Adsorption (2010) 16: 279–286
DOI 10.1007/s10450-010-9240-3

Study of chromium(VI) adsorption onto modified activated carbons with respect to analytical application

Ryszard Dobrowolski · Magdalena Otto

Received: 8 March 2010 / Accepted: 21 May 2010 / Published online: 25 June 2010

Abstract Two different types of modification of activated carbon, by treatment with concentrated solution of HNO_3 and outgassing treatment at high temperature, were studied in order to obtain the most effective adsorption of chromium(VI) ions from water solution. The basic parameters affecting the adsorption capacity of Cr(VI) ions on modified activated carbons were studied in details and the effect of modifications of activated carbons has been determined by studying the initial runs of adsorption isotherms. The obtained Cr(VI) adsorption isotherms were well fitted in the Freundlich equation. The reduction of Cr(VI) to Cr(III) and further ion exchange mechanism of adsorption onto oxidizing activated carbon and surface precipitation to $Cr(OH)_3$ in case of outgassing activated carbon were found as the main adsorption mechanisms of Cr(VI) ions onto modified activated carbons. Presence of chlorides and nitrates in studied adsorption system strongly decreased the adsorption ability of Cr(VI) onto outgassing activated carbon and mechanism of this behavior is proposed.

Keywords Chromium adsorption · Modified activated carbons · Enrichment · Atomic absorption spectrometry

1 Introduction

Chromium occurs in the environment due to natural sources and manmade activities in two oxidation states: trivalent Cr(III) and hexavalent Cr(VI). Cr(III) is considered as a essential trace nutrient for human, while Cr(VI), in turn, is highly toxic (Nriagu and Nieboer 1988). Owing to the different toxicities of Cr(VI) and Cr(III), there is a great interest in the speciation and determination of chromium species in environmental matrices (Stein and Schwedt 1994).

Flow injection analysis (FIA) combined with inductively coupled plasma-mass spectrometry (ICP-MS) (Séby et al. 2003), electrothermal atomic absorption spectrometry (ETAAS) (Siles Cordero et al. 2004) and flame atomic absorption spectrometry (FAAS) (Anthemidis et al. 2002; Saracoglu et al. 2002) are the most useful techniques in the determination of chromium in the environmental samples. Due to lack of compatibility between the low level of chromium in drinking waters and the detection limit of ETAAS preconcentration and separation steps are required to improve the detection capability of this technique. Several procedures have been used for the preconcentration and separation of Cr(VI) from Cr(III) species, e.g. ion exchange, precipitation and co-precipitation, chelation, electrolysis, extraction, solid phase (Narin et al. 2008) and cloud point extraction (Wang et al. 2010a) and activated carbon adsorption (Gil et al. 2006). Adsorption of heavy metals onto activated carbons is found to be the most effective for separation and enrichment of trace metals from aqueous solutions because of their extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity. However, the chemical nature of activated carbons determined by the amount and nature of surface functional groups is more important. The surface of activated carbons can be easily modified in various ways, e.g. by treatment with solutions of acids and alkalis resulting in increasing the amount of alkaline and acidic groups of carbon's surface, impregnation with metal salts or outgassing treatment at high temperature (above 1100 °C), resulting in

R. Dobrowolski (✉) · M. Otto
Department of Analytical Chemistry and Instrumental Analysis, Faculty of Chemistry, Maria Curie-Sklodowska University, M.C. Sklodowska Sq. 3, 20-031 Lublin, Poland
e-mail: rdobrow@poczta.umcs.lublin.pl

the removal of surface functional groups and the change in anions-exchange capacity (Dobrowolski 1998). Latva et al. (2003) proposed the procedure of separation and determination of Cr(III) and Cr(VI) from aqueous solutions onto iron-loaded activated charcoal.

The mechanism of sorption of metal ions onto activated carbon is still under investigation taking into account the influence of surface acid groups resulting in the adsorption capacity. Moreover the role of raw material used for the activated carbon preparation and the influence of suspension parameters for particular adsorption system are not clear. Less attention is devoted in recognizing the mechanism and adsorption capacity for particulars surface groups because of complexity of sorption phenomenon. It can be expected that the most active adsorption centers will be occupied by ions of very diluted solutions and for high concentration these centers will be exhausted and unavailable. This behavior will be marked in the initial part of adsorption isotherms. Up until now almost every studied isotherms were fitted by well known Langmuir and Freundlich equations and some efforts were undertaken for interpretation of calculated parameters (Mohan and Pittman 2006).

