

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Comparison of the Thermodynamic Parameters Estimation for the Adsorption Process of the Metals from Liquid Phase on Activated Carbons

Svetlana Lyubchik, Andrey Lyubchik, Olena Lygina,
Sergiy Lyubchik and Isabel Fonseca

*REQUIMTE, Faculdade Ciência e Tecnologia, Universidade Nova de Lisboa
Quinta de Torre, Campus da Caparica, 2829-516 Caparica
Portugal*

1. Introduction

Over the past decades investigation of the adsorption process on activated carbons has confirmed their great potential for industrial wastewater purification from toxic and heavy metals. This chapter is focused on the adsorption of Cr (III) in high-capacity solid adsorbents such as activated carbons. There are abundant publications on heavy metal adsorption on activated carbons with different oxygen functionalities covering wide-range conditions (solution pH, ionic strength, initial sorbate concentrations, carbon loading and etc. (Brigatti et al., 2000; Carrott et al., 1997; Li et al., 2011; Lyubchik et al., 2008; Tikhonova et al., 2008; Kołodziejka, 2010; Anirudhan & Radhakrishnan, 2011). Although much has been accomplished in this area, less attention has been given to the kinetics, thermodynamics and temperature dependence of the adsorption process, which is still under continuing debates (Ramesh et al., 2007; Myers, 2004). The principal problem in interpretation of solution adsorption studies lies in the relatively low comparability of the data obtained by different research groups. These are due to the differences in the nature of the carbons, conditions of the adsorption processes and the chosen methodology of the metals adsorption analysis. Furthermore, the adsorption from the solution is much more complex than that from the gas phase.

In general, the molecules attachment to the solid surface by adsorption is a broad subject (Myers, 2004). Therefore, only complex investigation of the metal ions/carbon surfaces interaction at the aqueous-solid interface can help to understand the metals adsorption mechanism, which is an important point in optimization of the conditions of their removal by activated carbons (Anirudhan & Radhakrishnan, 2008; Argun et al., 2007; Aydin & Aksoy, 2009; Ramesh et al., 2007; Liu et al., 2004). Particularly, thermodynamics has the remarkable ability to connect seemingly unrelated properties (Myers, 2004). The most important application of thermodynamics is the calculation of equilibrium between phases of the adsorption process profile. The basis for thermodynamic calculations is the adsorption isotherm, which gives the amount of the metals adsorbed in the porous structure as a function of the amount at equilibrium in the solutions. Whether the adsorption isotherm has been experimentally determined, the data points must be fitted with analytical equations for interpolation, extrapolation, and for the calculation of thermodynamic properties by numerical integration or differentiation (Myers, 2004; Ruthven, 1984).

It has to be noted, that the thermodynamics applies only to equilibrium adsorption isotherms. The equilibrium of heavy metals adsorption on activated carbons is still in its infancy due to the complexity of operating mechanisms of metal ions binding to carbon with ion exchange, complexation, and surface adsorption as the prevalent ones (Brown et al., 2000). Furthermore, these processes are strongly affected by the pH of the aqueous solution (Liu et al., 2004; Chen and Lin, 2001; Brigatti et al., 2000). The influence of pH is generally attributed to the variation, with pH, in the relative distribution of the metal and carbon surface species, in their charge and proton balance (Csobán et al., 1998; Kratochvil and Volesky, 1998). Therefore, the equilibrium constants of each type of the species on each type of the activated sites are very important for the controlling of metals ions capture by activated carbons (Carrott et al., 1997; Chen & Lin, 2001).

Another area of the debates is an optimum contact time to reach the adsorption equilibrium and, once again, regardless of the solution pHs, the differences in metal ions speciation, adsorbents charge and potential, complicate the overall process and make a comparison of the results of a metals capture by activated carbons difficult. The majority of studies on the sorption kinetics have revealed a two-step behaviour of the adsorption systems (Brigatti et al., 2000; Csobán et al., 1998; Raji et al., 1998) with fast initial uptake and much slower gradual uptake afterwards, which might take days even months (et al., 2000; Csobán et al., 1998; Raji et al., 1998; Kumar et al., 2000; Ajmal et al., 2001; Lakatos et al., 2002; Chakir et al., 2002; Leist et al., 2000; Csobán & Joó, 1999). Some of the authors reported the optimum contact time of minutes (Kumar et al., 2000; Ajmal et al., 2001), whereas, at the other extreme, that of hundred hours (Brigatti et al., 2000; Lakatos et al., 2002) for equilibrium to be attained; and the average values reported for the heavy metal binding were of 1–5 hours (Csobán et al., 1998; Raji et al., 1998; Chakir et al., 2002; Leist et al., 2000; Csobán and Joó, 1999). It has been also stressed that adsorption thermodynamics is drastically affected by the equilibrium pH of the solutions. Regardless of the equilibrium pH, adsorption of the heavy metals by a single adsorbent could be completed in a quite different contact time (Carrott et al., 1997; Lalvani et al., 1998; Farias et al., 2002; Perez-Candela et al., 1995). Taking into account that equilibration of metal ions uptake by activated carbons depends on the equilibrium pH, authors agreed (Lyubchik et al., 2003) with the statement (Carrott et al., 1997) that it would be appropriate to express adsorption results in terms of the final solution pH. However, this practice is not widely used by the investigators.

Due to the prolonged time is needed to accomplish thermodynamic equilibrium conditions, the adsorption experiments are often carried out under pseudo-equilibrium condition, when the actual time is chosen either to accomplish the rapid adsorption step or, rather arbitrary, to ensure that the saturation level of the carbon is reached (Kumar et al., 2000). However, once again, the adsorption models are all valid only and, therefore, applicable only to complete equilibration.

The study presented herein is part of the work aimed the exploration of the mechanism of Cr (III) adsorption on activated carbons associated with varying of surface oxygen functionality and porous texture. The mechanism of chromium adsorption was investigated through a series of equilibrium and kinetic experiments under varying pH, temperature, initial chromium concentration, carbon loading for wide-ranging carbons of different surface properties (i.e. texture and surface groups) (Lyubchik et al., 2004; Lyubchik et al., 2005; Lyubchik et al., 2008); and particular objective of the current study is evaluation of the thermodynamics (entropy, enthalpy, free energy) parameters of the adsorption process in the system “Cr (III) – activated carbon”.

Thermodynamics were evaluated through a series of the equilibrium experiments under varying temperature, initial chromium concentration, carbon loading for two sets of the commercial activated carbons and their oxidised by post-chemical treatment forms with different texture and surface functionality. This approach served the dual purpose: i) gained deep insight into various carbon's structural characteristics and their effect on thermodynamics of the Cr (III) adsorption; and ii) gained insight, which often very difficult or impossible to obtain by other mean, into equilibrium of the Cr (III) adsorption on activated carbon. The thermodynamics parameters were evaluated using both the thermodynamic equilibrium constants and the Langmuir, Freundlich and BET constants. The obtained data on thermodynamic parameters were compared, when it was possible.

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 their oxidative post treatments. Chemical treatment aimed at introduction of the surface oxygen functional groups on the carbon surface. In some conditions, the chemical treatments also changed the carbons porous texture.

2.1.1 Surface modification

Commercial activated charcoals GR MERCK 2518 and GAC Norit 1240 Plus (A- 10128) have been subjected to the post-chemical treatment with 1 M nitric acid at boiling temperature during 6 h. The oxidized materials, were subsequently washed with distilled water until neutral media, and dried in an oven at 110 °C for 24 h.

2.1.2 Surface characterization

The textural characterization of the carbon samples was based on nitrogen adsorption isotherms at 77K. These experiments were carried out with Surface Area & Porosimetry Analyzer, Micromeritics ASAP 2010 apparatus. Prior to the adsorption testing, 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-Raduskhevich and B.J.H. methods were applied respectively to determine the micro- and mesopores volume. The oxidation treatment resulted in reduction of the apparent surface area with mesopores formation (Table 1).

The carbon's point zero charge (pH_{PZC} values) were obtained by acid-base titration (Sontheimer, 1988). pH_{PZC} decreases when the carbon surface is treated with nitric acid (Table 1). 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 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 CO₂ 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, 1999). Thus, a CO₂ 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 CO₂ at the same temperature (around 650 °C). Ether (700 °C), phenol (600-700 °C) and carbonyls/quinones (700-980 °C) decompose as CO. The treatment by nitric acid resulted in an increase in carboxylic acids and anhydrous carboxylic, lactones and phenol groups.

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}
Merck_initial	755	0.33	0.31	41	714	7.02
Merck_1 M HNO ₃	1017	0.59	0.55	40	977	3.41
Norit_initial	770	0.40	0.32	41	729	6.92
Norit_1 M HNO ₃	945	0.43	0.41	72	873	4.41

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

Carbons	Proximate analysis (wt %)			Elemental analysis (wt %)			
	Moisture	Volatile	Ash	C	H	N	O
Norit_initial	3.9	6.7	2.8	95.2	0.40	0.48	3.90
Norit_1M HNO ₃	1.8	7.9	2.0	87.9	0.60	2.60	8.90
Merck_initial	2.0	9.1	3.2	92.8	0.25	0.40	6.50
Merck_1M HNO ₃	1.7	12.8	2.0	86.3	0.30	0.54	12.80

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

Carbons	Oxygen evolved, (g/100g)		
	CO ₂	CO	CO/CO ₂
Norit_initial	0.49	1.18	2.41
Norit_1M HNO ₃	3.18	5.94	1.86
Merck_initial	0.44	1.15	2.61
Merck_1M HNO ₃	3.05	18.7	6.22

Table 3. Surface oxygen functionality of the studied activated carbons

All chemicals used were of an analytical grade. Salt Cr₂(SO₄)₂OH₂, which is used in the tanning industry, was used as a sources of trivalent chromium. Metal standard was prepared by dissolution of Cr (III) salt in pure water, which was first deionized and then doubly distilled. The initial pH of the resulting Cr (III) solution was 3.2. The chromium solution was always freshly prepared and used within a day in order to avoid its aging.

2.2 Adsorption process analysis

2.2.1 Batch experiments

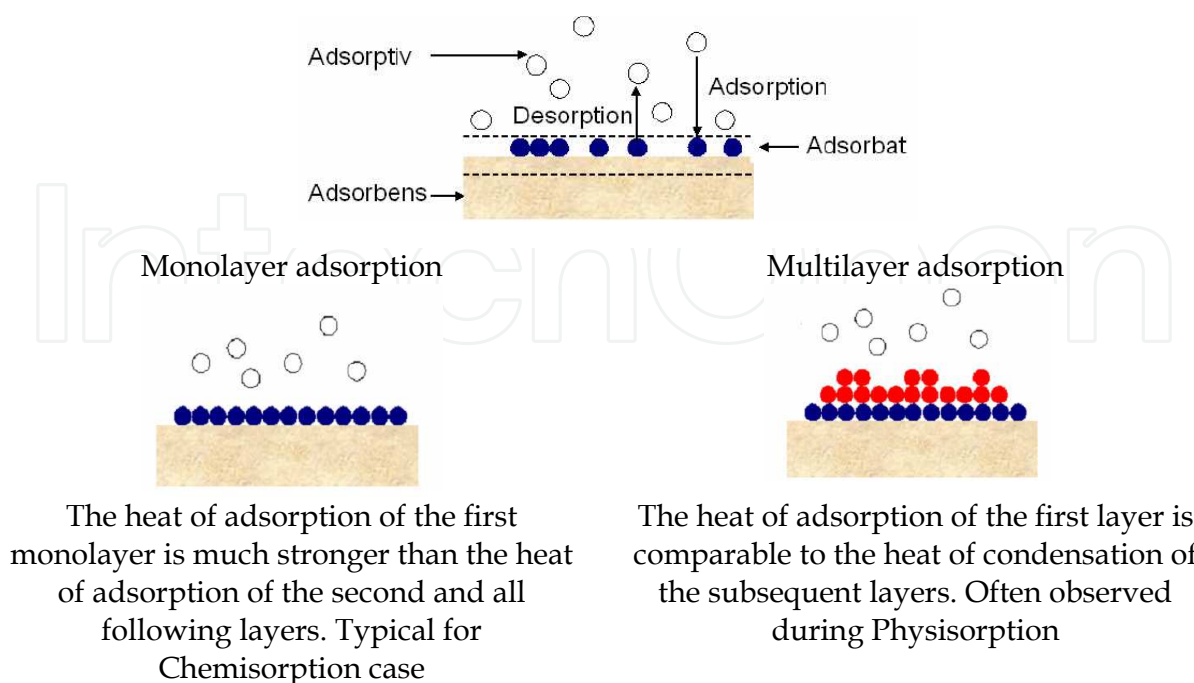
Batch laboratory techniques were utilized to study the equilibrium of Cr (III) adsorption on Norit and Merck activated carbons. The adsorption isotherms were obtained at four different temperatures: 22, 30, 40 and 50 °C. All adsorption isotherms were determined at initial pH of the resulting Cr (III) solution i.e. 3.2, without adding any buffer to control the pH to prevent introduction of any new electrolyte into the systems.

