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Electrochemical studies of the interaction between a modified activated carbon surface and heavy metal ions

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Abstract

Cyclic voltammetric studies of the influence of surface chemistry on the electrochemical behaviour of powdered activated carbon electrodes (PACE) in the presence of selected heavy metal ions (Pb^{2+}, Hg^{2+}, Cd^{2+}) in bulk solution and pre-adsorbed on carbon were carried out. The variety of surfaces was achieved via the modification of carbon samples by heat treatment under vacuum and in an oxygen/ammonia atmosphere, as well as oxidation with conc. nitric acid. The chemical structures of the modified carbon surfaces were characterised by XPS and standard pH-titration. The adsorption capacities of the modified carbon samples towards the heavy metal ions in question were estimated. The mechanisms of adsorption processes of metal species on carbon surfaces were analysed and described on the basis of their electrochemical behaviour. The nature of the interactions between the modified carbon surfaces and adsorbed cations is discussed.

1. Introduction

Although heavy metals are considered harmful to the environment, their concentrations in surface water have increased considerably in recent times. As they are among the most toxic of water pollutants, investigations concerning their removal or at least their minimisation are of considerable importance. A variety of techniques are now being applied in the treatment of surface water or waste water to reduced the levels of these pollutants to a minimum. Activated carbon has been an effective adsorbent for the removal of inorganic metal ions because of their highly developed surface area and microporosity, high chemical, thermal and ionising radiation stability, and their distinctive sorptive behaviour in solutions of electrolytes [1–3]. Although the selectivity and sorptive capacity of commercial carbon adsorbents towards metal ions is rather low, these parameters can be altered by the introduction of functional groups through surface modification [4–12]. The following phenomena may occur on a carbon surface during adsorption: (i) active proton/cation exchange, (ii) surface complex formation of metal ions, (iii) spontaneous reduction of metals with low standard redox potentials (charge-transfer processes), (iv) interaction of metal cations with the π electrons of the carbon network. Thus, modification of the activated carbon surface can affect adsorption mechanisms and the ways in which surface and sorbed cation interact.

In the present investigations, we studied the influence of surface oxygen and/or nitrogen groups on the adsorption of Pb^{2+}, Hg^{2+}, Cd^{2+} ions from aqueous solution on modified activated carbon. We further attempted to ascertain the real nature of the adsorbed ionic species – modified carbon surface interactions using X-ray photoelectron spectroscopy and cyclic voltammetric measurements.

2. Experimental

2.1. *Materials*

A commercial active carbon ROW 0.8 Supra (Norit, The Netherlands) was washed (demineralised) with concentrated HF and HCl acids (ash content 0.2 wt. %) and subsequently modified by:

(i) heating at 1173 K under vacuum (HTV),
(ii) heating in a stream of 1:1 oxygen–ammonia at 673 K (OPA),
(iii) oxidation with concentrated nitric acid at 355 K (ONA).

The physicochemical properties of the carbon samples obtained in these ways have been described elsewhere [13, 14].

2.2. *Surface chemistry*

2.2.1. *XPS measurements*

The XPS method was used to characterise the chemical properties of the modified carbon surface. XP spectra were obtained with an EscaLab 210 (V.G. Scientific Ltd.) photoelectron spectrometer using non-monochromatised Al K_α radiation (1486.6 eV), the source being operated at 15 kV and 34 mA. Prior to XPS measurement the powdered carbon samples were dried for 2 h at 100 °C (373 K). The vacuum in the analysis chamber was always better than 5×10^{-10} Pa. The high-resolution scans were performed over the 280–294, 395–407 and 527–540 eV ranges (C 1s , N 1s and O 1s spectra, respectively). In order to obtain an acceptable signal-to-noise ratio the spectral region was scanned 20 times. After subtraction of the base line (Shirley-type), curve fitting was performed using the non-linear least-squares algorithm and assuming a mixed Gaussian/Lorenzian peak shape of variable proportion (mainly 0.3). This peak-fitting was repeated until an acceptable fit was obtained (error – 5%). The positions of the deconvoluted peaks (binding energy – BE) were determined from both literature data [15–17] and empirically derived values.

2.2.2. *pH-metric titration*

The pH-metric titrations were carried out using the point-by-point method [18, 19]. Known portions of each carbon were added to the mixtures containing various quantities of NaCl, NaOH and HCl (pH = 1–13).The ionic strength was kept constant ($I = 0.1$).

2.3. *Adsorption studies*

The active carbon samples (ca. 0.2 g) were immersed in the metal (Pb, Hg, Cd) nitrate solution (10 cm^3) of concentration 0.01 M and pH = 1.33 adjusted by the addition of 0.1 M HNO_3. Each mixture was shaken in a dark bottle for 48 h, after which the cation concentration and the pH of the solutions were determined. The metal ion concentrations were determined as follows: Pb^{2+} by colorimetric analysis using PAR as complexing agent [20], Hg^{2+} by spectrophotometry according to the procedure described in the literature [21], and Cd^{2+} by atomic absorption spectroscopy (Philips PU9100 AAS).