The studies of adsorption equilibrium have lead to the conclusion that pH is the dominant parameter controlling the adsorption of Cr(VI) ions onto activated carbons (Chen and Lin 2001; Di Natale et al. 2007; Wang et al. 2010b). The role of the surface chemical and physical properties of activated carbon and the influence of heteroatoms, e.g sulfur, nitrogen, hydrogen and oxygen on the removal of chromium by its adsorption onto activated carbon was investigated by Valix et al. (2008). There is no doubt that heteroatoms provide the net charge in the activated carbon structure. By forming heterocyclic rings they can reside within the carbon layers, or they are bonded to edges of carbon in defect position. It can be expected that this sites are the main adsorbing ions centers and modification of carbon by building heteroatoms into its structure will be resulted in specific adsorption properties of carbon.

Recently, a slurry sampling graphite furnace atomic absorption spectrometry technique (GF AAS) for determination of trace elements has been proposed (Dobrowolski 1998). This technique seems to be very attractive especially in the case of direct introduction of carbon slurry with adsorbed trace elements after enrichment into the electrothermal graphite atomizer. Direct injection of carbon slurry into atomizer is possible in the case of application of fine powdered activated carbon and it requires very fine purification of carbons from mineral additives. This technique is irreplaceable when complete desorption of an analyte from activated carbon is impossible, despite the application of very aggressive agents as desorption medium. When almost all analyte is adsorbed onto activated carbon the batch system of enrichment is suitable for further determination of trace metals by carbon slurry sampling GF AAS technique. For this reason new adsorbents with specific adsorption properties are needed.

The aim of this study was the evaluation of modified activated carbons application for separation and enrichment of Cr(VI) from aqueous solutions. For this purpose modifications of powdered activated carbon (C*) by treatment with concentrated HNO_3 solution (OC*) and outgassing treatment at high temperature (OGC*) were proposed. The basic parameters affecting the adsorption capacity of Cr(VI) ions on modified activated carbons were studied in details and the effect of modifications of activated carbons has been determined by setting the initial runs of adsorption isotherms. Taking into account further analytical application of prepared carbons the removing of chromium species from loaded activated carbons was studied using inorganic acids in respect to their concentrations. Determination of chromium in solid materials requires the introduction of digestion steps in the analytical procedure, which usually involves the application of aqua regia. It means that after this step the excess of used acids will be presented in the solution before preconcentration stage. For this reason the influence of chlorides and nitrates on adsorption ability of Cr(VI) ions onto modified activated carbon for diluted aqueous solution was studied additionally.

2 Experimental

2.1 Reagents and materials

Standard stock solution of Cr(VI) (520 mg/L) were prepared by proper dissolution of powdered $K_2Cr_2O_7$ (POCH, Gliwice, Poland) in double-distillated water. Hydrochloric acid Suprapure (36%) (Merck, Darmstadt, Germany), nitric acid Suprapure (65%) (Merck, Darmstadt, Germany), sodium chloride (POCH, Gliwice, Poland), potassium nitrate (POCH, Gliwice, Poland) were used. NaOH and HCl solutions were used for pH adjustment. Throughout all analytical work, double-distilled water was used.

The powdered activated carbon, Medical Carbon (Carbo Medicinalis), produced from charcoal by Gryfskand in Hajnówka, Poland, after pretreatment with hydrochloric acid (POCH, Gliwice, Poland) was used as the initial adsorbent. It was stated experimentally that this pretreatment reduced ash contents in the carbon up to 0.01%.

2.2 Apparatus

Measurements of chromium concentration in studied adsorption system were carried out with a Varian SpectrAA 800 atomic absorption spectrometer equipped with a GTA 100 graphite furnace Zeeman background correction. A hollow cathode lamp (Varian) was used for the measurement

of Cr at wavelength 357.9 nm, and a 0.5 nm slit width was selected. Pyrolytic graphite coated tubes (Varian) were used in all experiments. The temperature program employed in Cr(VI) determinations was as follows: drying: 120 °C for 10 s; ashing: 1000 °C for 3 s; atomisation: 2600 °C for 2 s. Pure argon was used as the inert gas with a flow rate of 3.0 L/min except the atomization stage.

2.3 Activated carbon modification and measurements

Commercially available activated carbon was leached by concentrated hydrochloric acid using a Soxhlet apparatus made of quartz and by hydrofluoric acid in the Teflon vessel. Then two portions of the purified activated carbon were modified using two different methods, e.g. oxidation by concentrated nitric acid and outgassing treatment at high temperature (1100 °C) in argon atmosphere as inert gas. The procedure of oxidation was as follows: 100 mL of concentrated nitric acid was added to 10 grams of the activated carbon and the suspension was heated at 90 °C until dry. The residue was washed with distilled water until conductivity of the water eluent was close to that of the distilled water. Outgassing treatment was held in fluidized furnace at 1100 °C in argon atmosphere. In this way three different activated carbons were obtained: C*—discharging carbon, OC*—oxidized by concentrated nitric acid carbon and OGC*—outgassing carbon. The surface characteristic of obtained carbons is summarized in Table 1. The reaction of the activated carbon with the oxidants cannot change only the chemical nature of its surface but also its texture characteristics. Carbon oxidation by concentrated nitric acid caused the decrease in the surface area in the greatest extent. Probably, some of macropores were destroyed because of the loss of pore walls as result of carbon partial digestion by strong hot acid. On the other hand outgassing process caused the increase of the surface area because of removing surface acidic groups which can block entering of the adsorbate into micropores. Adsorption experiments were carried out at 25 °C. Particular measuring points were obtained for the adsorption system: 50 mL of chromium solution and 0.2 g of an activated carbon. The equilibrium adsorption uptake in the solid phase a, (mg/g), was calculated as follows:

