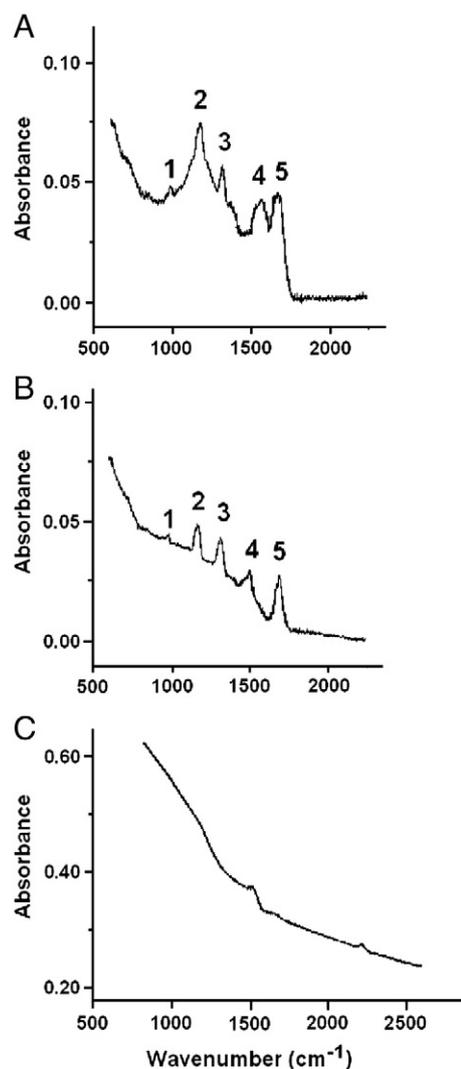
The results characterizing the prepared charcoals were summarized in Table 1. Charcoal C-1 was carbonized and activated by a conventional method applying sulfuric acid e.g. [11]. The obtained charcoal characterized by the maximum adsorption capacity was activated further by nitric acid. Charcoal C-3 was carbonized by a conventional physical carbonization and further activated like charcoal C-2. Charcoal C-1 and charcoal C-3 were used as references in the comparison of characteristics of charcoal C-2. Charcoal C-1 and charcoal C-2 had quite the same specific surface considering the error limit and their value was more than three times less than in the case of charcoal C-3. The specific surface was in connection with the preparation method, and the physical carbonization at 900 °C resulted in the most porous structure of the carbon.

The other important data for the characterization of charcoals were the quality and the quantity of the surface functional groups. The weight ratios of the raw material, sulfuric acid and the consecutively used nitric acid were optimized through the measurement of functional groups by the Boehm titration. The results in the optimized cases were summarized in Table 1.

The Boehm titration revealed some important differences among the charcoals prepared in various ways. Charcoal C-1 and charcoal C-2 could be differentiated by the quantity of lactone groups which was significantly higher in the case of charcoal C-2 while the quantity of the other two functional groups was similar. Due to the difference between the activation methods of charcoal C-1 and charcoal C-2 the higher amount of lactone groups could be attributed to the effect of nitric acid. Furthermore in the case of charcoal C-3 the amount of carboxylic and lactone group remained below the detection limit and the quantity of phenol group was significantly lower than in the case of the other two carbons. According to these results the physical activation process at high temperature increased the specific surface area of carbon but did not promote the development of surface functional groups in spite of the similarly applied activation method.

The total carbon content of the raw material was found to be 52% m/m ( $\pm 2$ ) and this increased to about 60% m/m ( $\pm 3$ ) by the chemical carbonization and to 85% m/m ( $\pm 3$ ) by the physical one (see Table 1). The nitrogen and the sulfur content remained below 1% in the case of all samples.