2.4. *Cyclic voltammetry*

Electrochemical studies of all the activated carbon samples, both before and after metal cation adsorption, were performed as previously described [7, 10, 22]. Cyclic voltammetry measurements were carried out in blank electrolyte solutions (0.1 M $NaNO_3$ + 0.1 M HNO_3 (pH = 1.33)) using the powdered active carbon electrode (PACE) technique [10, 22]. After prior vacuum desorption (10^{-2} Pa), the powdered carbon (grain size 0.075–0.063 mm, mass 50 mg) was placed in an electrode container and drenched with a de-aerated solution to obtain a ~3 mm sedimentation layer. First, the potentiometric responses of the carbon electrodes were measured in an oxygen-free atmosphere once their values had stabilised (usually after 24 h). Next, cyclic voltammetry (CV) was performed using the typical three-electrode system and an Autolab (Eco Chemie) modular electrochemical system equipped with a PGSTAT 10 potentiostat, driven by GEPS3 software (Eco Chemie). All potentials were measured, and are reported against a potassium chloride saturated calomel electrode (SCE). A platinum gauze served as counter electrode. The cyclisations were started from zero to positive potentials and were carried out in potential ranges precluding the electrolysis of water. The cyclic voltammograms were recorded after curve shapes had stabilised. Although the electrode design ensures that the shape of the CV curves recorded is reproducible, the specific capacitance cannot now be estimated because the potential and current distribution in the electrode bed are unknown [23].

The electrochemical behaviour of prepared PACEs was compared with that of solid glassy carbon GC (3 mm disc diameter) and graphite RG (Radelkis, OP-C-711-C, 6 mm disc diameter) commercial electrodes [7, 10].

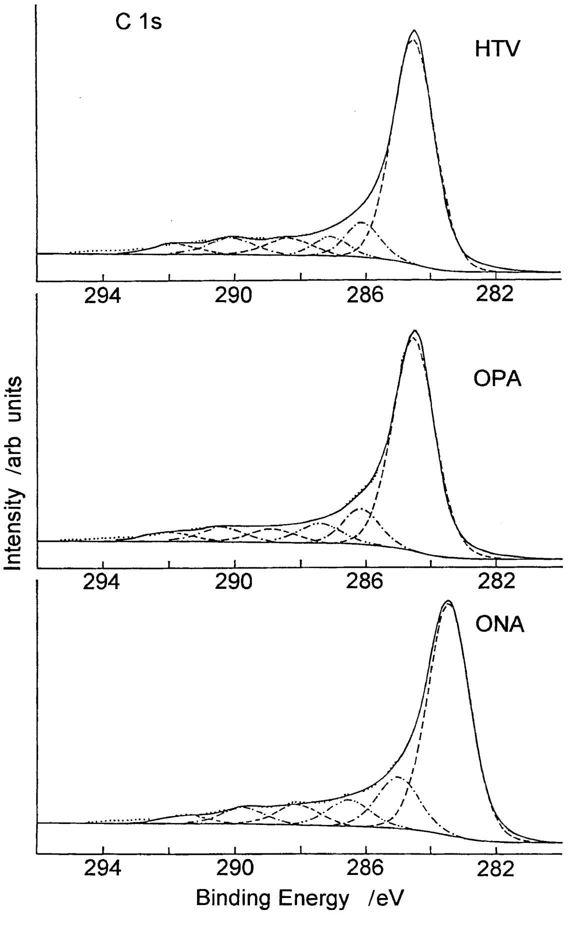

Fig. 1. High resolution XP spectra of C 1s for modified carbon samples.

3. Results and discussion

The surface properties of the activated carbon samples have in part already been described [13, 14]. The chemical structure of surface layer of the materials is highly diverse. Annealing under vacuum (HTV) gives basic properties on the carbon surface while the oxidised carbon sample (ONA) has acidic groups at different acidic strength. Amino-oxidative treatment (OPA) produces amphoteric characteristic with a slight excess of basic properties. The specific surface areas of the modified carbon samples obtained from nitrogen adsorption (at 77 K) were calculated by the BET method to be 1003, 1024 and 970 $m^2 g^{-1}$ for HTV, OPA and ONA, respectively. To facilitate the discussion of the later electrochemical studies performed in this work, the surface chemistry of the carbon samples was characterised by XPS and pH-metric titration.

The high-resolution XP spectra for the C 1s, N 1s and O 1s regions are presented in Figures 1–3, respectively: several peaks are present for each element. Deconvolution of the C 1s spectra (Figure 1) yields several peaks with different binding energies (BE), which probably represent: (i) graphitic carbon (284.5 eV), (ii) carbon atoms in phenolic, alcohol or ether groups (286.1 eV), (iii) carbonyl or quinone groups (287.4 eV), (iv) nitrogen-containing and/or ester groups (288.7 eV), (v) carboxylic acidic groups (289.3 eV), and (vi) carbon present in acid anhydride, carbonate groups and/or adsorbed carbon oxides (290.4 eV). These assignments agree very well with the extensive XPS studies done on the commercially available carbons used as catalyst supports [25–28]. Heat treatment under vacuum (HTV) or in an oxygen/ammonia atmosphere (OPA) enhanced the amount of total surface carbon and the relative concentration of graphitic carbon; oxidation with nitric acid (ONA) reduced these quantities.