$$a = \frac{(c_i - c) \cdot V}{m} \quad (1)$$

where c_i is the initial Cr(VI) concentration (mg/L), c is the equilibrium Cr(VI) concentration (mg/L), V is the volume of the solution (L) and m is the mass of the adsorbent (g). pH measurements of initial chromium solutions and carbon suspensions were made using a glass electrode combined with a calomel electrode, GK2302B (Radiometer). After the equilibrium reaching (180 min) the liquid phase was separated by a centrifuge.

3 Results and discussion

3.1 Effect of pH

The effect of pH on chromium(VI) adsorption onto modified activated carbons was studied by using of solutions with the same chromium concentration and different initial pH values for particular adsorption system. In Fig. 1 the adsorption ability of chromium as a function of the equilibrium pH is shown. The optimum pH for adsorption of Cr(VI) onto prepared activated carbons fit into wide ranges of pH values. OC* reaches a maximum adsorption ability between 1.8 and 5.5. Oxidized carbon possesses huge number of acidic groups on its surface (Dobrowolski 1998). Moreover surface charge density for this type of carbon is negative up to pH around 3.5 units (Dobrowolski et al. 1986). For the pH lower than 1.5 dissociation of surface acid group can be neglected. It means that for low values of pH the reduction of Cr(VI) to Cr(III) and adsorption by nonspecific sorption or formation of surface chelates are the main mechanism of adsorption. For the pH higher than 1.5 acidic surface groups enhanced

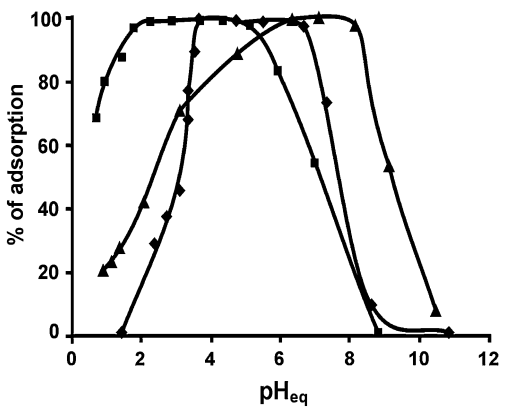

Fig. 1 The pH influence on Cr(VI) adsorption onto C* (◆), OC* (■), OGC* (▲); $m = 0.2$ g, $V = 50$ mL, $C_{Cr(C^*)} = 0.26$ mg/L, $C_{Cr(OC^*)} = 2.60$ mg/L, $C_{Cr(OGC^*)} = 1.20$ mg/L, $t = 3$ h, $T = 25$ °C

Table 1 Basic parameters of modified activated carbons

Carbon type	C*	OC*	OGC*
S_{BET} (m^2/g)	1200	620	1415
Micropore area (m^2/g)	790	380	880
Micropore volume (cc/g)	0.35	0.17	0.39

the Cr(III) adsorption. Chromic ions exist in aqueous solutions as $[Cr(H_2O)_5]^{3+}$. These associated water molecules are exchanged with the hydroxyl ions and the exchanged number depends on the pH of the solution. pH variations are caused by changes in amount of acidic surface groups. These cause the change of the extent of the positive charge on the chromic ion. Because of this, for higher values of pH (>5.5) the interaction between acidic surface groups and chromic ions becomes weak and adsorption ability decreases drastically. For carbon C* a maximum adsorption ability is between 3.8 and 7, while in case of OGC* carbon the shift of maximum adsorption ability toward alkaline pH, i.e. 6 to 8.5, is observed. That shift is caused mainly, due to the fact outgassing activated carbon does not indicate the presence of acidic groups on their surface (Dobrowolski 1998). Moreover, this type of carbon indicates a positive charge of surface in very wide range of pH values (Dobrowolski et al. 1986). The change of the positive charge density on negative around pH of 10.5 units causes the decrease of adsorption ability of Cr(VI) ions onto outgassing activated carbon. Adsorption of Cr(VI) onto OC* and C* is poor at pH value lower than one unit, where H_2CrO_4 is the main species, and in basic solutions where Cr(VI) exists in the form of chromate ion (CrO_4^{2-}). Cr(VI) is adsorbed the best in the pH range where hydrogen chromate ions ($HCrO_4^-$) and dichromate ions ($Cr_2O_7^{2-}$) are in equilibrium. It is worth to mention, that optimum equilibrium pH for adsorption of Cr(VI) onto C*, OC* and OGC* was obtained when initial pH of aqueous solutions were about 5.