FT-IR spectra demonstrated in Fig. 1 showed essential differences between absorption bands assigned to functional groups in the case of



**Fig. 1.** FT-IR spectra of charcoal C-2 (A), charcoal C-2 saturated with lead (B), (assignment of peaks: 1: 1035  $\text{cm}^{-1}$  –C–OH, alicyclic; 2: 1216  $\text{cm}^{-1}$  –C–O–C; 3: 1365  $\text{cm}^{-1}$  Ar(OH); 4: 1604  $\text{cm}^{-1}$  –COO–; 5: 1720  $\text{cm}^{-1}$  –CO, carboxylic group), and charcoal C-3 (C).

untreated (A) and lead saturated charcoals (B). According to the assignment alicyclic alcoholic group (1, wave number: 1035  $\text{cm}^{-1}$ ), ether group (2, wave number: 1216  $\text{cm}^{-1}$ ), phenol group (3, wave number: 1365  $\text{cm}^{-1}$ ), ionic carboxylic group (4, wave number: 1604  $\text{cm}^{-1}$ ), and carbonyl group of carboxylic group (5, wave number: 1720  $\text{cm}^{-1}$ ) could be identified. The ether group and the C–O–C part of the lactone

**Table 1**

Characterization of charcoals prepared from Lapsi seeds with different carbonization processes.

Type of charcoal	C-1	C-2	C-3
Carbonization procedure			
Physically (temperature; time; inert gas stream)	–	–	900 °C; 2 h; N <sub>2</sub>
Chemically (temperature; time)	150 °C; 24 h	150 °C; 24 h	150 °C; 24 h
Chemicals for carbonization and activation	cc H <sub>2</sub> SO <sub>4</sub>	cc H <sub>2</sub> SO <sub>4</sub>	cc H <sub>2</sub> SO <sub>4</sub>
Chemical for further activation	–	cc HNO <sub>3</sub>	cc HNO <sub>3</sub>
Specific surface area ( $\text{m}^2\text{g}^{-1}$ ) (SD)	11.9 ( $\pm 2.0$ )	11.4 ( $\pm 2.6$ )	39.4 ( $\pm 1.7$ )
Total carbon content % m/m (SD)	62.1 ( $\pm 2.9$ )	59.9 ( $\pm 2.2$ )	85.3 ( $\pm 3.1$ )
	mmol g <sup>-1</sup>		
Phenol group ( $\text{mmol g}^{-1}$ ) (SD)	51.75	49.92	71.08
Lactone group ( $\text{mmol g}^{-1}$ ) (SD)	3.742 ( $\pm 0.097$ )	3.625 ( $\pm 0.102$ )	0.017 ( $\pm 0.002$ )
Carboxyl group ( $\text{mmol g}^{-1}$ ) (SD)	0.786 ( $\pm 0.033$ )	1.966 ( $\pm 0.077$ )	0 ( $\pm 0.005$ )
Ratios of carbon atoms and functional groups	3.067 ( $\pm 0.130$ )	2.918 ( $\pm 0.113$ )	0 ( $\pm 0.004$ )
	C/phenol	~14	~4181
	C/lactone	~66	–
	C/carboxyl	~17	–

group appeared at the same wavelength (see the wide band 2 on Fig. 1A). The FT-IR results confirmed that the chemical treatment using concentrated sulfuric acid carbonized the cellulose structure of the raw material differently than the physical treatment. Therefore the further oxidation process (applying concentrated nitric acid) could significantly increase the number of functional groups. Furthermore the FT-IR spectrum of the physically carbonized C-3 (Fig. 1C) was significantly different from the spectra of C-1 and C-2. Functional groups could not be identified in the spectrum of C-3 by FT-IR technique.

In consequence of the adsorption of lead the band at  $1216\text{ cm}^{-1}$  became narrower and the absorbance decreased due to the reaction between the lead and the lactone group. Furthermore, the band at  $1604\text{ cm}^{-1}$  shifted towards a lower wave number due to the reaction between the lead and the carboxylic group. The same changes could be observed in the FT-IR spectra of charcoal treated with nickel. The lactone group and the carboxylic group formed coordinative bond with the metal ions, as it could be concluded from the differences between the FT-IR spectra of the metal ion free and the metal ion saturated charcoals. According to the typical SEM photos of the obtained charcoal-2 the average size of the carbon particles was  $50\text{ }\mu\text{m}$  and they showed granular character.