Following the modification procedures used here, the N 1s peak shape undergoes considerable change (Figure 2). Four types of nitrogen can be distinguished in the modified material according to the schematic representation put forward by Kapteijn et al. [29]: N-6 (pyridinic), N-5 (pyrrolic and pyridonic), N–Q (nitrogen substitutes in aromatic graphene structures – quaternary nitrogen) and N-X (nitrogen oxides, pyridine-*N*-oxides) with binding energies of 398.6, 400.2, 401.3 and 404.5 eV, respectively. Heat treatment under vacuum retains a small amount of surface nitrogen (0.3%)

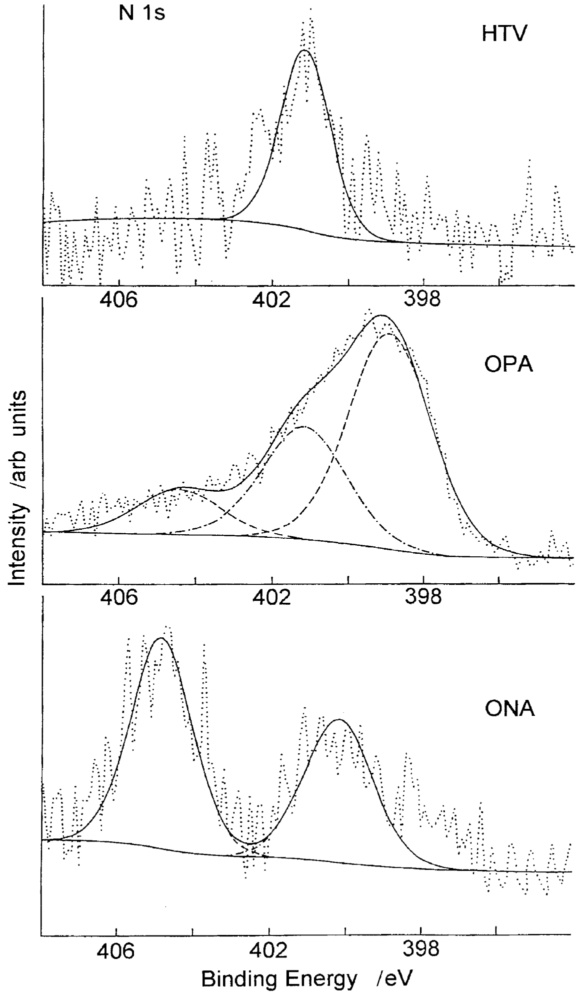

Fig. 2. High resolution XP spectra of N 1s for modified carbon samples.

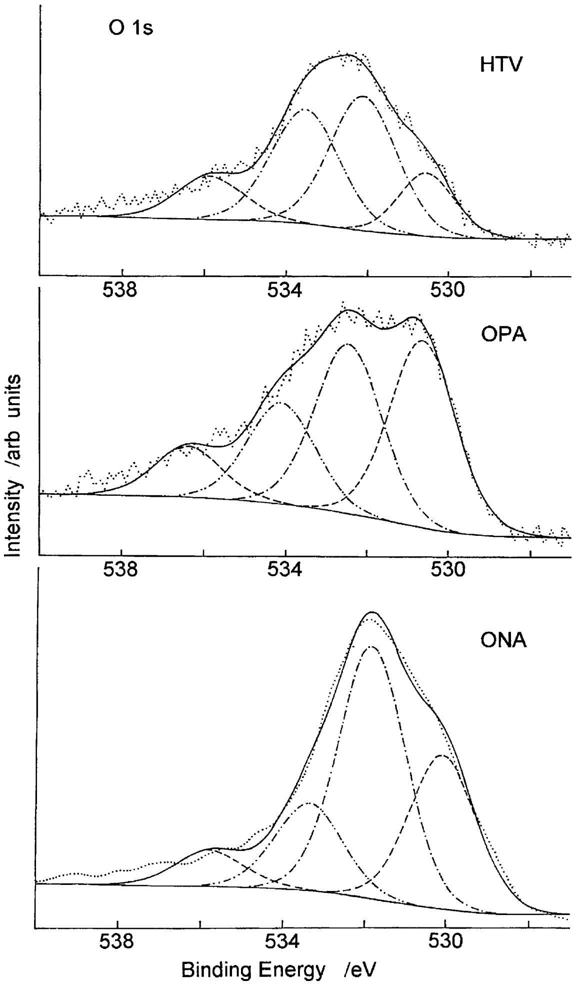

Fig. 3. High resolution XP spectra of O 1s for modified carbon samples.

Table 1. Physicochemical characteristic of modified carbon samples

Sample	S_{BET}/m g^{-1}	O/N (at.%/at.%)		pH[a]	H_3O^+ ads. /mM g^{-1}	OH^- ads. /mM g^{-1}	E_s[b]/mV	c_0[c] /mC g^{-1}
		Elemental	XPS					
HTV	1003	0.30/0.26	2.5/0.2	10.8	0.568	0.163	+380	74
OPA	1024	1.51/1.81	2.5/2.1	8.9	0.495	0.296	+298	68
ONA	970	3.87/0.62	7.0/0.7	4.5	0.348	1.125	+512	102

[a] pH of carbon slurry (1 g AC in 100 cm^{-3} of 0.1 M $NaNO_3^-$).

