



The role of surface chemistry and solution pH on the removal of Pb²⁺ and Cd²⁺ ions via effective adsorbents from low-cost biomass

Abdel-Nasser A. El-Hendawy*

Physical Chemistry Department, National Research Center, 12622 Dokki, Cairo, Egypt

ARTICLE INFO

Article history:

Received 16 July 2008

Received in revised form

30 November 2008

Accepted 23 December 2008

Available online 31 December 2008

Keywords:

Activated carbon

Surface modification

Solution pH

FTIR

Heavy metals removal

ABSTRACT

A deep understanding of adsorption of Pb²⁺ and Cd²⁺ ions from their aqueous solutions on activated carbons and their HNO₃-oxidized forms has been attempted. These activated carbons were obtained from date pits using different activation methods. Adsorption isotherms of Pb²⁺ and Cd²⁺ ions were determined from solutions at pH 3 and 5.9. The results revealed that all obtained isotherms exhibited the model fitting according to Langmuir equation. The oxidized samples prone, slightly, to the high affinity isotherm type. The results revealed also that the investigated carbons removed appreciable amounts of lead and cadmium ions which increased by increasing pH of solutions from 3 to 5.9. The adsorption capacity of the investigated carbons also increased by HNO₃ acid surface treatment. The results were discussed in light of a possible chemical modification by nitric acid resulting in the creation of a large number of surface functional oxygen species. This interpretation was confirmed by FTIR investigation. The solution-pH and the surface chemistry of the carbons were found to play a decisive role in the uptake of these heavy metal ions from aqueous solutions rather than the carbon texture characteristics.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Today, the removal of heavy metal contaminants is one of the most important environmental issues to be solved. In the last years, the importance of heavy metals pollution control has encouraged a major research effort to develop effective means to identify and remove these toxic pollutants from drinking water and wastewater. The presence of heavy metals in the environment is of major concern because of their threat to human life and the environment. The current regulatory trend is for heavy metal discharge limits approaching those of drinking water standards [1]. For effluents with high metal concentrations, chemical precipitation processes (e.g. hydroxide, sulphide, carbonate) are the oldest and most frequently used due to its low cost. However, many metal bearing wastes contain substances, such as complexing agents, that decrease the effectiveness of precipitation processes leading to relatively high metal concentrations in the effluent. Thus, additional treatment processes, down-line from the precipitation process, may be required to “polish” the effluent prior to discharge. These tertiary processes may be the primary metal removal process from waste streams having low concentrations of metal ions. Examples of such processes involving separation procedures are ion exchange, reverse osmosis cementation, electrochemical, membranes, solvent

extraction and adsorption. Ion exchange and reverse osmosis, while effective in producing and effluent low in metal ions, have high operation, and maintenance costs are subject to fouling [2].

Treatment with activated carbon (AC) has been reported to be efficient for removal of organic and inorganic pollutants from aqueous solutions [3,4]. Its application, in filters for removal of heavy metals (e.g. Hg) proved a competitive process in removal of trace amounts [5,6]. Adsorption on PAC indicated that the process was highly efficient in removing several metal ions from wastewater with an efficiency exceeding 80% [7]. Since then the adsorption by AC has become an established water treatment method for the removal of heavy metals, and hence received considerable attention [1,2,8–18]. These studies covered the removal of several metals including, essentially, Pb²⁺, Hg²⁺, Ca²⁺, Co²⁺, Zn²⁺, Cu²⁺, Cr³⁺, and many others such as rare earths and gold [19]. In particular, lead and cadmium occupy a prominent position as many investigators mentioned their treatment with activated carbons prepared from commercial products, agricultural wastes or from coal origin [1,2,5,9–11,14,16,18–20]. This is attributed to their specific toxicity effects, as there, with Hg²⁺, has been classified as priority pollutants by the US Environmental Protection Agency (EPA) [2].

Agricultural waste products are considered as a convenient source for preparation of activated carbons because of their continual availability, low cost, and feasibility for deriving wide spectra of activity. The adsorption characteristics of activated carbons are generally governed by the source of raw material and the preparation procedures used during carbonization and activation. Another

* Tel.: +20 50 223 2515; fax: +20 23 337 0931.

E-mail address: elhendawy@yahoo.com.

important factor is the surface chemistry of the carbons, particularly in case of metal ions removal [21].

The objective of the present study was to investigate the efficiency of removing lead and cadmium ions from aqueous solutions using activated carbon derived from a novel agricultural by-product; namely date pits. Several factors affecting this process are considered which include the solution-pH, conditions of preparation, texture characteristics, and surface modification through the treatment with nitric acid.

2. Experimental

2.1. Adsorbents

A series of activated carbons, obtained by various activation procedures, have been investigated [22,23]. One group of carbons was prepared by impregnation with phosphoric acid (30, 50, 70 vol%) followed by carbonization at 300, 500, or 700 °C for 3 h, then thoroughly washed with distilled water and finally dried at 110 °C. These carbons are denoted by the letters CP followed by two digits; the first indicating heat-treatment temperature 3, 5, or 7 and the second indicating acid concentration; 3, 5 or 7 respectively. Thus, e.g. CP-55 means a carbon activated by H₃PO₄ of 50 vol% and heat treated at 500 °C. The second group of carbons were prepared by the traditional steam activation, via carbonization at 500 °C for 3 h, followed by gasification by steam/N₂ at 850 °C up to various burn-off values. These carbons are denoted by the letters CS followed by the degree of burn-off (12–73%). Two more carbon samples were obtained by the one-step steam pyrolysis, at 600 or 700 °C, developed recently by Gergova et al. [24,25]. These are denoted by S-600 and S-700, respectively. A last carbon sample was prepared by impregnating the raw material with KOH followed by carbonization at 700 °C for 3 h, as recently suggested by Laine and Calafat [26]; this is denoted by K-700.

Portions of the activated carbons obtained under different activation conditions were subjected to oxidation by HNO₃ to introduce oxygen surface complexes [17]. The procedure was as follows: 50 cm³ of concentrated nitric acid was added to 5 g of activated carbon, and the suspension was heated on a hot plate until dryness. The residue was washed with distilled water until no nitrates were present, and dried overnight at 110 °C.

