Adsorption of hexavalent chromium on cationic cross-linked starches of different botanic origins

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ABSTRACT

The influence of origin of native starch used to obtain cationic cross-linked starch (CCS) on the adsorption of Cr(VI) onto CCS has been investigated. CCS granule size is influenced by the botanic source of native starch. The equilibrium adsorption of Cr(VI) onto CCS was described by the Langmuir, Freundlich, Dubinin–Radushkevich and Temkin models. The more equal the adsorption energy of the quaternary ammonium groups in CCS granule as indicated by low value of change of Temkin adsorption energy ΔE_T the greater amount of Cr(VI) was adsorbed onto CCS. The value of ΔE_T decreased and sorption capacity of CCS increased with the decrease of CCS granule size and with the increase of number of amorphous regions in CCS granules. The affinity of dichromate anions increases and adsorption proceeds more spontaneously when Cr(VI) is adsorbed onto more amorphous CCS. Adsorption process of Cr(VI) onto such CCS is more exothermic and order of system undergoes major changes during adsorption. After the adsorption on CCS Cr(VI) could be regenerated by incineration at temperature of 800 °C.

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1. Introduction

Soluble hexavalent chromium (Cr(VI)) is extremely toxic and exhibits carcinogenic effects on biological systems due to strong oxidizing nature. In aqueous waste Cr(VI) is present as either dichromate anion ($Cr_2O_7{}^{-2}$) in acidic environments or as chromate anion ($CrO_4{}^{-2}$) in alkaline environments [1]. The conventional process used for removal of Cr(VI) from wastewater is reduction and its precipitation as chromium (III) hydroxide [2]. This procedure is not completely satisfactory and has several disadvantages like generation of a large amount of secondary waste products due to various reagents used in a series of treatments such as reduction of Cr(VI), neutralization of acid solution and precipitation. There is a need for the development of low cost, easily available materials that could allow to remove and recover Cr(VI) economically.

Adsorption process is found to be a substantial method for the removal of chromium species from aqueous waste. A variety of natural and synthetic materials have been tested as chromium adsorbents. Amide groups containing pyridine copolymer [3] and amino-functionalized macroporous glycidyl methacrylate copolymer [4] have been synthesized and used for Cr(VI) adsorption. Also, activated carbon is versatile and has been proven to be an effective adsorbent for the removal of Cr(VI). Production of low-cost activated carbon becomes a great goal of many researchers. Activated carbons for Cr(VI) adsorption have been derived by burning of rice

straw [5], by treating rice husk and sawdust [6] or palm seed [7] with sulphuric acid. Tamarind wood activated carbon after activation with zinc chloride [8], activated carbon pre-treated by heating with sulphuric or nitric acid [9], also, were investigated as adsorbents of Cr(VI). Other kinds of adsorbents for Cr(VI) removal are various biomaterials, such as coir pith [10], succinic acid treated sugarcane bagasse [11], rubber wood sawdust alone or with immobilized *Acinetobacter haemolyticus* [12], seaweed *Hydrilla verticillata* [13], dead fungal biomass of marine *Aspergillus niger* [14] or thermophilic cyanobacterium *Phormidium* sp. [15]. However, some of these adsorbents have low adsorption capacity or adsorb chromium only from strong acid solutions.

Starch is a low-cost natural renewable polymer that can be cross-linked with epichlorohydrin or other agents. Obtained water-insoluble and modified with various reagents ionic products can be used to remove heavy metal ions from wastewater. It has been established [16] that water-insoluble cross-linked amphoteric starches containing phosphate groups and tertiary amine groups can remove Cr(VI), Pb^{2+} and phenol from solutions. The adsorption of the chromate ions follows the Langmuir adsorption isotherm, and it was confirmed that Cl^- of tertiary amine groups are exchanged by chromate ions. The adsorption of Cr(VI) on the cross-linked starches with cationic quaternary ammonium and anionic carboxymethyl groups has been also investigated [17]. The adsorption was found to follow the Langmuir isotherm, to be dependent on initial pH, Cr(VI) concentration, adsorbent dose, temperature and was of exothermic character. The adsorption capacity decreased with the increase of the degree of substitution of anionic groups. Cross-linked cationized starches are more