3.2 Kinetic study

The effect of time on adsorption of Cr(VI) onto modified activated carbons is shown in Fig. 2. The studies suggest that the process of adsorption is rather quick and depends on carbon modification. In case of C* and OGC* carbons the adsorption equilibrium is achieved after several minutes, while in case of OC* carbon getting equilibrium requires more time. Probably, the adsorption of Cr(VI) onto that activated carbon follows mainly by the surface reduction of Cr(VI) to Cr(III), and then as the aqueous complex or complexes with humic acids presented on the surface of that modified carbons adsorb on its surface. Due to the large size of the complex of $[Cr(H_2O)_5]^{3+}$ the adsorption onto the oxidized carbon can be carried out very slow. Finally, shaking time of 180 min was chosen to ensure to reach adsorption equilibrium in all cases.

In order to recognize the reaction order of kinetic sorption of Cr(VI) onto studied activated carbons all experimental kinetic data were fitted to the commonly applied pseudo-first-order equation (Lagergren 1898) and pseudo-second-order equation (Ho et al. 2000). These kinetic rate equations can be written as follows:

$$\ln(a_{eq} - a_t) = \ln a_{eq} - k_1 t, \tag{2}$$

$$\frac{t}{a_t} = \frac{1}{k_2 a_{eq}^2} + \frac{1}{a_{et}} t \tag{3}$$

where a_t (mg/g) is the amount adsorbed at time t. The k_1 (1/min) and k_2 (g/mg·min) are the rate constants of the pseudo-first-order equation and pseudo-second-order equation, respectively. In Fig. 3 the fitting plots using pseudo-

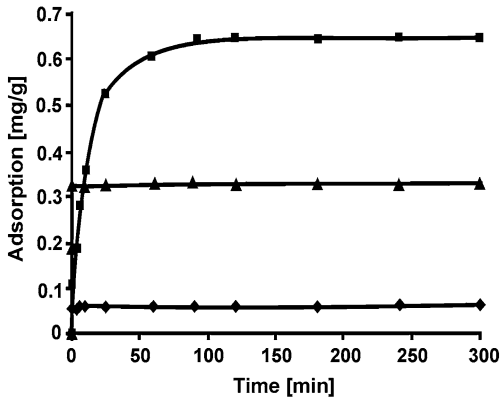

Fig. 2 Adsorption kinetics of Cr(VI) onto C* (◆), OC* (■), OGC* (▲); $m = 0.2$ g, $V = 50$ mL, pH optimal, $C_{Cr(C^*)} = 0.26$ mg/L, $C_{Cr(OC^*)} = 2.60$ mg/L, $C_{Cr(OGC^*)} = 1.20$ mg/L, pH = 5, $T = 25$ °C

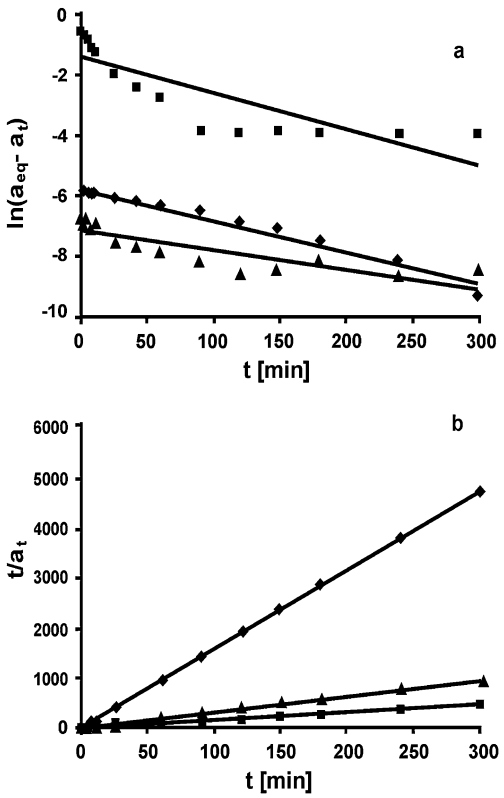

Fig. 3 The kinetic fitting plots (**a**) pseudo-first-order equation; (**b**) pseudo-second-order equation for the carbon C* (◆), OC* (■) and OGC* (▲)