The batch tests were conducted by loading a desirable amount of sorbent to the 250 ml Erlenmeyer flasks containing the Cr(III) solution of fixed (at 200 ppm, which is 10 times lower than the initial concentration present in the tannery wastewater) concentration. Each of the 10 samples used for one experiment consisted of a known carbon dosage from a range 1.2 – 20 g/l in 25 ml of Cr(III) 200 ppm solution, which were shaking on a gyratory shaker at 180 rev/min for 1-7 days (depending on the temperature of the experiment). Each experiment was performed for both initial and post-treated with peroxide, 1 M and acid forms of Norit and Merck carbons, thus generated a total of $10 \times 2 \times 2 = 40$ samples for each experimental temperature. Furthermore, in some cases, for the batch tests the conditions were changed for fixed carbon loading at 4.8 g/l, whereas Cr(III) concentration were varied from 50 to 2000 ppm. Experiments were duplicated for quality control. The standard deviation of the adsorption parameters was under 1.5 %.

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.

2.3 Supporting theory

In a typical adsorption process, species/materials in gaseous or liquid form (the adsorptive) become attached to a solid or liquid surface (the adsorbent) and form the adsorbate [Scheme 1], (Christmann, 2010).



Scheme 1. Presentation of the typical adsorption process (after Christmann, 2010)

Since the adsorptive and the adsorbent often undergo a chemical reactions, the chemical and physical properties of the adsorbate is not always just the sum of the individual properties of the adsorptive and the adsorbent, and often represents a phase with new properties (Christmann, 2010).

When the adsorbent and adsorptive are contacted long enough, the equilibrium is established between the amount of adsorptive adsorbed on the carbon surface (the adsorbate) and the amount of adsorptive in the solution. The equilibrium relationship is described by isotherms. Therefore, the adsorption isotherm for the metal adsorption is the relation between the specific amount adsorbed (q_{eq} , expressed in (mmol) of the adsorbate per (g) of the solid adsorbent) and the equilibrium concentrations of the adsorptive in liquid phase (C_{eq} , in expressed in (mmol) of the adsorptive per (l) of the solution), when amount adsorbed is equals q_{eq} .

Chemical equilibrium between adsorbate and adsorptive leads to a constant surface concentration (Γ) in [mmol/m²]. Constant (Γ) is maintained when the fluxes of adsorbing and desorbing particles are equal, thus the initial adsorptive concentration and temperature dependence of the liquid-solid phase equilibrium are considered (Christmann, 2010).

A common procedure is to equate the chemical potentials and their derivatives of the phases involved. Note: the chemical potential (μ) is the derivative of the Gibbs energy (dG) with respect to the mole number (n_i) in question (Christmann, 2010), which is for the adsorption process from the liquid phase is the equilibrium concentrations of the adsorptive in liquid phase (C_{eq}), when amount adsorbed on the carbon surface is equals (q_{eq}) [1]:

$$\mu_i = \left[\frac{dG}{dn_i} \right]_{P,T}, \text{ other mole numbers } (C_{eq}) \quad (1)$$

The decisive quantities when studying the adsorption process are the heat of adsorption and its coverage dependence to lateral particle-particle interactions, as well as the kind and number of binding states (Christmann, 2010). The most relevant thermodynamic variable to describe the heat effects during the adsorption process is the differential isosteric heat of adsorption (ΔH_x), kJ mol⁻¹, that represents the energy difference between the state of the system before and after the adsorption of a differential amount of adsorbate on the adsorbent surface (Christmann, 2010). The physical basis is the Clausius-Clapeyron equation [2]:

$$\frac{1}{(C_{eq})} \left[\frac{d(C_{eq})}{dT} \right]_{\Gamma} = \left[\frac{d \ln(C_{eq})}{d(\frac{1}{T})} \right]_{\Gamma} = - \frac{\Delta H_x}{R} \quad (2)$$

Knowledge of the heats of sorption is very important for the characterization and optimization of an adsorption process. The magnitude of (ΔH_x) value gives information about the adsorption mechanism as chemical ion-exchange or physical sorption: for physical adsorption, (ΔH_x) should be below 80 kJmol⁻¹ and for chemical adsorption it ranges between 80 and 400 kJmol⁻¹ (Saha & Chowdhury, 2011). It also gives some indication about the adsorbent surface heterogeneity.

Langmuir Isotherm: A model assumes monolayer coverage and constant binding energy between surface and adsorbate [3]:

$$q_{eq} = \frac{K_L \times q_{max} C_{eq}}{1 + K_L C_{eq}} \quad (3)$$

where q_{max} is the maximum adsorption capacity (monolayer coverage), i.e. mmol of the adsorbate per (g) of adsorbent;

K_L is the constant of Langmuir isotherm if the enthalpy of adsorption is independent of coverage.

The constant K_L depends on (i) the relative stabilities of the adsorbate and adsorptive species involved, (ii) on the temperature of the system, and (iii) on the initial concentration of the metal ions in the solution. Factors (ii) and (iii) exert opposite effects on the concentration of adsorbed species: the surface coverage may be increased by raising the initial metal concentration in the solution but will be reduced if the surface temperature is raised (Christmann, 2010).

If the desorption energy is equal to the energy of adsorption, then the first-order processes has been assumed both for the adsorption and the desorption reaction. Whether the deviation exists, the second-order processes should be considered, when adsorption/desorption reactions involving rate-limiting dissociation. From the initial slope of a log - log plot of a Langmuir adsorption isotherm the order of adsorption can be easily determined: if a slope is of 1, that is 1st order adsorption; if a slope is of 0.5, that is 2nd order adsorption process (Christmann, 2010).

BET (Brunauer, Emmett and Teller) Isotherm: This is a more general, multi-layer model.

It assumes that a Langmuir isotherm applies to each layer and that no transmigration occurs between layers. It also assumes that there is equal energy of adsorption for each layer except for the first layer [4]:

$$q_{eq} = \frac{K_{BET} \times q_{max} C_{eq}}{(C_{init} - C_{eq}) \times [1 + (K_{BET} - 1) \times (C_{eq} / C_{init})]} \quad (4)$$

where C_{init} is saturation (solubility limit) concentration of the metal ions (in mmol/l) and K_{BET} is a parameter related to the binding intensity for all layers;

Two limiting cases can be distinguished: (i) when $C_{eq} \ll C_{init}$ and $K_{BET} \gg 1$ BET isotherm approaches Langmuir isotherm ($K_L = K_{BET} / C_{init}$); (ii) when the constant $K_{BET} \gg 1$, the heat of adsorption of the very first monolayer is large compared to the condensation enthalpy; and adsorption into the second layer only occurs once the first layer is completely filled. Conversely, if K_{BET} is small, then a multilayer adsorption already occurs while the first layer is still incomplete (Christmann, 2010). In general, as solubility of solute increases the extent of adsorption decreases.

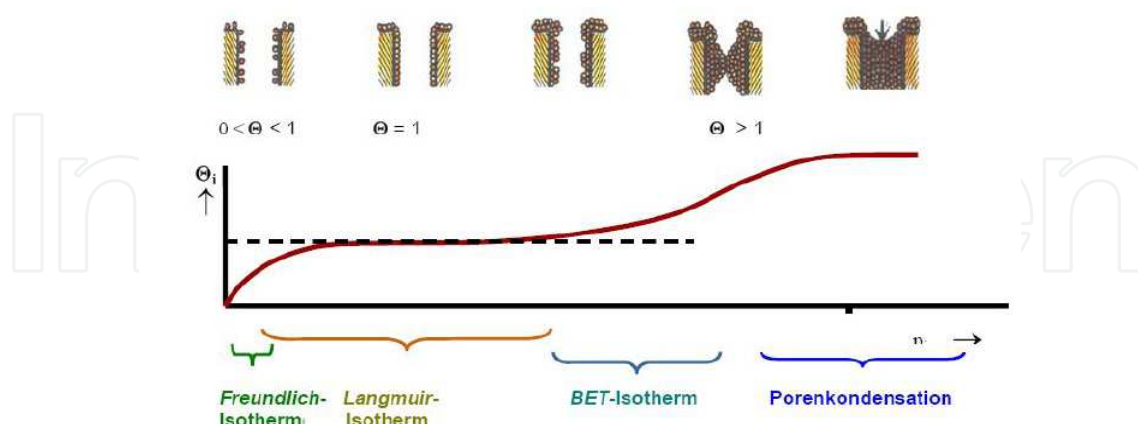
This is known as the "Lundelius' Rule". Solute-solid surface binding competes with solute-solvent attraction. Factors which affect solubility include molecular size (high MW- low solubility), ionization (solubility is minimum when compounds are uncharged), polarity (as polarity increases get higher solubility because water is a polar solvent).

Freundlich Isotherm: For the special case of heterogeneous surface energies in which the energy term (K_F) varies as a function of surface coverage the Freundlich model are used [5]:

$$q_{eq} = K_F \times C_{eq}^{1/n} \quad (5)$$

where K_F and $1/n$ are Freundlich constants related to adsorption capacity and adsorption efficiency, respectively.

To determine which model (Scheme 2) to use to describe the adsorption isotherms for particular adsorbate/adsorbent systems, the experimental data were analyzed using model's linearization.



Scheme 2. Models presentation of the adsorption process (after Christmann 2010), where symbol (θ) is the fraction of the surface sites occupied.

2.4 Theoretical calculations

2.4.1 Isotherms analysis

The results of Cr (III) adsorbed on activated carbons were quantified by mass balance. To test the system at equilibrium, the following parameters were used: adsorption capacity of the carbon (q_{eq}) expressed in terms of metal amount adsorbed on the unitary sorbent mass (mmol/g), i.e. $[Cr\ III]_{uptake}$; and sorption efficiency of the system ($R\%$) indicated from the percentage of removed metal ions relative to the initial amount, i.e. $[Cr_{Rem}]$, %. These parameters have been calculated as indicated below [6, 7]:

$$q_{eq} = \frac{(C_{init} - C_{eq})}{m} \quad (6)$$

$$R\% = \frac{(C_{init} - C_{eq})}{C_{eq}} 100 \quad (7)$$

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

The data for the uptake of Cr (III) at different temperatures has been processed in accordance with the linearised form of the Freundlich [8], Langmuir [9] and BET [10] isotherm equations.

For the Freundlich isotherm the log-log version was used [8]:

$$\log q_{eq} = \log K_F + 1/n \log C_{eq} \quad (8)$$

The Langmuir model linearization (a plot of $1/q_{eq}$ vs $1/C_{eq}$) was expected to give a straight line with intercept of $1/q_{max}$ [9]:

$$\frac{1}{q_{eq}} = \frac{1}{K_L q_{max}} \frac{1}{C_{eq}} + \frac{1}{q_{max}} \quad (9)$$

The BET model linearization equation [10] was used:

$$\frac{C_{eq}}{(C_{init} - C_{eq})q_{eq}} = \frac{K_{BET} - 1}{K_{BET}q_{max}} \frac{C_{eq}}{C_{init}} + \frac{1}{K_{BET}q_{max}} \quad (10)$$

For a successful determination of a BET model the limiting case of $K_{BET} \gg 1$ is required. In this case, a plot of $\left[\frac{C_{eq}}{(C_{init} - C_{eq})q_{eq}} \right]$ vs $\frac{C_{eq}}{C_{init}}$ yields a straight line with positive slope and intercept from which the constant (K_{BET}) and the monolayer sorption capacity (q_{max}) can be obtain.

2.4.2 Thermodynamic parameters

Thermodynamic parameters such as change in Gibb's free energy ΔG^0 , enthalpy ΔH^0 and entropy ΔS^0 were determined using the following equation [11]:

$$K_d = \frac{q_{eq}}{C_{eq}} \quad (11)$$

where K_d is the apparent equilibrium constant, q_{eq} (or $[Cr\ III]_{uptake}$); is the amount of metal adsorbed on the unitary sorbent mass (mmol/g) at equilibrium and C_{eq} (or $[Cr\ III]_{eq}$) equilibrium concentrations of metal ions in solution (mmol/l), when amount adsorbed is equals q_{eq} ;

$\frac{q_{eq}}{C_{eq}}$ - relationship depends on the type of the adsorption that occurs, i.e. multi-layer, chemical, physical adsorption, etc.

The thermodynamic equilibrium constants (K_d) of the Cr III adsorption on studied activated carbons were calculated by the method suggested by (Khan and Singh, 1987) from the intercept of the plots of $\ln(q_{eq}/C_{eq})$ vs. q_{eq}

Then, the standard free energy change ΔG^0 , enthalpy change ΔH^0 and entropy change ΔS^0 were calculated from the Van't-Hoff equation [12].

$$\Delta G^0 = -RT \ln K_d, \quad (12)$$

where K_d is the apparent equilibrium constant; T is the temperature in Kelvin and R is the gas constant ($8.314\text{ Jmol}^{-1}\text{K}^{-1}$):

The slope and intercept of the Van't-Hoff plot [13] of $\ln K_d$ vs. $1/T$ were used to determine the values of ΔH^0 and ΔS^0 ,

$$\ln K_d = \left(\frac{-\Delta H^0}{R} \right) \frac{1}{T} + \frac{\Delta S^0}{R} \quad (13)$$

Then, the influence of the temperature on the system entropy was evaluated using the equations [14]

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (14)$$

The thermodynamic parameters of the adsorption were also calculated by using the Langmuir constant (K_L), Freundlich constants (K_F) and the BET constant (K_{BET}) for the

equations [12–14] instead of (K_d) . The obtained data on thermodynamic parameters were compared, when it was possible.