[b] For pH = 1.33.

[c] c_0 – cathodic peak capacity (see Figure 5).

bound as quaternary nitrogen (N–Q). After modification in an oxygen/ammonia atmosphere, the total nitrogen surface concentration increases to 2.1%. This is probably due to the partial replacement of surface oxygen atoms by nitrogen-containing species. After oxidative modification a new type of bonded nitrogen (like nitric oxides) appears.

The O 1s spectra (Figure 3) for the carbon samples display several peaks whose binding energies depend on the modification procedure. Three main peaks corresponding to C=O (530.6 eV), C—O (532.3 eV) and adsorbed water (536.3 eV) are present for all the samples studied. The other two peaks with binding energies 533.5 and 534.3 eV can be ascribed to C—O—C and C=N—O structures, respectively, in different surface oxygen-as well as oxygen- and nitrogen-containing functional groups [17]. The higher concentration of surface carbonyl groups on oxygen/ammonia treated carbons suggests their higher ability to chemisorb dioxygen with the formation of a superoxide species (in the first stage) and then carbonyl moieties (surface autocatalytic oxidation) [27].

The surface elemental composition was estimated on the basis of the XPS data. The surface oxygen and nitrogen atomic percentages are set out in Table 1.

The results of pH titration for the modified carbon samples are shown in Figure 4. Basic properties are dominant for HTV samples up to pH 11.5, for the OPA sample up to about pH 10. This stands in contrast to the acid–base behaviour of the nitric-acid-oxidised sample (ONA), which exhibits acidic properties above pH 3. These values are similar to the results obtained by mass titration (10.87, 7.36, 3.48) and the pH of a carbon slurry in 0.1 M $NaNO_3$ (10.8, 8.9, 4.5), respectively. Titration of the samples with 0.1 M hydrochloric acid and sodium hydroxide solutions yielded the capacities listed in Table 1.

The electrochemical behaviour of electrodes prepared from the tested carbons was investigated at potential ranges from −0.8 to +1.8 V (vs SCE) and for sweep

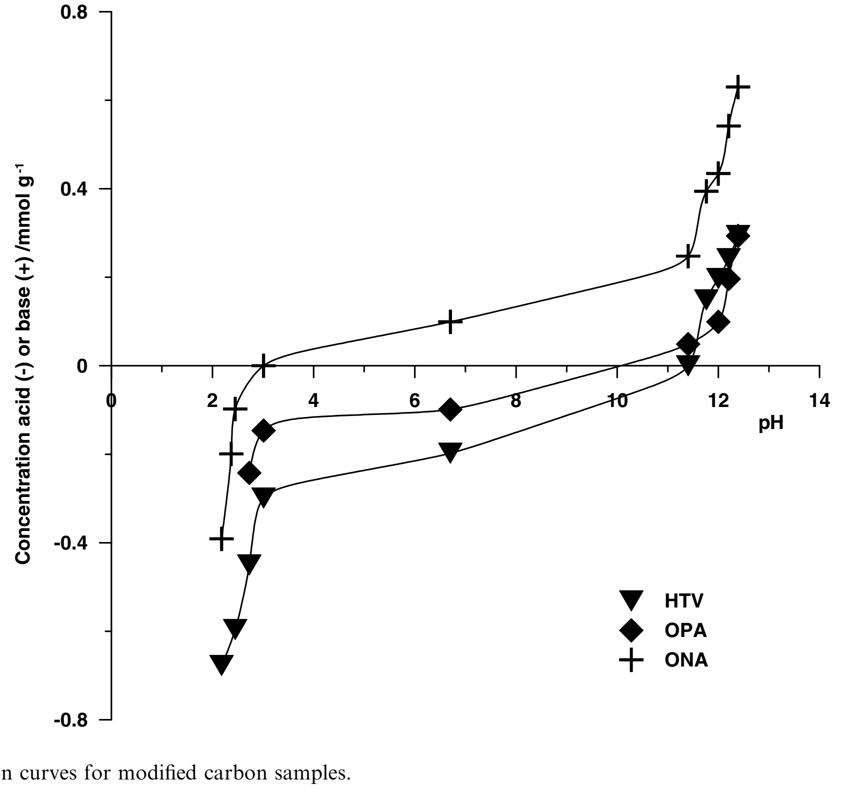

Fig. 4. pH-metric titration curves for modified carbon samples.