### 3.2. Sorption kinetics

The sorption kinetics was evaluated using a pseudo-first order and a pseudo-second-order kinetic model. The pseudo-first order models did not give any acceptable results therefore the pseudo-second order kinetic model was applied on the basis of the following differential equation [e.g. 12]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (1)$$

where  $k_2$  is the rate constant of pseudo-second order adsorption ( $\text{g mg}^{-1} \text{ min}^{-1}$ ). The integration of Eq. (1) for the boundary condition  $q_t = 0$  at  $t = 0$  gives:

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

which can be linearized as

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

According to the experimentally measured data the pH decreased simultaneously with the decreasing concentration of the metal ions of the aqueous phase, which means that the binding of the metal ions to the surface functional groups was accompanied by hydrogen ion development (see Figs. 2 and 3). The quantity of the released hydrogen ions and the adsorbed metal ions was compared in Table 2. The hydrogen ion development was about 1.5 times more than the concentration of adsorbed lead while in the case of nickel it was the half of its adsorbed concentration. Furthermore the sorption process using charcoal C-2 was about two times faster compared to the value obtained by charcoal C-1 for both metal ions (Table 2). The difference between the resulted rate constants in the case of the two carbons could be considered to the different amount of lactone groups which bound the metal ions by coordinative bonds.

### 3.3. Sorption equilibrium

The sorption isotherms were modeled by using various models: the Langmuir, the Redlich–Peterson, the Freundlich and the Langmuir–Freundlich [e.g. 12]. According to the interpretation of the Langmuir adsorption isotherm it was assumed that the adsorption takes place on specific homogeneous sites on the adsorbent. This isotherm was applied in non-linear form (Eq. (4)) or most commonly in linear form (Eq. (5)):

$$\frac{q_e}{q_m} = \frac{bC_e}{1 + bC_e} \quad (4)$$

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (5)$$

where  $q_m$  (maximum adsorption capacity) was the maximum amount of adsorbed cation per unit weight of carbon ( $\text{mg g}^{-1}$ ), forming a complete monolayer on the surface;  $b$  is the Langmuir constant ( $\text{L mg}^{-1}$ ) which corresponds to  $k_a/k_d$  (where  $k_a$  and  $k_d$  were the rate constants for adsorption and desorption processes), and  $C_e$  ( $\text{mg L}^{-1}$ ) and  $q_e$  ( $\text{mg g}^{-1}$ )

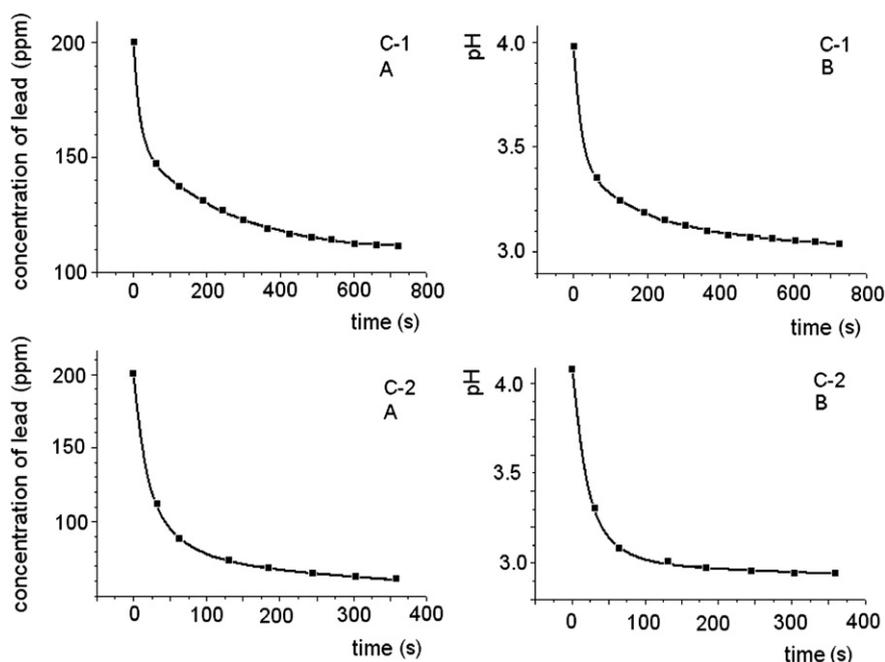


Fig. 2. Experimentally measured concentration of lead (A) and the change of pH (B) in function of time using charcoal C-1 and charcoal C-2.