The differential isosteric heat of adsorption (ΔH_x) at constant surface coverage was calculated using the Clausius-Clapeyron equation [15]:

$$\frac{d \ln(C_{eq})}{dT} = - \frac{\Delta H_x}{RT^2} \quad (15)$$

Integration gives the following equation [16]:

$$\ln(C_{eq}) = - \left[\frac{\Delta H_x}{R} \right] \frac{1}{T} + K \quad (16)$$

where K is a constant.

The differential isosteric heat of adsorption was calculated from the slope of the plot of $\ln(C_{eq})$ vs $1/T$ and was used for an indication of the adsorbent surface heterogeneity. For this purpose, the equilibrium concentration (C_{eq}) at constant amount of adsorbate adsorbed was obtained from the adsorption isotherm data at different temperatures according to (Saha & Chowdhury, 2011).

3. Results and discussion

3.1 Adsorption isotherms

The equilibrium measurements focused on the determination of the adsorption isotherms. Figures 1–4 show the relationship between the amounts of chromium adsorbed per unit mass of carbon, i.e. $[\text{Cr(III)}]_{\text{uptake}}$ in mmol/g, and its equilibrium concentration in the solution, i.e. $[\text{Cr(III)}]_{\text{eq}}$ in mmol/l, at the temperatures of 22, 30, 40 and 50 °C. The carbon adsorption capacity improved with temperature and gets the maximum at 40 °C in the case of the oxidized Norit and Merck carbons and slightly improved with temperature in the case of the parent Norit and Merck activated carbons. The isotherms showed two different shapes. There are isotherms of type III (Fig. 1, 2) for the oxidized samples and of type IV (Fig. 3, 4) for the parent Norit and Merck carbons. Therefore in all cases, the adsorption of the polar molecules (like Cr III solution) on unpolar surface (like the studied activated carbons) is characterized by initially rather repulsive interactions leading to a reduced uptake (Fig. 1, 2), while the increasing presence of adsorbate molecules facilitate the ongoing adsorption leading to isotherms of type III. Furthermore, the porous adsorbents are used and additional capillary condensation effects appeared leading to isotherms of type IV (Fig. 3, 4).

Batch adsorption thermodynamics was described by the three classic empirical models of Freundlich (Eq. 8), Langmuir (Eq. 9) and BET (Eq.10). Regression analysis of the linearised isotherms of Freundlich ($\log q_{eq}$ vs $\log C_{eq}$) and Langmuir ($1/q_{eq}$ vs $1/C_{eq}$) and

$\left(\left[\frac{C_{eq}}{(C_{init} - C_{eq})q_{eq}} \right] \text{ vs } \frac{C_{eq}}{C_{init}} \right)$ using the slope and the intercept of the obtained straight line

gave the sorption constants (K_F , $1/n$ and K_L , K_{BET} , q_{max}). The related parameters for the fitting of Freundlich, Langmuir and BET equations and correlation coefficients (R^2) at different temperatures are summarized in Tables 4.

Based on the results, we can concluded that the Freundlich model appeared to be the most “universal” to describe the equilibrium conditions for all studied activated carbons over the

entire range of temperatures, when the Langmuir and BET models were appropriate for one or another of the adsorption systems only.

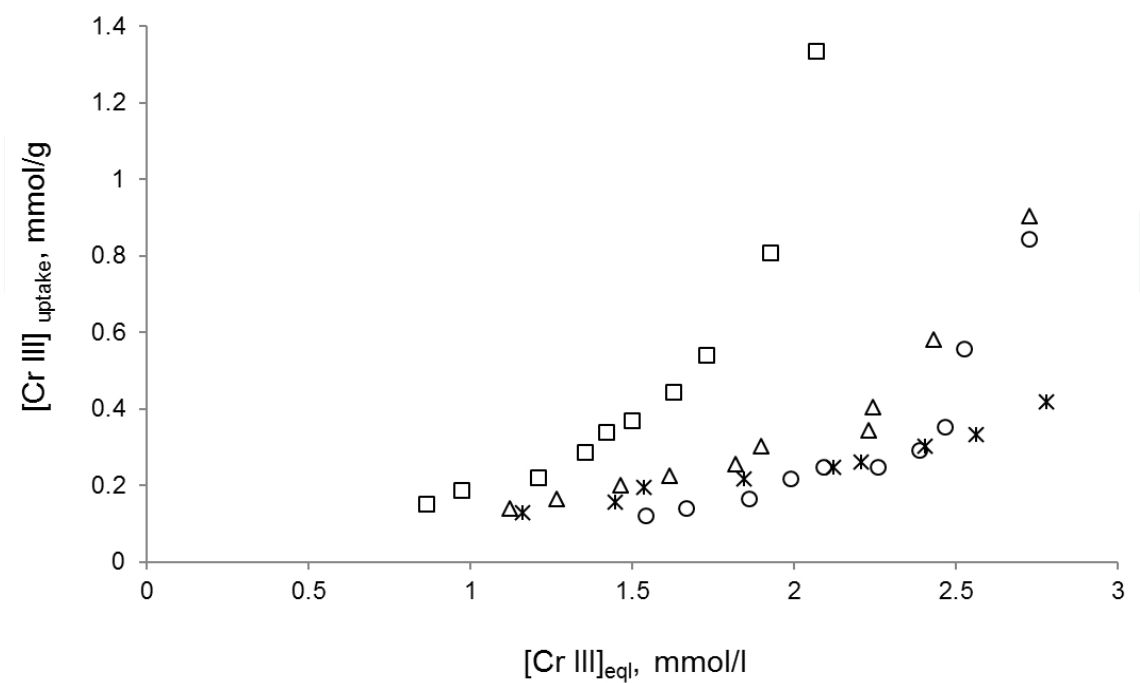


Fig. 1. Isotherms of the Cr (III) adsorption on modified by 1M HNO₃ Norit activated carbon at different temperatures: (*) – 22; (○) – 30; (□) – 40 and (△) – 50 °C.

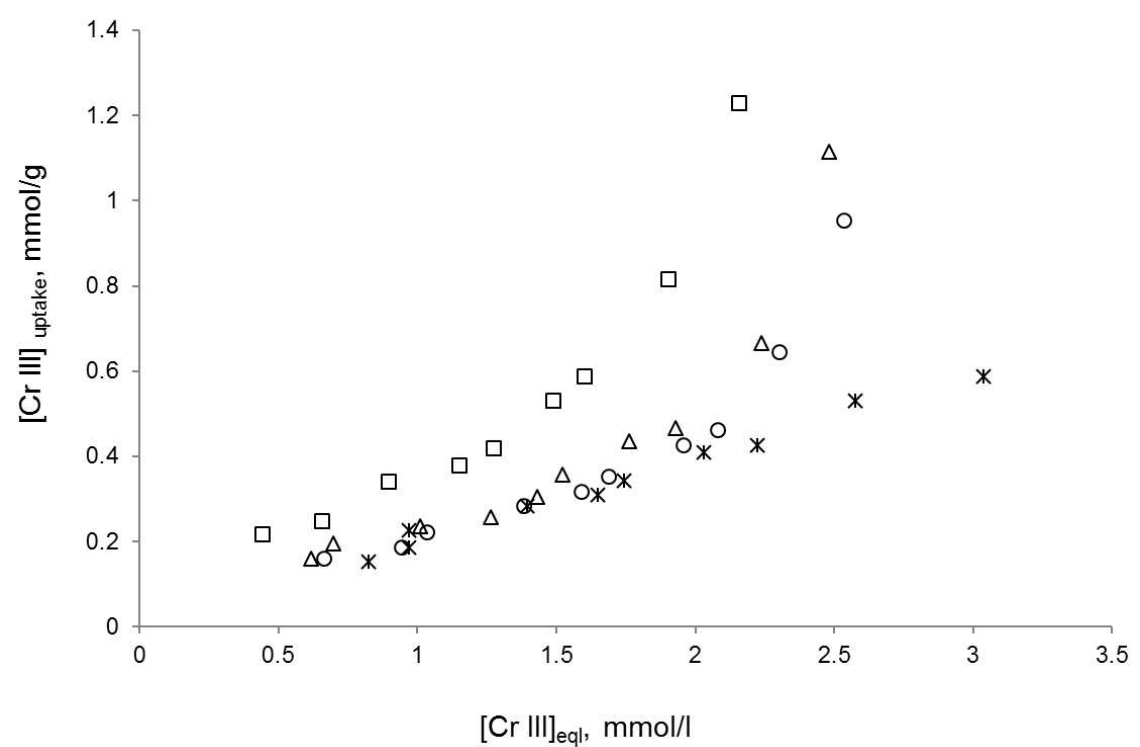


Fig. 2. Isotherms of the Cr (III) adsorption on modified by 1M HNO₃ Merck activated carbon at different temperatures: (*) – 22; (○) – 30; (□) – 40 and (△) – 50 °C.

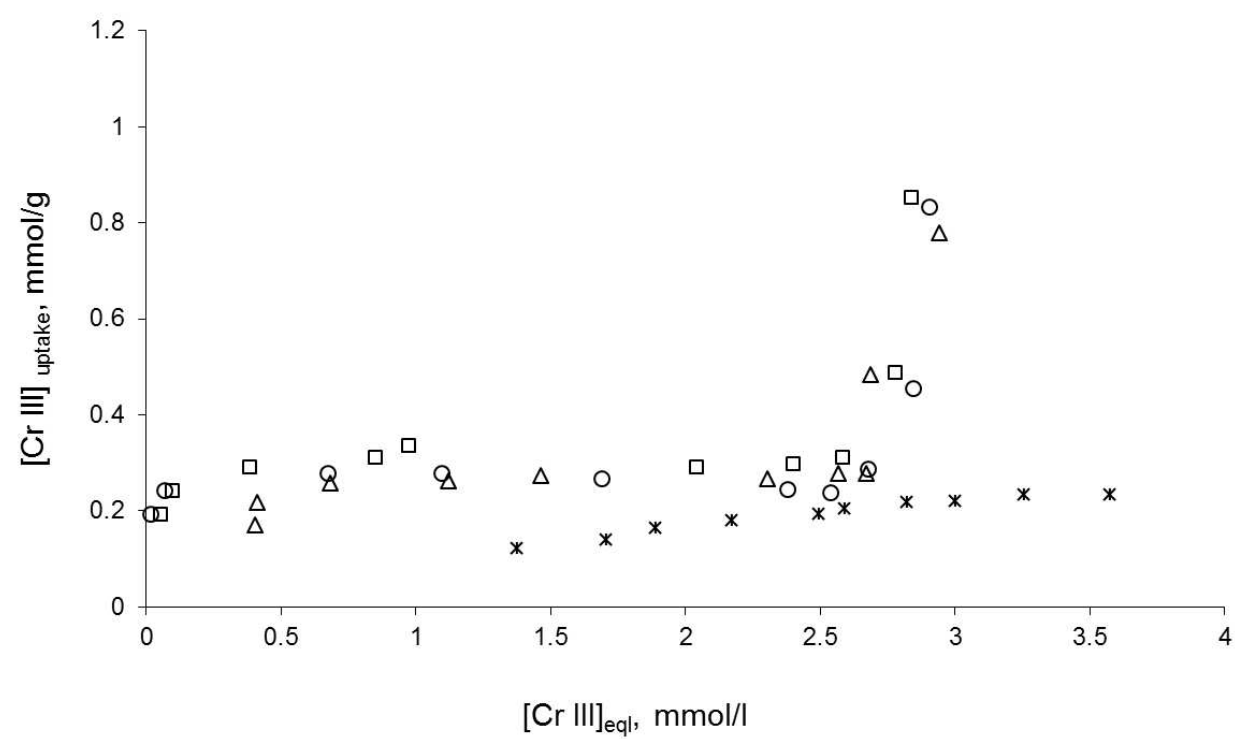


Fig. 3. Isotherms of the Cr (III) adsorption on initial Merck activated carbon at different temperatures: (*) – 22; (○) – 30; (□) – 40 and (△) – 50 °C.