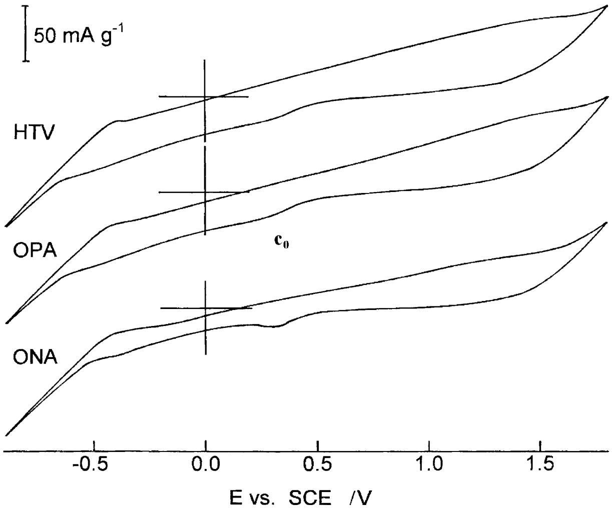

Fig. 5. Cyclic voltammograms for the PACEs prepared from tested carbons recorded in blank electrolyte solution (pH = 1.33, $v = 3 \times 10^{-3}$ V s^{-1}).

rates from 0.1 to 0.001 V s^{-1}. In acidic blank solutions (pH = 1.33) the presence of a cathodic peak (or wave) (c$_o$) was recorded for all samples (Figure 5). The shape of the cyclic voltammograms (CVs) obtained may be indicative of the reduction of electrochemically active surface groups that were oxidised in the 1.2–1.3 V potential range. The charge transferred during reduction processes depends on the carbon modification procedure and is the highest for the ONA sample (Table 1).

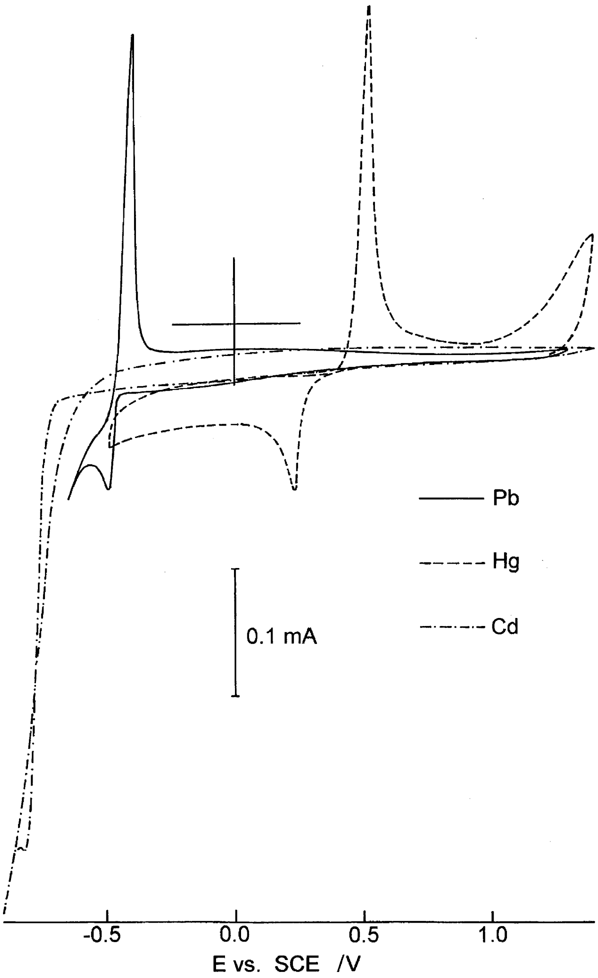

Fig. 6. Cyclic voltammograms for the glassy carbon electrode recorded in blank electrolyte solution containing 0.01 M metal (Pb, Hg, Cd) nitrate, (pH = 1.33, $v = 3 \times 10^{-3}$ V s^{-1}).

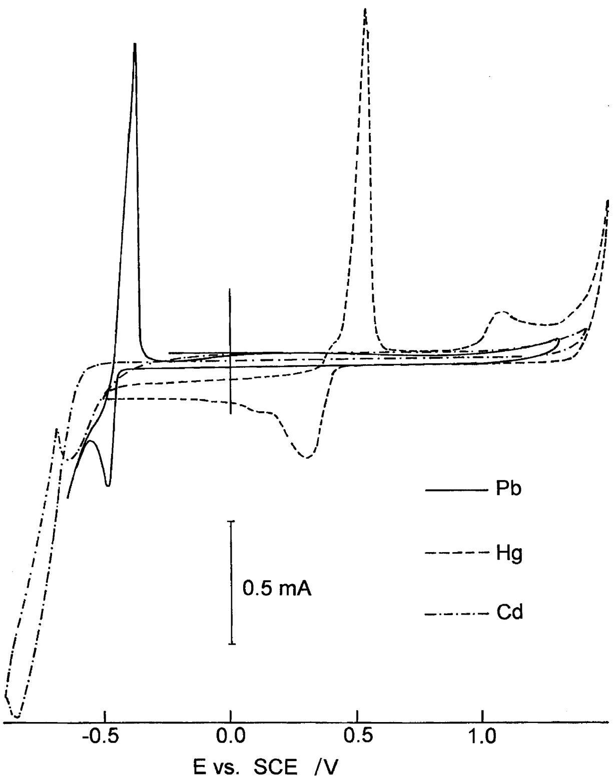

Fig. 7. Cyclic voltammograms for the graphite electrode recorded in blank electrolyte solution containing 0.01 M metal (Pb, Hg, Cd), nitrate (pH = 1.33, $v = 3 \times 10^{-3}$ V s^{-1}).