Nomenclature

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ARE	average relative error (%)
BTMAOH	benzyltrimethylammonium hydroxide
C_{Ae}	amount of adsorbate adsorbed per dm^3 of solution at equilibrium (mol/l)
C_e	equilibrium concentration of solute in the bulk solution (mmol/l)
C_o	initial concentration of the solute in the bulk solution (mmol/l)
CCS	cationic cross-linked starch
CCSP	cationic cross-linked starch obtained from potato starch
CCSC	cationic cross-linked starch obtained from corn starch
CCSWA	cationic cross-linked starch obtained from type A wheat starch
CCSWB	cationic cross-linked starch obtained from type B wheat starch
CCSPO	cationic cross-linked starch from potato starch obtained using benzyltrimethylammonium hydroxide as catalyst
DS	degree of substitution calculated according to N-(2-hydroxypropyl)-3-N,N,N-trimethylammonium groups
f	Temkin constant related to the heat of adsorption (J/mol)
EF	effectiveness of the cationic groups in the binding of Cr(VI) (equiv./equiv.)
EPTMAC	2,3-epoxypropyltrimethylammonium chloride
E_{DR}	Dubinin–Radushkevich mean free energy of adsorption (kJ/mol)
ΔE_T	change of the Temkin adsorption energy (kJ/mol)
$\Delta G°$	Gibbs free energy of adsorption (kJ/mol)
$\Delta H°$	change of enthalpy (kJ/mol)
K_C	thermodynamic distribution constant
K_F	Freundlich constant concerned with the relative adsorption capacity
K_L	Langmuir equilibrium constant (l/mol)
K_T	Temkin equilibrium constant (l/mol)
n_F	Freundlich constant concerned with the intensity of adsorption
N	number of experimental points
q_e	amount of the adsorbate adsorbed by adsorbent at the equilibrium (mmol/g)
Q_{DR}	Dubinin–Radushkevich saturation capacity (mmol/g)
Q_L	Langmuir maximum adsorption capacity (mmol/g)
R	universal gas constant (J/mol K)
R^2	linear correlation coefficient
R_L	Langmuir dimensionless constant (the separation factor)
S	place of active site in adsorbent
$\Delta S°$	change of entropy (kJ/K mol)
T	temperature (K)

Greek symbol

β	constant related to the Dubinin–Radushkevich mean free energy (mol^2/kJ^2)
ε	Polanyi potential (J/mol)
Θ	fractional coverage

favourable for the adsorption of Cr(VI) species. Chan and Ferng [18] investigated dynamic adsorption behaviour between Cr(VI) ions and water-insoluble tertiary amine groups containing starch derivatives and found that the sorption proceeds as a two stage process. The external mass transport occurs in the early stage and the intraparticle diffusion process is long-term. The external mass transport is an endothermic process while the intraparticle diffusion is exothermic. It has been found that adsorption of Cr(VI) onto ethylenediamine modified cross-linked starch can be described by pseudo-second-order kinetic model and Freundlich isotherm equation [19]. Maximum adsorption of Cr(VI) was observed at pH 4 and adsorption equilibrium was achieved within 4 h. The adsorption of Cr(VI) on cross-linked cationic starches with quaternary ammonium groups has been investigated by Xu et al. [20]. The adsorption process was found to be dependent on the initial pH of the solution, the initial concentration of Cr(VI), the dose of the adsorbent and adsorption temperature. The adsorption reaches equilibrium in a short time and follows the Langmuir isotherm. The adsorption capacity increased with the increase of the amount of cationic groups. An adsorption thermodynamics study shows that adsorption processes are exothermic and the adsorption of Cr(VI) favours lower temperature. Insoluble quaternary ammonium groups containing cationic starch with degree of substitution of 0.2 have been used to remove Cr(VI) by ultrafiltration [21].

The particles size can have a great influence on the sorption properties of adsorbent. The smaller the particles of adsorbent the greater the amount of dyes [22] or metal ions [23] could be adsorbed. In our previous work we have investigated the influence of the cross-linking density on the adsorption of Cr(VI) by cationic cross-linked starch containing quaternary ammonium groups (CCS) [24]. It was found that with increase of the quantity of cross-links the size of CCS microgranules in aqueous solutions decreases and at the same time the quantity of adsorbed dichromate anions increases. When the cross-linking density is the same, the size of CCS microgranules will depend on the size of native starch microgranules. The present work examines the influence of botanical source of native starch used to obtain CCS on the adsorption of Cr(VI). Additionally, the influence of the conditions of cationization reaction on the ability to adsorb Cr(VI) of cross-linked starch has been investigated. The Langmuir, Freundlich, Dubinin–Radushkevich and Temkin adsorption models have been used to evaluate adsorption results.