2.2. Adsorbates

Pb(II) and Cd(II) metal ions were studied, the salts used were lead acetate for Pb(II) and cadmium nitrate for Cd(II). A stock solution of each metal salt was prepared (1000 mg/l) by dissolving the required amount of metal salt in its acidified double distilled water (in 1% HNO₃ or acetic acid solution) to prevent hydrolysis formation. All the chemicals or reagents used were of AR grade. The stock solutions of Pb(II) and Cd(II), were diluted with distilled water to obtain standard solutions.

2.3. Methodology of the equilibrium isotherms

Batch mode sorption studies of Pb(II) and Cd(II) from aqueous solutions were carried out to obtain the equilibrium isotherms at 25 °C. For determining the adsorption isotherms, 100 ml of metal solution of varying concentrations, ranged between 25 and 250 mg/l, was treated with 100 mg of adsorbent and agitated immediately for 24 h. This period of time was determined on the basis of our preliminary studies which was sufficient for the equilibrium uptake of these metal ions. Two series of experiments were carried out for each metal ions at two initial pH of 3 and 5.9. The pH values were adjusted by adding a controlled amount of 0.1 M nitric acid

for Cd(II) or 0.1 M acetic acid for Pb(II) solutions, where the adsorption is significant but below the pH at which the metal hydroxide precipitation occurs. It is known that the metal hydroxide species begin to form at about pH 6 for lead and at about pH 8 for cadmium, for this reason the chosen-pHs here were below these limits. After equilibrium period, the solution was filtered. The residual metal concentrations for each metal in their test solutions were measured by using a Perkin-Elmer model 2380 Atomic Absorption Spectrometer. The metal concentration retained in the sorbent phase q_e (mg/g) was calculated by using the equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of the metal ion in solution (mg/l), V is the solution volume (liters) and W is dry weight of the sorbent mass (g).

3. Results and discussion

3.1. General consideration

The adsorption capacities Q_0 (mg/g) for all investigated adsorbents towards every metal ions were calculated using the following the linear portion of the Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \quad (2)$$

where C_e is the equilibrium metal ion concentration (mg/l or ppm), q_e the amount of lead or cadmium ions adsorbed at equilibrium (mg/g) and Q_0 (mg/g) and b (l/mg) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

An interesting relationship is also plotted to demonstrate the removal capacity (%R) for the various prepared carbons as function of initial metal ions, Pb²⁺ or Cd²⁺, concentrations. It is defined as the ratio of difference in metal concentration before and after adsorption ($C_0 - C_e$) to the initial concentration of metal ions.

$$\%R = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

Such relationship is useful to predict the performance or the efficiency of each carbon in treatment of wastewaters with variable loadings of these heavy metals, Pb²⁺ or Cd²⁺ ions.

3.2. Uptake of Pb²⁺ ions by activated carbons

Fig. 1 depicts the adsorption isotherms of Pb²⁺ by some investigated carbons in both forms oxidized and non-oxidized, in aqueous solutions at pH 3 and 5.9. All isotherms exhibit the L-type, Langmuir, as classified by Giles [27], despite a slight tendency to a high affinity isotherm, H-type, was shown by the oxidized carbons. It is clearly shown from Fig. 1 that the isotherms of the oxidized carbons attained the plateau or the monolayer coverage more faster than the non-oxidized forms. This finding indicates that the oxidized carbons are more efficient in adsorption of Pb²⁺ than the non-oxidized ones. Such behaviour could be ascribed to an effective formation of abundance of oxygen functional groups on the oxidized carbon surface. These functional groups could act as acidic active sites that increased progressively the sequestration of Pb²⁺ from aqueous solutions. The monolayer capacity, Q_0 (mg/g), was evaluated from the linear Langmuir plots (Table 1). Since, in aqueous solution, the Pb²⁺ should be hydrated, a hydration number was suggested to be 4–7.5 [28]. The diameter of Pb_{aq}²⁺ then might be equal to 8.02 nm whereas the diameter of a water molecule is 0.276 nm. Therefore, with the exception of the ultra-micropores (less than 0.8 nm in diameter), all the surfaces areas corresponding to super-micropores, meso- and macropores would be effective and

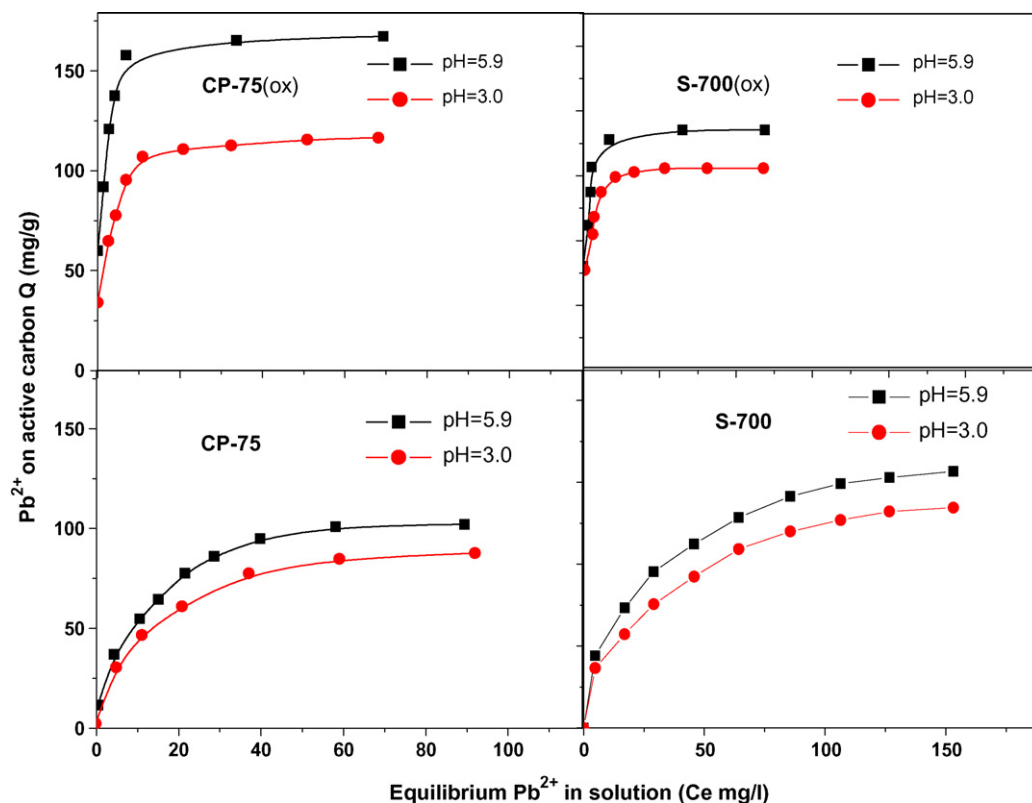


Fig. 1. Adsorption isotherms of Pb^{2+} by selected activated carbons under different conditions (HNO_3 -oxidation, pH 3 and 5.9).

accessible to remove Pb^{2+} from aqueous solutions. By considering the hydrated radius of Pb_{aq}^{2+} , an estimate of the surface area covered by adsorbed Pb^{2+} ions was calculated [2] and given in Table 1. Since many factors affect the adsorption of metal ions from their aqueous solutions, many variables are considered here so as to assess the relative effect of each on the removal capacity.