The electrochemical properties of the oxidised/reduced forms of the couples to be tested were characterised using commercial glassy carbon (GC) and graphite (RG) electrodes. The cyclic voltammograms obtained in acidic blank solutions (pH = 1.33) containing the cations to be tested are presented in Figures 6 and 7. Both these CVs are similar and approach the literature data [30–33]. A two-electron cathodic reduction and anodic response according to the scheme: $Me^{2+} + 2e \Leftrightarrow Me^0$ may explain the peaks on the CV curves.

Next, the electrochemical behaviour of the couples to be tested was investigated using the powdered activated carbon electrode technique. The potential responses for the respective systems are given in Table 2.

The electrochemical behaviour of PACE–lead ion systems is illustrated in Figure 8. This shows cyclic voltammograms recorded in acidic electrolyte solution containing Pb^{2+} ions for modified activated carbon with pre-adsorbed lead. Generally, besides the c$_0$ of the cathodic peak, the presence of a second cathodic peak (c$_1$) and a broad anodic peak (a$_1$) is observed for all samples. For ONA carbon a distinctly shaped second anodic peak (a$_2$) is present. The following reactions may explain the observed cathodic peaks and waves [34–36]:

Table 2. Adsorption capacity, response potential and peaks potentials (for adsorbed cations) of modified carbon samples

Carbon sample	Lead				Mercury					Cadmium			
	A[a] /mM g^{-1}	E_s[b] /mV	$E_{p,c1}$ /mV	$E_{p,a2}$ /mV	A[a] /mM g^{-1}	E_s[b] /mV	$E_{p,c1}$ /mV	$E_{p,a2}$ /mV	$E_{p,a1}$ /mV	A[a] /mM g^{-1}	E_s[b] /mV	$E_{p,c1}$ /mV	$E_{p,a2}$ /mV
GC	–	–	−535	−390	–	–	+230	+530	–	–	–	−830	–
RG	–	–	−490	−380	–	–	+300	+550	+1100	–	–	−850	−690
HTV	0.053	+466	+980	–	0.155	+593	−300	+1300	+1550	0.010	+375	−660	−70
OPA	0.084	+486	+990	–	0.162	+605	+50	+1150	+1600	0.010	+486	−540	−70
ONA	0.071	+619	+930	−460	0.158	+618	–	+750	+1200	0.014	+505	−580	−100

[a] From 0.01 M. Me(NO$_3$)$_2$ (Me = Pb^{2+}, Hg^{2+}, Cd^{2+}) + 0.1 M HNO$_3$, pH = 1.33.

[b] In 0.01 M Me(NO$_3$)$_2$ + 0.1 M HNO$_3$ + 0.1 M NaNO$_3$, pH = 1.33.

$$(c_0) \quad >C{=}O + H^+ + e = \ >C{-}OH \qquad (E_{p,c_0} \cong +250\ \text{mV}) \qquad (1)$$

$$(c_1) \quad Pb^{4+} + 2e = Pb^{2+} \qquad (E_{p,c_1} \cong +950\ \text{mV}) \qquad (2)$$

The broad anodic peak (a$_1$) for HTV and OPA can be explained by the following processes:

$$Pb^{2+} - 2e = Pb^{4+} \qquad (3)$$

$$O_2 - 2e = O_2^{2-} \quad (E_{p,a_1} \cong +1600\ \text{mV}) \qquad (4)$$

$$Pb^{2+} + O_2^{2-} + 4H^+ = Pb^{4+} + 2H_2O \qquad (5)$$

and that for ONA carbon by the reaction:

$$Pb^{2+} - 2e = Pb^{4+} \qquad (6)$$

$$> C{-}OH - e => C{=}O + H^+ \quad (E_{p,a_1} \cong +1000\,\text{mV}) \qquad (7)$$

$$2 > C{=}O + Pb^{2+} + 2H^+ = Pb^{4+} + 2 > C{-}OH \qquad (8)$$

Figure 8 also shows that for the potential range used here (<−500 mV) a Pb^{2+} reduction wave is observed only for ONA carbon. The anodic response yields peak a$_2$ with a potential of −460 mV.

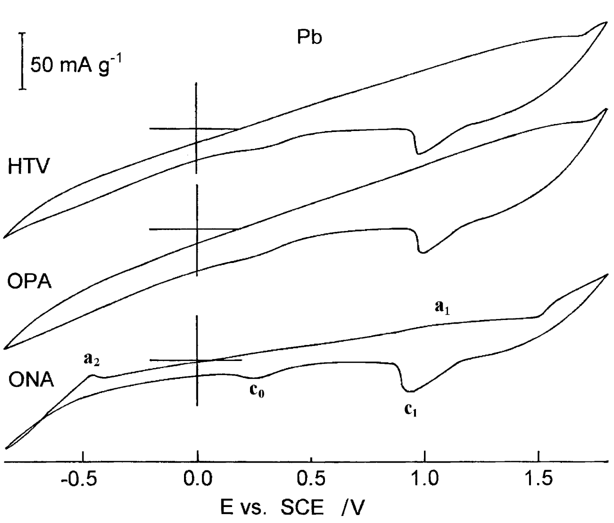

Fig. 8. Cyclic voltammograms for PACEs prepared from tested carbons with pre-adsorbed lead recorded in blank electrolyte solution containing 0.01 M lead nitrate (pH = 1.33, $v = 3 \times 10^{-3}$ V s^{-1}).