2. Materials and methods

2.1. Materials

The native potato starch (Antanavas Starch Plant, Lithuania), wheat starch type A and type B (Malsena Starch Plant, Lithuania) and corn starch (Cerestar, Holland) were dried at 104 °C temperature before the use. 2,3-Epoxypropyltrimethylammonium chloride (70%, Fluka), epichlorohydrin (99%, Aldrich) and benzyltrimethylammonium hydroxide (40%, Aldrich) were used as received

2.2. Preparation of CCS

The molecular mass of the anhydroglucoside unit (AGU) was assumed as a mole of starch. The starch was cross-linked with 0.1 mol/AGU of epichlorohydrin (EPCH) in the presence of sodium hydroxide, washed with cold water, dried and then cationized with 2,3-epoxypropyltrimethylammonium chloride (EPTMAC) in the presence of sodium hydroxide or benzyltrimethylammonium hydroxide (BTMAOH) as catalysts (the molar ratio AGU:EPTMAC:catalyst:H_2O was 1:0.4:0.04:16) at 45 °C for 24 h. After the reaction CCS was washed five times with water and two

times with water–isopropanol mixture and dried. The number of cationic groups in CCS was expressed as the degree of substitution (DS), which was calculated from the nitrogen content estimated by the Kjeldahl method [25] after purification by Soxhlet extraction with methanol for 16 h.

Cross-linked starch obtained in the reaction of starch with EPCH gathers additionally only hydroxyalkyl groups and it is very difficult to determine the number of formed cross-links. The degree of cross-linking of CCS was expressed as the amount of EPCH used in the cross-linking reaction (0.1 mol/AGU).

2.3. Equilibrium adsorption studies

Cr(VI) solutions were prepared from $K_2Cr_2O_7$ fixanal by dilution with distilled water to required concentrations. The pHs of Cr(VI) solutions were in the range 5.4–5.6 in all experiments.

0.1 g of dry CCS was placed into Erlenmeyer flask and 100 cm^3 of Cr(VI) solution of desired concentration was added. The flask was stoppered and shaken for 60 min at different temperatures and fixed shaking intensity in a thermostating water bath with temperature control of $\pm 1\,°C$ (Memmert GmbH, Germany). Then the mixture was filtered through a filter paper and the residual concentration of Cr(VI) in solution was estimated.

2.4. Determination of Cr(VI) concentration

The concentration of Cr(VI) in the samples was determined spectrophotometrically at 540 nm according to the standard 1,5-diphenyl-carbazide method [26].

2.5. Measurement of particle size

The size distribution of native starch granules was measured with a COULTER LS200 Particle Size Analyzer equipped with a Coulter Fluid Module (Beckman Coulter, USA). The results were calculated as a geometric mean value of the particle diameter.

3. Mathematical description

The adsorption equilibrium information is the most important part of information in understanding an adsorption process. In the case of the models with two parameters, the Langmuir and Freundlich equations are largely used. Other models such as Dubinin–Radushkevich or Temkin allow the determination of the energy of adsorption and could give the additional information about adsorption mechanism.

The Langmuir isotherm model [27] assumes that adsorption takes place at the specific homogeneous sites within the adsorbent and once an adsorbate molecule occupies a site, no further adsorption can take place. Also, all sorption sites are identical and energetically equivalent. The Langmuir equation may be presented as:

$$q_e = \frac{Q_L K_L C_e}{1 + K_L C_e} \tag{3.1}$$

where q_e (mol/g) is the amount of the adsorbate adsorbed by adsorbent at the equilibrium, C_e (mol/l) is the equilibrium concentration of the adsorbate, Q_L (mol/g) is the maximum adsorption capacity and K_L (l/mol) is the Langmuir equilibrium constant.