Table 2 Kinetic parameters for the for the studied adsorption systems

Carbon type	Pseudo-first-order equation			Pseudo-second-order equation		
	a_{eq} (mg/g)	k_1 (1/min)	R^2	a_{eq} (mg/g)	k_2 (g/mg·min)	R^2
C*	0.063	0.010	0.976	0.063	26.06	0.999
OC*	0.666	0.011	0.706	0.666	0.23	0.999
OGC*	0.325	0.006	0.720	0.325	163.23	1

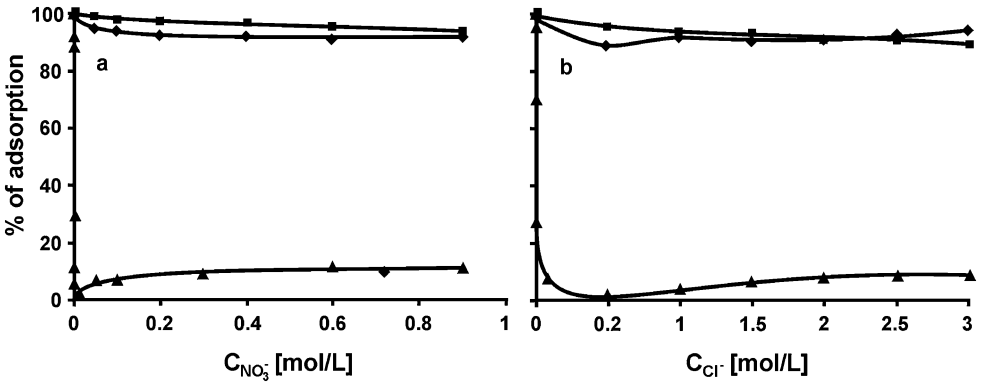

Fig. 4 The influence of (**a**) NO_3^- and (**b**) Cl^- on Cr(VI) adsorption onto C* (◆), OC* (■), OGC* (▲); $m = 0.2$ g, $V = 50$ mL, pH = 5, $C_{Cr(C^*)} = 2.60$ mg/L, $C_{Cr(OC^*)} = 14.50$ mg/L, $C_{Cr(OGC^*)} = 5.20$ mg/L, $t = 3$ h, $T = 25$ °C

first-order equation and pseudo-second-order equation are shown. The kinetic parameters acquired from fitting results are summarized in Table 2. The correlation coefficients for the linear plots of t/a_t against time from the pseudo-second order rate law are greater than 0.999 for all studied activated carbons. Obtained results suggest that this sorption system is not a first order reaction and that the pseudo-second order model provides the best correlation of the data, based on the assumption that the rate-limiting step may be caused by chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate (Ho et al. 2000).

3.3 Effect of NO_3^- and Cl^-

The influence of oxidants and reducing agents on chromium(VI) adsorption ability on the modified activated carbon is very important from the analytical point of view, mentioned earlier. In Fig. 4 the influence of nitrates and chlorides on the Cr(VI) adsorption is shown. In the case of C* and OC* carbons the effect of nitrates and chlorides is non-significant. In turn drastic decrease of adsorption of Cr(VI), even above 90%, is observed in case of OGC* carbon. This may be caused by the competitiveness of chloride, nitrate and Cr(VI) ions towards adsorption centers of activated carbon, because Cr(VI) in the range of 6–8 of pH value (around the maximum adsorption ability of Cr(VI) on OGC*) is in the form of hydrogen chromate ions ($HCrO_4^-$) and dichromate ions ($Cr_2O_7^{2-}$) and the main mechanism of sorption of Cr(VI) in this range is associated with the exchange of these forms of chromium with basic carbon surface groups. From the analytical point of view, it means that in case of

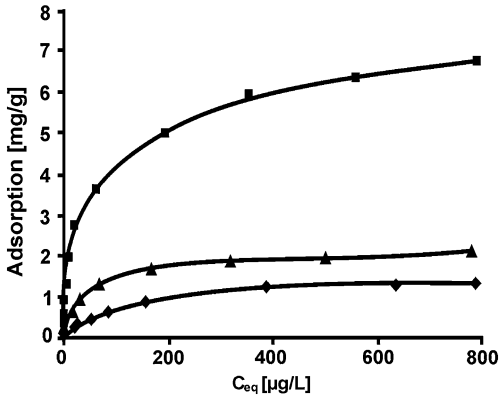

Fig. 5 Initial runs of adsorption isotherms of Cr(VI) onto C* (◆), OC* (■), OGC* (▲); $m = 0.2$ g, $V = 50$ mL, pH = 5, $t = 3$ h, $T = 25$ °C

OGC* carbon the excess of oxidants and reducing agents, used for a solid sample digestion, should be removed from the solution before the chromium sorption step of the analytical procedure. On the other hand, that property takes advantage of the application of this carbon in chromium speciation studies involving the separation of Cr(III) from the sample solution through its adsorption on OGC* and determination of Cr(VI) in solution. This study will be undertaken in near future.