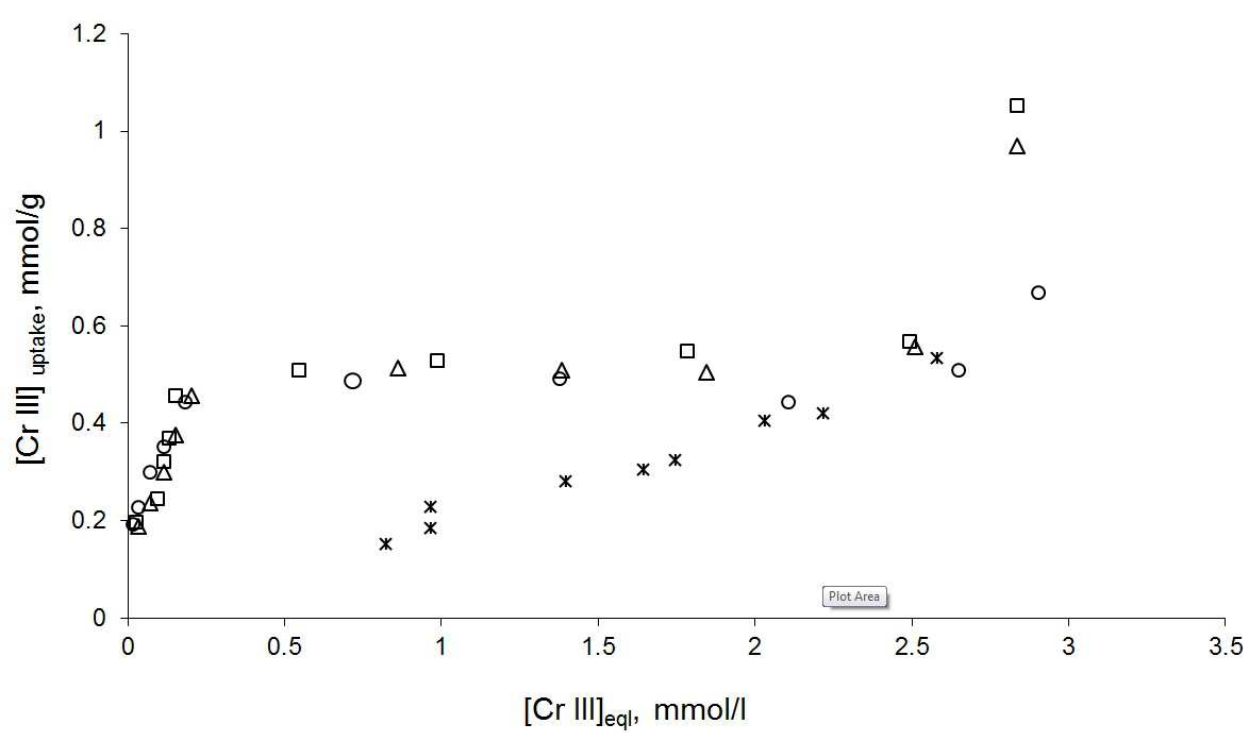


Fig. 4. Isotherms of the Cr(III) adsorption on initial Norit activated carbon at different temperatures: (*) – 22; (○) – 30; (□) – 40 and (△) – 50 °C.

		Langmuir constants			Freundlich constants			BET constants			Equilibrium constants	
T, °C		R ²	q _{max} , mmol/g	K _L l/mmol	R ²	K _F , mol/g	1/n	R ²	q _{max} , mmol/g	K _{BET}	R ²	K _d
Fixed [Cr III] = 200 ppm, pH3.2												
Merck												
22	Initial	0.7671	0.1290	75.9837	0.9795	10.6608	0.7836	0.9641	0.1197	9.1498	0.0945	4.701
30	Initial	0.7921	0.2617	138.7455	0.5253	3.9487	0.0508	0.9608	0.1092	3.4681	0.1976	6.688
40	Initial	0.7711	0.3332	23.7812	0.6158	3.2485	0.1351	0.9443	0.1164	-16.8765	0.2040	5.445
50	Initial	0.7730	0.3027	4.2890	0.6773	4.2274	0.1748	0.8825	0.0997	-9.3369	0.1677	4.754
22	1M HNO ₃	0.9877	-3.7564	-0.0466	0.9898	5.4386	1.0756	0.9214	0.3525	3.1462	0.9630	3.9361
30	1M HNO ₃	0.9606	2.3453	0.1021	0.9595	4.7632	1.2235	0.6241	0.3164	2.5019	0.9717	4.7063
40	1M HNO ₃	0.9042	2.1961	0.2201	0.9671	2.5448	1.0175	0.5632	0.5651	2.6392	0.9636	5.6350
50	1M HNO ₃	0.9403	2.2412	0.1245	0.9680	4.1034	0.9795	0.8566	0.2990	3.8750	0.9745	5.2799
Norit												
22	Initial	0.9728	0.3509	22.0336	0.6793	3.7895	0.1017	0.9436	0.1931	9.7116	0.1412	3.5450
30	Initial	0.9411	0.4684	31.7875	0.8272	3.7895	0.1820	0.9973	0.4087	176.2481	0.2345	5.0420
40	Initial	0.8679	0.5344	15.4698	0.8058	2.1710	0.2360	0.9899	0.4127	130.3293	0.1845	3.9250
50	Initial	0.9576	0.5419	12.7623	0.8327	1.9333	0.2320	0.9854	0.4020	148.4132	0.0945	4.6290
22	1M HNO ₃	0.9728	-1.0185	-0.0954	0.9644	0.1022	1.2550	0.9641	0.3525	9.5353	0.7945	3.1000
30	1M HNO ₃	0.9688	-0.1399	-0.2946	0.9701	28.9194	2.6228	0.3015	0.2937	3.2066	0.9727	4.3925
40	1M HNO ₃	0.9810	-0.3438	-0.3443	0.9677	9.7227	1.6942	0.7065	0.2134	2.7445	0.9672	5.0415
50	1M HNO ₃	0.9827	-0.4389	-0.2106	0.9588	9.4387	1.6454	0.7735	0.1910	2.7281	0.9860	4.6223
Fixed [Carbon] = 4 g/l, pH3.2												
Merck												
22	Initial	0.9915	0.1159	84.5720	0.9752	1.1620	0.0615	0.9670	0.0689	10.4093	0.0667	3.1676
22	1M HNO ₃	0.9661	1.0690	0.3985	0.9868	3.1705	0.8362	0.9746	0.4179	2.3340	0.9701	5.2972
Norit												
22	Initial	0.9716	0.2756	28.0537	0.9792	3.2751	0.3748	0.9786	0.1157	9.5029	0.1740	3.2031
22	1M HNO ₃	0.9851	0.5617	0.8277	0.9891	0.2496	1.5384	0.9817	0.1720	8.0431	0.9758	4.7848

Table 4. Parameters of the Cr(III) adsorption on studied activated carbons at different temperatures

The Langmuir model was applicable (R^2 ca. 0.96) for the parent Norit carbon, which has low apparent surface area and poor surface oxygen functionality (Tabl. 1, 3), thus indicating strong specific interaction between the surface and the adsorbate and confirmed the monolayer formation on the carbon surface. The lower values of the correlation coefficients (R^2 ca. 0.76) for the parent Merck carbon indicated less strong fitting of the experimental data, most

probably due to less developed porous structure of this carbon. Large values of the Langmuir constant (K_L) of ca. 75-140 (which are relative to the adsorption energy) implied a strong bonding on a finite number of binding sites. Langmuir constants (Table 4) slightly increased with temperature increase indicating an endothermic process of the Cr (III) adsorption on studied activated carbons. This observation could be attributed to the increasing an interaction between adsorbent and adsorbate at higher temperatures for the endothermic reactions (Kapoor & Viraraghavan, 1997). There were unfavourable data correlations (the negative values of q_{max} and K_L) for the Langmuire model application (Tabl. 4). It can be seen that the Langmuir model did not fit the adsorption run for the Norit oxidized sample, while it fitted it for the Merck oxidized carbon. Although the Langmuir isotherm model does not correspond to the ion-exchange phenomena, in the present study it was used for oxidized forms of carbon to evaluate their sorption capacity (q_{max}). According to the obtained results the oxidized Merck carbon possessed the highest adsorbate uptake (c.f. q_{max} data, Tabl. 4).

A more general BET (Brunauer, Emmett and Teller) multi-layer model was also used to establish an appropriate correlation of the equilibrium data for the studied carbons. The model assumes the application of the Langmuir isotherm to each layer and no transmigration between layers. It also assumes equal adsorption energy for each layer except the first. It was shown, that in all cases, when Langmuir model failed, the BET model fitted the adsorption runs with better correlations, and an opposite, when Langmuire model better correlated the equilibrium data, BET model was less applicable (c.f. the related parameters for the fitting of Langmuir and BET equations for parent Merck and oxidized Norit, Tabl. 4). Still, in some cases, BET isotherm could not fit the experimental data well (as pointed by the low correlation values) or not even suitable for the adsorption equilibrium expression (for instance, negative values of K_{BET} Tabl. 4). From the obtained data, three limiting cases are distinguished: (i) when $C_{eq} \ll C_{init}$ and $K_{BET} \gg 1$, BET isotherm approaches Langmuir isotherm ($K_L = K_{BET}/C_{init}$), it was the case of the parent Norit carbon; and (ii) when the constant $K_{BET} \gg 1$, the heat of adsorption of the very first monolayer is large compared to the condensation enthalpy and adsorption into the second layer only occurs once the first layer is completely filled, these were the cases of the Cr (III) adsorption by oxidized Merck and Norit carbons; (iii) when K_{BET} is small, which was the case of the parent Merck carbon, then a multilayer adsorption already occurs while the first layer is still incomplete. In the last case that is most probably connected to the less developed porous structure of the parent Merck.

Based on the obtained results (Tabl. 4), the Freundlich model appeared to be the most “universal” to describe the equilibrium conditions in all studied adsorption systems over the entire range of temperatures. The linear relationships ($R^2 \sim 0.95-0.99$) were observed among the plotted parameters at different temperatures for oxidized samples indicating the applicability of the Freundlich equation. The Cr (III) isotherms showed Freundlich characteristics with a slope of ~ 1 in a log-log representation for the oxidized Merck and Norit activated carbons. These values were in the range of ~ 0.2 for the parent Merck and Norit carbons; and $1/n$ was found to be more than 2.6 in the case of oxidized Norit carbon. Larger value of n (smaller value of $1/n$) implies stronger interaction between adsorbent and adsorbate [39]. It is known that the values of $0.1 < (1/n) < 1.0$ shows that adsorption of Cr (III) is favorable (Mckay et al., 1982) and the magnitude of $(1/n)$ of to 1 indicates linear adsorption leading to identical adsorption energies for all (Weber & Morris, 1963). Freundlich constants (K_F) related to adsorption capacity. In average, these values were in a range of (2-9) and decreased by rising the temperature for all studied carbons.

While Langmuir and BET isotherms indicate the homogeneity of the adsorbent surface and uniform energies of the adsorption, the Freundlich type isotherm hints towards transmigration of sorbate in the plane of the surface and its heterogeneity. Therefore, the surface of studied activated carbons could be made up of small heterogeneous adsorption patches which are very much similar to each other in respect of adsorption phenomenon. Since here the Norit and Merck activated carbons were used as supplied and after post-chemical oxidative treatment, Cr(III) uptake on initial carbons, i.e. those without surface functionality, taken place mainly due to physisorption and increased with the increase in temperature. For oxidized samples total adsorption increases with the temperature until certain temperature, and further temperature rising led to the reversal adsorption capacity when the total adsorption decreases with the temperature. The cross over appears at 40^oC. This can be explained by the fact that for carbon reached by surface functionality there is more than one mechanism of chromium sorption: along with the normal physisorption the chemisorption of chromium on the active sites takes place leading to increased adsorption via surface exchange reactions, then with the rise in temperature, i.e. T > 40 °C, the ionic exchange is no longer the main mechanism of sorption.

3.2 Adsorption thermodynamics

The adsorption process involves a solid phase (adsorbent) and a liquid phase containing a dissolved species (adsorptive) to be adsorbed (adsorbate). The affinity of the adsorbent for the adsorbate determines its distribution between the solid and liquid phases. When the sorption equilibrium is established, the adsorbate immobilized in the solid sorbent is in equilibrium with the residual concentration of adsorptive remaining in the liquid phase.

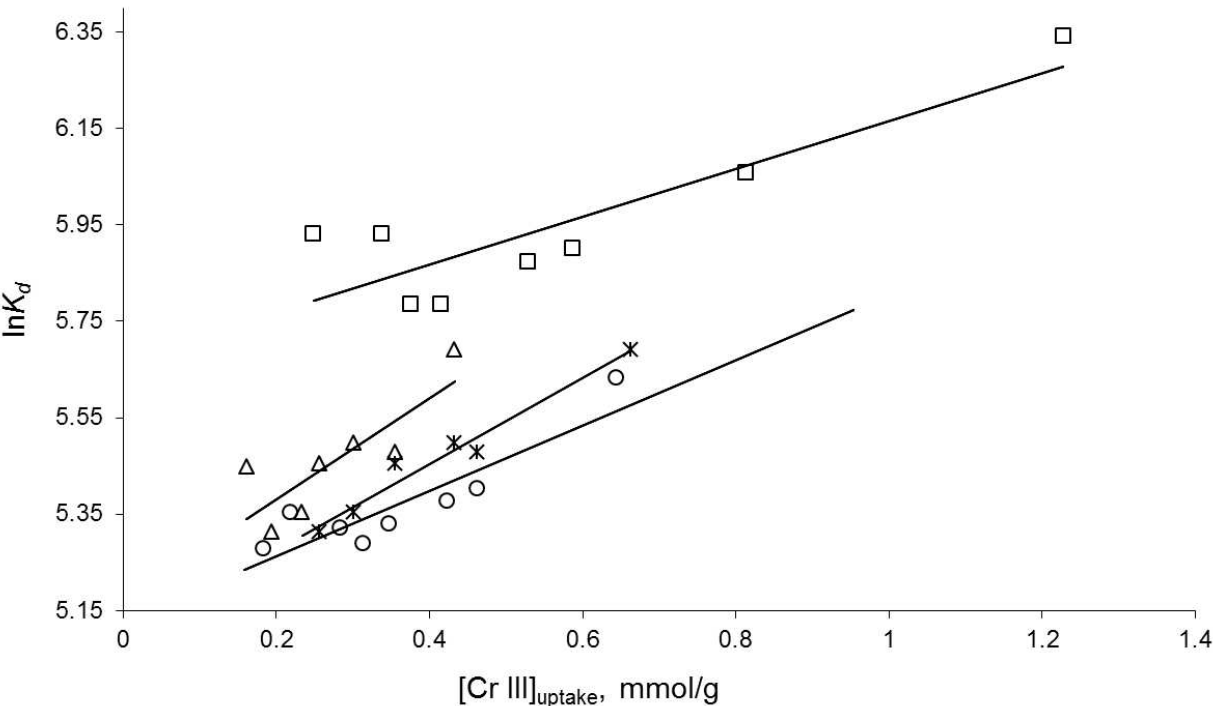


Fig. 5. Plots of $\ln [Cr\ III]_{uptake}/[Cr\ III]_{eq}$ vs. $[Cr\ III]_{uptake}$ for the Cr(III) adsorption on modified by 1M HNO₃ Merck activated carbon at (*) – 22; (O) – 30; (□) – 40 and (△) – 50 °C.