3.2.1. Dependence of Pb^{2+} removal on carbon texture characteristics

The investigated carbons displayed a wide range of porous characteristics where their specific surface areas (S_{BET}) ranged between 30 and 945 m^2/g , their total pore volumes (V_p) ranged between 0.011 and 0.533 ml/g, and their mean pore radii (\bar{r}) ranged between 7.1 and 45.4 Å. Details regarding their textural characteristics have

been reported elsewhere [22,23]. Most of the tested carbons are typically microporous (mean radii of 7–15 Å) the upper limit of wide-pores shown by few carbons. As mentioned before, the ultramicropores are inaccessible to the diameter of lead hydrated ions in aqueous solutions. Thus the surface characteristics for those carbons were found to play a limited role in the Pb^{2+} adsorption process. The high adsorption capacities of the investigated carbons might be due to another factors such as the solution-pH and the surface chemical nature. Based on the values of surface areas covered by Pb^{2+} (Table 1), it seems that a reasonable fraction of the total surface area takes part in the removal of lead ions 12–77% in relation to S_{BET} of nitrogen surface areas. It is noticeable that the present carbons adsorb significant amounts of lead ions from aqueous solution ranged between 42 and 182 mg/g (for both carbon forms and

Table 1

Adsorption of Pb^{2+} from aqueous solution by the activated carbons at pH 5.9 and 3.0.

| Sample (Oxidized) | at pH 5.9 | | at pH 3.0 | | Sample (Non-oxidized) | at pH 5.9 | | at pH 3.0 | |
|-------------------|--------------|---------------------------|--------------|---------------------------|-----------------------|--------------|---------------------------|--------------|---------------------------|
| | Q_0 (mg/g) | $S^{Pb^{2+}}$ (m^2/g) | Q_0 (mg/g) | $S^{Pb^{2+}}$ (m^2/g) | | Q_0 (mg/g) | $S^{Pb^{2+}}$ (m^2/g) | Q_0 (mg/g) | $S^{Pb^{2+}}$ (m^2/g) |
| CP-33 (ox) | 87 | 128 | 50 | 73 | CP-33 | 59 | 86 | 42 | 62 |
| CP-35 (ox) | 91 | 134 | 57 | 84 | CP-35 | 62 | 91 | 45 | 66 |
| CP-37 (ox) | 98 | 144 | 60 | 88 | CP-37 | 66 | 97 | 44 | 65 |
| CP-53 (ox) | 144 | 211 | 94 | 138 | CP-53 | 95 | 139 | 76 | 112 |
| CP-55 (ox) | 151 | 221 | 70.5 | 103 | CP-55 | 139 | 204 | 54 | 79 |
| CP-57 (ox) | 112 | 164 | 68 | 100 | CP-57 | 80 | 117 | 50 | 73 |
| CP-73 (ox) | 134 | 196 | 89 | 131 | CP-73 | 89 | 130 | 74 | 108 |
| CP-75 (ox) | 162 | 237 | 101 | 148 | CP-75 | 117 | 172 | 84 | 123 |
| CP-77 (ox) | 157 | 230 | 105 | 154 | CP-77 | 119 | 175 | 87 | 17 |
| CS-12 (ox) | 96 | 141 | 87 | 128 | CS-12 | 88 | 129 | 70 | 103 |
| CS-37 (ox) | 133 | 195 | 98 | 144 | CS-37 | 127 | 186 | 105 | 154 |
| CS-54 (ox) | 101 | 148 | 81 | 119 | CS-54 | 80 | 117 | 66 | 97 |
| CS-73 (ox) | 169 | 248 | 146 | 214 | CS-73 | 138 | 202 | 131 | 192 |
| S-600 (ox) | 131 | 192 | 86 | 126 | S-600 | 115 | 169 | 77 | 113 |
| S-700 (ox) | 182 | 267 | 162 | 237 | S-700 | 157 | 230 | 143 | 210 |
| K-700 (ox) | 139 | 204 | 117 | 172 | K-700 | 127 | 186 | 92 | 135 |

Table 2Removal efficiency (%R) of the activated carbons towards Pb^{2+} , estimated for various initial concentrations at $C_0 = 25$ and 75 (mg/l).

| Sample (Oxidized form) | $C_0 = 25$ (mg/l) | $C_0 = 75$ (mg/l) | Sample (Non-oxidized) | $C_0 = 25$ (mg/l) | $C_0 = 75$ (mg/l) |
|------------------------|-------------------|-------------------|-----------------------|-------------------|-------------------|
| CP-33 (ox) | 69 | 50 | CP-33 | 61 | 38 |
| CP-35 (ox) | 71 | 53 | CP-35 | 60 | 41 |
| CP-37 (ox) | 55 | 45 | CP-37 | 48 | 36 |
| CP-53 (ox) | 52 | 41 | CP-53 | 41 | 32 |
| CP-55 (ox) | 54 | 44 | CP-55 | 43 | 33 |
| CP-57 (ox) | 50 | 52 | CP-57 | 39 | 37 |
| CP-73 (ox) | 73 | 58 | CP-73 | 62 | 50 |
| CP-75 (ox) | 97 | 91 | CP-75 | 81 | 55 |
| CP-77 (ox) | 81 | 55 | CP-77 | 75 | 51 |
| CS-12 (ox) | 58 | 40 | CS-12 | 49 | 31 |
| CS-37 (ox) | 91 | 71 | CS-37 | 52 | 33 |
| CS-54 (ox) | 63 | 47 | CS-54 | 47 | 35 |
| CS-73 (ox) | 73 | 45 | CS-73 | 68 | 34 |
| S-600 (ox) | 71 | 57 | S-600 | 46 | 28 |
| S-700 (ox) | 56 | 41 | S-700 | 35 | 30 |
| K-700 (ox) | 70 | 53 | K-700 | 64 | 44 |

both pHs) as indicated in Tables 1 and 2. These amounts are much bigger than previously reported values (20–40 mg/g) [1,2,14]. So, The solution-pH and the surface chemistry of the carbons play the decisive roles in the uptake of these metal ions from their aqueous solutions and the texture characteristics show very limited effect.