3.4 Equilibrium isotherm study

The adsorption isotherms of Cr(VI) from the aqueous solutions on modified activated carbons are shown in Fig. 5. The equilibrium isotherm studies were carried out at initial pH of 5, temperature of 25 °C and equilibrium time of 3 h. The

adsorption isotherms show the Langmuirian behaviour and may be described by the generalized Langmuir equation:

$$a = a_m \frac{(Kc)^n}{1 + (Kc)^n} \tag{4}$$

where a is the adsorbed amount of Cr(VI) in mg/g at the equilibrium of Cr(VI) concentration c, a_m is the maximum adsorbed amount (sorption capacity), K is the Langmuir constant and n, varying from zero to unity, characterizes the quasi Gaussian energetic heterogeneity of the adsorption system (Jaroniec and Choma 1997). For $n = 1$ (4) becomes the classical Langmuir isotherm, characteristic of homogeneous adsorbents. For very low concentration, the factor $(Kc)^n \ll 1$ and (4) reduces to the Freundlich equation:

$$a = a_m (Kc)^n \tag{5}$$

which can be rewritten in the linear form:

$$\ln a = \ln(a_m K) + n \ln c \tag{6}$$

By including c_o which denotes the Freundlich constant connected with the sorption capacity and substituting K by $(c_o)^{-n}$ (6) can be transformed into:

$$\ln a = \ln[a_m (c_o)^{-n}] + n \ln c \tag{7}$$

The above relation is presented in Fig. 6 and it can be observed that the studied isotherms are in good agreement with the linear form of the Freundlich equation for lower Cr(VI) concentrations. The adsorption heterogeneity increases when the value of n decreases to zero. The maximum sorption capacity evaluated from the adsorption isotherms presented in Fig. 5 equals to 1.28 mg/g for carbon C*, 2.07 mg/g for carbon OGC* and 6.92 mg/g for carbon OC*. The parameters K and n evaluated from (7) are summarized in Table 3. Additionally the maximum sorption capacities for the studied carbons are listed in this table. The smallest value of n is obtained for carbon OGC* however, the greatest value of n is obtained for carbon OC*. It means that energetic heterogeneity of the studied carbons is the greatest for carbon OGC*, smaller for carbon C* and the smallest for carbon OC*.

3.5 Desorption study

The desorption kinetic studies of Cr(VI) by 6 M HCl from modified activated carbons (Fig. 7) and the desorption studies of Cr(VI) in relation to HCl and HNO_3 concentration were carried out. The desorption kinetics studies are helpful for the estimation of desorption equilibrium at studied system. By comparing adsorption and desorption kinetics it is visible that the desorption process is relatively slow. For OGC* carbon nearly half of adsorbed chromium passes into bulk solution after 25 minutes, while for OC* carbon only 8% chromium desorbs from activated carbon to 6 M HCl solution. These data confirm thesis that the main mechanism of Cr(VI) adsorption onto OC* carbon is reduction to Cr(III)

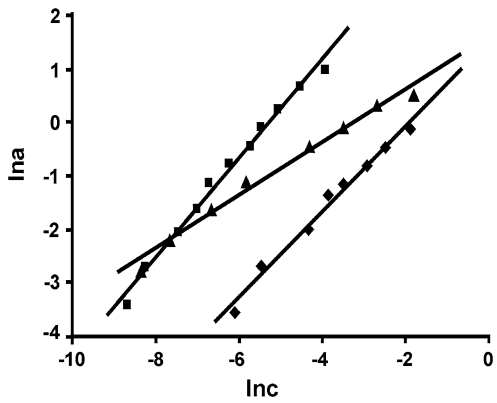

Fig. 6 Linear dependences plotted according to (4) for the carbon C* (◆), OC* (■) and OGC* (▲)

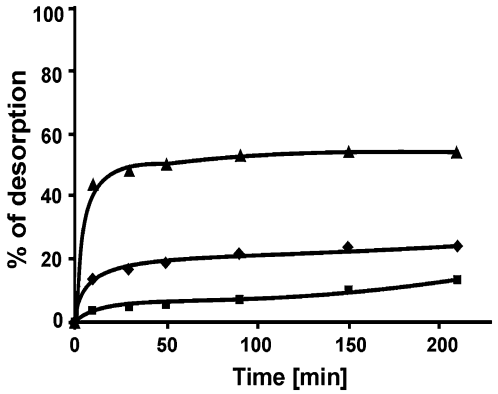

Fig. 7 Desorption kinetics of Cr(VI) from C* (◆), OC* (■), OGC* (▲) by 6 mol/L of HCl; $m = 0.006$ g, $V = 1.5$ mL, $A_{Cr(C^*)} = 66$ μg/g, $A_{Cr(OC^*)} = 325$ μg/g, $A_{Cr(OGC^*)} = 650$ μg/g, $T = 25$ °C

