Simultaneous removal of 3d transition metals from multi-component solutions by activated carbons from co-mingled wastes

Svetlana B. Lyubchik\textsuperscript{a,d,}\textasteriskcentered, Andrej I. Lyubchik\textsuperscript{d}, Elena S. Lygina\textsuperscript{b}, Sergej I. Lyubchik\textsuperscript{d}, Tatiana L. Makarova\textsuperscript{c}, Joaquim Vital\textsuperscript{d}, Ana M.B. do Rego\textsuperscript{f}, Isabel M. Fonseca\textsuperscript{d,}\textasteriskcentered

\textsuperscript{a} L.M. Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Science of Ukraine, R. Luxemburg Str. 70, 83114 Donetsk, Ukraine
\textsuperscript{b} Donetsk State University of Economics and Trade, Department of Chemistry, Teatral’naya ave. 28, 83054 Donetsk, Ukraine
\textsuperscript{c} Ioffe Physico-Technical Institute, 26 Politechnicheskaya, 194021 St. Petersburg, Russia
\textsuperscript{d} REQUIMTE, CQFB, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Quinta da Torre, 2829-516 Monte da Caparica, Portugal
\textsuperscript{f} Centro de Química-Física Molecular, Instituto Superior Técnico, Complexo Interdisciplinar Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

Received 7 December 2006; received in revised form 25 August 2007; accepted 27 August 2007

Abstract

The main purpose of the present work was to study the simultaneous removal of 3d transition metals from multi-component solutions by novel porous material obtained from carbon-containing liquid and solid waste. The activated carbon was prepared from co-mingled natural organic waste: 25% sunflower husks, 50% petroleum waste and 25% low-grade bituminous coal. The porous carbon material was obtained via stages of pre-oxidation with binary eutectic Na/K carbonates (in order to avoid melting and coke formation), followed by “step by step” carbonization at 100–400 °C in an inert atmosphere and activation with steam at 850 °C.

The adsorption of the 3d transition metals: copper (II), cobalt (III), nickel (II), iron (III), and chromium (III), on novel activated carbons has been investigated using multi-component model solutions. Experiments have been carried out on the thermodynamics of the simultaneous adsorption of the 3d transition metals in a static mode. The total metal removal combines the process of metal hydroxide precipitation in the solution with the metal cation adsorption on negatively charged carbon surface in a single operation unit. The carbon/metals interaction at the surface of spent adsorbents is discussed.

Keywords: Activated carbon; 3d transition metals; Adsorption; X-ray photoelectron spectroscopy

1. Introduction

Promptly increasing technogenic impact on the natural sources resulting in creation of the problems related to the limited supply of water. The volume of sewage constantly increases and accordingly, the needs for their purification are growing. Ions of heavy metals are concerned to the numbers of the most dangerous impurities.

Research of heavy metals adsorption on the activated carbons of different nature attracts the attention of researchers all over the world [1–7]. However, the available information published in the literature about metals adsorption from the liquid phase is mainly devoted to the heavy metals removal from mono-component solutions. A relatively small number of studies have examined the adsorption processes from multi-component solutions of heavy metals [8–10]. However, the most encountered in industrial operation modes systems are the multi-component solutions and, consequently, heavy metals are frequently encountered in a mixture in industrial wastewater. Thus, there is a definite need for the investigation of heavy metals adsorption process from multi-component solutions to suit the problems in the area of wastewater treatment.