The value for the apparent equilibrium constant (K_d) of the adsorption process of the Cr (III) in aqueous solution on studied activated carbons were calculated with respect to temperature using the method of [Khan and Singh] by plotting $\ln (q_{eq}/C_{eq})$ vs. q_{eq} and extrapolating to zero q_{eq} (Fig. 5, 6) and presented in Table. 4. In general, K_d values increased with temperature in the following range of the studied activated carbons: Merck_initial < Norit_initial < Norit_ treated by 1M HNO₃ < Merck_treated by 1M HNO₃ (Tabl. 4.). However, it should be noted that in the case of the parent Norit and Merck activated carbons, the experimental data did not serve well for the apparent equilibrium constants calculation (as pointed by the low correlation values (R^2) on Fig. 7).

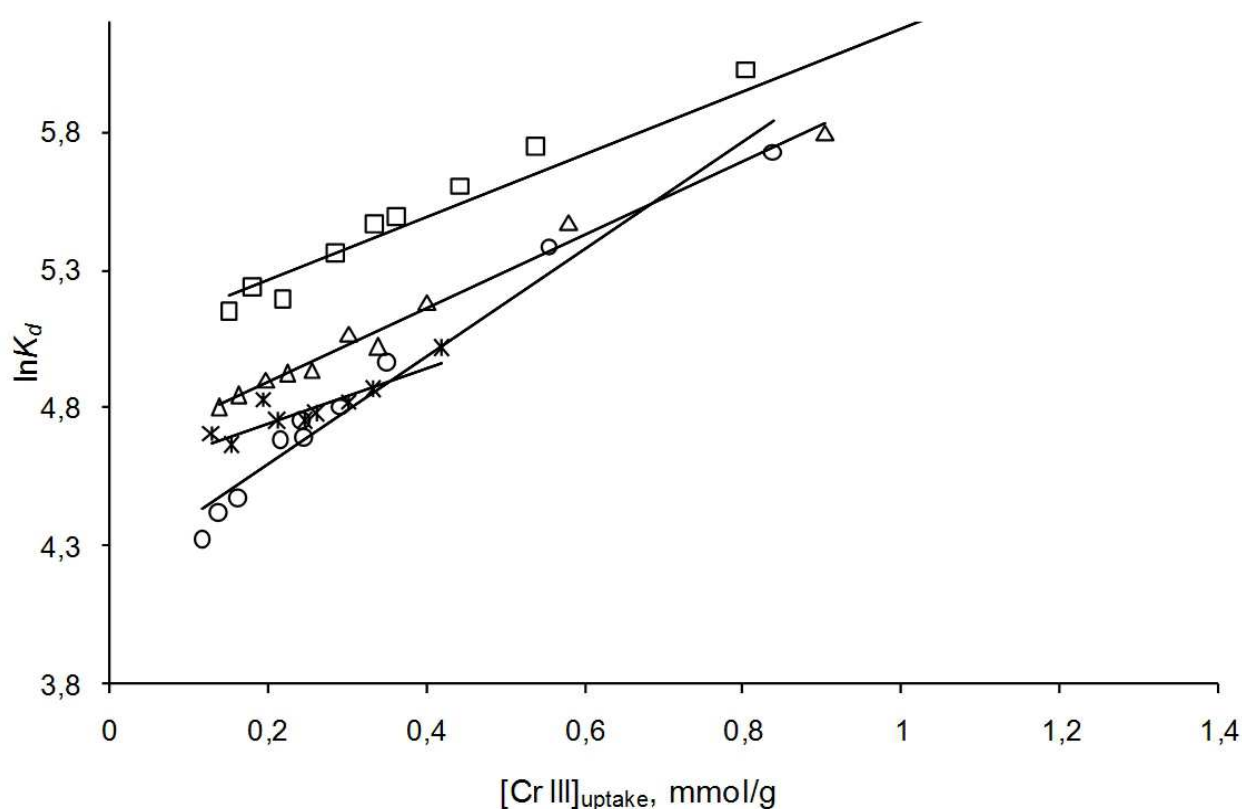


Fig. 6. Plots of $\ln [Cr III]_{uptake}/[Cr III]_{eq}$ vs. $[Cr III]_{uptake}$ for the Cr(III) adsorption on modified by 1M HNO₃ Norit activated carbon at (*) – 22; (O) – 30; (□) – 40 and (△) – 50 °C.

As-depicted irregular pattern of linearised forms of $[\ln (q_{eq}/C_{eq})$ vs. $q_{eq}]$, (Fig. 7) are likely to be caused by less developed porous structure of the parent materials and their poor surface functionality, thus low adsorption and, consequently, by the pseudo-equilibrium conditions in the systems with parent activated Norit and Merck carbons.

Thermodynamic parameters for the adsorption were calculated from the variations of the thermodynamic equilibrium constant (K_d) by plotting of $\ln K_d$ vs. $1/T$. Then the slope and intercept of the lines are used to determine the values of ΔH^0 and the equations (13) and (14) were applied to calculate the standard free energy change ΔG^0 and entropy change ΔS^0 with the temperature (Table 5).

Based on the results obtained using the thermodynamic equilibrium constant (K_d) some tentative conclusions can be given. The free energy of the process at all temperatures was

negative and decreased with the rise in temperature (Fig. 9 (II) and 10 (II)), which indicates that the process is spontaneous in nature is more favourable at higher temperatures. The entropy change (ΔS^0) values were positive, that indicates a high randomness at the solid/liquid phase with some structural changes in the adsorbate and the adsorbent (Saha, 2011). This could be possible because the mobility of adsorbate ions/molecules in the solution increase with increase in temperature and that the affinity of adsorbate on the adsorbent is higher at high temperatures (Saha, 2011). The positive values of ΔH^0 indicate the endothermic nature of the adsorption process, which fact was evidenced by the increase in the adsorption capacity with temperature (Tabl. 5). The magnitude of ΔH^0 may also give an idea about the type of sorption. As far as physical adsorption is usually exothermic process and the heat evolved is of 2.1–20.9 kJ mol⁻¹ (Saha 2011); while the heats of chemisorption is in a range of 80–200 kJ mol⁻¹ (Saha 2011), and the enthalpy changes for ion-exchange reactions are usually smaller than 8.4 kJ/mol (Nakajima & Sakaguchi, 1993), it is appears that sorption of Cr(III) on studied activated carbons is rather complex reaction. It has to be pointed out, that owing to different operating mechanisms for the Cr (III) adsorption on studied samples, given the K_d values are not vary linear with the temperature (see Fig. 8 (IV) and the regression coefficients in Tabl. 5) and hence applying of the van't Hoff type equation for the computation of the thermodynamic parameters for the adsorption on the studied carbons is not fully correct, especially in a case of parent carbons (see Fig. 9 (IV) and 10 (IV)).

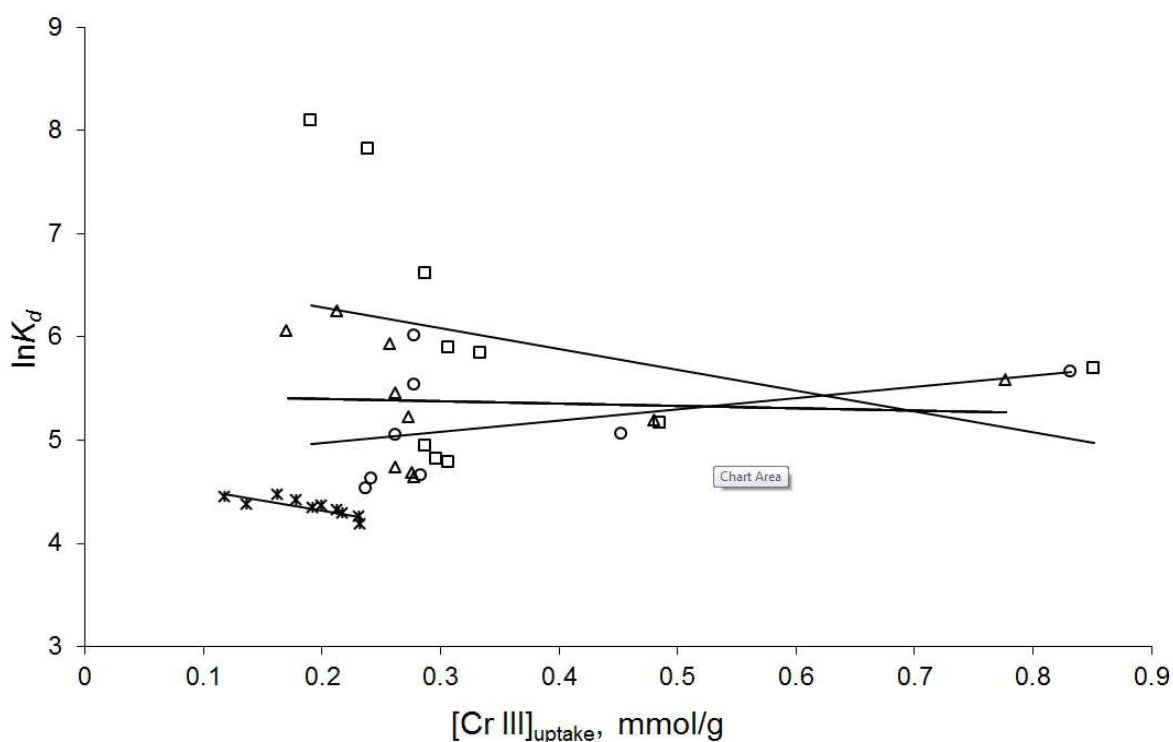


Fig. 7. Plots of $\ln [\text{Cr III}]_{\text{uptake}}/[\text{Cr III}]_{\text{eq}}$ vs. $[\text{Cr III}]_{\text{uptake}}$ for the Cr(III) adsorption by parent Merck activated carbon at (*) – 22; (O) – 30; (□) – 40 and (△) – 50 °C.

On the other hand, Langmuir, Freundlich and BET constants showed similar variation with temperature (Fig. 8 (I), (II) and (III)), and hence were also used to calculate the thermodynamic parameters (compare the R^2 for different calculations, Table 5).

T. °C	For Langmuir isotherms				For Freundlich isotherms				For BET isotherms				For Thermodynamic equilibrium constants			
	G kJ mol ⁻¹	R ²	S kJ mol ⁻¹ kJmol ⁻¹	H kJ mol ⁻¹	G kJ mol ⁻¹	R ²	S kJ mol ⁻¹	H kJ mol ⁻¹	G kJ mol ⁻¹	R ²	S kJ mol ⁻¹	H kJ mol ⁻¹	G kJ mol ⁻¹	R ²	S kJ mol ⁻¹	H kJ mol ⁻¹
Merck																
22	Initial 10.6544	-	-0.2649	-	-5.8225	-	-0.0631	-	-5.4464	-	-0.0714	-	-3.8080	-	0.0069	-
30	Initial 12.4649	0.7514	-0.2519	-88.8023	-3.4706	0.4097	-0.0692	-24.4253	-3.1426	0.999	-0.0771	-26.5045	-4.8021	0.0476	0.0100	-1.7635
40	Initial -8.2721	-	-0.2573	-	-3.0756	-	-0.0682	-	-	-	-	-	-4.4239	-	0.0085	-
50	Initial -3.9223	-	-0.2628	-	-3.8834	-	-0.0636	-	-	-	-	-	-4.1996	-	0.0075	-
22	1M HNO ₃ -	-	-	-	-4.1666	-	-0.0281	-	-2.8200	-	0.0297	-	-3.3711	-	0.0415	-
30	1M HNO ₃ 5.7662	0.4910	0.0095	8.6466	-3.9445	0.1867	-0.0281	-12.4485	-2.3174	0.3768	0.0273	5.9464	-3.9141	0.8734	0.0422	8.8801
40	1M HNO ₃ 3.9513	-	0.0150	-	-2.4383	-	-0.0320	-	-2.5333	-	0.0297	-	-4.5134	-	0.0428	-
50	1M HNO ₃ 5.6124	-	0.0094	-	-3.8032	-	-0.0268	-	-3.6489	-	0.0271	-	-4.4823	-	0.0414	-
Norit																
22	Initial -7.7178	-	-0.0466	-	-3.2777	-	-0.0436	-	-5.5931	-	0.2376	-	-3.1136	-	0.0253	-
30	Initial -8.7411	0.4508	-0.0420	-21.4743	-1.9589	0.5719	-0.0468	-16.1303	-13.0695	0.6100	0.2560	64.4903	-4.0882	0.4316	0.0279	4.3579
40	Initial -7.1497	-	-0.0458	-	-1.7209	-	-0.0460	-	-12.7129	-	0.2467	-	-3.5694	-	0.0253	-
50	Initial -6.8598	-	-0.0452	-	-1.9399	-	-0.0439	-	-13.4691	-	0.2414	-	-4.1279	-	0.0263	-
22	1M HNO ₃ -	-	-	-	-	-	-	-	-5.4464	-	-0.0876	-	-2.7836	-	0.0470	-
30	1M HNO ₃ -	-	-	-	-8.5022	0.7330	-0.1237	-45.9976	-2.9445	0.6414	-0.0936	-31.2994	-3.7397	0.7670	0.0489	11.0731
40	1M HNO ₃ -	-	-	-	-5.9373	-	-0.1280	-	-2.6355	-	-0.0916	-	-4.2229	-	0.0489	-
50	1M HNO ₃ -	-	-	-	-6.0471	-	-0.1237	-	-2.7035	-	-0.0885	-	-4.1239	-	0.0470	-

Table 5. Thermodynamic parameters of the Cr III adsorption on studied activated carbons at different temperatures

According to the calculation using (K_L), (K_F) and (K_{BET}) constants (Tabl. 6), the free energy of the processes at all temperatures was negative and increased with the temperature rise (Fig. 9 (I), (II), (III) and Fig. 10 (I), (II), (III)), which indicates spontaneous in nature adsorption processes. While, an increase in the negative value of ΔG^0 with temperature indicates that the adsorption process is more favorable at low temperatures indicating the typical tendency for physical adsorption mechanism.