Table 3 Freundlich isotherm parameters for the studied adsorption systems

Carbon type	a_m (mg/g)	K ((L/mg)^n)	n	c_0 (mg/L)	R^2
C*	1.28	3.49	0.80	0.21	0.985
OC*	6.92	19.33	0.93	0.04	0.990
OGC*	2.07	2.30	0.49	0.18	0.987

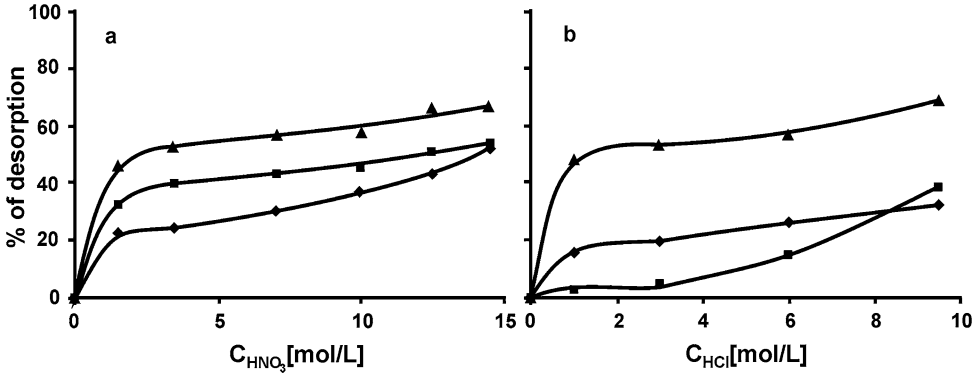

Fig. 8 Desorption of Cr(VI) from C* (◆), OC* (■), OGC* (▲) in respect to (**a**) HNO_3 and (**b**) HCl concentration; $m = 0.006$ g, $V = 1.5$ mL, $A_{Cr(C^*)} = 66$ μg/g, $A_{Cr(OC^*)} = 325$ μg/g, $A_{Cr(OGC^*)} = 650$ μg/g, $t = 2$ h, $T = 25$ °C

species. While, in case of OGC carbon nearly half of adsorbed chromium forms a film of $Cr(OH)_3$ on the external surface of carbon and this film can be easily dissolved in 6 M HCl solution.

Basing on above data the desorption studies of Cr(VI) in respect to concentration of HCl and HNO_3 were undertaken. It was stated that even the application of concentrated nitric or hydrochloric acids did not cause the total desorption of chromium ions from the surface of modified activated carbons. As it is shown in Fig. 8 the greatest desorption of chromium ions, i.e. about 60%, was observed for the OGC*. On this basis, it can be concluded that the process of adsorption of Cr(VI) onto these modified activated carbons is irreversible. The mechanism of adsorption of Cr(VI) in the case of unmodified and oxidized carbons is associated with a surface reduction of chromium(VI) to chromium(III) and further sorption by ion exchange and in the case of outgassing carbon with the surface precipitation of $Cr(OH)_3$. From the analytical point of view, this low desorption of Cr(VI) from activated carbons, despite the concentrated acids (HNO_3 and HCl) application, indicates that the most effective technique for determination of chromium in environmental samples after its enrichment on activated carbon is the slurry sampling atomic absorption spectrometry with electrothermal atomization (SS GF AAS).

4 Conclusions

Chemical modifications in general improve the adsorption capacity of activated carbons probably due to a higher number of active binding sites after modification, better ion-exchange properties, and formation of new functional groups that favor chromium(VI) uptake. It was pointed out, by fitting Freundlich equation to experimental data, that optimal removal of Cr(VI) from solution will also depend on suitable choice of carbon textural properties. The adsorption process was found to have followed the pseudo-second order equation and Freundlich isotherm very well.

The studied activated carbons are characterized by different chromium sorption capacities. Carbon OC* possesses the best properties for analytical applications and the highest maximum sorption capacity. The Cr(VI) adsorption onto C* and OC* carbons was almost independent on nitrates and chlorides, indicating in opposite to OGC* carbon, that Cr(VI) removal from solution was not principally carry out by anionic adsorption mechanism. OGC* carbon seems to be promising adsorbent for study of chromium speciation in aqueous solution because of the much decrease, practically to zero, of the adsorption capacity toward Cr(VI) ions in presence of nitrates and chlorides excess.

Adsorption of Cr(VI) onto modified activated carbons is partially irreversible process even of the application of strong nitric or hydrochloric acids as eluents. It also proves that reduction of Cr(VI) to Cr(III) is the main mechanism of Cr(VI) ions sorption onto C* and OC* carbons.