The electrochemical behaviour of PACE – mercury ion systems is shown in Figure 9: cyclic voltammograms recorded in acidic electrolyte solution containing Hg^{2+} ions for modified activated carbon with pre-adsorbed cations. Generally, besides the c$_0$ cathodic peak, a second cathodic peak/wave (c$_1$) and a broad, double anodic peak (a$_1$,a$_2$) is observed for all samples. The following reactions may explain the observed cathodic peaks and waves [31, 37, 38]:

$$(c_0) \quad > C{=}O + H^{++}e => C{-}OH \qquad (E_{p,c_0} \cong +250\text{mV}) \qquad (9)$$

$$(c_1) \quad Hg^{2+} + 2e = Hg^0 \quad \text{(see Table 2)} \qquad (10)$$

$$(a_2) \quad Hg^0 - e = Hg^+ \quad \text{(see Table 2)} \qquad (11)$$

$$(a_1) \quad Hg^+ - e = Hg^{2+} \quad \text{(see Table 2)} \qquad (12)$$

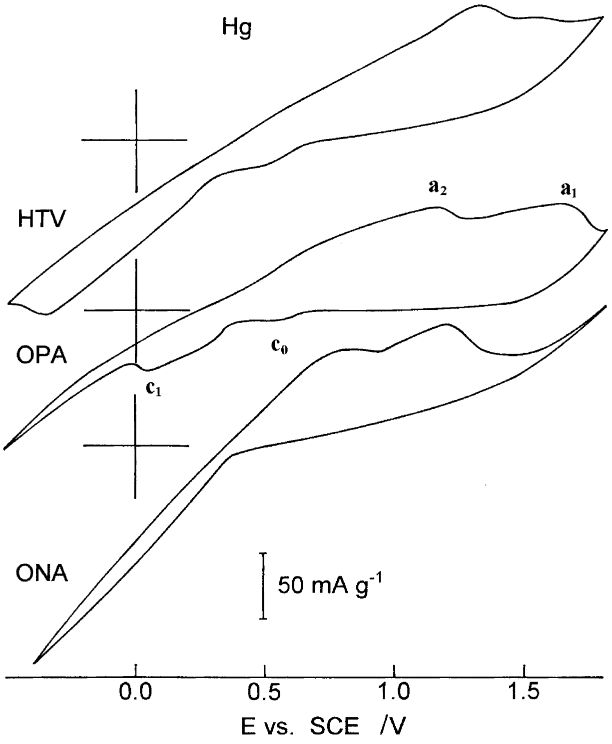

Fig. 9. Cyclic voltammograms for PACEs prepared from tested carbons with pre-adsorbed mercury recorded in blank electrolyte solution containing 0.01 M mercury nitrate (pH = 1.33, $v = 3 \times 10^{-3}$ V s^{-1}).

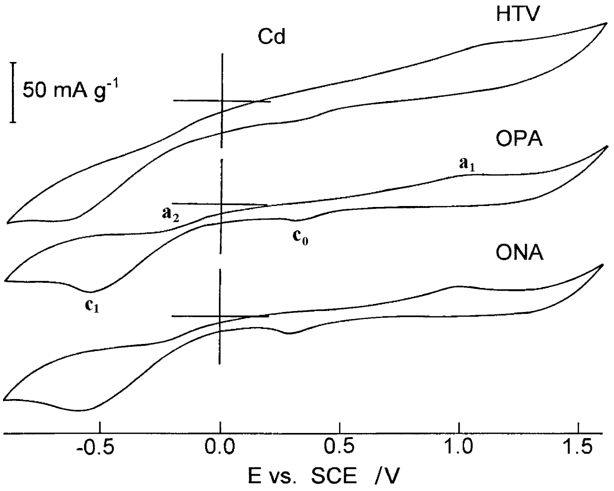

Fig. 10. Cyclic voltammograms for PACEs prepared from tested carbons with pre-adsorbed cadmium recorded in blank electrolyte solution containing 0.01 M. cadmium nitrate, (pH=1.33, $v=3 \times 10^{-3}$ V s^{-1}).

Anodic oxidative processes may be accompanied by the following reactions:

$$2Hg^{+} = Hg^{2+} + Hg^{0} \quad (13)$$

$$> C{=}O + Hg^{+} + H^{+} = Hg^{2+} + > C{-}OH \quad (14)$$

$$Hg^{+} + 4H^{+} = Hg^{2+} + 2H_2O \quad (15)$$

Figure 10 illustrates the electrochemical behaviour of PACE–cadmium ion systems: cyclic voltammograms recorded in acidic electrolyte solution containing Cd^{2+} ions for modified activated carbon with pre-adsorbed cadmium. In general, apart from a c_0 cathodic peak, a second cathodic peak (c_1) and a broad anodic peak (a_1) are present for all samples. Additionally, there is an anodic wave (a_2) in the potential range from −100 to −70 mV. The following reactions may explain the observed cathodic peaks and waves [32, 33]:

$$(c_0) \quad > C{=}O + H^{+} + e => C{-}OH \quad (E_{p,c_0} \cong +250\,\text{mV}) \quad (16)$$

$$(c_1) \quad Cd^{2+} + 2e = Cd^{0} \quad (E_{p,c_1} \cong -600\,\text{mV}) \quad (17)$$

$$(a_1) \quad > C{-}OH - e => C{=}O + H^{+} \quad (E_{p,a_1} \cong +1000\,\text{mV}) \quad (18)$$

$$(a_2) \quad Cd^{0} - 2e = Cd^{2+} \quad (E_{p,c_1} \cong -80\,\text{mV}) \quad (19)$$

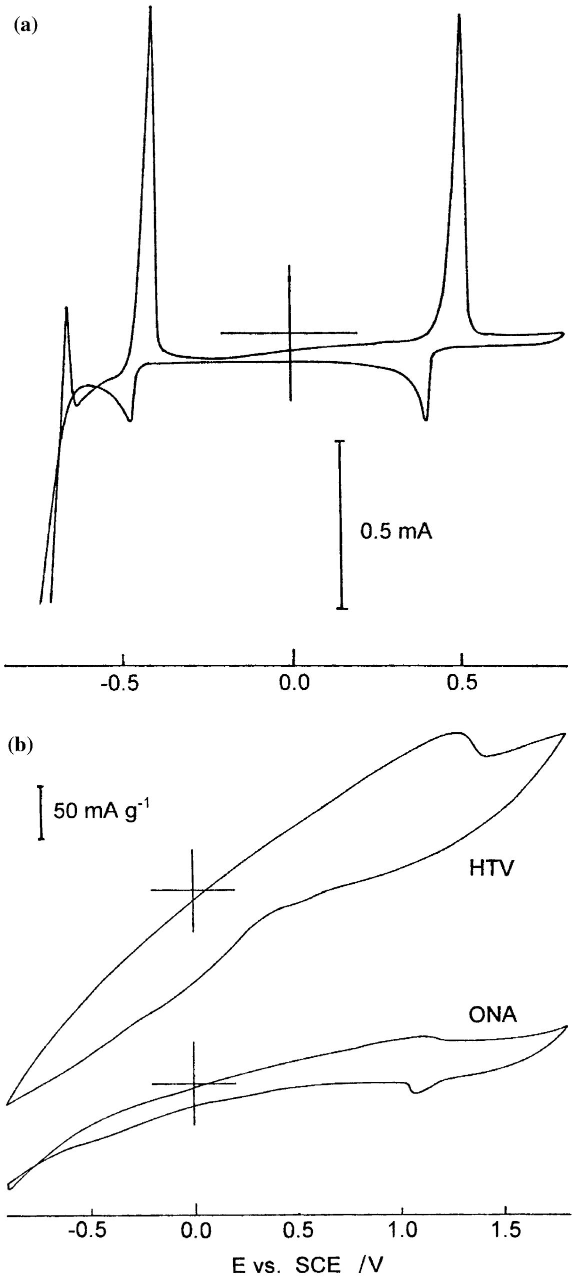

Fig. 11. Cyclic voltammograms for ternary system containing together Pb^{2+}, Hg^{2+} and Cd^{2+} nitrate solution ($[Me^{2+}] = 0.0033$ M) recorded for RG (a) as well as for PACE (b) electrodes (pH = 1.33, $v = 3 \times 10^{-3}$ V s^{-1}).

The surface modification procedures applied to the carbons tested alter its surface area only slightly (see Table 1). The nearly 10% differences in apparent surface area (S_{BET}) could not explain the marked differences in adsorption capacity towards cations (Table 2). The contact of active carbon materials with an aqueous solution containing the tested cations may lead to the adsorption of cations and metal-containing species (i.e. $MeOH^{+}$), partial reduction of adsorbed cations and the formation of an imperfect metallic layer deposited on the carbon surface (especially for mercury) [37, 39]. Modification of the carbon surface chemistry strongly influences the extent and mechanisms of metal cation adsorption (Table 2) and the electrochemical activity of the cations present in the system studied here (Figures 8–10). However, knowledge of the acid–base properties of a carbon surface is insufficient to explain the adsorption capabilities of this system. Generally speaking, the electrochemical activity (magnitude of the metal oxidation–reduction peaks) of cation/activated carbon surface systems in nitrate solution depends on the ion uptake, as Figures 8–11 clearly show. The electrochemical behaviour of a mixture of cations in solution on a commercial carbon electrode (GC) (Figure 11(a)) is close to the literature data [30–37], but for studied PACE depends on the surface chemistry of modified carbon samples and correlates with their adsorption ability. For this particular mixture of cations in solution the dominant electrochemical process is connected with mercury oxidation-reduction reactions (Figure 11(b)), which can be explained by the highest adsorption of this cation on the carbon surface (Table 2).

4. Conclusion

The various methods of chemically modifying the activated carbon surfaces investigated here led to a differentiation in the electrochemical properties of PACE in the aqueous solutions used. Mechanisms of electrode behaviour (oxidation–reduction) of the heavy metal ions investigated (Pb, Hg, Cd) with respect to the chemical properties of the PACE surface are put forward. In the case of a mixture of heavy metal ions, the extent of their adsorption (especially mercury) on the electrode processes was established.

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