The overall process on oxidized carbons seems to be endothermic; whereas that on initial Norit and Merck activated carbons is more evident being exothermic, the negative values of ΔH^0 in the last case indicate that the product is energetically stable (Tabl. 6). Had the physisorption been the only adsorption process, the enthalpy of the system should have been exothermic. The result suggests that Cr (III) sorption on initial activated carbons is either physical adsorption nor simple ion-exchange reactions, whereas it on oxidized carbons is much more complicated process. Probably, the transport of metal ions through the particle solution interface into the porous carbon texture followed by the adsorption on the available surface sites are both responsible for the Cr (III) uptake.

The negative ΔS^0 value shows a greater order of reaction during the adsorption on initial activated carbons that could be due to fixation of Cr (III) to the adsorption sites resulting in a decrease in the degree of freedom of the systems. In some cases of oxidized Merck carbon the entropy at all the temperatures positive and is slightly decreases with the temperature with an exception for 40°C. It means that with the temperature the ion-exchange and the replacement reactions have taken place resulted in creation of the steric hindrances (Helfferich, 1962) which is reflected in the increased values for entropy of the system, but at 50°C, these processes are completed and the system has returned to a stable form. Thus it can be concluded that physisorption occurs at a room temperature, ion-exchange and the replacement reactions start with the rise in the temperature and they became less important at $T > 40^\circ\text{C}$.

Based on adsorption in-behind physical meaning, some general conclusions can be drawn. When the activated carbon is rich by surface oxygen functionality and has well developed porous structure, including mesopores, the evaluation of the thermodynamic parameters can be well presented by all of (K_d), (K_L), (K_F) and (K_{BET}) constants. When similar, but more microporous carbon is used, the thermodynamic parameters is better to present by (K_d), (K_F) and (K_{BET}) constants. However, when the carbon has less developed structure and surface functionality, thermodynamic parameters is better to evaluate based on (K_L) and (K_F) constants. As a robust equation, Freundlich isotherm fits nearly all experimental adsorption data, and is especially excellent for highly heterogeneous carbons. Therefore (K_F) constants can be used for the comparison of the calculated thermodynamic parameters for different activated carbons. However, predictive conclusions can be hardly drawn from systems operating at different conditions and proper analysis will require relevant model as one of the vital basis.

3.3 Isosteric heat of the adsorption

The equilibrium concentration $[\text{Cr III}]_{\text{eq}}$ of the adsorptive in the solution at a constant $[\text{Cr III}]_{\text{uptake}}$ was obtained from the adsorption data at different temperatures (Fig. 1 - 4). Then isosteric heat of the adsorption (ΔH_x) was obtained from the slope of the plots of $\ln[\text{Cr III}]_{\text{eq}}$ versus $1/T$ (Fig. 11, 12) and was plotted against the adsorbate concentration at the adsorbent surface $[\text{Cr III}]_{\text{eq}}$, as shown in Fig. 13.

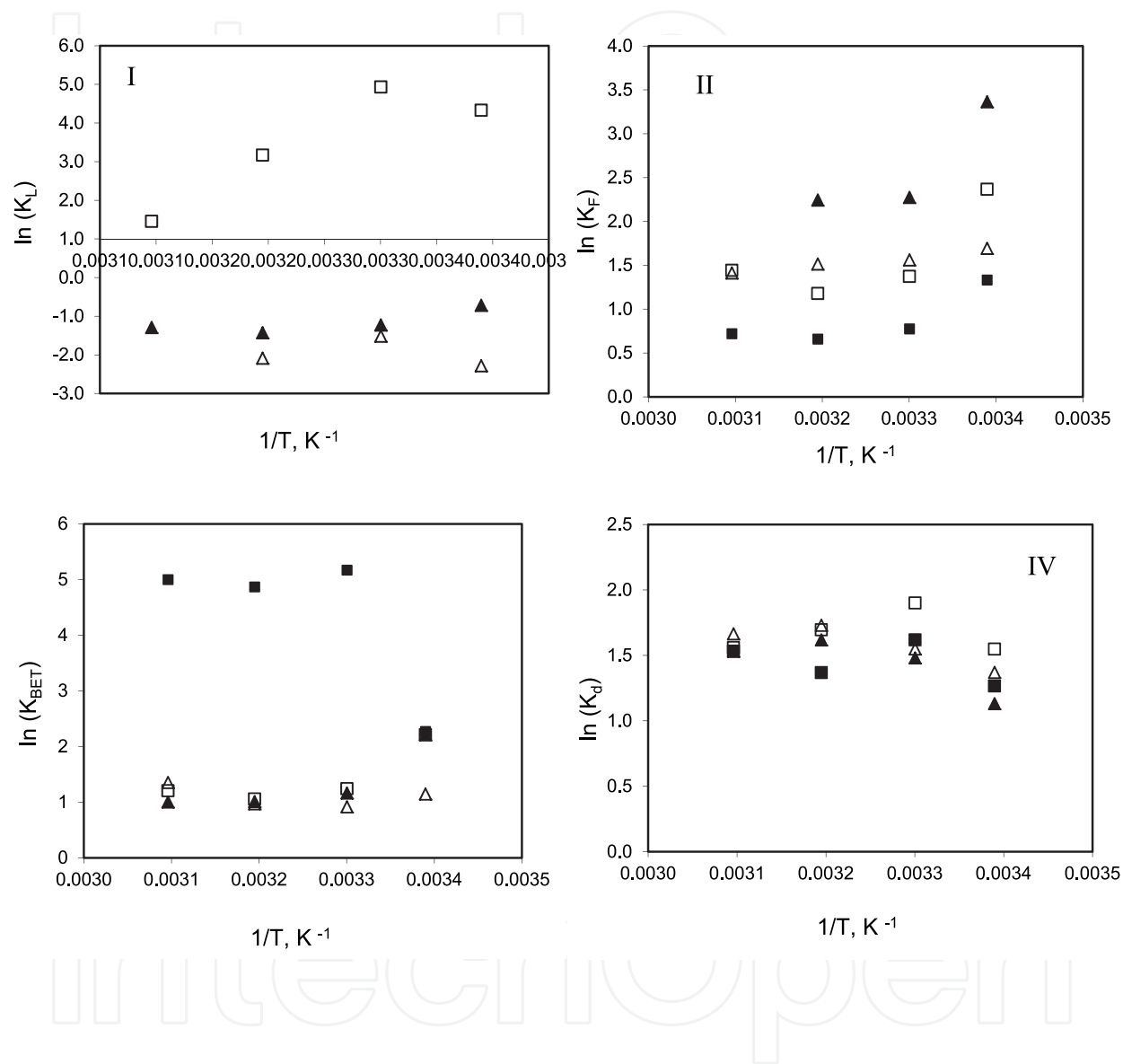


Fig. 8. Plots of Langmuir (K_L); Freundlich (K_F), BET (K_{BET}) and thermodynamic equilibrium constants (K_d) *vs* temperature for the adsorption of Cr(III) on parent Norit (■) and Merck (□) and modified by 1M HNO₃ Norit (▲) and Merck (Δ) activated carbons.

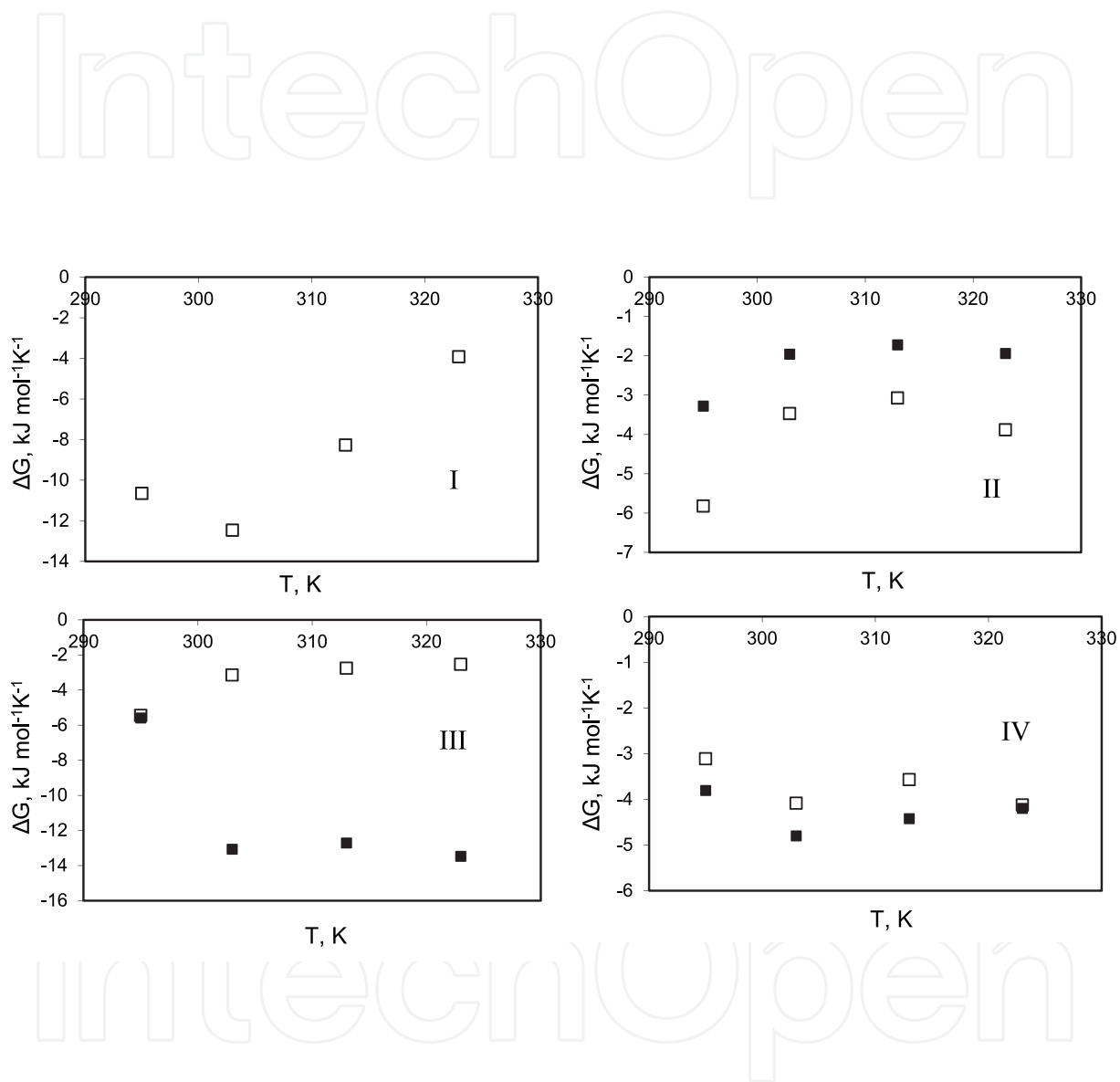


Fig. 9. Plot of Gibb’s free energy change (ΔG^0) vs temperature, calculated on Langmuir (I); Freundlich (II), BET (III) and thermodynamic equilibrium (IV) constants for Cr(III) adsorption on parent Norit (■) and Merck (□) activated carbons