The Langmuir equation can be linearized to five different linear forms but for the adsorption of Cr(VI) onto CCS the best fittings were obtained when first linear equation was used:

$$\frac{C_e}{q_e} = \frac{1}{Q_L K_L} + \frac{1}{Q_L} \cdot C_e \tag{3.2}$$

Then C_e/q_e versus C_e was plotted and Q_L was calculated from the slope and K_L from the intercept. The favourable nature of adsorption can be expressed in terms of dimensionless constant that is called the separation factor and defined as [28]:

$$R_L = \frac{1}{1 + K_L C_o} \tag{3.3}$$

where C_o (mmol/l) is the initial highest concentration of the adsorbate. The value of R_L indicates the type of obtained isotherm: unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich equilibrium isotherm equation is used for the description of multilayer adsorption with the interaction between adsorbed molecules. The model predicts that the adsorbate concentration on the adsorbent will be increasing as long as the adsorbate concentration in the solution will be increasing. The model applies to the adsorption onto heterogeneous surfaces with uniform energy distribution and reversible adsorption. The Freundlich equation may be written as:

$$q_e = K_F C_e^{1/n_F} \quad \text{(non-linear form)} \tag{3.4}$$

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \quad \text{(linear form)} \tag{3.5}$$

where K_F (l/mmol) is the Freundlich isotherm constant concerned with the relative adsorption capacity and n_F is constant related to the intensity of adsorption. By plotting of $\ln q_e$ versus $\ln C_e$ the value of K_F was obtained from the intercept and n_F from the slope.

The magnitude of the exponent n_F gives an indication on the favourability of adsorption. In general it is stated that values of n_F in the range 2–10 represent good, 1–2 moderately difficult and less than 1 poor adsorption characteristics [29].

The Dubinin–Radushkevich isotherm equation is more general than the Langmuir equation because it does not assume a homogeneous surface or constant adsorption potential. It was used to distinguish between the chemical and physical adsorption. The model is based on the adsorption potential theory by Polanyi. Dubinin suggested that the adsorption proceeds in the volume of adsorbent micropores as opposed to layer-by-layer adsorption on micropore walls [30]. The Dubinin–Radushkevich isotherm equation may be written as:

$$q_e = Q_{DR} \exp(-\beta \varepsilon^2) \quad \text{(non-linear form)} \tag{3.6}$$

$$\ln q_e = \ln Q_{DR} - \beta \varepsilon^2 \quad \text{(linear form)} \tag{3.7}$$

where Q_{DR} (mmol/g) is the theoretical saturation capacity, β (mol^2/kJ^2) is the constant related to the mean free energy of adsorption per mole of adsorbate. ε is the Polanyi potential which is equal to:

$$\varepsilon = RT \ln \left(1 + \left(\frac{1}{C_e}\right)\right) \tag{3.8}$$

Hence by plotting $\ln q_e$ versus ε^2 it is possible to obtain the value of Q_{DR} from the intercept, and the value of β from the slope. The constant β gives an idea about the Dubinin–Radushkevich mean free energy E_{DR} (kJ/mol) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship:

$$E_{DR} = \frac{1}{\sqrt{2\beta}} \tag{3.9}$$

The mean free energy gives information about the adsorption mechanism: if the value of E_{DR} is between 8 and 16 kJ/mol, the adsorption process followed ion-exchange mechanism, if the value of E_{DR} is less than 8 kJ/mol, the nature of adsorption process is physical [31].

Table 1
Diameter (geometric mean value) of native starch granules in water, characteristics of obtained CCS and amount of Cr(VI) adsorbed onto CCS at equilibrium[a].

Native starch	Diameter of granules in water (μm)	Type of CCS	Diameter of CCS granules in water, (μm)	DS of CCS	Amount of cationic groups in CCS, ($\times 10^{-3}$ equiv./g)	Amount of Cr(VI) adsorbed at equilibrium		EF (equiv./equiv.)
						mmol/g	10^{-3} equiv./g	
Potato	32.3	CCSP	69.9	0.37	1.70	0.625	1.25	0.74
Corn	11.8	CCSC	35.9	0.375	1.71	0.65	1.30	0.76
Wheat A	13.6	CCSWA	42.7	0.37	1.70	0.655	1.31	0.77
Wheat B	7.75	CCSWB	26.6	0.29	1.41	0.57	1.14	0.81

[a] Adsorption temperature 20 °C.

The Temkin adsorption model assumes that adsorption sites in the adsorbent are unequal and have the different adsorption coefficients and adsorption energies [32]. If the adsorption sites to arrange according to decrease in their adsorption energy the change of the Temkin adsorption energy (ΔE_T) will be proportional to the difference of adsorption energy between two neighbouring active sites:

$$E_0 - E_S = S \cdot \Delta E_T \tag{3.10}$$

where E_0 (kJ/mol) is the highest possible adsorption energy of the active site (than $S=0$), E_S (kJ/mol) is the adsorption energy of whatever other active site and S is the place of active site.