3.2.2. Influence of activation conditions on Pb^{2+} removal

Inspection of the results in Table 1 indicates that the scheme of activation appears to affect the efficiency of active carbon in removal of lead ions. Generally, steam-activated, and KOH-treated, carbons are relatively more efficient adsorbents than those activated by H_3PO_4 . Naturally this could be attributed to the basic nature of these carbons ($pH > 8$) [22,23] in comparison to the acid-treated ones.

The fact that the phosphoric acid carbons showed high Pb^{2+} adsorption capacities (cf. Table 1) could be attributed to the pres-

ence of some PO_4^{3-} which could act as active centers contribute in Pb^{2+} sequestration. The observed increase in the uptake capacity of acid-activated carbons by increasing the calcination temperature of the samples activated within 300–700 °C could be attributed to the possible increase in the amount of PO_4^{3-} that may formed and retained on their surfaces.

3.2.3. Effect of solution-pH on adsorption of Pb^{2+}

The solution-pH may have a role in their adsorption capacities towards Pb^{2+} . This parameter was investigated in the present work. The results of this investigation are given in Table 1. Examination of this table shows that the increase in the pH of solution from 3 to 5.9 resulted in a significant increase in the Pb^{2+} uptake capacities by these activated carbons. The increase was attained about 62, 53 and 37% for three modes of activations as displayed by the samples CP-75 (ox), S-600 (ox) and

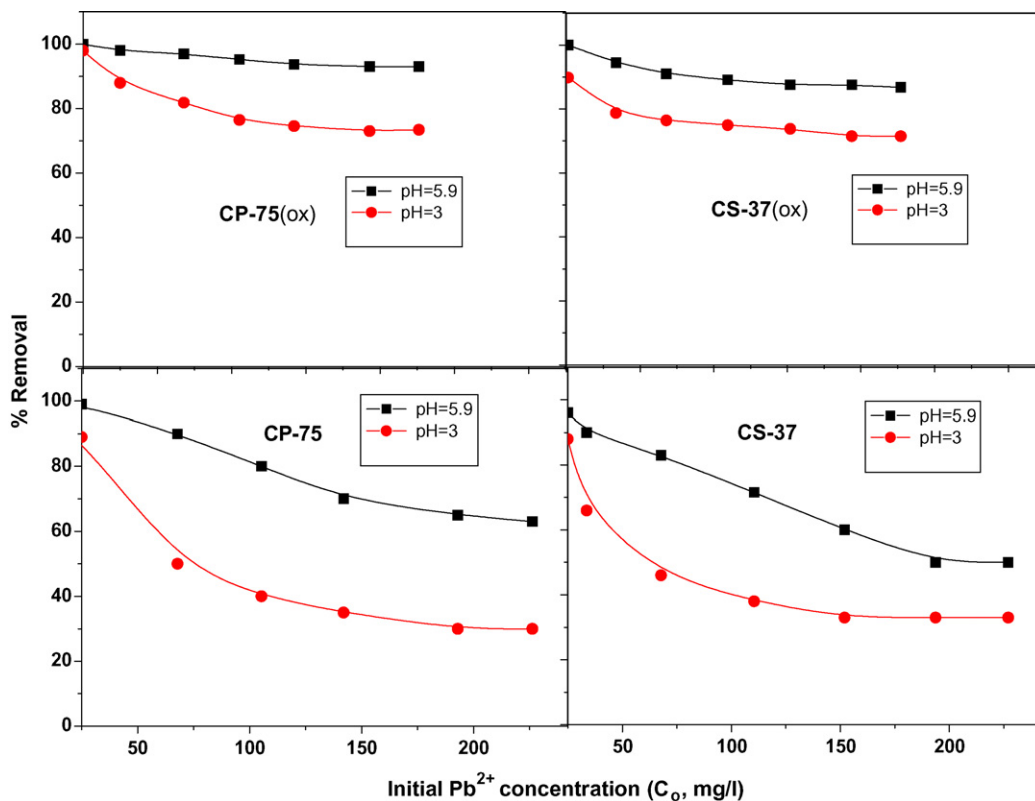


Fig. 2. Removal capacity of Pb^{2+} (%R) by activated carbons under different conditions (oxidation, pH 3 and 5.9).