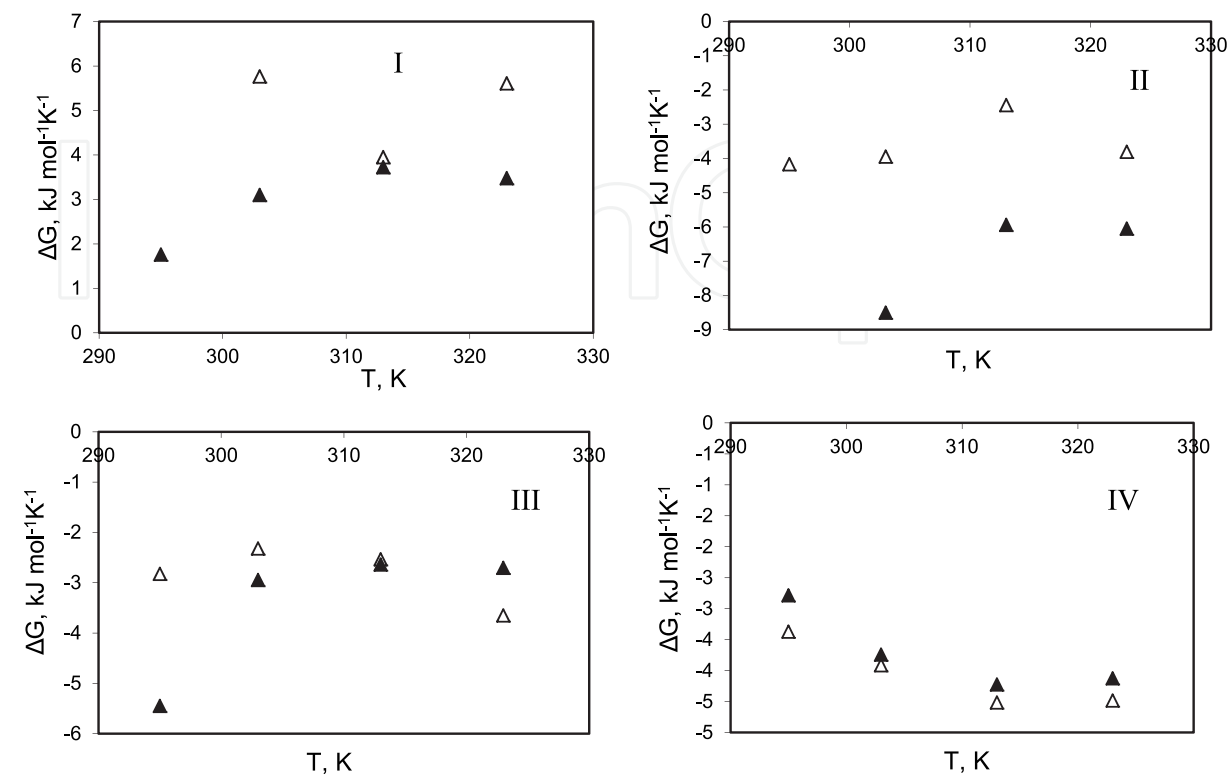


Fig. 10. Plot of Gibb’s free energy change (ΔG^0) vs temperature, calculated on Langmuir (I); Freundlich (II), BET (III) and thermodynamic equilibrium(IV) constants for Cr(III) adsorption on modified by by 1M HNO_3 Norit (\blacktriangle) and Merck (\triangle) activated carbons

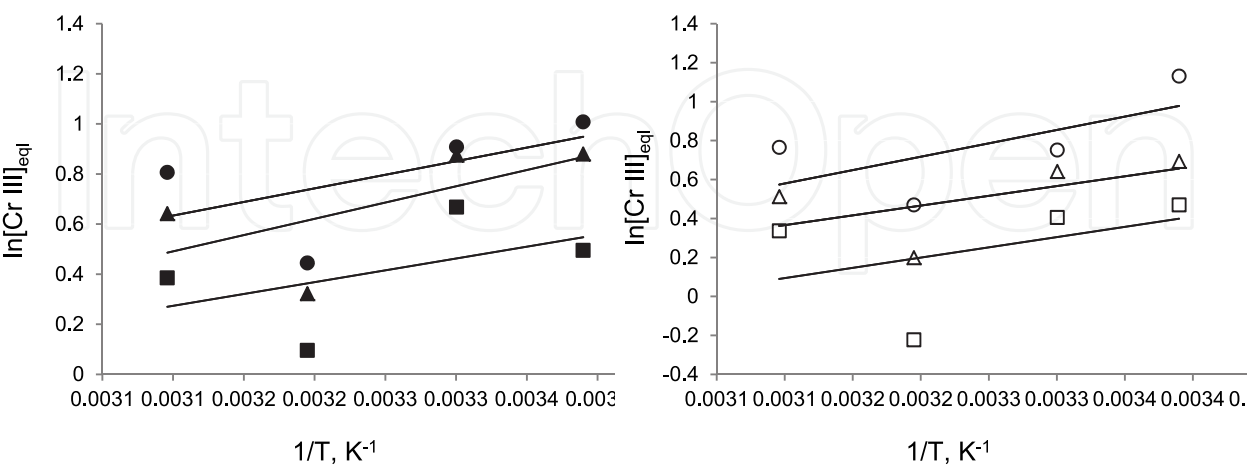


Fig. 11. Plot of $\ln[\text{Cr III}]_{\text{eq}}$ vs $1/T$, K^{-1} , calculated for the modified activated carbons 1M HNO_3 Norit : at $[\text{Cr III}]_{\text{uptake}}$ (\bullet) - 0.4; (\blacksquare) - 0.3; (\blacktriangle) - 0.2 mmol/g; and 1M HNO_3 Merck: at $[\text{Cr III}]_{\text{eq}}$ (\circ) - 0.6; (\square) -0. 4 and (\triangle) -0.3 mmol/g.

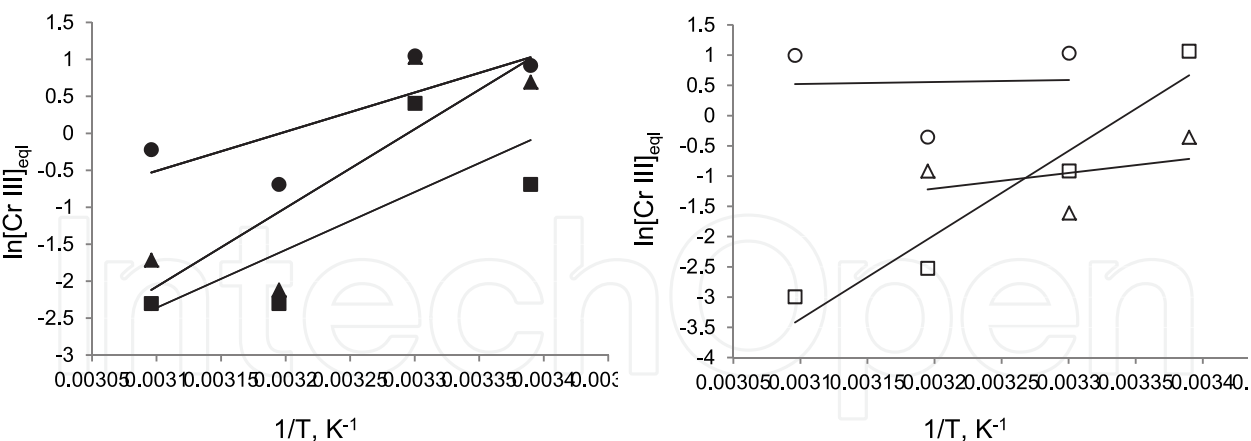


Fig. 12. Plot of $\ln[\text{Cr III}]_{\text{eq}}$ vs $1/T, \text{K}^{-1}$, calculated for the parent Norit : at $[\text{Cr III}]_{\text{uptake}}$ (●) – 0.5; (■) – 0.4; (▲) – 0.26 mmol/g; and parent Merck: at $[\text{Cr III}]_{\text{eq}}$ (○) – 0.3; (□) – 0.26 and (△) – 0.22 mmol/g.

The plots revealed that (ΔH_x) is dependent on the loading of the sorbate, indicating that the adsorption sites are energetically heterogeneous towards Cr III adsorption. For oxidized by 1M HNO_3 Norit and 1M HNO_3 Merck activated carbons (Fig. 13), the isosteric heat of adsorption steadily increased with an increase in the surface coverage, suggesting the occurrence of positive lateral interactions between adsorbate molecules on the carbon surface (Do 1998). In contrary, for the parent Norit and Merck activated carbons (Fig. 13), the (ΔH_x) is very high at low coverage and decreases sharply with an increase in $[\text{Cr III}]_{\text{uptake}}$. It has been suggested that the high (ΔH_x) values at low surface coverage are due to the existence of highly active sites on the carbon surface. The adsorbent-adsorbate interaction takes place initially at lower surface coverage resulting in high heats of adsorption. Then, increasing in the surface coverage gives rise to lower heats of the adsorption (Christmann, 2010). The magnitude of the (ΔH_x) values ranged in 10-140 kJ mol^{-1} revealed that the adsorption mechanism for the studied activated carbons is complex and can be attributed to the combined chemical-physical adsorption processes.

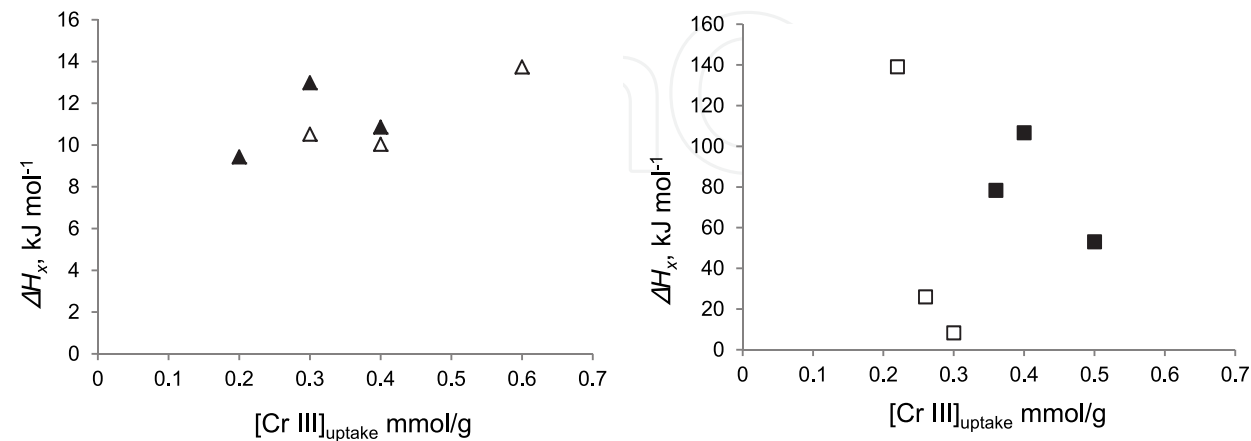


Fig. 13. Plot of isosteric heating (ΔH_x) as a function of the amount adsorbed of the parent Norit (■) and Merck (□) activated carbons and their oxidized by 1M HNO_3 Norit (▲) and 1M HNO_3 Merck(△) forms.

3.4 General remarks

It should be stressed, however, that the interpretation of the results presented here is tentative. According to our previous investigation on the equilibrium for the studied systems at different pHs and at a room temperature there are both slow and fast Cr(III) uptakes by Norit and Merck carbons (Lyubchik, 2005). The actual time to reach equilibrium is strongly depended on the initial and equilibrium pH of the solution, as well as on the surface functionality and material texture, and was varied between 0.5 and 3 months for different carbons at different pHs. The process did not appear to achieve equilibrium over the time interval used for the batch experiment of ca. 0.5-1 month, especially for the carbons reached by surface functionality (i.e. those modified by nitric acid), as well as for the all systems at moderated acidic pH values, i.e. pH 2 and 3.2. Thus, for the Norit and Merck carbons treated by 1 M HNO₃ the chromium removal increased from 40–50 % to 55–65 % as the contact time is increased from 0.5 to 3 months at pH 3.2. At pH 3.2 the carbon's surface might have different affinities to the different species of chromium existing in the solution. Under real equilibrium conditions our results showed that studied Merck activated carbons adsorb Cr (III) from the aqueous solution more effective then corresponded Norit samples. It is related to the microporous texture of Norit carbons that could be inaccessible for large enough Cr (III) cations (due to their surrounded layers of adsorbed water).

This finding points out that the chosen current conditions for batch experiment at different temperatures could be out of the equilibrium conditions for the studied systems. Therefore current analysis of the thermodynamic parameters should be corrected taking into account the behaviors of the systems in complete equilibrium state.

4. Conclusion

The adsorption isotherms are crucial to optimize the adsorbents usage; therefore, establishment of the most appropriate correlation of an equilibrium data is essential. Experimental data on adsorption process from liquid phase on activated carbon are usually fitted to several isotherms, where Langmuir and Freundlich models are the most reported in literature. To determine which model to use to describe the adsorption isotherms the experimental data were analyzed using linearised forms of three, the widespread-used, Langmuir, Freundlich and BET models for varied activated carbons.

As a robust equation, Freundlich isotherm fitted nearly all experimental adsorption data, and was especially excellent for highly heterogeneous adsorbents, like post-treated by HNO₃ Merck and Norit activated carbons. It was shown, that in all cases, when Langmuir model fall-short to represent the equilibrium data, the BET model fitted the adsorption runs with better correlations, and an opposite, when Langmuir model better correlated the equilibrium data, BET model was less applicable. In some cases, chosen models were not able to fit the experimental data well or were not even suitable for the equilibrium data expression. As-depicted irregular pattern of experimental data and applied linearised models are likely to be caused by the complex nature of the studied activated carbons. Different adsorption behavior is related to the varied porous structure, nature and amount of surface functional groups, as well as to the different operating mechanism of the Cr (III) with temperatures rising.