The main idea of present work was to study simultaneous removal of 3d transition metals (Cu (II), Co (II), Ni (II), Fe (III), and Cr (III)) from multi-component solutions by activated carbon obtained from carbon-containing liquid and solid waste. Using the co-mingled sunflower husks, petroleum waste...
Table 1
Elemental and proximate analyses of the chosen waste materials

<table>
<thead>
<tr>
<th>Samples, waste source</th>
<th>Elemental composition (%)</th>
<th>Proximate analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C&lt;sub&gt;daf&lt;/sub&gt;</td>
<td>H&lt;sub&gt;daf&lt;/sub&gt;</td>
</tr>
<tr>
<td>Bituminous coal</td>
<td>80.0</td>
<td>5.3</td>
</tr>
<tr>
<td>Sunflower husks</td>
<td>54.6</td>
<td>6.7</td>
</tr>
<tr>
<td>Aromatic tar stock</td>
<td>79.2</td>
<td>8.9</td>
</tr>
</tbody>
</table>

and low-grade bituminous coal we have observed a synergistic effect during co-mingled waste co-activation [11]. The adsorption capacity of the resulting activated carbon towards Cr (III), 1.09 mmol/g, was found to be higher than the one obtained using the commercial GAC Norit 1240 Plus (A-10128) under similar conditions [12,13]. Therefore, there is a strong incitement to develop the innovative processes which can produce secondary environmentally friendly adsorbents from co-mingled waste and to develop the methodology for their use in water purification from heavy metals.

2. Experimental

2.1. Preparation of the activated carbon from co-mingled waste

The activated carbon was prepared from co-mingled natural organic liquid and solid waste. For the blending process the components were combined in a fixed proportion of 25% biomass, 25% low-grade coal and 50% petroleum wastes. In order to avoid coke formation during the activation process, 5% (by weight of blends) of binary eutectic additives of Na/K carbonates were used. The blend components were collected from the Donbass region of the Ukraine. Bituminous coal b<sub>8</sub> were supplied from Lidievka mine located at Donetsk in Eastern Ukraine. The biomass selected was sunflower husks. Sunflower husks were graciously provided by the Oil Process Plan “Cargil” of Joint Ukrainian-USA Oil Corporation, Donetsk, Eastern Ukraine. A petroleum feedstock component was graciously supplied by Coke Process Plan “Rutchenkovo”, Donetsk, Eastern Ukraine.

The nature of petroleum component (i.e. the degree of its “aromaticity” as a ratio of aromatic-to-aliphatic fractions) has been estimated by 1H NMR spectroscopy. The chosen feedstock had 44.6% of aromatic fraction and, within present study it is referred to “aromatic tar stock”. The parent materials were characterized by elemental and proximate analyses (Table 1) using an Automatic CHNS-O elemental analyzer and Flash EATM 1112 instrument.

For the preparation of the activated carbons, low-temperature carbonization in an inert atmosphere followed by high-temperature activation with steam at 850 °C were used. Carbonization was performed using a stepwise temperature increase from 100 to 400 °C for 3.5 h following by heating at constant temperature of 400 °C for 2 h. The yield of char was 56.2%. After carbonization, the char carbon (5 g) was subjected to steam activation (heating rate 5 °C/min; steam flow rate 300 ml/min) at 850 °C in a tubular furnace for 2 h. The yield of the activated carbon was 26.4% (by total components loading). Sample is labelled as “ACW-Ar2”, where “ACW” is activated carbon from co-mingled waste, and “Ar2” is the reference to the source of a petroleum feedstock component, i.e. “aromatic tar stock” supplied by Coke Process Plan “Rutchenkovo”, Donetsk, Eastern Ukraine.

2.1.1. Surface characterization

The structural parameters of the resulting carbon were evaluated using nitrogen gas adsorption at 77 K and temperature-programmed desorption techniques (Table 2). The experiments were carried out using Micromeritics ASAP 2010 and Micromeritics TPD/TPR 2900 instrument. Prior to the adsorption test the samples were outgassing at 240 °C for 24 h under
a pressure of 10^{-3} Pa. The apparent surface areas were determined from the adsorption isotherms using the BET equation. The Dubinin-Radushkevich and B.J.H. methods were applied respectively to determine the micro- and mesopores volume. The assignment of the TPD peaks to the specifics surface groups was based on the data published in literature [14]. Thus, a CO\(_2\) peak results from decomposition of the carboxylic acid groups at low temperatures (below 400 °C), or lactones at high temperatures (650 °C); carboxylic anhydrides decompose as CO and CO\(_2\) at the same temperature (around 650 °C). Ether (700–700 °C) and carbonyls/quinones (700–980 °C) decompose as CO.

The pH at the point of zero charge (pH\(_{PZC}\)) for the carbon was measured using the pH drift method [15].

For the adsorption tests, the activated carbons were used as received and after post-oxidative treatment with 1 M HNO\(_3\) for 6 h at reflux in order to vary the amount of the surface oxygen groups. The data obtained were compared with those for commercial GAC Norit 1240 Plus (A-10128) and its oxidized (with 1 M HNO\(_3\)) counterpart, which according to our previous investigation was found to be highly efficient towards Cr (III) adsorption [12,13].

Spent activated carbons were analyzed by X-ray photoelectron spectroscopy (XPS) using a XSAM800 (KRATOS) X-Ray Spectrometer operated in the fixed analyzer transmission (FAT) mode with pass energy of 20 eV and the non-monochromatised Mg K\(_\alpha\) X-radiation. Samples were supported on double-face tape and analyzed in ultra high vacuum (UHV), and typical base pressure in the sample chamber was in the range of 10^{-6} Pa. Sun SPARC Station 4 with Vision software (Kratos) was used for spectra acquisition. The curve fitting for component peaks was carried out with XPS Peak 4.1 using a product of Gaussian and Lorentzian (pseudo-Voigt) profiles, and Shirley background. Constraints were constant widths and constant Lorentzian/Gaussian ratio for all the peaks within each region. C 1s, O 1s, and Cr 2p regions were analyzed with a step of 0.1 eV. Also complete spectra were acquired for each sample with a step of 0.3 eV. For quantification purposes, sensitivity factors provided by VISION element library were used [16].

### 2.2. Analysis of the heavy metal adsorption from model multi-component solutions

The adsorption process was studied in batch experiments for individual metals and their two-, three-, four- and five-component mixtures. The process was carried out at room temperature (27 ± 1 °C), for a fixed carbon loading of 0.6–0.8 g/l and varying the metal concentration in the range of 20–1000 mg/l of each of the metals, either in multi- or mono-component solutions. Metal salts which are largely used in different industrial processes, such as (CH\(_3\)COO)\(_2\)Ni × 4H\(_2\)O; (CH\(_3\)COO)\(_2\)Co × 4H\(_2\)O; (CH\(_3\)COO)\(_2\)Cu × H\(_2\)O; Fe(NO\(_3\))\(_3\) × 9H\(_2\)O and Cr\(_2\)(SO\(_4\))\(_3\)×(OH)\(_2\), were used as a source of the 3d transition metals. In order to evaluate the changes in coordination geometry, [Me\(^{n+}\)/ligands] complexes were studied by UV–visible spectrophotometry using GBC 918 instrument.

All the adsorption runs were performed using the initial pH\(_{init}\) of the chosen salt, i.e. pH\(_{init}\) 1.99 for Fe\(^{3+}\); pH\(_{init}\) 3.2 for Cr\(^{3+}\); pH\(_{init}\) 7.04 for Ni\(^{2+}\); pH\(_{init}\) 6.83 for Cu\(^{2+}\) and pH\(_{init}\) 6.93 for Co\(^{2+}\), without adding any buffer for the pH control, in order to prevent the introduction of any new electrolyte into the system. At the end of the experiment the final pH of the solution was measured.

When the adsorption process was completed, the solutions were filtered through membrane filters of 0.45 µm; and the metal equilibrium concentrations were measured by inductively coupled plasma (ICP) atomic emission spectroscopy according to the standard procedure [17], using ISP Jobin-Yvon Ultima instrument.

All the adsorption tests were performed on the novel carbon from co-mingled waste (ACW-Ar2), on the commercial GAC Norit 1240 Plus (A-10128) and its oxidized counterpart. The experiments were duplicated for quality control and statistical purposes; the standard deviation of the sorption parameters was below 2.4%.

The amount of the adsorbed metal on the activated carbon was quantified by mass balance. The following parameters were used: adsorption capacity of the carbon expressed in terms of the metal amount adsorbed on the unit adsorbent mass, i.e. Me uptake (mmol/g), and sorption efficiency of the system determined as the percentage of metal ions removed relatively to their initial amounts, i.e. Me\(_{Rem}\) (%).

### 3. Results and discussion

#### 3.1. Thermodynamic data for simultaneous metal adsorption from mono- and multi-component model solutions

We have found that the novel carbon ACW-Ar2 adsorbed an appreciable amount of each of the individual metals (Fig. 1). The individual metals uptake is in the range of Ni (III) > Cr (III) > Fe (III) ≈ Cu (II) > Co (II), which is in agreement with the metals’ hydrated radii. The high uptake of Cr\(^{3+}\) ions could be due to hydrolysis occurring at certain pH ranges, when a decrease in
a charge of the hydrated chromium ion species results in an increase in their adsorption on carbon surface.

It is well known [18] that water molecules in hexa-aqueous metal complexes are replaced by ligands, which have a hydrophobic–hydrophilic molecular structure. Such metal–ligand complexes tend to gather at the aqueous–solid interface more efficiently than the hydrated metal ions do [18]. As a result, the metal ion concentration at the solid interface becomes higher, thus accelerating the overall adsorption kinetics.

In order to evaluate the competitive effect of the individual metal removal from multi-component solutions, equilibrium experiments were carried out for the solutions containing two to five metals ions: (i) three two-component systems: [Ni (II)–Co (II)], [Ni (II)–Cr (III)] and [Co (II)–Cr (III)], (ii) one three-component system [Co (II)–Ni (II)–Cr (III)], (iii) two four-components systems: [Co (II)–Ni (II)–Cr (III)–Cu (II)] and [Co (II)–Ni (II)–Cr (III)–Fe (III)], and (iv) one five-component system [Co (II)–Ni (II)–Cr (III)–Fe (III)–Cu (II)]. The initial concentration of each metal in these experiments was varied from 20 to 1000 mg/l and carbon loading was fixed at (0.7–0.8) g/l.

An improved removal of the 3d transition metal ions was found for their multi-component solutions. In the presence of additional metals in aqueous solutions, higher removal of each individual metal was observed with an enhancement of the removal in the order: Ni (II) < Cr (III) < Fe (III) < Cu (II) < Co (II) (Figs. 1 and 2). Thus, adsorption of Co (II) drastically increases in the presence of Ni (II) for all the studied multi-component systems, while adsorption of the other metals is only slightly increased in these conditions.

Typical results are presented in Fig. 2 for the three-component system [Co (II)–Ni (II)–Cr (III)]. The synergism for cobalt (II) adsorption in the presence of nickel (II) can be related to the changes in the coordination geometry for cobalt (II) complexes. According to the cobalt adsorption spectra, instead of the octahedral coordination of Co (II) in mono-component solution, the Co (II) tetrahedral coordination was found when Ni (II) was added. In contrast, Ni (II), Cr (III), Fe (III) and Cu (II) maintained their octahedral configurations in both mono- and multi-component solutions. Cr (III), Cu (II), Fe (III) and Ni (II) ions were adsorbed more efficiently than Co (II) from mono-component solutions. Consequently, the addition of cobalt did not affect their adsorption from multi-component solutions.

The trend for the 3d transition metals removal from four and five-component systems was almost the same. Due to the similar coordination geometry and hydrophobic–hydrophilic molecular structure of [Me\(^{n+}\)--ligand] complexes, the surface-adsorption properties and the hydrolysis proceeding of certain metal species were similar in all multi-components systems.

### 3.2. pH depletion/rinsing: final pH

It is well known that the adsorption process is related to the carbon pH\(_{PZC}\). For our systems, the studied activated carbons significantly altered the final pH of the solution, always in the direction of their pH\(_{PZC}\). The changes in the surface charge caused by the adsorption of metals ions are exemplified by Fig. 3A–C, which show the pH drift (expressed as the ratio of the initial and final concentration of hydrogen ions [H\(^+\)]\(_{init}\)/[H\(^+\)]\(_{final}\)) for the activated carbon obtained from co-mingled waste with a pH\(_{PZC}\) of 5.85. The final pH of the solution is sufficiently affected by the carbon dosage and the initial pH, causing the different sorption mechanisms.

For the adsorption of Cu (II), Ni (II) and Co (II) from mono-component solutions, the initial pH ~ 6–7 remained almost unchanged after the adsorption run (Fig. 3B). Similarly, no changes in pH was observed for the adsorption of Fe (III) having low initial pH\(_{init}\) = 1.99 (Fig. 3A), whereas in the case of Cr (III) the initial pH\(_{init}\) = 3.21 was drastically increased to its final pH values of 6–7.6 depending on the carbon loading (Fig. 3C).

Simultaneous adsorption experiments showed that Fe (III) and Cr (III) did not affect the Co (II), Ni (II) and Cu (II) removal, whereas removal of Fe (III) and Cr (III) is drastically increased in the presence of Co (II), Ni (II) and Cu (II). On removal of Cr (pH\(_{init}\) = 3.21) and Fe (pH\(_{init}\) = 1.99) simultaneously with Ni (II), Co (II) and Cu (II) (pH\(_{init}\) ~ 6–7 for mono-component solutions) over activated carbon (pH\(_{PZC}\) 5.85) the final pH is increased by pH\(_{final}\) ~ 6.5–7.5, and consequently, an increased removal of these metals is particularly due to precipitation of Fe and Cr hydroxides in the solution at higher pH.

At pH\(_{final}\) ~ 6.5–7.5 the net carbon surface is negatively charged facilitating adsorption of positively charged species. Removal by precipitation reactions in the solution is likely to have occurred, as the initial metal concentrations in the experiments are quite high. Thus, an increase in the final pH improved the removal of each metal due to both the enhancement of the adsorption on negatively charged carbon surface and precipitation in the form of hydroxides (Fig. 4). The total removal for each metal from multi-component solution under equilibrium conditions were found as high as 65–75%, whereas the metals removal by adsorption was only 15–20% (Fig. 4) when the rest of the metal being removed by precipitation in the solution.

The same trends for the metals adsorption were found for commercial GAC Norit (pH\(_{PZC}\) = 6.92) and its oxidized counter-

![Fig. 2. Simultaneous adsorptions of (Δ) Ni (II), (●) Co (II) and (□) Cr (III) from three-component model solution on ACW-Ar2 carbon.](image-url)
part (pH_{PZC} = 4.41) (Fig. 5). Here again, simultaneous removal of the 3d transition metals from aqueous solutions involved both metal precipitation in a form of hydroxide and metal cation adsorption on the negatively charged carbon surface. However, for oxidized Norit carbon the metals removal occurs preferentially by adsorption compared to removal by precipitation due to its lower pH_{PZC} and, consequently, lower pH_{final} of the solution.

3.3. Influence of the adsorbent texture and surface on the adsorption process

All the studied carbons adsorbed appreciable amount of 3d transition metals (Figs. 2 and 5) under chosen experimental conditions, but the sorption efficiency is influenced by their texture and surface functionalities.

The effect of the texture is related to the carbon porous structure and, particularly to the accessibility of the adsorbent internal surface for large-size high-hydrated metal ions (e.g. 0.922 nm for [Cr(H_2O)_6]^{3+} [19]). The absolute value of the apparent surface area is a less important factor in this case: the parent Norit carbon, which has higher surface area than the ACW-Ar2 carbon is less efficient for metals adsorption (Table 2). This fact emphasizes the dominating role of the pore size distribution in the adsorption process in the case of carbons with lack of surface oxygen functionality.

Oxidation with nitric acid essentially modifies the structure of the parent carbons. The specific surface area of the parent Norit carbon slightly increases after oxidation due to further development of the microporosity (Table 2). Considering purely physisorption process, an increase of the pore size should increase an uptake of the metals. Among all the studied carbons, the oxidized Norit carbon with predominantly microporous structure and developed surface oxygen functionality (Table 2) exhibited the highest efficiency in metals adsorption (cf. Figs. 5A and B and 2). This clearly demonstrates the importance of the ion exchange on the overall
adsorption process with participation of the oxygen surface groups.

The adsorption increases when the carbon surface is oxidized (cf. Fig. 5A vs. B), although the nature and the amount of the surface oxygen groups play an important role in the adsorption process. We should mention that in contrast to the parent GAC Norit, the ACW-Ar2 carbon already contains certain amount of carboxylic, lactones, quinones and phenolic surface groups (Table 2). The oxidation of parent GAC Norit with 1 M HNO3 increased significantly the concentration of functional oxygen groups (Table 2). However, “non-oxidized” carbon ACW-Ar2 shows the adsorption efficiency similar to that for oxidized GAC Norit (cf. Figs. 2 and 5B), confirming the importance of chemisorption.

3.4. The carbon/metals interaction at the surface of spent adsorbents: XPS data

In order to deep insight into the metal bonding with the carbon active sites, we monitored the carbon/metals interac-

tion at the surface of spent adsorbents by X-ray photoelectron spectroscopy. Parent and oxidized GAC Norit before and after adsorption of Cr (III) ions were chosen for the analysis.

Fitting pseudo-Voigt profiles to peak regions gives seven components for all C 1s regions and four to five components for O 1s regions, depending on the nature of the carbon. The seventh component in the C 1s regions, centered at ∼7.5 eV from the main peak, is assigned to a shake-up satellite corresponding to a π−π* excitation typical of aromatic systems. Positions of some of C 1s core level signal, assignment and area percentage are given in Table 3. The first main difference between the samples is the ratio of aliphatic and aromatic carbons at the surface. Due to chromium adsorption on the parent GAC Norit the amount of aromatic group increases and aliphatic group decreases. In the case of oxidized Norit carbon we have observed the remarkable destruction of the aromatic system of the sample. The carbon surface is enriched in aliphatic carbon content resulting from graphitic bonds rupture due to chromium interaction with oxygen surface groups.

Differences between the O 1s region peaks for the studied samples were observed. In the case of oxidized GAC Norit sample, it is evident that the O 1s high BE energy tail is less important after chromium adsorption than before (Fig. 6). This tail corresponds, in principle, to adsorbed or entrapped water, strongly bound to the surface (through hydroxyl and/or carboxylic groups) by hydrogen bonds. The adsorption of chromium substitutes the superficial molecules of water. Oxidized GAC Norit surface is richer in C–X–H groups bound to aliphatic carbons, rather than in aromatic carbons and C–X–R groups (Table 3).

Fig. 7 shows typical Cr 2p XPS spectra with fitted components and Shirley baseline for oxidized Norit carbon. The spectra show doublet peaks with the binding energy at 577.9 ± 0.2 and 587.8 ± 0.2 eV (Fig. 7) corresponding respectively to the components Cr 2p3/2 and Cr 2p1/2.
Table 3
Component peaks for C 1s region. XPS data for ACW-Ar2, parent and oxidized GAC Norit carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>Position of the peaks for samples before Cr (III) adsorption</th>
<th>Position of the peaks for samples after Cr (III) adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position of the peaks</td>
<td>C 1s core level signal</td>
</tr>
<tr>
<td></td>
<td>284.7 285 286.3</td>
<td>287.4 289.9 291.2</td>
</tr>
<tr>
<td>Parent GAC Norit</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidized GAC Norit</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACW-Ar2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>284.7 285 286.3</td>
<td>287.7 290.4 291.6</td>
</tr>
<tr>
<td>Peak Assignment</td>
<td>C--sp²  C--sp³  C--OH, C--O--C, C--S</td>
<td>C=O, O--C--O, O--C--N</td>
</tr>
<tr>
<td></td>
<td></td>
<td>COOH, COOC, O--COO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O==COO</td>
</tr>
</tbody>
</table>

Carbon atomic% for the samples before Cr (III) adsorption

<table>
<thead>
<tr>
<th>Sample</th>
<th>43.4 23.8 9.4</th>
<th>6.3 4.6 4.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent GAC Norit</td>
<td>5.1 60.8 9.1</td>
<td>6.4 5.1 3.9</td>
</tr>
<tr>
<td>Oxidized GAC Norit</td>
<td>55.3 19.2 8.2</td>
<td>6.5 7.6 3.2</td>
</tr>
<tr>
<td>ACW-Ar2</td>
<td>37.2 30.2 11.2</td>
<td>5.4 4.4 3.3</td>
</tr>
<tr>
<td>Carbon atomic% for the samples after Cr (III) adsorption</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>37.2 50.5 10.1</th>
<th>5.9 4.3 3.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent GAC Norit</td>
<td>16.9 50.5 10.1</td>
<td>5.9 4.3 3.7</td>
</tr>
<tr>
<td>Oxidized GAC Norit</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7. Cr 2p XPS spectra with fitted components and Shirley baseline for oxidized GAC Norit.

According to literature data [16], the binding energy of single peak of chromium inorganic oxide is located at 576.6 ± 0.2 eV which is about 1.3 eV lower than our assignment. Doublet peaks with binding energy near 577.2 and 587.5 eV correspond to Cr (III) species bounded to oxygen [16] hence we could considered our finding to be chromium (III) bounded to the carbon surface oxygen groups.

In order to fit the peak regions of the Cr 2p spectra we applied the multiplet-splitting models (Fig. 7). The appearance of multiplet structures results from the presence of pronounced amount of unpaired electrons that could be due to the complexation reactions of chromium with weak field ligand, such as π-system in carbon matrix.

The data obtained from XPS, are in agreement with those obtained for liquid phase adsorption, suggesting that the main mechanism of 3d transition metal adsorption is an ion exchange on the surface groups accompanied by surface complexation reactions.

4. Conclusion

The use of the activated carbon from co-mingled waste as the 3d transitional metal adsorbent offers an attractive approach to simultaneous metal removal from multi-component solutions. The total metal removal combines the process of metal hydroxide precipitation (up to 50–55% by total removal) with the metal cation adsorption on negatively charged carbon surface (up to 15–20% by total removal) in a single operation unit. While metal hydroxide precipitates are rarely processed for metal recovery, the adsorption and/or ion exchange on carbon surface allow the metals recovery.

In order to facilitate the access of the high-hydrated metal ions to the internal surface of the carbon, the adsorbent should have an optimum balance of micro- and mesopores. This aspect is especially significant in the case of carbon material with lack of the oxygen functional groups. The presence of surface oxygen functional groups enhances the 3d transition metals adsorption. According to XPS data, the carbon/metals interaction at the spent adsorbent surface occurs due to the complexation reactions of metal ions with weak field ligand, such as π-system in carbon matrix and due to metals binding to the carbon surface groups. The mechanism of the 3d transition metals adsorption on the activated carbon from co-mingled waste is a combined physical and chemisorption.

Acknowledgements

Authors would like to thank to the NATO “Science for Peace” Programme, project SfP 977984 and FCT Programme, SFRH/BPD/7150/2001, Portugal for financial support. Elena S. Lygina would like to thank to Prof. Isabel M. Fonseca and Prof. Tatiana M. Makarova for the training visit to Universidade Nova de Lisboa, Faculdade de Ciências e Tecnologia, Portugal and for the financial support form the NATO “Science for Peace” Programme.
References