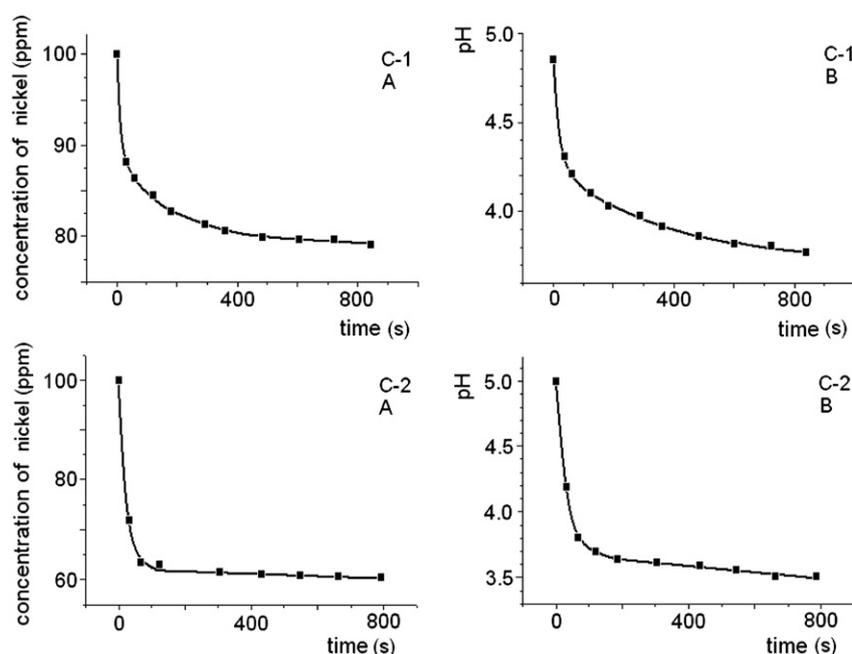


Fig. 3. Experimentally measured concentration of nickel (A) and the change of pH (B) in function of time using charcoal C-1 and charcoal C-2.

were the equilibrium cation concentrations in liquid phase and in solid phase, respectively. By further analysis of the Langmuir equation a dimensionless equilibrium parameter ( $R_L$ ) could be obtained which was considered as a separation factor:

$$R_L = \frac{1}{1 + bC_0} \quad (6)$$

The Redlich–Peterson (R–P) equation contained three parameters and unified the features of the Langmuir and the Freundlich isotherms. The R–P isotherm could be described by Eq. (7):

$$q_e = \frac{K_{RP}C_e}{1 + \alpha_{RP}C_e^\beta} \quad (7)$$

where  $K_{RP}$ ,  $\alpha_{RP}$  and  $\beta$  were the R–P parameters. The values of  $\beta$  were  $0 < \beta \leq 1$ . In the case of  $\beta = 1$  the R–P equation gave the Langmuir equation. The constants of R–P isotherm could be calculated by a parameter estimation program (e.g. Origin version 6) since they could not be obtained by using a graphical method because of three unknown parameters.

The experimentally measured and calculated adsorption isotherms were demonstrated in Fig. 4 at various pH values applying the Langmuir model in the case of charcoal C-1 and charcoal C-2 using lead and nickel. The experimentally measured equilibrium sorption capacities and the

calculated data were summarized in Table 3 for lead and in Table 4 for nickel. All of the measured equilibrium sorption capacities were in good correlation with the calculated ones. The absorbed concentrations of lead and nickel obtained indirectly from the residual concentrations of liquid phase (determined by atomic absorption spectroscopy) were established by XRF measurements of heavy metal saturated charcoals in comparison with an internal standard. The experimentally measured maximal equilibrium sorption capacities using C-2 were 423 and 85  $\text{mg g}^{-1}$  for lead and nickel respectively and these results were significantly higher compared to the literary data (50–300  $\text{mg g}^{-1}$  for lead [7] and 3–36  $\text{mg g}^{-1}$  for nickel [20]). The correlation coefficient ( $0.971 < R^2 < 0.999$ ) indicated a very good fit of data to the model. The values of separation factor were  $0 < R_L < 1$ ,  $R_L = 1$  and  $R_L = 0$  which means favorable, linear and irreversible adsorption respectively. In the case of all Lapsi charcoals  $R_L$  was between 0 and 1 at every applied initial concentration which data indicated favorable adsorption at each pH and the Langmuir constants resulted in quite high values signifying that the rate of adsorption overwhelmed the rate of desorption in all cases. The monolayer adsorption capacity was significantly higher in the case of charcoal C-2 due to the higher amount of lactone groups while the charcoal C-3 showed subordinate adsorption in comparison with the other two carbons.