The thermodynamics parameters were evaluated using both the thermodynamic equilibrium constants and the Langmuir, Freundlich and BET constants. The obtained data were compared, when it was possible. Based on adsorption in-behind physical meaning general conclusions were drawn. However, it should be stressed, that the interpretation of the results presented here is tentative. The principal drawback of adsorption studies in a liquid phase is associated with the relatively low precision of the measurements and the long equilibration time that is requires. These factors imply that an extensive experimental effort is needed to obtain reliable adsorption data in sufficient quantity to allow evaluated the process thermodynamics. Therefore, the adsorption experiments are carried out either under pseudo-equilibrium condition when the actual time is chosen to accomplish the rapid adsorption step or under equilibrium condition when the contact time is chosen rather arbitrary to ensure that the saturation level of the carbon is reached. While, the adsorption models are all valid only and, therefore, applicable only to completed equilibration.

5. References

- Anirudhan, T. & Radhakrishnan, P. (2011). Adsorptive Removal and Recovery of U(VI), Cu(II), Zn(II), and Co(II) from Water and Industry Effluents. *Bioremediation Journal*, Vol.15, No1, pp. 39-56
- Anirudhan, T. & Radhakrishnan, P. (2008). Thermodynamics and Kinetics of Adsorption of Cu(II) from Aqueous Solutions onto a New Cation Exchanger Derived from Tamarind Fruit Shell. *Journal of Chemical Thermodynamics*, Vol.40, pp. 702-709. ISSN: 0021- 9614.
- Ajmal, M.; Rao, R.; Ahmad, R.; Ahmad, J. & Rao, L. (2001). Removal and Recovery of Heavy Metals from Electroplating Wastewater by using Kyanite as an Adsorbent. *Journal of Hazardous Materials*, Vol.87, pp. 127-137
- Araújo, M. & Teixeira, J. (1997). Trivalent Chromium Sorption on Alginate Beads. *Int. Biodeterioration and Biodegradation* Vol.40, pp. 63-74
- Argun, M.; Dursun, S.; Ozdemir, C. & Karatas, M. (2007). Heavy Metal Adsorption by Modified Oak Sawdust: Thermodynamics and Kinetics. *Journal of Hazardous Materials*, Vol.141, pp. 77-85. ISSN: 0304-3894.
- Aydin, Y.A. & Aksoy, N.D. (2009). Adsorption of Chromium on Chitosan: Optimization, Kinetics and Thermodynamics. *Chemical Engineering Journal*, Vol. 151, pp. 188-194. ISSN: 1385-8947.
- Bailey, S.; Olin, T.; Bricka R. & Adrian D. (1999). A Review of Potentially Low-cost Sorbents for Heavy Metals. *Water Research*, Vol.33, No.11, pp. 2469-2479
- Brigatti, M.; Franchini, G.; Lugli, C.; Medici, L.; Poppi L. & Turci, E. (2000). Interaction between Aqueous Chromium Solutions and Layer Silicates. *Applied Geochemistry*, Vol.15, pp. 1307-1316
- Brown, P.; Gill, S. & Allen, S. (2000). Metal Removal from Wastewater using Peat. *Water Research*, Vol.34, No.10, pp. 3907-3916
- Carrott, P.; Ribeiro Carrott, M.; Nabais, J. & Prates Ramalho, J. (1997). Influence of Surface Ionization on the Adsorption of Aqueous Zinc Species by Activated Carbons, *Carbon*, Vol.35, pp. 403-410

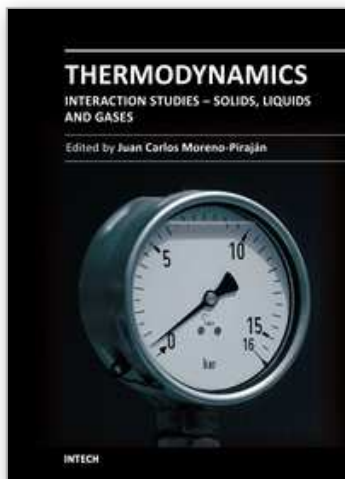
- Chakir, A.; Bessiere, J.; Kacemi, K. & Marouf, B. (2002). A Comparative Study of the Removal of Trivalent Chromium from Aqueous Solutions by Bentonite and Expanded Perlite. *Journal of Hazardous Material*, Vol.95, No1-2, pp. 29-46
- Chen, J. & Lin, M. (2001). Surface Change and Metal Ion Adsorption on H-type Activated Carbon: Experimental Observation and Modelling Simulation by the Surface Complex Formation Approach. *Carbon*, Vol.39, pp. 1491-1504
- Christmann, K. (2010). Adsorption. Lecture Series 2010/2011: "Modern Methods in Heterogeneous Catalysis Research", Institut für Chemie und Biochemie, Freie Universität, Berlin, Available from http://www.fhierlin.mpg.de/acnew/departement/pages/teaching/pages/teaching_wintersemester_2010_2011/klaus_christmann_adsorption_101105.pdf
- Csobán, K.; Párkányi-Berka, M.; Joó P. & Behra, Ph. (1998). Sorption Experiments of Cr(III) onto Silica. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, Vol.141, pp. 347-364
- Csobán, K. & Joó, P. (1999). Sorption of Cr (III) on Silica and Aluminium Oxide: Experiments and Modelling. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, Vol.151, pp. 97-112
- Do, D.D. (1998). *Adsorption Analysis: Equilibria and Kinetics*. Series on Chemical Engineering, Vol. 2. Imperial College Press, London.
- Farias, R.; Souza, A.; Nunes, L. & Cardoso, V. (2002). Adsorption of Cr(III) and Fe(III) on an Inorganic Organic Silicon Hybrid Surface. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, Vol.211, No.2-3, pp. 295-298
- Ferro-García, M.; Rivera-Utrilla, J.; Bautista-Toledo, I. & Moreno-Castilla, C. (1998). Adsorption of Humic Substances on Activated Carbon from Aqueous Solutions and Their Effect on the Removal of Cr(III) Ions. *Langmuir*, Vol.14, pp. 1880-1886
- Figueiredo J.; Pereira M.; Freitas M. & Orfão J. (1999). Modification of the surface chemistry of activated carbons. *Carbon*, Vol.37, pp. 1379-1389
- Helfferrich, F. (1962). *Ion Exchange*, McGraw-Hill, New York, 624 pp.
- Indraswati, N. & Ismadjia, S. (2009). Equilibrium and Kinetic Studies in Adsorption of Heavy Metals using Biosorbent: A
- Kapoor, A. & Viraraghavan, T. (1997). Nitrate Removal from Drinking Water. *Journal of Environmental Engineering*, Vol.123, No.4, pp. 370-379
- Khan, A. & Singh, R. (1987). Adsorption Thermodynamics of Carbofuran on Sn(IV) a Rsenosilicate in H⁺, Na⁺ and Ca⁺ Forms. *Colloids and Surfaces*, Vol.24, pp. 33-42.
- Kołodzyńska, D. (2010). The Effects of the Treatment Conditions on Metal Ions Removal in the Presence of Complexing Agents of a New Generation. *Desalination*, Vol.263, No1-3, pp. 159-169
- Kratochvil, D. & Volesky, B. (1998) Advances in the Biosorption of Heavy Metals, *Trends in Biotechnology*, Vol.16, pp. 291-300
- Kumar, A.; Rao, N. & Kaul, S. (2000). Alkali-treated Straw and Insoluble Straw Xanthate as Low Cost Adsorbents for Heavy Metal Removal - Preparation, Characterization and Application. *Bioresource Technology*, Vol.71, pp. 133-142
- Lakatos, J.; Brown S. & Snape, C. (2002). Coals as Sorbents for the Removal and Reduction of Hexavalent Chromium from Aqueous Waste Streams. *Fuel*, Vol.81, pp. 691-698

- Lalvani, S.; Wiltowski, T.; Hübner, Weston, A. & Mandich, N. (1998). Removal of Hexavalent Chromium and Metal Cations by a Selective and Novel Carbon Adsorbent. *Carbon*, Vol.39, pp. 1219-1226
- Leist, M.; Casey R. & Caridi, D. (2000). The Management of Arsenic Wastes: Problems and Prospects. *Journal of Hazardous Materials*, Vol.76, pp. 125-138
- Li, Y.; Xia, B.; Zhao, Q.; Liu, F.; Zhang, P.; Du, Q.; Wang, D.; Li, D.; Wang, Z. & Xia, Y. (2011). Removal of Copper Ions from Aqueous Solution by Calcium Alginate Immobilized Kaolin. *Journal of Environmental Sciences*, Vol.23, No3, pp. 404-411
- Liu, X.; Goodfellow, M. & Zheng, O. (2004). Correlation of pH Dependant Equilibrium Isotherms of Heavy Metal Biosorption with a Modified Freundlich Model *Environmental Technology*, Vol.25, No12, pp. 1341-1348
- Lyubchik, S.; Melo, R., Palma, C. & Fonseca I. (2003). Adsorption Equilibrium in the System "Cr (III) – Activated Carbon, In: *NATO Science Series IV. Earth and Environmental Science*, V.24, *Role of Interfaces in Environmental Protection*, S. Barany (Ed.), 355-377, Kluwer Academic Publishers, ISSN 1568-1238, Dordrecht, The Netherlands
- Lyubchik, S.; Lyubchik, A.; Lygina, E.; Lyubchik, S.I., Makarova, T.; Vital, J.; Rego, A. & Fonseca, I. (2008). Simultaneous Removal of 3d Transition Metals from Multi-Component Solutions by Activated Carbons from Co-mingled Wastes. *Separation and Purification Technology*, Vol.60, No3, pp. 264-271
- Lyubchik, S.; Perepichka, I.; Galushko, O.; Lyubchik, A.; Lygina, E. & Fonseca, I. (2005). Optimization of the Conditions for the Cr (III) Adsorption on Activated Carbon. *Adsorption*, Vol.11, No5-6, pp. 581-593
- Mckay, G.; Blair, H. & Garden, J. Adsorption of dyes on chitin. I. Equilibrium studies. *Journal of Applied Polymer Science*, Vol.27, pp. 3043-3057
- Myers, L. (2004). Thermodynamics of Adsorption, In: *Chemical Thermodynamics for Industry*, T.M. Letcher, (Ed.), 243-252, Royal Society of Chemistry, ISBN 0-85404-591-0, Cambridge, UK
- Nakajima, A. & Sakaguchi, T. (1993). Uptake and recovery of gold by immobilized persimmon tannin. *Journal of Chemical Technology and Biotechnology*, Vol.57, No4, pp. 321-326
- Perez-Candela, M.; Martin-Martinez, J. & Torregrosa-Macia, R. (1995). Chromium (VI) Removal with Activated Carbons. *Water Research*, Vol.29, pp. 2174-2180
- Raji, C. & Anirudhan, T. (1998). Batch Cr(VI) Removal by Polyacrylamide-grafted Sawdust: Kinetics and Thermodynamics. *Water Research*, Vol.32, pp. 3772-3780
- Ramesh, A.; Lee, D. & Wong, J. (2005). Thermodynamic Parameters for Adsorption Equilibrium of Heavy Metals and Dyes from Wastewater with Low-cost Adsorbents. *Journal of Colloid and Interface Science*, Vol.291, pp. 588-592
- Ruthven, D. (1984). *Principles of Adsorption and Adsorption Processes*, John Wiley & Sons, New York
- Saha, P. & Chowdhury S. (2011). *Insight into Adsorption Thermodynamics*, InTech, ISBN:978-953-307-544-0, Vienna, Austria
- Sonthimer H.; Crittenden J. & Summers R. (1988). *Activated Carbon for Water Treatment*. DVGW-Forschungsstelle am Engler-Bunte-Institut der Universität Karlsruhe (TH), AWWA Research Foundation, Karlsruhe, 126 pp.

- Tikhonova, L.; Goba, V.; Kovtun, M.; Tarasenko, Yu.; Khavryuchenko, V.; Lyubchik, S. & Boiko, A. (2008). Sorption of Metal Ions from Multicomponent Aqueous Solutions by Activated Carbons Produced from Waste. *Russian Journal of Applied Chemistry*, Vol.81, No8, pp. 1348-1355
- Weber, W. & Morris, J. (1963). Kinetics of adsorption on carbon from solutions. *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* Vol.89, pp. 31-60

IntechOpen

IntechOpen



Thermodynamics - Interaction Studies - Solids, Liquids and Gases

Edited by Dr. Juan Carlos Moreno Piraján

ISBN 978-953-307-563-1

Hard cover, 918 pages

Publisher InTech

Published online 02, November, 2011

Published in print edition November, 2011

Thermodynamics is one of the most exciting branches of physical chemistry which has greatly contributed to the modern science. Being concentrated on a wide range of applications of thermodynamics, this book gathers a series of contributions by the finest scientists in the world, gathered in an orderly manner. It can be used in post-graduate courses for students and as a reference book, as it is written in a language pleasing to the reader. It can also serve as a reference material for researchers to whom the thermodynamics is one of the area of interest.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Svetlana Lyubchik, Andrey Lyubchik, Olena Lygina, Sergiy Lyubchik and Isabel Fonseca (2011). Comparison of the Thermodynamic Parameters Estimation for the Adsorption Process of the Metals from Liquid Phase on Activated Carbons, Thermodynamics - Interaction Studies - Solids, Liquids and Gases, Dr. Juan Carlos Moreno Piraján (Ed.), ISBN: 978-953-307-563-1, InTech, Available from:
<http://www.intechopen.com/books/thermodynamics-interaction-studies-solids-liquids-and-gases/comparison-of-the-thermodynamic-parameters-estimation-for-the-adsorption-process-of-the-metals-from->

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](https://creativecommons.org/licenses/by/3.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen