Adsorption 11: 581–593, 2005

Optimization of the Conditions for the Cr (III) Adsorption on Activated Carbon*

SVETLANA B. LYUBCHIK[†]
REQUIMTE, CQFB, Departamento de Quimica, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Quinta da Torre, 2829-516 Monte da Caparica, Portugal

IRENE I. PEREPICHKA
Donetsk National University, Universitetskaya str. 24, Donetsk 83055, Ukraine

OLGA L. GALUSHKO
L.M. Litvinenko Institute of Physical–Organic and Coal Chemistry, National Academy of Sciences of Ukraine, R. Luxemburg 70, 83114 Donetsk, Ukraine

ANDREY I. LYUBCHIK AND ELENA S. LYGINA
Donetsk National University, Universitetskaya str. 24, Donetsk 83055, Ukraine

ISABEL M. FONSECA
REQUIMTE, CQFB, Departamento de Quimica, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Quinta da Torre, 2829-516 Monte da Caparica, Portugal

Received July 13, 2005; Revised October 8, 2005; Accepted October 8, 2005

Abstract. In order to understand the patterns of the adsorption equilibrium of Cr (III) on activated carbon, the adsorption process was studied by two different ways: classical batch experiments on commercial Norit and Merck activated carbons and their oxidized forms in a wide range of pHs; and extended time-based tests at the same pH values on the same adsorbents. This approach allowed us to understand the role of texture, chemical carbon surface functionality and experimental conditions (initial pH of the solution, contact time and adsorbate/adsorbent ratio) on the effectiveness of Cr (III) removal. The adsorption process of Cr (III) at (24 ± 1°C) on Merck and Norit activated carbons and their oxidized forms were studied at pH values between 1.5 and 5 (either adjusted or buffered). Chromium concentration was fixed at 200 ppm. The carbon loading ranged from 1.2 to 20 g/l. The carbon/Cr (III) solution contact time was varied from 0.5–1 month to 5 months, to ensure that the saturation of the carbon level was reached. According to the data obtained, the presence of carboxylic groups on carbon surface seems to enhance Cr (III) uptake at initial pH of the solution in the range between 2 and 4. Depending on the nature of the adsorbent surface chemistry, the contact time to reach equilibrium may range from 3 to 5 months. There is an optimum carbon loading which limits the Cr (III) uptake/removal at given pH value. In order to understand the adsorption process, an ion exchange, surface complex and surface precipitation were considered.

Keywords: heavy metals, adsorption, activated carbon, surface chemistry

---

*This paper was presented in the 5th Brazilian Meeting on Adsorption, held at Natal, Brazil, 18-21 July, 2004.

[†] To whom correspondence should be addressed.

1. Introduction

In the last decades, the problems of water deficiency and exhaustion of water sources on our planet, has been becoming more and more evident. Thus, 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. The highly efficient systems of wastewater purification from heavy metals, such as reverse osmosis and ionic exchange, existing in industrial scale, are rather expensive (Brown et al., 2000), whereas others, such as chemical sedimentation and ionic flotation, do not provide the necessary efficiency of purification. From this point of view the adsorption process on activated carbons from natural organic raw material allows providing necessary balance cost/quality of sewages clean-up. Research of heavy metals adsorption on the activated carbons of different nature attracts the attention of researchers all over the world (Ajmal et al., 2001; Brigatti et al., 2000; Carrott et al., 1997; Chen and Lin, 2001; Csobán and Joó, 1999; Ferro-Garcia et al., 1998; Kumar et al., 2000; Kratochvil and Volesky, 1998). However, the available information published in the literature about metals adsorption from the liquid phase is ambiguous.

The aim of the present work was the optimization of the adsorption conditions for the effective removal of heavy metals using activated carbons. For this purpose, it has been investigated the influence of various textural and surface characteristics of carbon materials, i.e. porosity, surface area, oxygen functional groups, as well as the conditions of the adsorption process (initial solution acidity, contact time, components ratio) on chromium trivalent adsorption from water solutions.

2. Experimental

2.1. Materials

Two commercially available activated charcoals GR MERCK 2518 and GAC Norit 1240 Plus (A-10128) were chosen as adsorbents. The activated carbons were used as supplied (parent carbons) and after different oxidative treatments. These chemical surface treatments aim to introduce surface oxygen functional groups on the carbon surface. In some conditions, the chemical treatments also changed the carbons' porous texture.

The chemical surface treatments were carried out either with 1 M hydrogen peroxide at room temperature or 1 and 13 M nitric acid at boiling temperature during 6 h. The details of the oxidation treatments are described elsewhere (Lyubchik et al., 2003). The oxidized materials, were subsequently washed with distilled water until neutral media, and dried in an oven at 110°C for 24 h.

Table 1. Textural and surface characteristics of the studied activated carbons.

Carbons	S_{BET}, (m^2/g)	V_{total}, (cm^3/g)	V_{micro}, (cm^3/g)	S_{meso}, (m^2/g)	S_{micro}, (m^2/g)	pH_{PZC}
Norit_initial	770	0.40	0.32	41	729	6.92
Norit_H_2O_2	956	0.60	0.55	85	871	6.59
Norit_1 M HNO_3	945	0.43	0.41	72	873	4.41
Norit_13 M HNO_3	612	0.29	0.26	71	541	4.47
Merck_initial	1017	0.59	0.55	40	977	7.02
Merck_H_2O_2	739	0.31	0.30	25	714	6.48
Merck_1 M HNO_3	755	0.33	0.31	41	714	3.41
Merck_13 M HNO_3	702	0.32	0.29	72	630	3.91

Source: Adapted from Lyubchik et al. (2003).

The textural characterization of the carbon samples was based on nitrogen adsorption isotherms at 77 K. These experiments were carried out with Surface Area & Porosimetry Analyzer, Micromeritics ASAP 2010 apparatus (Table 1). Prior to the adsorption the samples were outgassed 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-Raduskhevich and B.J.H. methods were applied respectively to determine the micro- and mesopore volumes. The oxidation treatment resulted in reduction of the apparent surface area and total pore volume (Table 1). The pore size distribution is changed in the direction of mesopore formation. The carbons' point zero charge (pH_{PZC} values) were obtained by acid–base titration (Rivera-Utrilla et al., 2001). pH_{PZC} decreases when the carbon surface is treated with nitric acid (Table 1). Low pH_{PZC} values mean higher carbon surface acidity.

The parent carbons and their oxidized forms were characterized by elemental and proximate analyses using an Automatic CHNS-O Elemental Analyzer and a Flash EATM 1112 (Table 2). The oxygen content significantly increases when the carbon surface is treated with nitric acid.

The carbon surface was also characterized by temperature-programmed desorption with a Micromeritics TPD/TPR 2900 equipment. A quartz

Table 2. Proximate and elemental analyses of the studied activated carbons.

	Proximate analysis (wt.%)			Elemental analysis (wt.%)			
Carbons	Moisture	Volatile	Ash	C	H	N	O
Norit_initial	3.9	6.7	2.8	95.2	0.40	0.48	3.90
Norit_H_2O_2	2.6	7.3	1.9	94.2	0.40	0.54	4.90
Norit_1 M HNO_3	1.8	7.9	2.0	87.9	0.60	2.60	8.90
Norit_13 M HNO_3	2.2	14.8	1.9	85.8	0.90	1.10	12.30
Merck_initial	2.0	9.1	3.2	92.8	0.25	0.40	6.50
Merck_H_2O_2	1.6	10.2	2.8	91.7	0.35	0.65	7.30
Merck_1 M HNO_3	1.7	12.8	2.0	86.3	0.30	0.54	12.80
Merck_13 M HNO_3	1.8	18.6	1.7	82.1	0.90	1.00	16.10

Source: Adapted from Lyubchik et al. (2003).

microreactor was connected to a mass spectrometer set up (Fisons MD800) for continuous analysis of gases evolved in a MID (multiple ion detection) mode. Surface oxygen groups on carbon materials decomposed upon heating by releasing CO and CO_2 at different temperatures (Table 3). The assignment of the TPD peaks to the specifics surface groups was based on the data published in the literature (Figueiredo et al., 1999). 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 anhydrous decompose as CO and CO_2 at the same temperature (around 650°C). Ether (700°C), phenol (600–700°C) and carbonyls/quinones (700–980°C) decompose as CO. TPD profiles for all the studied carbon materials are shown in Fig. 1. The treatment by nitric acid resulted in an increase in carboxylic acids and anhydrous carboxylic, lactones and phenol groups. Treatment with hydrogen peroxide introduces only carbonyl and quinone groups at a low proportion (Fig. 1, Table 3).

Table 3. Surface oxygen functionality of the studied activated carbons.

	Oxygen evolved (g/100 g)		
Carbons	CO_2	CO	CO/CO_2
Norit_initial	0.49	1.18	2.41
Norit_H_2O_2	1.12	1.46	1.30
Norit_1 M HNO_3	3.18	5.94	1.86
Norit_13 M HNO_3	11.4	12.6	1.10
Merck_initial	0.44	1.15	2.61
Merck_H_2O_2	1.92	6.95	3.6
Merck_1 M HNO_3	3.0	18.7	6.2
Merck_13 M HNO_3	15.9	17.9	1.12

Source: Adapted from Lyubchik et al. (2003).

The solutions of Cr (III), with a fixed concentration of 200 ppm, were prepared from the salt of $Cr_2(SO_4)_2OH_2$, which is used in the tanning industry. The initial pH of the resulting Cr (III) solution was 3.2.

2.2. *Adsorption Process Analyses*

2.2.1. *Batch Experiments.* The adsorption process was studied in a static mode, under equilibrium conditions, using the oxidized and the parent carbons as adsorbents. The chromium concentration was fixed at 200 ppm, which is 10 times lower than the initial concentration present in the tannery wastewater. In order to increase the rate of the adsorption to reach equilibrium, the Cr/carbon solutions were stirred up on a shaker at 160–180 rpm. for 0.5–1 month. This process was carried out at constant temperature (24 ± 1°C). The initial pH was adjusted (either with 0.1 M HCl or 0.1 M NaOH) in the range of 1.5–5.0.

Each of the 10 samples used for one experiment, consisted of a known carbon dosage between 1.2 and 20 g/l, which were added to 25 ml of Cr (III) solution (200 ppm). The experiments were duplicated for quality control and statistical purposes. The percent standard deviation of the sorption parameters was under 1.5%. All the adsorption isotherms were determined without adding any buffer to control the pH, in order to prevent the introduction of any new electrolyte into the systems.

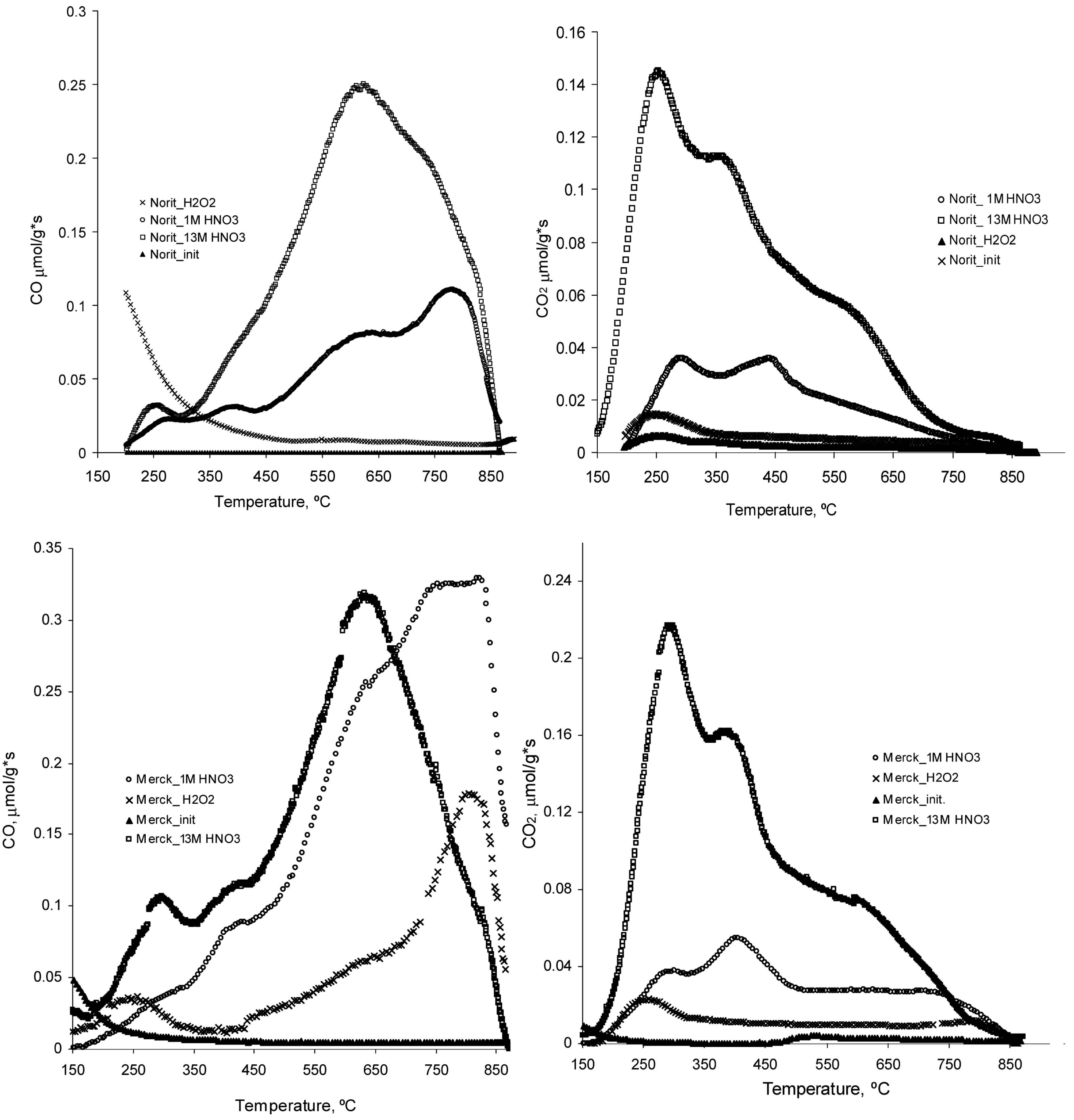

Figure 1. TPD profiles for studied carbon materials.

Time-based experiments were carried out separately for 40 systems, in order to establish the carbon-solution contact time necessary to attain the equilibrium state, which depends on the initial pH of the solution. The adsorption runs were performed at a fixed sorbate concentration of 200 ppm and fixed carbon loading of 4 g/l at (24 ± 1)°C, for 5 different pH values between 1.5 and 5. The kinetics adsorption studies were carried out in a buffer solution to eliminate the deviation in Cr and the surface group speciation.

The influence of pH on the efficiency of chromium retention was evaluated under pseudo-equilibrium conditions. The carbon/Cr (III) solution contact time was fixed at 0.5–1 month to ensure that the saturation level of the carbon was reached. The adsorption runs were performed using a fixed sorbate concentration

(200 ppm) and fixed carbon loading (4 g/l) at (24 ± 1) °C. The pH range chosen was limited to pH values less or equal to 5, due to chromium hydroxide formation which precipitation interfere in the adsorption process. The pH of the solutions was buffered and carefully controlled over the entire period of contact until the sorption equilibrium was completed. This methodology allowed preventing the change of the chromium speciation and the change of surface groups charge, along the equilibrium studies (Kratochvil and Volesky et al., 1998).

At the end of the experiments, the adsorbent was removed by filtration through membrane filters with a pore size of 0.45 μm. The chromium equilibrium concentration was measured spectrophotometrically, using UV-Visible GBC 918 spectrometer, at fixed wavelength $\lambda = 420$ nm according to the standard procedure.

The chromium adsorbed on activated carbons at equilibrium was quantified by mass balance. The following parameters were used:

Adsorption capacity of the carbon (q_{eql}) expressed in terms of metal amount adsorbed on the unitary sorbent mass (mg/g), i.e. Cr (III) uptake:

$$q_{\mathrm{eql}} = \frac{(C_{\mathrm{init}} - C_{\mathrm{eql}})}{m} \tag{1}$$

and Sorption efficiency of the system (*Rem%*) indicated from the percentage of removed metal ions relative to the initial amount, i.e. Cr removal, %:

$$Rem\% = \frac{(C_{\mathrm{init}} - C_{\mathrm{eql}})}{C_{\mathrm{eql}}} 100 \tag{2}$$

where C_{init} and C_{eql} are, respectively, the initial and equilibrium concentrations of metal ions in solution (mg/l) and m is the carbon dosage (g/l).

The optimum conditions for Cr (III) adsorption were evaluated based on the analysis of the data obtained from thermodynamic and kinetics tests, combining several experimental conditions.

3. Results and Discussion

3.1. *Influence of the Components Contact Time on the Cr (III) Adsorption Process*

It was generally observed that the adsorption of metals on activated carbons increases when the contact time increases. There was an evidence of both slow and fast chromium uptakes on the studied activated carbons. The actual time to reach equilibrium was strongly depended on the initial pH of the solution and on the nature of carbons, i.e. surface functionality and material texture. The contact time to reach equilibrium varied between 0.5 and 3 months for different carbons, at different initial pH. The process did not reach the equilibrium over the time interval of 0.5–1 month, for the carbons enriched with oxygen surface groups (i.e. those modified with nitric acid), at moderated acidic pH values of 2 and 3.2. Therefore, it was decided to leave the carbons in contact with the solution of Cr (III) for a longer time. Then, the equilibrium tests were performed after the 3rd and the 5th months. We observed that in two weeks chromium uptake was strongly slowed down, and it is possible to assume an establishment of the pseudo-equilibrium. However, the saturation with chromium ions, for all the adsorbents, was completed only after 3 months, when the maximum Cr (III) uptake was observed. Further increase of the contact time (up to 9 months) did not affect the additional Cr (III) uptake.

The "classical" bell trend of the pH influence on the Cr (III) removal was observed only in the case of acid treated samples, at the equilibrium state. The highest Cr (III) removal (nearly 70–80%) was attained at pH 3.2 on Merck and Norit carbons oxidized with 13 M HNO_3 (Fig. 2). Similar observations, for the Cr (III) removal, were reported by some authors (Kumar et al., 2000; Burns et al., 1999; Lee et al., 1995). In contrast, others referred maximal removal of Cr (III) by activated carbon at pH 5–6 (Kratochvil and Volesky, 1998; Aggarwal et al., 1999; Ranganathan, 2000).

Generally, the adsorption increases when the carbon surface is oxidized, although there is a dependence on the nature of the surface oxygen groups. Thus, it was observed that an increase in uptake was maximal in the case of a sample oxidized with nitric acid, and it was minimal in the case of samples oxidized with hydrogen peroxide. The oxidation with hydrogen peroxide slightly increases the amount of carbonyl and quinone surface groups, while oxidation with 13 M HNO_3 increased significantly the concentration of carboxylic and lactone groups (Fig. 1). Therefore, the surface groups evolved as CO_2 might have had a major influence on the adsorption of Cr (III) ions.

It is well known that the adsorption process is drastically affected by the equilibrium pH of the solutions. Considering that the uptake of metal ions at equilibrium depends on the equilibrium pH, we agreed with

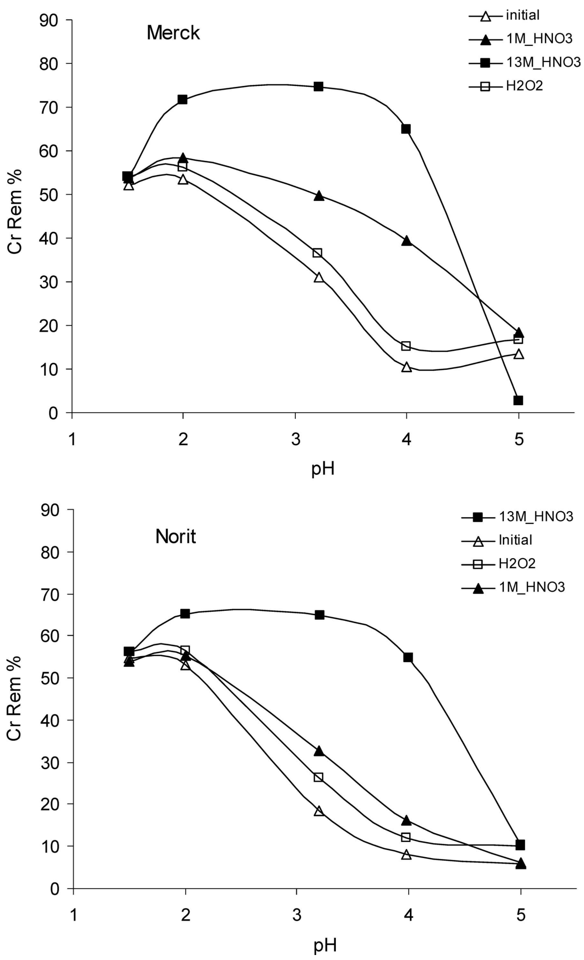

Figure 2. Influence of the solution pH on of the sorption efficiency of Merck and Norit activated carbons (data are given for 3 months of the adsorption process, for full equilibrium in the studied systems). (Adapted from Lyubchik et al., 2003).

the statement (Carrott et al., 1997) that it would be appropriate to express the adsorption results in terms of the final solution pH (see discussion of the adsorption thermodynamic at part 3.4 of the present paper).

However, the study of the pH influence on the adsorption kinetics was carried out at buffered pH values and carefully controlled over the entire period of contact, until the sorption equilibrium was completed. In fact, a different time was needed to saturate the carbon depending on the initial pH of the solution. The results obtained for the chromium removal after 0.5 month and 3 months of contact time at initial solution pH 2, 3.2 and 4 are summarized in Table 4.

In a previous work (Lyubchik et al., 2003), using the same adsorbents it was observed that at pH2 and 3.2 the chromium removal was initially rapid for all the adsorbents studied. As the contact time increases, the rate of adsorption decreases depending on the chemical surface characteristics.

Thus, for the Norit and Merck carbons treated with 13 M $HNO_{3,}$ the chromium removal increased from 40–48% to 66–69% (i.e. by 1.4–1.7 times) as the contact time was increased from 0.5 to 3 months at pH 2 and 3.2. For the other samples, the increase of chromium removal was of 2.0–2.6 times (from 20–30% to 50–60%) at pH 2 and of 1.6–2.0 at pH 3.2. These findings suggested that, in the pH range of maximal adsorption (i.e. pH of 2–3.2), the carbon's surface might have different affinities to the different species of chromium existing in the solution, and their affinity towards chromium ions are strongly affected by the solution pH.

The adsorption at pH 4 was found to be rapid and almost accomplished within 0.5 month. However, at pH∼5, when the chromium started largely to precipitate, the adsorption remained unaffected. The chromium removal at pH 4–5, was slightly increased (by 5–11%) only in the case of carbons treated with nitric acid. Some desorption (no more then 5%) was also observed in the case of hydrogen peroxide treated samples, which confirms the reversibility of the Cr (III) sorption on those carbons at pH 4 and 5.

Thus, for all the studied systems at the equilibrium state, the maximal Cr (III) uptake occurred at pH 2 and 3.2. Therefore, the pH influence on the adsorption process from batch experimental data should be analyzed considering that the adsorption equilibrium is completed. A contact time of 0.5 month was enough to achieve significant Cr (III) removal at pH higher than 3.5 and lower than 2; however an elapsed contact time was necessary to establish equilibrium at the pH range of a maximal chromium adsorption, i.e. 2 < pH > 3.5. Therefore, one should take care with data presented for acidic pH values, and ensure that the chosen contact time is enough to accomplish the adsorption equilibrium.

3.2. Influence of the Sorbent—Sorbat Ratio on the Cr (III) Adsorption Process

It was observed, that the sorption efficiency of the carbon adsorbents increases and their sorption capacity decreases with carbon loading (Fig. 3). The reduction

Table 4. Sorption efficiency. Influence of time at certain initial pH values.

	pH 2			pH 3.2			pH 4		
Carbons	Rem% 0.5 month	Rem% 3 months	Rem$_{0.5}$/ Rem$_3$	Rem% 0.5 month	Rem% 3 months	Rem$_{0.5}$/ Rem$_3$	Rem% 0.5 month	Rem% 3 months	Rem$_{0.5}$/ Rem$_3$
Norit_initial	20.91	54.74	2.62	18.21	34.06	1.87	22.10	11.72	0.53
Norit_H_2O_2	25.28	56.19	2.22	23.72	37.81	1.59	25.40	19.52	0.77
Norit_1 M HNO_3	30.43	60.49	1.99	28.70	51.79	1.80	39.66	35.31	0.89
Norit_13 M HNO_3	50.55	75.74	1.50	48.08	74.50	1.55	60.81	69.64	1.15
Merck_initial	22.99	50.84	2.21	11.7	12.00	1.02	8.02	8.12	1.01
Merck_H_2O_2	23.88	53.08	2.22	12.01	18.78	1.56	19.42	12.00	0.62
Merck_1 M HNO_3	25.47	56.34	2.21	18.08	36.37	2.01	32.2	36.0	1.11
Merck_13 M HNO_3	40.54	69.06	1.70	48.21	66.30	1.38	57.69	61.29	1.06

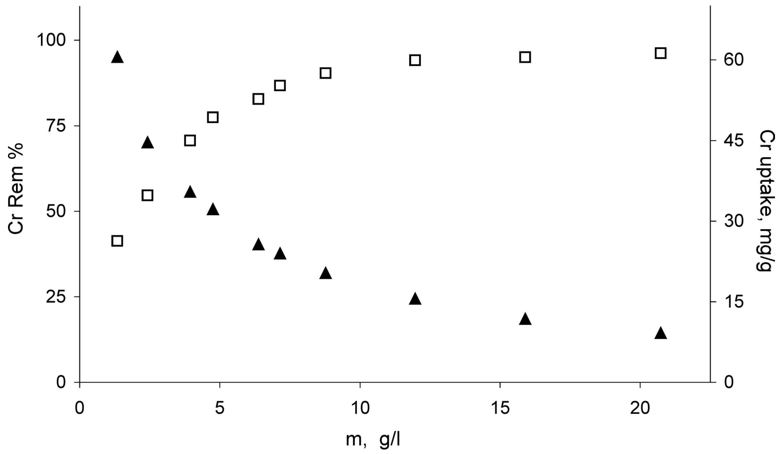

Figure 3. Dependence of the sorption efficiency (□ Rem%) and capacity (▲ Cr uptake, mg/g) on carbon loading (data are given for Merck post-treated by 13 M HNO_3 for 2 weeks of the adsorption process at pH 3.2).

of the sorption capacity is related to the fact that some of the active centers remain unsaturated during adsorption process. However, with the increase of carbon content the absolute amount of active centers increases, resulting in an increase of the overall sorption efficiency of the systems. This fact shows that, at a given pH for the adsorption in static mode, there is an optimum carbon loading which limits the Cr (III) uptake/ removal.

Thus, for the studied systems, the sorption efficiency of the activated carbons continuously increases until carbon loading of 6–8 g/l. A further an increase of the carbon loading does not affect the sorption process and the chromium removal remains practically constant. The decrease of the sorption capacity is more pronounced to carbon loading up to 8 g/l. For higher carbon loadings, the decrease on the sorption capacity is less pronounced.

Maximal Cr (III) uptake of 45–60 mg/g was found for the oxidized samples treated with 13 M HNO_3. For the parent activated carbons the chromium uptake at pH 3.2, obtained under pseudo equilibrium conditions (i.e. 2 weeks of the adsorption process) was 8–20 mg/g.

The data obtained for the sorption capacities are in agreement with those referred in the literature for the most efficient heavy metals adsorbents (Ferro-Garcia et al., 1998; Kumar et al., 2000; Kratochvil et al., 1998; Kratochvil and Volesky, 1998).

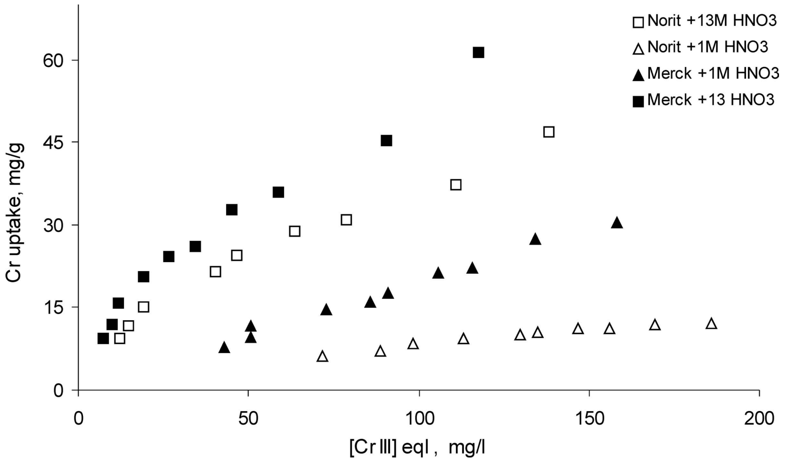

Figure 4. Isotherms of Cr (III) adsorption for activated carbons Merck and Norit oxidized by nitric acid (data are given for 2 weeks of the adsorption process at pH 3.2).

3.3. *Influence of the Adsorbent Texture on the Cr (III) Adsorption Process*

All the carbon samples adsorbed appreciable amounts of Cr (III), but the sorption efficiency of the carbons is influenced by their texture and surface functionalities.

The texture effect is related to the porous structure of the adsorbents (Table 1), specially when the micropores with diameter less than 1 nm are inaccessible for highly-hydrated $[Cr(H_2O)_6]^{3+}$ ions of 0.922 nm (Bautista-Toledo et al., 2001). The second structural parameter, the absolute value of the apparent surface area, seems to be the less important factor (despite the high surface area of the parent Merck, it was less effective in adsorbing chromium than the parent Norit carbon). 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 hydrogen peroxide does not change significantly the structure of the parent carbon materials. The structure of the modified samples (surface area, pore size distribution, pore volume) is practically identical to the initial ones; and their behavior during adsorption corresponds to the behavior of the parent materials.

Oxidation with nitric acid essentially modifies the structure of the initial Norit and Merck carbons. The specific surface area of Merck decreased due to partial destruction of the initial micropores along with the formation of a mesoporous structure. This observation was more evident in case of the materials treated with 13 M HNO_3, resulting in deeper degree of oxidation (Table 3). The specific surface area of the parent Norit carbon slightly increases with oxidation with 1 M HNO_3 due to further development of the microporosity. However, deep oxidation of the parent Norit carbon treated with 13 M HNO_3 causes a reduction on the apparent surface area and on the micropore volume. There is an increase of mesoporosity, probably due to an enlargement of micropores (Table 1). We should expect a higher uptake when the pore size increases, as referred previously, but in this case it seems that the surface chemistry plays major role on chromium adsorption (Fig. 4).

3.4. *Influence of the Solution pH on the Cr (III) Adsorption Process*

According to the approach pioneered by Kratochvil and Volesky (1998) for two-metals equilibrium data, the adsorption isotherms at different pH for the studied carbons were analysed as three-dimensional pH dependent sorption-isotherm surfaces (the details are published elsewhere (Lyubchik et al., 2003). Such approach reflected the complicated relationship between the Cr (III) removal capacity and the solution pH. Furthermore, due to the lack of precise control over the thermodynamic tests, whether the systems reached full equilibrium state or not, the pH influence on the adsorption process at equilibrium seems to be even much more complicated.

The sorption isotherms exhibited different shapes. At pH 1.5 and 4 they are of type IV according to Brunauer classification indicating the existence of optimum sorbent dosage, which limits the amount of chromium adsorbed. At pH 2 and 3.2 they could be attributed to types II and III, i.e. adsorption in micropores, accompanied by adsorbate-adsorbate interaction. These suggest that solutes had a higher affinity for the new layer formed by the solute molecules already adsorbed then for the solvent. Therefore, along with the ion-exchange, surface complex formation and surface precipitation might be involved in the sorption process.

3.4.1. pH Depletion/Rinsing: Final pH. The final pH of the solution after sorption was measured for all the studied systems (see Appendix Table 5). This value is affected by the carbon loading. Generally, the final pH for the solutions with higher carbon content differs significantly from the initial pH, comparing to the systems with lower carbon loading. Thus, at the maximum carbon loading of 20 g/l, for parent and hydrogen peroxide treated samples, $\Delta(\mathrm{pH}_{\mathrm{final}}\text{-}\mathrm{pH}_{\mathrm{initl}})$ was about 3–4 units the studied initial pH range.

It should be noted that for the solutions with low initial pH 1.5, the carbon loading had virtually no effect on the final pH values, whereas this influence was pronounced at higher initial pH (2, 3.2 or 4). For all the studied adsorbents, it was observed that the final pH drift always to the value of PZC. Thus, in the case of acid treated samples the highest decrease in the initial pH was found in the systems at pH 3.2, resulting in the final pH values in the interval from 2.0 to 2.3. Only a slight decrease of the initial pH was found in the systems at pH 4 yielding the final pH of 3.0–3.2. In contrast, initial pH 2 was increased during the sorption to the final pH value of 2.8 and almost no change in the pH was found at initial pH 1.5 (final pH $\approx$ 1.8).

A significant shift in the initial pH of the solution was observed in the case of parent Norit and Merck carbons and their hydrogen peroxide oxidized forms. At initial moderate pH 3.2 and 4 the presence of carbon changed significantly the initial pH of the solution to a final alkaline pH $\approx$ 6–7.6. At initial pH 2, the addition of carbon to the solution kept the acid conditions till the end of the experiment (final pH $\approx$ 4–5.5).

With regard to the changes in the carbon surface charge caused by the adsorption of chromium ions, Figs. 5 and 6 show the profile of hydrogen ion concentration drift (expressed as $[\mathrm{H}^+]_{\mathrm{final}}/[\mathrm{H}^+]_{\mathrm{init}}$) to carbon loading for the studied adsorbents.

It should be noted, that despite the differences in the initial pH conditions, the adsorption of Cr (III) on the carbon surface always occurred at certain pH values close to the $\mathrm{pH}_{\mathrm{PZC}}$ of the adsorbents, i.e. at pH $\approx$ 7 for all parent Merck, Norit and H_2O_2 treated samples and at pH $\approx$ 3 for the carbons treated with nitric acid. It is referred in the literature (Chen, and Lin, 2001; Chakir et al., 2002) that changes of the carbon's zeta potential in the presence of chromium are directly related to the properties of the adsorbent, which was modified due to the adsorbed cationic Cr (III) species.

The influence of the pH of the solution on the uptake is generally attributed to the change in the relative distribution of the carbon surface groups charge and of the overall proton balance (Csobán et al., 1998; Kratochvil and Volesky, 1998). Therefore, each type of oxygen surface groups (that might be protonated, neutral or deprotonated) plays an important role on the adsorption of the metals ions (Chen and Lin, 2001; Carrott et al., 1997; Csobán et al., 1998).

It could be expected that the efficiency of removal of positively charged metal species increased with increasing pH, due to the fact that the net surface charge is gradually changing from positive in acid solution to negative in basic solutions. However, since the adsorption in the studied systems occurred at pH values lower (1–2 units) to the carbons $\mathrm{pH}_{\mathrm{PZC}}$, a complete explanation of the adsorption mechanism is complex. Furthermore, we believe that there is more than one mechanism to explain the chromium sorption on the studied activated carbons at pH between 1.5 and 5.

The mechanisms shall consider the change of adsorbent properties with pH and chromium speciation in the solution.

Thus, at pH 2 and 3.2, the removal of Cr (III) required elapsed time to achieve equilibrium and the Cr (III) uptake reached the maximum. It is difficult to explain the role of each of the mechanisms that affected Cr III uptake since the protons participate in several reactions at the same time. To be able to explain the sorption of Cr (III) on activated carbon at the studied pH range several reactions between chromium ions and carbon surface should be assumed.

At pH 3.2, there is a significant decrease of the initial pH (Figs. 5 and 6, Table 5) during batch adsorption. The chromium cations could be both the aqueous metal ions $[\mathrm{Cr(H_2O)_6}]^{3+}$ and their hydrolyzed form

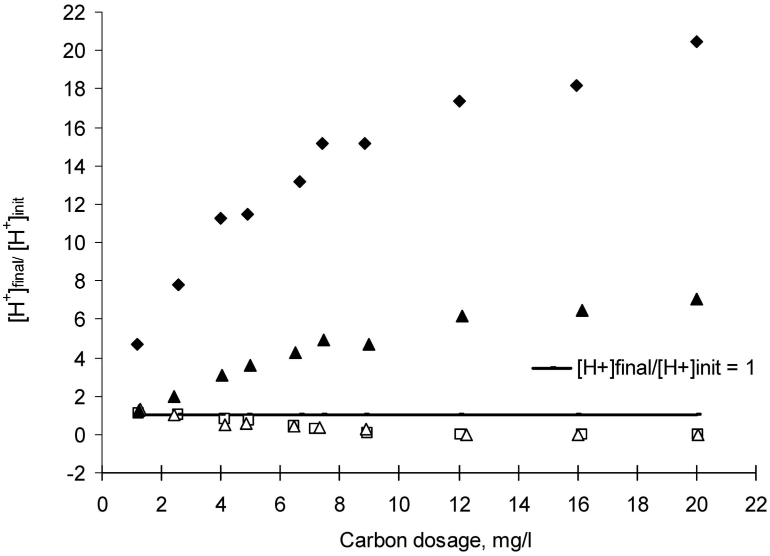

Figure 5. Influence of Norit carbons loading on the final solution pH (initial pH 3.2). (△) Initial Norit; (□) Norit treated by H_2O_2; (▲) Norit treated by 1 M HNO_3; (■) Norit treated by 13 M HNO_3.

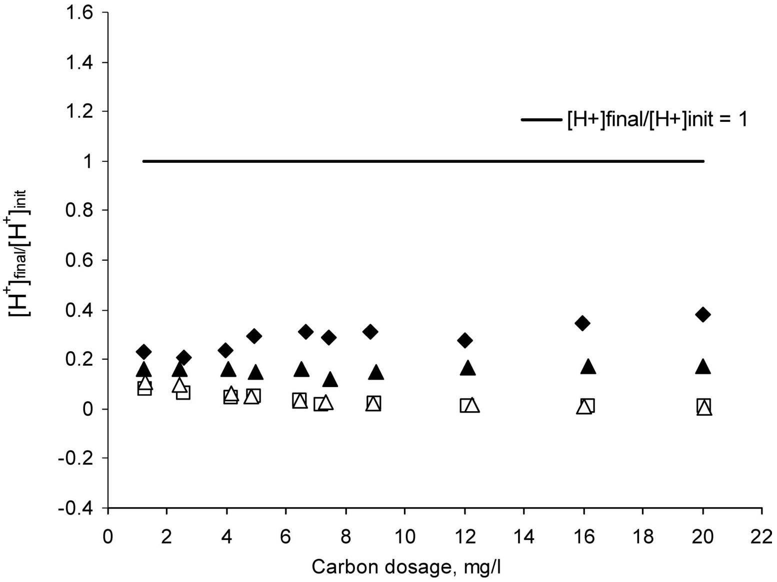

Figure 6. Influence of Merck carbons loading on the final solution pH (initial pH 2). (△) Initial Merck; (□) Merck treated by H_2O_2; (▲) Merck treated by 1 M HNO_3; (■) Merck treated by 13 M HNO_3.

$[Cr(H_2O)_5OH]^{2+}$, while the adsorption sites could be neutral or/and protonated surface groups:

$$ROOH + Cr^{3+} \rightarrow ROCr^{2+} + H^+ \quad (1)$$

$$ROOH_2^+ + Cr^{3+} + H_2O \rightarrow ROCr(OH) + 3H^+ \quad (2)$$

We think that at pH 3.2, according to these mechanisms the chromium species are not equally attracted. Both Langmuir and Freundlich equations were used to simulate the ion-exchange and the adsorption-complexation reactions (Lyubchik et al., 2004). The obtained correlation coefficients were of 0.98 and

0.99, respectively. Thus, it seems that the mechanism of chromium uptake at pH 3.2 can be explained considering an outer-sphere complexation, most probably with the first hydrolyzed hydrolytic species, which is converted with time to an inner-sphere complexation:

$$\begin{aligned} &ROOH + [Cr(H_2O)_5OH]^{2+} \\ &\quad \rightarrow ROOH \ldots [Cr(H_2O)_5OH]^{2+} \\ &\quad \rightarrow RO\text{-}O[Cr(H_2O)_4OH]^{+} + H^{+} + H_2O \qquad (3) \end{aligned}$$

At pH 2, $[Cr(H_2O)_6]^{3+}$ is considered as the adsorbing ion. The adsorption mechanism may be explained assuming that there is a fast aqueous chromium ion-exchange, followed by their surface hydrolysis and slower chemisorption. The observed increase of the final pH during the batch experiments, forces to shift the equilibrium of the hydrolysis reaction (4).

$$Cr^{3+} + H_2O \rightleftarrows Cr(OH)^{2+} + H^{+} \qquad (4)$$

When the chromium is adsorbed as Cr^{3+} the reaction (4) drifts to the left resulted in protons depletion and hence the pH rise. Furthermore, the pH of a solution increased also due to significant protonation of the adsorption sites (Lyubchik et al., 2003).

4. Conclusions

According to the data obtained for the chromium (III) adsorption on activated carbon, the following conditions should be used in order to obtain maximum chromium uptake:

1. The initial pH of the solution should be varied between pH 2 and 4.
2. The presence of surface oxygen functional groups, mainly carboxylic, enhances chromium adsorption at pH 2–4.
3. The adsorbents should have an optimum balance of micro-and mesopores in order to facilitate the access of the high-hydrated metal ions to the adsorbent internal surface. This aspect is especially significant in the case of carbon materials with lack of the oxygen functional groups.
4. The effect of contact time, to reach total equilibrium, is very important for the adsorption processes performed in a static mode. In this case, the efficiency of the adsorbent can be increased 2–2.5 (!) times.

Furthermore, it is necessary to take into account that for each kind of adsorbent there is an optimum carbon loading. A further increase of the carbon content does not result in an increase of the adsorption capacity and efficiency.

Optimization of the experimental conditions in accordance to the suggested above, could favor the use of activated carbons in real industrial scale, when the balance cost/quality of heavy metal removal is provided.

Appendix

Table 5. Final pH in the studied system.

		pH initial			
	Carbon	pH 1.5	pH 2	pH 3.2	pH 4
Studied carbons	dosage (g/l)	pH final			
Norit_init	20	1.87	5.76	7.3	7.69
Norit_init	16	1.81	4.92	6.84	7.25
Norit_init	12	1.83	4.28	6.59	6.89
Norit_init	10	1.78	4	5.12	6.58
Norit_init	8	1.75	3.84	4.03	6.37
Norit_init	6	1.56	3.78	3.91	5.94
Norit_init	5	1.72	3.65	3.58	4.45
Norit_init	4	1.74	3.5	3.39	4.15
Norit_init	2.5	1.74	3.15	3.29	3.93
Norit_init	1.2	1.79	2.97	3.19	3.78
Norit_H_2O_2	20	1.63	4.69	6.26	7.1
Norit_H_2O_2	16	1.61	4.37	5.95	6.79
Norit_H_2O_2	12	1.6	4.05	4.54	6.78
Norit_H_2O_2	10	1.56	3.88	3.73	6.57
Norit_H_2O_2	8	1.55	3.87	3.62	4.9
Norit_H_2O_2	6	1.55	3.8	3.54	4.91
Norit_H_2O_2	5	1.51	3.56	3.4	4.38
Norit_H_2O_2	4	1.54	3.43	3.34	4.18
Norit_H_2O_2	2.5	1.53	3.13	3.22	3.87
Norit_H_2O_2	1.2	1.46	2.94	3.16	3.97
Norit_1 M HNO_3	20	1.69	2.88	2.5	3.43
Norit_1 M HNO_3	16	1.49	2.86	2.51	3.57
Norit_1 M HNO_3	12	1.55	2.86	2.64	3.53
Norit_1 M HNO_3	10	1.56	2.87	2.73	3.6
Norit_1 M HNO_3	8	1.53	2.87	2.76	3.67
Norit_1 M HNO_3	6	1.55	2.88	2.77	3.69
Norit_1 M HNO_3	5	1.53	2.87	2.83	3.71

(*Continued on next page.*)

Table 5. (*Continued*).

		pH initial			
	Carbon	pH 1.5	pH 2	pH 3.2	pH 4
Studied Carbons	dosage (g/l)	pH final			
Norit_1 M HNO_3	4	1.59	2.99	2.86	3.76
Norit_1 M HNO_3	2.5	1.58	2.98	3.09	3.71
Norit_1 M HNO_3	1.2	1.59	3	3.13	4.02
Norit_13 M HNO_3	20	1.63	2.56	2.03	3.08
Norit_13 M HNO_3	16	1.62	2.59	2.05	3.08
Norit_13 M HNO_3	12	1.66	2.6	2.08	3.11
Norit_13 M HNO_3	10	1.61	2.64	2.1	3.16
Norit_13 M HNO_3	8	1.54	2.7	2.19	3.24
Norit_13 M HNO_3	6	1.53	2.7	2.24	3.36
Norit_13 M HNO_3	5	1.54	2.8	2.27	3.45
Norit_13 M HNO_3	4	1.65	2.69	2.34	3.42
Norit_13 M HNO_3	2.5	1.52	2.74	2.48	3.4
Norit_13 M HNO_3	1.2	1.45	2.89	2.59	3.51
Merck_init	20	1.75	4.33	5.96	7.05
Merck_init	16	1.41	4.05	4.88	7.57
Merck_init	12	1.93	3.85	4.13	6.16
Merck_init	10	1.69	3.65	3.67	4.57
Merck_init	8	1.66	3.53	3.5	4.46
Merck_init	6	1.3	3.49	3.48	4.4
Merck_init	5	1.68	3.29	3.29	4.25
Merck_init	4	1.67	3.19	3.18	4.29
Merck_init	2.5	1.76	3	3.18	3.98
Merck_init	1.2	1.69	2.97	3.08	3.87
Merck_H_2O_2	20	1.59	4.11	6.16	7.04
Merck_H_2O_2	16	1.6	4.05	5.69	6.89
Merck_H_2O_2	12	1.58	3.97	4.23	6.25
Merck_H_2O_2	10	1.51	3.7	3.75	5.03
Merck_H_2O_2	8	1.55	3.73	3.48	4.58
Merck_H_2O_2	6	1.62	3.49	3.45	4.34
Merck_H_2O_2	5	1.6	3.28	3.27	4.12
Merck_H_2O_2	4	1.56	3.33	3.25	4.11
Merck_H_2O_2	2.5	1.67	3.21	3.14	3.99
Merck_H_2O_2	1.2	1.61	3.1	3.06	3.95
Merck_1 M HNO_3	20	1.77	2.76	–	3.15
Merck_1 M HNO_3	16	1.78	2.77	–	3.19
Merck_1 M HNO_3	12	1.6	2.78	–	3.21
Merck_1 M HNO_3	10	1.65	2.82	–	3.33
Merck_1 M HNO_3	8	1.71	2.92	–	3.31
Merck_1 M HNO_3	6	1.66	2.8	–	3.37
Merck_1 M HNO_3	5	1.56	2.82	–	3.44
Merck_1 M HNO_3	4	1.47	2.79	–	3.51
Merck_1 M HNO_3	2.5	1.85	2.79	–	3.7
Merck_1 M HNO_3	1.2	1.78	2.8	–	3.9
Merck_13 M HNO_3	20	1.55	2.44	1.80	2.68
Merck_13 M HNO_3	16	1.55	2.46	1.86	2.74
Merck_13 M HNO_3	12	1.56	2.56	1.92	2.76
Merck_13 M HNO_3	10	1.58	2.51	2.02	2.82
Merck_13 M HNO_3	8	1.56	2.54	205	2.82
Merck_13 M HNO_3	6	1.75	2.51	206	2.88
Merck_13 M HNO_3	5	1.61	2.53	2.18	2.94
Merck_13 M HNO_3	4	1.66	2.63	2.21	2.95
Merck_13 M HNO_3	2.5	1.68	2.68	2.33	3.11
Merck_13 M HNO_3	1.2	1.65	2.64	2.59	3.33

(*Continued.*)

Acknowledgments

Authors are thankful to NATO Science for Peace Programme SfP project 977984 and FCT Programme, SFRH/BPD/7150/2001, Portugal for the financial support.

References

Aggarwal, D., M. Goyal, and R.C. Bansal, "Adsorption of Chromium by Activated Carbon from Aqueous Solution," *Carbon*, **37**, 1989 (1999).

Ajmal, M., R.A.K. Rao, R. Ahmad, J. Ahmad, and L.A.K. Rao, "Removal and Recovery of Heavy Metals from Electroplating Wastewater by Using Kyanite as an Adsorbent," *Journal of Hazardous Materials*, **87**, 127 (2001)

Bautista-Toledo, I., J. Rivera-Utrilla, M.A. Ferro-García, and C. Moreno-Castilla "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**, 93–100 (1994).

Brigatti, M.F., G. Franchini, C. Lugli, L. Medici, L. Poppi, and E. Turci, "Interaction Between Aqueous Chromium Solutions and Layer Silicates," *Applied Geochemistry*, **15**, 1307 (2000).

Brown, P.A., S.A. Gill, and S.J. Allen, "Metal Removal from Wastewater Using Peat," *Water Research*, **34**, 3907 (2000).

Burns, C.A., P.J. Cass, I.H. Harding, and R.J. Crawford, "Adsorption of Aqueous Heavy Metals onto Carbonaceous Substrates," *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **155**, 63 (1999).

Carrott, P.J.M., M.M.L. Ribeiro Carrott, J.M.V. Nabais, and J.P. Prates Ramalho, "Influence of Surface Ionization on the Adsorption of Aqueous Zinc Species by Activated Carbons," *Carbon*, **35**, 403 (1997).

Chakir, A., J. Bessiere, K.E.L. Kacemi, and B. Marouf, "A Comparative Study of the Removal of Trivalent Chromium from Aqueous Solutions by Bentonite and Expanded Perlite," *Journal of Hazardous Materials*, **95**, 29, (2002).

Chen, J.P. and M. Lin, "Surface Change and Metal Ion Adsorption on H-type Activated Carbon: Experimental Observation and Modelling Simulation by the Surface Complex Formation Approach," *Carbon*, **39**, 1491 (2001).

Csobán, K. and P. Joó, "Sorption of Cr (III) on Silica and Aluminium Oxide: Experiments and Modeling," *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **151**, 97 (1999).

Csobán, K., M. Párkányi-Berka, P. Joó, and Ph. Behra, "Sorption experiments of Cr(III) onto silica," *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **141**, 347 (1998).

Ferro-García, M.A., J. Rivera-Utrilla, I. Bautista-Toledo, and C. Moreno-Castilla, "Adsorption of Humic Substances on Activated Carbon from Aqueous Solutions and Their Effect on the Removal of Cr(III) Ions," *Langmuir*, **14**, 1880 (1998).

Figueiredo, J.L., M.F.R. Pereira, M.M.A. Freitas, and J.J.M. Órfão, "Modification of the Surface Chemistry of Activated Carbons," *Carbon*, **37**, 1379, (1999).

Kratochvil, D., P. Pimentel, and B. Volesky, "Removal of Trivalent and Hexavalent Chromium by Seaweed Biosorbent," *Environmental Science Technology*, **32**, 2693 (1998).

Kratochvil, D. and B. Volesky, "Advances in the Biosorption of Heavy Metals," *Trends in Biotechnology*, **16**, 291 (1998).

Kumar, A., N.N. Rao, and S.N. Kaul, "Alkali-Treated Straw and Insoluble Straw Xanthate as Low Cost Adsorbents for Heavy Metal Removal—Preparation, Characterization and Application," *Bioresource Technology*, **71**, 133 (2000).

Lee, K.C., S.K. Low, and K.L. Kek, "Removal of Chromium from Aqueous Solution," *Bioresource Technology*, **54**, 183 (1995).

Lyubchik, S., R. Melo, C. Palma, and I.M. Fonseca, "Adsorption Equilibrium in the System "Cr (III)—Activated Carbon," in S. Barany, (ed.), *Role of Interfaces in Environmental Protection, NATO ASI Series IV: Earth and Environmental Science*, Vol. 24, Kluwer, pp. 355—377 (2003).

Lyubchik, S.I., A.I. Lyubchik, O.L. Galushko, L.P. Tikhonova, J. Vital, I.M. Fonseca, and S.B. Lyubchik, "Kinetics and Thermodynamics of the Cr (III) Adsorption on the Activated Carbon from Co-mingled Wastes," *Colloids and Sufaces A: Physicochem. Eng. Aspects*, **242**, 151 (2004).

Ranganathan, K., "Chromium Removal by Activated Carbons Prepared from *Casurina Equisetifolia* Leaves," *Bioresource Technology*, **73**, 99 (2000).

Rivera-Utrilla, J., I. Bautista-Toledo, M.A. Ferro-García, and C. Moreno-Castilla, "Activated Carbon Surface Modifications by Adsorption of Bacteria and Their Effect on Aqueous Lead Adsorption," *J. Chem. Technol. Biotechnol.*, **76**, 1209 (2001).