Tables 3 and 4 contained the data obtained also by using the Redlich–Peterson model. The values were  $\beta \approx 1$  in most of the cases (except charcoal C-3) which indicated the applicability of the Langmuir

Table 2

Calculated equilibrium concentrations of metal ions and pHs and pseudo-second order rate constants for lead and nickel using charcoal-1 and charcoal-2.

	Lead(II)		Nickel(II)	
	C-1	C-2	C-1	C-2
Equilibrium concentration ( $\text{mg g}^{-1}$ ) <sup>1</sup> (RSD %)	96.2 ( $\pm 1.2$ )	147.1 ( $\pm 0.5$ )	21.3 ( $\pm 1.5$ )	39.9 ( $\pm 0.5$ )
Concentration of adsorbed metal ion ( $\text{mmol g}^{-1}$ ) <sup>1</sup>	0.464	0.710	0.362	0.608
Concentration of developed hydrogen ion ( $\text{mmol g}^{-1}$ ) <sup>2</sup>	0.766	1.065	0.164	0.306
Ratio of hydrogen ions and metal ions	1.65	1.51	0.45	0.50
Pseudo-second order rate constant <sup>3</sup> ( $\text{g mg}^{-1} \text{min}^{-1}$ ) (RSD %)	0.011 ( $\pm 8$ )	0.020 ( $\pm 6$ )	0.083 ( $\pm 12$ )	0.165 ( $\pm 10$ )
$R^2$	0.999	0.999	0.999	0.999

Notes:

<sup>1</sup> Calculated from the measured data obtained by atomic spectroscopy.

<sup>2</sup> Calculated from the measured pH changes (Figs. 2, 3).

<sup>3</sup> Calculated from the kinetic model.

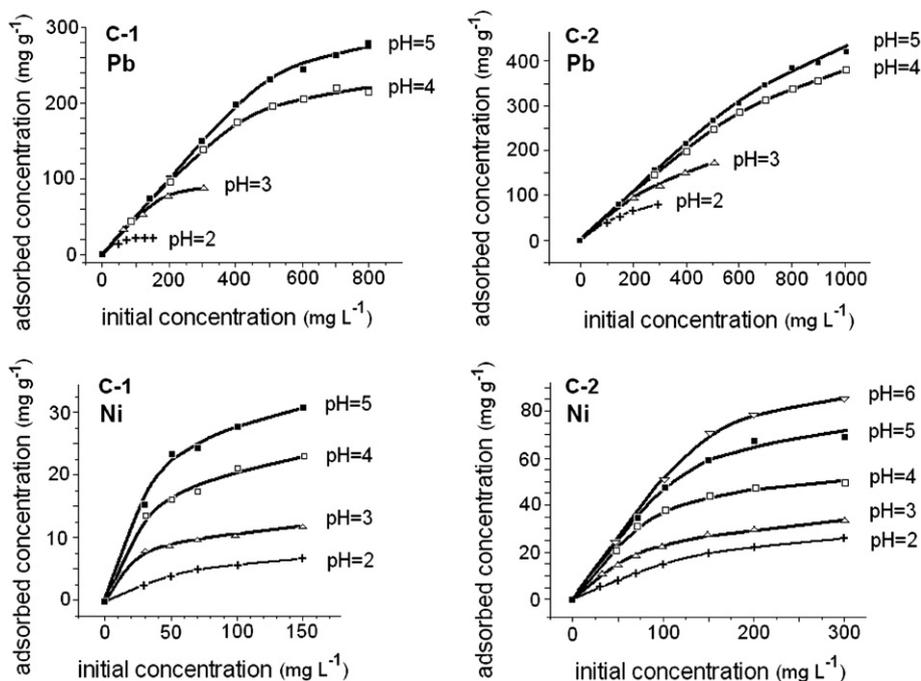


Fig. 4. Comparison of the adsorbed concentrations measured experimentally (symbols) and calculated by Langmuir model (line) in function of the initial concentration of aqueous phase, using charcoal C-1 and charcoal C-2 at various pHs applying lead and nickel respectively.

model. The Freundlich and the Langmuir–Freundlich models did not provide acceptable straight line and correlation coefficients in the case any of the charcoals and pH.

The separation factor of the Langmuir model was very close to zero in some cases and this result raised the possibility of irreversible adsorption. The comparison of sorption and desorption processes was

summarized in Fig. 5. The diagrams showed a hysteresis loop in all cases indicating the reduced desorption compared to the sorption. Desorption was blocked for both lead and nickel at pH above 5 and 6 respectively. The detained leaching indicates that the bond between the heavy metals and the functional groups of charcoals is quite strong.

Table 3 Summarization of sorption results evaluated by the Langmuir and Redlich–Peterson equation in the case of lead applying different types of activated charcoals (C-1, C-2, C-3) and pHs (n = 3).

		pH			
		2.0	3.0	4.0	5.0
<i>Experimental values</i>					
$q_e$ (mg g <sup>-1</sup> ) (RSD %)	C-1	19.2 (±2.3)	84.0 (±1.8)	217.8 (±2.0)	323.0 (±1.1)
	C-2	70.7 (±1.7)	162.2 (±1.3)	374.9 (±1.6)	422.9 (±0.9)
	C-3	5.8 (±2.1)		28.9 (±1.7)	
<i>Calculated values</i>					
Langmuir $q_{max}$ (mg g <sup>-1</sup> )	C-1	19.9	87.1	208.3	277.8
	C-2	63.6	127.9	390.6	423.7
	C-3	5.2		26.7	
$b$ (L mg <sup>-1</sup> )	C-1	0.535	0.639	0.541	0.209
	C-2	0.233	0.568	0.610	0.339
	C-3	0.035		0.222	
$R_L$	C-1	0.006 < $R_L$ < 0.06	0.005 < $R_L$ < 0.05	0.002 < $R_L$ < 0.006	0.006 < $R_L$ < 0.01
	C-2	0.02 < $R_L$ < 0.13	0.004 < $R_L$ < 0.02	0.02 < $R_L$ < 0.03	0.003 < $R_L$ < 0.004
	C-3	0.22 < $R_L$ < 0.49		0.03 < $R_L$ < 0.13	
$R^2$	C-1	0.998	0.999	0.999	0.997
	C-2	0.998	0.999	0.995	0.999
	C-3	0.971		0.996	
Redlich–Peterson $K_{RL}$ (L g <sup>-1</sup> )	C-1	18.3	50.3	216.3	332.7
	C-2	33.0	99.8	334.4	402.6
	C-3	1.1		16.6	
$\alpha_{RL}$ ((L mg <sup>-1</sup> ) <sup><math>\beta</math></sup> )	C-1	0.848	0.672	0.887	2.580
	C-2	0.975	0.889	2.257	1.189
	C-3	2.343		1.737	
$\beta$	C-1	1.020	0.968	1.026	0.857
	C-2	0.858	0.971	0.840	0.957
	C-3	0.484		0.761	
$R^2$	C-1	0.996	0.999	0.997	0.998
	C-2	0.999	0.999	0.998	0.998
	C-3	0.989		0.992	

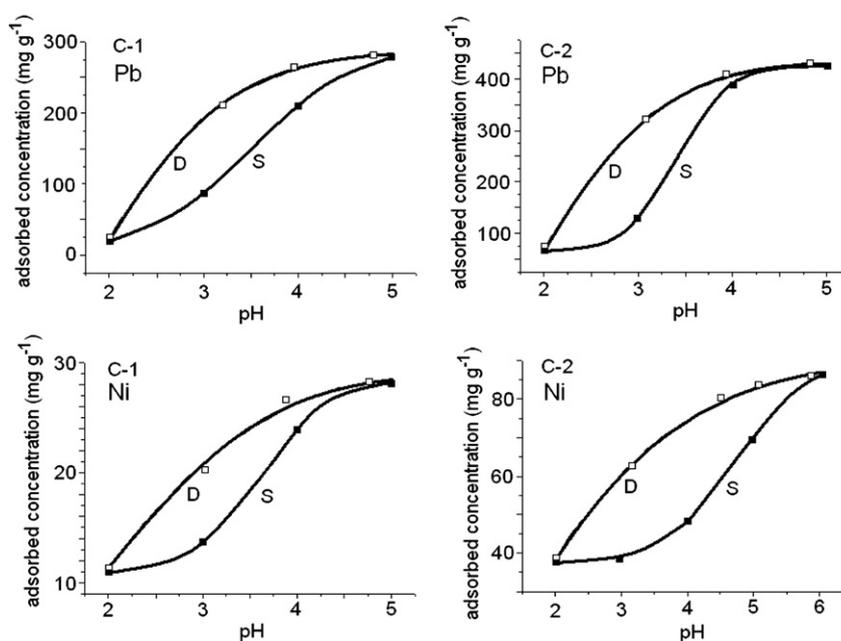
**Table 4**

Summarization of sorption results evaluated by the Langmuir and Redlich–Peterson equation in the case of nickel applying different types of activated charcoals and pHs (n = 3).

		pH				
		2	3	4	5	6
<i>Experimental values</i>						
$q_e$ (mg g <sup>-1</sup> ) (RSD %)	C-1	7.1 (±2.2)	12.3 (±1.0)	22.1 (±1.1)	30.5 (±1.2)	
	C-2	24.0 (±1.3)	31.8 (±0.8)	45.8 (0.9)	68.2 (±1.0)	85.0 (±0.9)
<i>Calculated values</i>						
Langmuir $q_{max}$ (mg g <sup>-1</sup> )	C-1	11.0	13.6	24.0	28.2	
	C-2	38.1	38.5	48.5	69.5	85.5
$b$ (L mg <sup>-1</sup> )	C-1	0.012	0.054	0.112	2.410	
	C-2	0.008	0.003	0.224	0.439	0.661
$R_L$	C-1	0.29 < $R_L$ < 0.74	0.09 < $R_L$ < 0.38	0.03 < $R_L$ < 0.23	0.002 < $R_L$ < 0.01	
	C-2	0.29 < $R_L$ < 0.81	0.53 < $R_L$ < 0.92	0.53 < $R_L$ < 0.92	0.02 < $R_L$ < 0.08	0.008 < $R_L$ < 0.03
$R^2$	C-1	0.992	0.995	0.998	0.998	
	C-2	0.997	0.999	0.998	0.999	0.999
Redlich–Peterson $K_{RL}$ (L g <sup>-1</sup> )	C-1	1.35	8.3	10.1	26.9	
	C-2	0.50	3.3	50.8	64.2	90.9
$\alpha_{RL}$ ((L mg <sup>-1</sup> ) <sup>β</sup> )	C-1	2.474	1.979	2.447	0.591	
	C-2	0.153	0.280	1.986	1.152	1.187
$\beta$	C-1	0.485	0.785	0.782	1.111	
	C-2	0.542	0.795	0.866	0.957	0.979
$R^2$	C-1	0.995	0.996	0.996	0.998	
	C-2	0.980	0.998	0.999	0.999	0.999

Knowing the total carbon content and the titrated concentrations of the functional groups the ratios of functional groups and the carbon could be calculated (Table 1). The charcoal-3 obtained by physical carbonization consisted of graphene layers which contained phenol groups per carbon atoms in the ratio of 1:4181 after chemical activation. The graphene structure was very resistant against the further chemical reaction therefore it could not be functionalized considerably. In the case of the other two charcoals only the ratio of the lactone group differed significantly. Under the effect of concentrated sulfuric acid double bonds were generated from the cellulose chain due to the dehydration processes [15]. According to our results a supposed chemical structure and mechanism were suggested to characterize the functionalized surface layer. The double bonds obtained during the dehydration process were oxidized by nitric acid producing lactone groups (Fig. 6). The design of the surface functionalization was

performed by the optimization of the number of double bonds varying the quantity of sulfuric acid and by the optimization of the number of lactone groups varying the quantity of nitric acid. The chemical structure took into consideration the ratios of carbon atoms and functional groups (Fig. 7A), the binding of the metal ions and the hydrogen ion development. Meanwhile the metal ion bound to the carboxylic group, the coordinative bond transformed to ionic one in the midst of hydrogen ion development (Fig. 7B,C). Anyhow, there was some difference between lead and nickel when the metal ion bound to lactone group. From the point of view of hydrolysis the lactone group–metal ion complex (Fig. 7B) was experienced to be more sensitive in the case of lead than in the case of nickel. The concentration of the developed hydrogen ions was 1.5 times more than the concentration of adsorbed lead ions, while it was the half of the concentration of the adsorbed nickel ions (Table 2). This difference can be explained

**Fig. 5.** Experimentally measured sorption (S) and desorption (D) diagrams in function of pH using charcoal C-1 and charcoal C-2 in the case of lead and nickel.

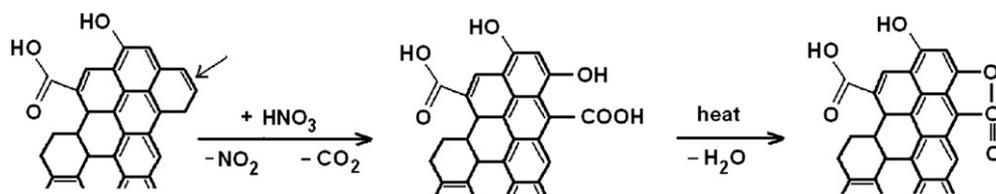


Fig. 6. Proposed oxidation mechanism of double bonds of charcoal-1 by nitric acid.

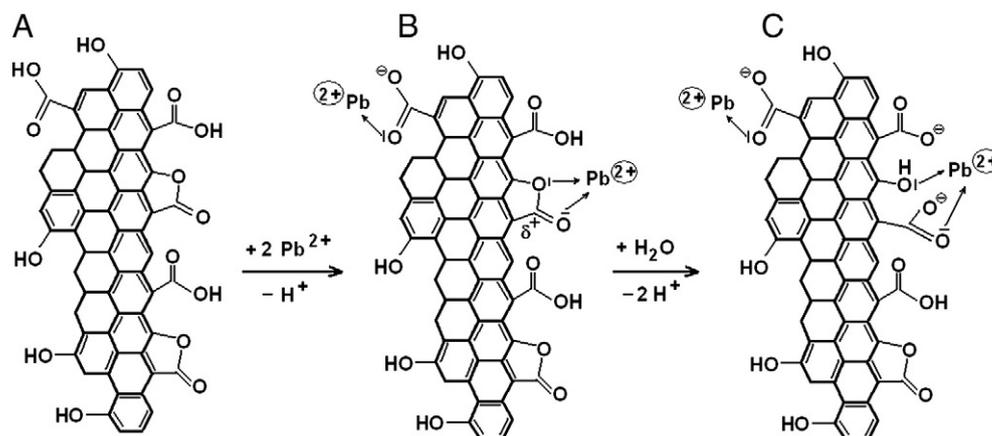


Fig. 7. Proposed structure of functionalized charcoal-2 and binding mechanism of lead ion.

by the higher electronegativity of lead (2.33) compared to the same of nickel (1.91). Consequently the delta positive charge on the carbon atom became higher facilitating the attack of the water molecule. As a result of the hydrolysis of the lactone group–metal ion complex the coordinative bond was transformed to ionic one which has higher binding strength. This process was fulfilled during the drying. As a result of the previous conversion a hysteresis loop could be observed between the sorption and desorption processes (Fig. 5). Desorption process consequently required higher acidic medium than the sorption. These results indicated that the sorbent prepared in dried form behaved as a cation exchange resin.

#### 4. Conclusion

The above demonstrated results revealed that high capacity charcoal C-2 could be prepared from Lapsi seeds by the use of chemical carbonization and further activation within a precise optimization. The experimentally determined sorption capacities [ $q_m(\text{Pb}) = 424 \text{ mg g}^{-1}$  and  $q_m(\text{Ni}) = 70 \text{ mg g}^{-1}$  at  $\text{pH} = 5$ ] in the model solutions were significantly higher compared to the literary values of the same. Therefore the obtained charcoal can be successfully applied for heavy metal removal also from industrial waste waters. Various functionalized charcoals could be designed by the use of this carbonization procedure and the method could be adapted in application of other waste materials as it was demonstrated by Varga et al. [19]. The experimental results could be explained quantitatively by the suggested chemical structure and reaction mechanism.

The irreversible bond between the specific heavy metal and the charcoal experienced at  $\text{pH} \geq 5$  has a promising effect in industrial waste water cleaning technologies. The reason is that after drying the heavy metal saturated charcoals can be recycled into the environment without any risk of heavy metal ion leaching at natural pHs, as it was experimentally demonstrated during the desorption measurements. While using diluted strong acids (e.g. 1 M HCl) the heavy metals can be reclaimed for other ways of utilization.

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