References

Anthemidis, A.N., Zachariadis, G.A., Kougoulis, J.-S., Stratis, J.A.: Flame atomic absorption spectrometric determination of chromium(VI) by on-line preconcentration system using a PTFE packed column. Talanta **57**, 15–22 (2002)

Chen, J.P., Lin, M.: Surface charge and metal ion adsorption on an H-type activated carbon: experimental observation and modeling simulation by the surface complex formation approach. Carbon **39**, 1491–1504 (2001)

Di Natale, F., Lancia, A., Molino, A., Musmarra, D.: Removal of chromium ions form aqueous solutions by adsorption on activated carbon and char. J. Hazard. Mater. **145**, 381–390 (2007)

Dobrowolski, R.: Application of activated carbons for the enrichment of toxic metals and their determination by atomic spectroscopy. In: Dąbrowski, A. (ed.) Adsorption and its Application in Industry and Environmental Protection, pp. 777–806. Elsevier, Amsterdam (1998)

Dobrowolski, R., Jaroniec, M., Kosmulski, M.: Study of Cd(II) adsorption from aqueous solution on activated carbons. Carbon **24**, 15–20 (1986)

Gil, R.A., Cerutti, S., Gásquez, J.A., Olsina, R.A., Martinez, L.D.: Preconcentration and speciation of chromium in drinking water samples by coupling of on-line sorption on activated carbon to ETAAS determination. Talanta **68**, 1065–1070 (2006)

Ho, Y.S., Ng, J.C.Y., McKay, G.: Kinetics of pollutant sorption by biosorbents: review. Sep. Purif. Methods **29**, 189–232 (2000)

Jaroniec, M., Choma, J.: Characterization of geometrical and energetic heterogeneities of active carbons by using sorption measurements. Stud. Surf. Sci. Catal. B **104**, 715 (1997)

Lagergren, S.: Zur theorie der sogenannten adsorption gelöster stoffe. K. Sven. Vetensk. Handl. **24**, 1–39 (1898)

Latva, S., Jokiniemi, J., Peraniemi, S., Ahlgren, M.: Separation of picogram quantities of Cr(III) and Cr(VI) species in aqueous solutions and determination by graphite furnace atomic absorption spectrometry. J. Anal. At. Spectrom. **18**, 84–86 (2003)

Mohan, D., Pittman, C.U. Jr.: Activated carbons and low-cost adsorbents for remediation of tri- and hexavalent chromium from water: a review. J. Hazard. Mater. B **137**, 762–811 (2006)

Narin, I., Kars, A., Soylak, M.: A novel solid phase extraction procedure on Amberlite XAD-1180 for speciation of Cr(III), Cr(VI) and total chromium in environmental and pharmaceutical samples. J. Hazard. Mater. **150**, 453–458 (2008)

Nriagu, J.O., Nieboer, E.: Chromium. In: Natural and Human Environment. Wiley, New York (1988)

Saracoglu, S., Soylak, M., Elci, L.: On-line solid phase extraction system for chromium determination in water samples by flow injection-flame atomic absorption spectrometry. Anal. Lett. **35**, 1519–1530 (2002)

Séby, F., Charles, S., Gagean, M., Garraud, H., Donard, O.F.X.: Chromium speciation by hyphenation of high-performance liquid chromatography to inductively coupled plasma-mass spectrometry—study of the influence of interfering ions. J. Anal. At. Spectrom. **18**, 1386–1390 (2003)

Siles Cordero, M.T., Vereda Alonso, E.I., de Torres, A.G., Cano Pavon, J.M., Development of a new system for the speciation of chromium in natural waters and human urine samples by combining ion exchange and ETA-AAS. J. Anal. At. Spectrom. **19**, 398–403 (2004)

Stein, K., Schwedt, G.: Speciation of chromium in the waste water from a tannery. Fresenius J. Anal. Chem. **350**, 38–43 (1994)

Valix, M., Cheung, W.H., Zhang, K.: Textural and surface chemistry of activated bagasse and its role in the removal of chromium ions from solution. Adsorption **14**, 711–718 (2008)

Wang, L.-L., Wang, J.-Q., Zheng, Z.-X., Xiao, P.: Cloud point extraction combined with high-performance liquid chromatography for speciation of chromium(III) and chromium(VI) in environmental sediment samples. J. Hazard. Mater. **177**, 114–118 (2010a)

Wang, X.S., Chen, L.F., Li, F.Y., Chen, K.L., Wan, W.Y., Tang, Y.J.: Removal of Cr(VI) with wheat-residue derived black carbon: reaction mechanism and adsorption performance. J. Hazard. Mater. **175**, 816–822 (2010b)