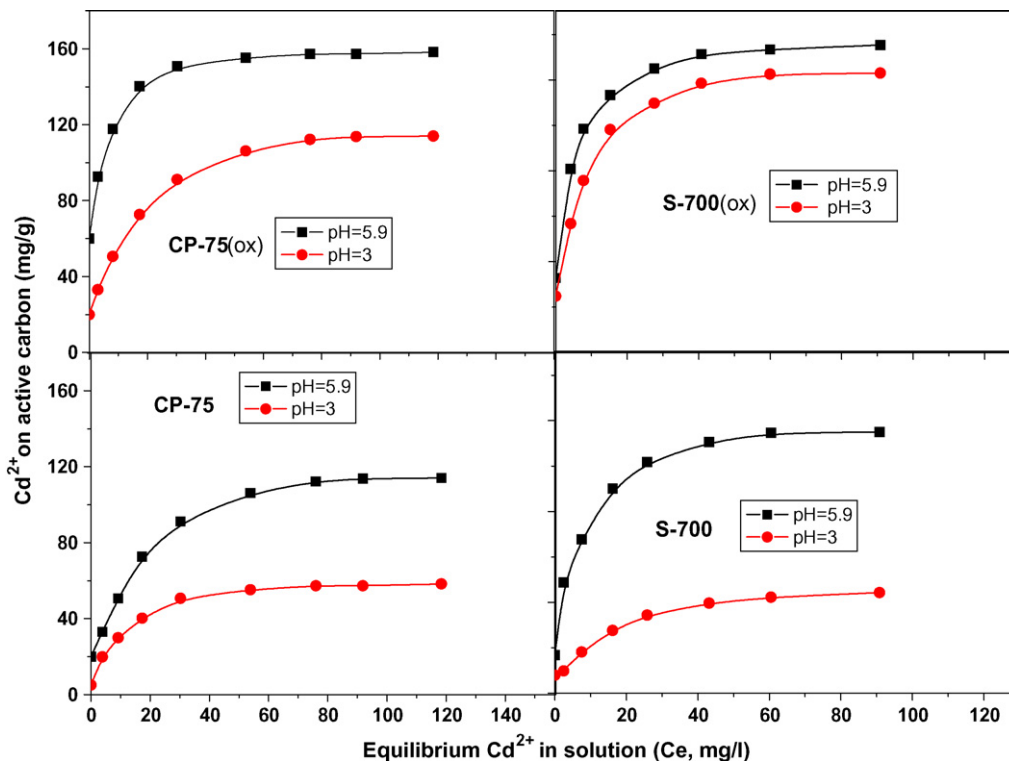


Fig. 3. Adsorption isotherms of Cd²⁺ on some activated carbons under different conditions (oxidation, pH 3 and 5.9).

CS-37 (ox), respectively (Fig. 1, Table 1). The enhanced increase in the Pb²⁺ uptake by active carbons due to increasing the pH of solution has been reported by several authors [1,5,9]. This trend has been discussed in terms of a possible hydrolysis of

adsorbate species and the formation of some surface compounds [8,9,17,29–31].

In fact, activated carbons are characterized by the presence of surface functional groups such as hydroxyl and carboxylic groups.

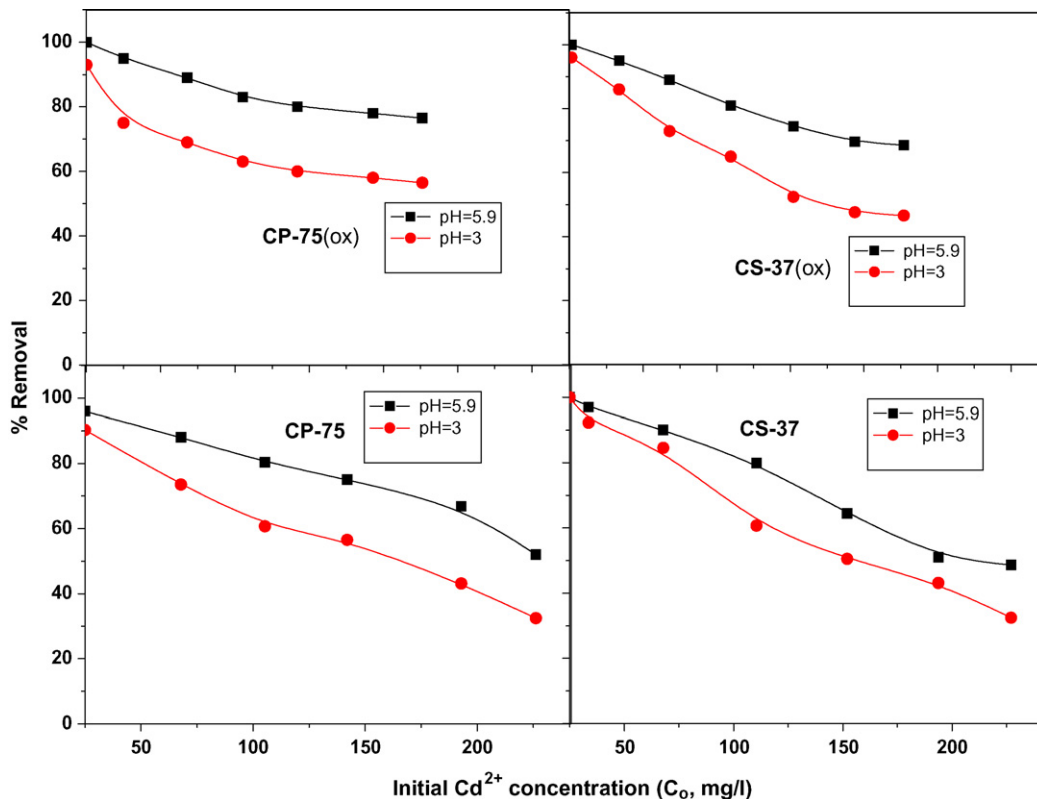


Fig. 4. Removal capacity of Cd²⁺ (%R) by some activated carbons under different conditions (oxidation, pH 3 and 5.9).

These groups may interact with metal cations to release protons H_3O^+ in aqueous solution [8,9,16,32]. Accordingly, this will account for the impact of pH on metal adsorption equilibria which was demonstrated to be very sensitive, and mostly increasing with pH, Table 1. The pattern of increase varies for individual metals as driven by solution phase equilibria of oxide/hydroxide complexes and precipitates [1].

Another suggested factor that might play an equally important role in determining adsorption in the present study, is the presence of the additional controlled-amount of acetate species, through acidification with acetic acid to stabilize the adsorption process at pH 3. This might act through competitive adsorption on the established hydrophobic carbon surface. The presence of dilute acetic acid was noticed to reduce significantly the lead removal capacity in column experiments [1]. It was hypothesized that acetic acid reacted with the carbon associated OH^- (on the surface and in the pore liquid) which produced a more rapid decrease in adsorbent pH and subsequent decrease in lead removal. Acetic acid (through common ion effect) might favour the stabilization of dissolved species of Pb^{2+} in solution and thus decreases its affinity towards the adsorbent. One can conclude that at low pH, both the adsorbent and the adsorbate are positively charged which arising an electrostatic repulsion between them. In addition, the presence high concentration of protons (H_3O^+) at lower pH of solution, these protons will be in competition with the positively charged metal ions for the adsorption sites on the carbon surface. Thus, both electrostatic repulsion and competition hinder or hampering the metal adsorption leading to a sharp decrease in adsorption capacity.

3.2.4. Estimated partial removal at different initial metal concentration

Based on the initial and equilibrium concentrations of Pb^{2+} , percentage removal capacities were evaluated at specific values (Table 2). From the practical point of view, most of the tested carbons seem to remove appreciable amounts of lead at a level of 25 mg/l, which is usually encountered in some contaminated waste streams. Activated carbons obtained under different preparation conditions remove in average from 50 up to 77% at such lead level and at the equilibrium in batch treatment conditions. Inspection of Table 2 appears, clearly, that the oxidized-carbons, in general, remove the biggest amounts of Pb^{2+} than the non-oxidized ones. At an initial low level of $C_0 = 25$ mg/l, they reported the highest metal removals, as %R (50–97%), and at a high level of $C_0 = 75$ ppm they removed 41–91%. It was noticed also that the investigated carbons adsorbed considerable amounts of lead ions than cadmium ions, this could be ascribed to the fact that the lower the pH at which metal hydroxide species form, the better the removal and thus, it was expected that lead would be better removed compared to cadmium, as obtained in this study (Fig. 2).

One fixed bed experiment (column) was conducted using an influent solution containing 20 mg Pb^{2+} in liter (20 ppm) of aqueous solution, and employing carbon CP-77. At a flow rate of 150 ml l^{-1} the AC column produced an effluent containing only 0.3–0.5 ppm of Pb^{2+} up-to 3 h, this consider as a pre-indication shows the efficiency of these carbons in the removal of lead ions from aqueous solution through column mode.

3.3. Efficiency of activated carbons in the removal of Cd^{2+} ions

A series of experiments were carried out to elucidate the efficiency of the prepared carbons in removing cadmium ions from aqueous solution, with the aim of comparison with Pb^{2+} removal. Fig. 3 illustrates the adsorption isotherms of Cd^{2+} ions on some representative carbon samples that clearly show their matching with the Langmuirian type. Fig. 4 shows their corresponding removal capacities towards Cd^{2+} under different conditions (oxidation, pH

3 and 5.9). The corresponding monolayer capacities Q_0 (mg/g) are given in Table 3. Cadmium seems to be removed, relatively, in smaller amounts than lead ions. This was appeared at the lower pH of 3, for the three modes of activation that can be represent with the three oxidized carbons CP-75 (ox), CS-37 (ox) and S-700 (ox). Their uptake capacities ranged 48–153 mg/g for Cd^{2+} in comparison to 50–162 mg/g for Pb^{2+} . However, the comparison of these values with their data obtained at pH 5.9, in this case these representative samples removed increasing comparable amounts of both metal ions. They removed 160, 131 and 169 mg/g of Cd^{2+} ions compared to 162, 133 and 182 mg/g of Pb^{2+} ions, respectively.

Compared to the fractional removal of lead at $C_0 = 25$ mg/l, cadmium ions are removed at a higher rate ($R \geq 83\%$) (Fig. 4). It might be assumed that the superior removal of cadmium could be attributed to faster migration in solution, and to probably lower hydration number surrounding them. This makes more micropores available to their adsorption.

3.4. Surface chemistry investigation

Fig. 5 shows the FTIR spectra of a representative carbon sample, CP-55 and its oxidized form CP-55 (ox). It is well known that many direct information about the surface chemical nature of the carbons may be obtained from their IR spectra. Thus, from the comparison of the spectra of both oxidized and non-oxidized carbons (Fig. 5) we can see the following: broad bands were observed in the spectra of both carbons forms in the range above 3000 cm^{-1} . These bands together with that appearing at 1717 cm^{-1} could be ascribed to stretching vibration of hydroxyl groups involved in hydrogen bonding probably participating with water adsorbed molecule on the carbon. These bands were appeared more intense and sharp in the spectra of the oxidized form which indicating an increase in surface hydrophilicity and thus water adsorption as a consequence to HNO_3 oxidation [17]. New bands at 1577, 1538 and 1334 cm^{-1} were found in the spectrum of the oxidized carbon indicating the presence of nitro and nitrates groups on the carbon surface. The bands centered and appeared at 1720 cm^{-1} in the spectra of both investigated carbons are more prominent in carbon spectra and is ascribed to stretching vibration of C=O in carboxylic acid and lactones groups. [17,33]. Two new weak bands were observed in the spectra of the oxidized carbon at 890 and 730 cm^{-1} which can be assigned to bending vibration (in-plane δ) of NO_2 and bending vibration (out-of-plane γ) of NO_2 of aromatic nitro compounds [33].

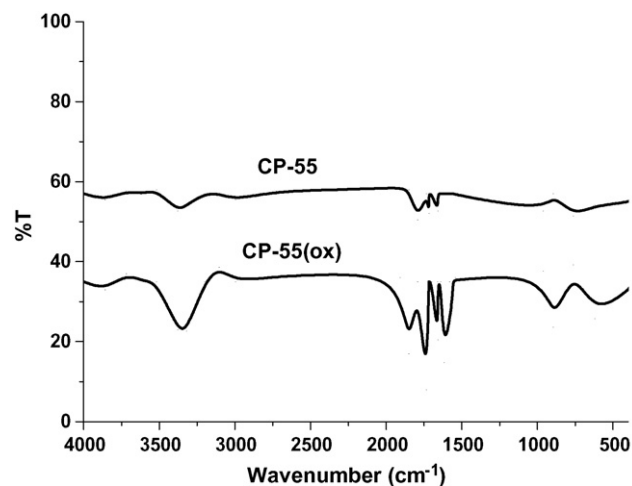


Fig. 5. A representative FTIR spectra of CP-55 carbon sample and its oxidized form CP-55 (ox).

Table 3
Adsorption of Cd²⁺ from aqueous solution by the activated carbons at pH 5.9 and 3.0.

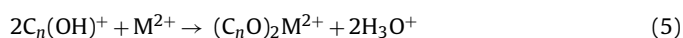
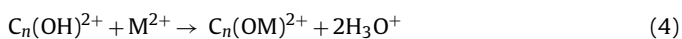
| Sample (Oxidized form) | Q ₀ (mg/g) | | Sample (Non-oxidized) | Q ₀ (mg/g) | |
|------------------------|-----------------------|-----------|-----------------------|-----------------------|-----------|
| | at pH 5.9 | at pH 3.0 | | at pH 5.9 | at pH 3.0 |
| CP-33 (ox) | 85 | 48 | CP-33 | 57 | 38 |
| CP-35 (ox) | 88 | 55 | CP-35 | 60 | 41 |
| CP-37 (ox) | 91 | 59 | CP-37 | 61 | 36 |
| CP-53 (ox) | 130 | 91 | CP-53 | 86 | 32 |
| CP-55 (ox) | 143 | 70 | CP-55 | 127 | 33 |
| CP-57 (ox) | 103 | 66 | CP-57 | 77 | 37 |
| CP-73 (ox) | 127 | 87 | CP-73 | 83 | 50 |
| CP-75 (ox) | 160 | 99 | CP-75 | 115 | 55 |
| CP-77 (ox) | 155 | 103 | CP-77 | 117 | 51 |
| CS-12 (ox) | 93 | 85 | CS-12 | 80 | 31 |
| CS-37 (ox) | 131 | 91 | CS-37 | 121 | 33 |
| CS-54 (ox) | 97 | 77 | CS-54 | 73 | 35 |
| CS-73 (ox) | 160 | 140 | CS-73 | 129 | 34 |
| S-600 (ox) | 130 | 83 | S-600 | 111 | 28 |
| S-700 (ox) | 169 | 153 | S-700 | 151 | 30 |
| K-700 (ox) | 131 | 108 | K-700 | 124 | 44 |

Therefore, one can conclude that the liquid phase nitric acid oxidation of carbon brought about the fixation of a large amount of oxygen functional groups in the form of carboxylic acid groups as well as nitro- and nitrates complexes. These groups, consequently, increase the surface polarity that may contribute the sequestration of these polar metals ions from aqueous solutions, as will be discussed in the next section.

3.5. Effect of surface modification on the uptake of Pb²⁺ and Cd²⁺ ions

Figs. 1 and 3 illustrate the adsorption isotherms of Pb²⁺ and Cd²⁺ by the HNO₃⁻ oxidized activated carbons (denoted by ox). Oxidation of the investigated carbons brought about a significant effect on the adsorption of lead and cadmium ions. This finding is clearly observed through the big adsorbed amounts of Pb²⁺ or Cd²⁺ by the oxidized form of the investigated carbons (Tables 1 and 3, Figs. 1–4). The observed increase in their metal adsorption capacities, as a consequence to oxidation process, was attained (in average) about 31 and 19% for lead and cadmium ions, respectively (Tables 1 and 3). This could be attributed to the oxidation process resulted in abundant of the adsorption sites that could sequester these big fractions of these metals from their aqueous solutions.

Nitric acid is recognized as a strong aggressive oxidant for the carbon surface. Its effect appears in generating and increasing the oxygen complexes; which have been reported by many investigators [9,16,17,21,23,31]. A considerable increase in the total acidic carboxylic and phenolic groups, appears which is dependent on the temperature of treatment with HNO₃ [17]. A relative greatest increase appears in the carboxylic groups which might dissociate in the aqueous media to release H⁺ ions. The released H⁺ will create electron donor centers that may facilitate and increase Pb²⁺ or Cd²⁺ deposition on the carbon surface. It has been reported that sorption of metal ions could be explained on the basis of an ion-exchange mechanism [32] or surface complexation [16,17]. As the carbon surface attracts the metal ions an equivalent amount of H⁺ are released into solution [34,35]. It is well known that the nitric-acid treatment increases the oxygen-containing functional groups which include acidic phenolic, hydroxyl, carbonylic and nitro groups on the carbon surface. Lead and cadmium adsorption may include formation of surface complexes with these functional groups on the carbon surface. The suggested equations for the reactions between metal ions, M²⁺, and surface functional groups to form complexes may be expected as follows in the aqueous medium:



Now the determining factor will be the surface chemistry rather than the texture characteristics of the carbon adsorbent. Where, although the uptake capacity seems to be limited by the available nitrogen-S_{BET}, nevertheless, the surface areas covered by Pb²⁺ ions, S^{Pb²⁺}, represents a significant fraction of the total surface areas (cf. Table 1). Oxidation by HNO₃ is believed to increase the carbon hydrophilic nature to become more wettable by water, as confirmed in this study via appearing a strong water IR-band in the oxidized form spectrum. Under these modified oxidation conditions and in water as a transport medium, an enhanced migration, diffusion and adsorption of Pb²⁺ or Cd²⁺ ions could take place, as observed in the obtained results in this study.

4. Conclusions

Date pits offer a promising raw material for the production of activated carbons for water treatment purposes. The investigated carbons exhibited good to high uptake capacities for metal ions. From slightly acidified lead acetate solutions (at pH 3) the HNO₃-oxidized carbons adsorbed 50–162 mg/g of Pb²⁺ that increased, significantly, by increasing the solution-pH to 5.9 and reported the range 87–182 mg/g. This uptake was found to be dependent on the preparation and activation procedure. Uptake of Pb²⁺ increases as function of heat-treatment temperature for the H₃PO₄ activated carbons which could be attributed to the presence of some PO₄³⁻ that may act as active centers contribute in Pb²⁺ sequestration. Steam-activation, generally enhances adsorption of lead ions probably due to the basic nature of these carbons. Many factors affect the uptake of metal ions: (1) scheme of activation of the adsorbent, (2) pH of the adsorption medium or solution, (3) surface oxygen complexes of the adsorbent (consequent to HNO₃-treatment) and (4) texture characteristic of the carbon (no apparent effect). The surface chemical nature of the activated carbon and pH of solution were found to play the major roles to inflict the highest impact on Pb²⁺ and Cd²⁺ ions removal. Lead is removed in somewhat higher amounts than cadmium due to its lower solubility and lower pH for complexation or deposition, which promotes its removal in comparison to Cd²⁺. Lead ions at the level of 25 mg/l, which is considered a low level and usually encountered in contaminated streams, the activated carbons increase their fractional removal with pH (from 3 to 5.9), then with HNO₃ oxidation to attain up to 97%. At same level of Cd²⁺, oxidation with HNO₃ has a limited effect or affects slightly the partial removal.

References

- [1] B.E. Reed, S. Arunachalam, B. Thomas, Removal of lead and cadmium from waste streams using granular activated carbon (GAC) columns, *Environ. Progress* 13 (1994) 60–64.
- [2] M. Ferro-García, A. Rivera-Utrilla, J. Bautista-Toledo, Removal of lead from water by activated carbons, *Carbon* 28 (1990) 545–552.
- [3] J.W. Patrick, *Porosity in Carbons: Characterization and Applications*, Edward Arnold, 1995, pp. 227–252.
- [4] D. Rivin, J.H. Atkins, Sorption of bioactive materials on carbon, *Carbon* 25 (1987) 135–145.
- [5] R.C. Bansal, J.B. Donnet, H.F. Stoeckli, *Active Carbon*, Marcel Dekker, New York, 1988, pp. 1–25.
- [6] C.P. Huang, D.W. Blankenship, The removal of mercury(II) from dilute aqueous solution by activated carbon, *Water Res.* 18 (1984) 37–46.
- [7] A.A. El-Hendawy, S.E. Samra, B.S. Girgis, Adsorption characteristics of activated carbons obtained from corncobs, *Colloids Surf. A* 180 (2001) 209–221.
- [8] J.P. Chen, M. Lin, Surface charge and metal ion adsorption on an H-type activated carbon: experimental observation and modeling simulation by the surface complex formation approach, *Carbon* 39 (2001) 1491–1504.
- [9] M.M. Rao, G.P.C. Rao, K. Seshiah, N.V. Choudary, M.C. Wang, Activated carbon from *Ceiba pentandra* hulls, an agricultural waste, as an adsorbent in the removal of lead and zinc from aqueous solutions, *Waste Manage.* 28 (2008) 849–858.
- [10] S. Satoa, K. Yoshihara, K. Moriyama, M. Machida, H. Tatsumoto, Influence of activated carbon surface acidity on adsorption of heavy metal ions and aromatics from aqueous solution, *Appl. Surf. Sci.* 253 (2007) 8554–8559.
- [11] C.A. Toles, W.E. Marshal, M.M. Johns, Granular activated carbons from nutshells for uptake of metals and organic compounds, *Carbon* 35 (1997) 1407–1414.
- [12] J. Goel, K. Kadirvelu, C. Rajagopal, V.K. Garg, Removal of lead (II) by adsorption using treated granular activated carbon: batch and column studies, *J. Hazard. Mater. B1* (25) (2005) 211–220.
- [13] A.A. El-Hendawy, A.A. Attia, W.E. Rashwan, Monitoring changes in textural and adsorptive properties of porous carbons modified by oxidizing agent, *Mans Sci Bull.* 31 (2004) 227–243.
- [14] T. Budinova, N. Petrov, J. Parra, V. Baloutzov, Use of activated carbon from antibiotic waste for the removal of Hg(II) from aqueous solution, *J. Environ. Manage.* 88 (2008) 165–172.
- [15] A.A. El-Hendawy, Surface and adsorptive properties of carbons prepared from biomass, *Appl. Surf. Sci.* 252 (2005) 287–295.
- [16] Z. Zhang, S. Chen, H. Lin, H. Zhang, Simultaneous determination of copper, nickel, lead, cobalt and cadmium by adsorptive voltammetry, *Anal. Chim. Acta* 272 (1993) 227–232.
- [17] A.A. El-Hendawy, Influence of HNO₃ oxidation on the structure and adsorptive properties of corncob-based activated carbon, *Carbon* 41 (2003) 713–722.
- [18] A.M. Youssef, M.R. Mostafa, Removal of copper ions by modified activated carbons, *Ind. J. Technol.* 130 (1992) 413–416.
- [19] A.M. Youssef, Th. El-Nabarawy, S.E. Samara, Sorption properties of chemically-activated carbons. 1. Sorption of cadmium (II) ions, *Colloids Surf. A* 235 (2004) 153–163.
- [20] P. Navarro, P. Vargas, M. Alonso, F.J. Alguacil, Towards a more environmentally friendly process for gold: models on gold adsorption onto activated carbon from ammoniacal thiosulfate solutions, *Desalination* 211 (2007) 58–63.
- [21] D. Mohan, S. Chander, Single component multi-component adsorption of metal ions by activated carbons, *Colloids Surf. A* 177 (2001) 183–196.
- [22] B.S. Girgis, A.A. El-Hendawy, Porosity development in activated carbons obtained from date pits under chemical activation with phosphoric acid, *Micro-porous Mesoporous Mater.* 52 (2002) 105–117.
- [23] A.A. El-Hendawy, Ph.D. Thesis, Mansoura University, Egypt, 1997.
- [24] K. Gergova, N. Petrov, S. Eser, Adsorption properties and microstructure of activated carbons produced from agricultural by-products by steam pyrolysis, *Carbon* 32 (1994) 693–702.
- [25] K. Gergova, N. Petrov, S. Eser, Effect of activation method on the pore structure of activated carbons from apricot stones, *Carbon* 34 (1996) 879–888.
- [26] J. Laine, Calafat A, Factors affecting the preparation of activated carbons from coconut shell catalyzed by potassium, *Carbon* 29 (1991) 949–953.
- [27] C.H. Giles, T.H. MacEwan, S.N. Nakhwa, D. Smith, *Studies in adsorption Part XI. A system of classification of adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids*, *J. Chem. Soc.* (1960) 3973.
- [28] J. Burges, *Metal Ions in Solution*, Ellis Harwood Ltd., New York, 1978.
- [29] A. Netzer, D.E. Hughes, Adsorption of copper, lead and cobalt by activated carbon, *Water Res.* 18 (1984) 927–933.
- [30] B.E. Reed, J. Maqbul, B. Tomas, Effect of pH, empty bed contact time and hydraulic loading rate on lead removal by granular activated carbon columns, *Water Environ. Res.* 68 (1996) 877–882.
- [31] E.H. Smith, Removal of cadmium, zinc, and lead from wastewater using recycled shot-blast fines, *Metal Finishing* 93 (1995) 13–25.
- [32] J. Karthikeyan, M. Chaudhuri, Enhancement of mercury (II) sorption from water by coal through chemical pretreatment, *Water Res.* 20 (1986) 449–452.
- [33] A.A. El-Hendawy, Variation of the FTIR spectra of a biomass under impregnation, carbonization and oxidation conditions, *J. Anal. Appl. Pyrol.* 75 (2006) 159–166.
- [34] M.A. Lillo-Ródenas, D. Cazorla-Amorós, A. Linares-Solano, Behaviour of activated carbons with different pore size distributions and surface oxygen groups for benzene and toluene adsorption at low concentrations, *Carbon* 43 (2005) 1758–1767.
- [35] I. Bautista-Toledo, J. Rweru-Utrilla, M.A. Ferro-García, C. Moreno-Castella, Influence of the oxygen surface complexes of activated carbons on the adsorption of chromium ions from aqueous solutions. Effect of sodium chloride and humic acid, *Carbon* 32 (1994) 93–100.