The Temkin isotherm equation may be written as [32]:

$$\Theta = \frac{1}{f} \cdot \ln(K_T \cdot C_e) \tag{3.11}$$

where Θ is the fractional coverage, C_e (mol/l) is the equilibrium concentration of the adsorbate, K_T is the Temkin equilibrium constant and f is the Temkin constant related to the heat of adsorption:

$$f = \frac{\Delta E_T}{RT} \tag{3.12}$$

where ΔE_T (J/mol) is the change of the Temkin adsorption energy between two neighbouring adsorption sites, T (K) is the adsorption temperature and R (kJ/mol K) is the universal gas constant.

The linear form of the Temkin isotherm equation is as follows:

$$\Theta = \frac{1}{f} \cdot \ln C_e + \frac{1}{f} \cdot \ln K_T \tag{3.13}$$

Hence by plotting Θ versus $\ln C_e$ it is possible to obtain the value of K_T from the intercept, and the value of f from the slope. The greater are the values of f or ΔE_T, the greater are the differences between the adsorption energy of the neighbouring active sites of adsorbent.

It can be emphasized that Temkin adsorption equation describes the experiment data satisfactorily if the values of Θ are moderate [32].

The average relative error (ARE), in percent, was calculated according to the equation:

$$ARE = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{q_{e_i,\exp} - q_{e_i,calc}}{q_{e_i,\exp}} \right| \tag{3.14}$$

where $q_{e_i,\exp}$ and $q_{e_i,calc}$ are the experimental and the calculated value of the adsorbate concentration in the adsorbent (mmol/g) and N is the number of the data points.

4. Results and discussion

4.1. Adsorption of Cr(VI) on CCS obtained from different native starches

CCS of different granule sizes have been obtained by cross-linking the starches from different botanical sources with EPCH and subsequent cationization with EPTMAC in the presence of NaOH as catalyst. The diameters of granules (in water) of native starches used to obtain CCS are given in Table 1. The potato starch granules are of the largest. Two separate fractions are characteristic of wheat granules according to their size and shape: large, oval type A granules and smaller, more spherical type B granules [33]. The wheat B starch is obtained as by-product in wheat A starch production. Depending on the production conditions wheat B starch could, also, have some amounts of wheat A starch granules. From this point of view the wheat B starch is more polydisperse. The size of modified starch granules depended on the size of native starch granules (see Table 1).

The Cr(VI) was adsorbed onto CCS obtained from potato (CCSP), corn (CCSC), wheat A (CCSWA) and wheat B (CCSWB) starches from the solutions of potassium dichromate. The adsorption proceeded very fast and all content of Cr(VI) was adsorbed during first 5–10 min of the process. In order to allow the adsorption to be completed and to reach the equilibrium the experiment was extended to 60 min.

The DS of CCS along with the amount of cationic groups per gram of adsorbent and the amount of adsorbed Cr(VI) in moles per gram of CCS at equilibrium are presented in Table 1. Furthermore, the amount of adsorbed Cr(VI) is, also, expressed as the number of equivalents of dichromate adsorbed by gram of CCS. Two quaternary ammonium groups participate in the interaction with one dichromate anion. The DS of CCSWB is slightly lower compared to that of CCSP, CCSC or CCSWA. The lower amount of Cr(VI) adsorbed onto CCSWB could be related both to DS and the size of granules. To compare the sorption properties of investigated CCS the value of effectiveness (EF) of cationic groups in the binding of Cr(VI) expressed as an equivalent of dichromate per equivalent of cationic groups was calculated (see Table 1). The value of EF increases with the decrease of CCS granule size. In this case dichromate ions interact with the cationic groups of CCSWB more effectively compared to those of CCS obtained from the potato, corn or wheat A starches.

More information about the driving forces of Cr(VI) adsorption onto CCS could be obtained from the adsorption models suited to describe the adsorption isotherms of Cr(VI) on different CCS. The adsorption isotherms of Cr(VI) on CCSP, CCSC, CCSWA and CCSWB are given in Fig. 1. The symbols in Fig. 1 represent the experimental adsorption values and lines represent the curves fitted according to the Langmuir, Freundlich, Dubinin–Radushkevich and Temkin adsorption models. The calculated values of adsorption model constants along with the values of the linear correlation coefficient (R^2) and average relative error (ARE) are given in Table 2.

The values of R^2 support the fact that the adsorption data closely follow the adsorption model while the value of ARE indicate the quality of the fit between the experimental and predicted data of the adsorption capacity used for the plotting of the isotherm curves. The high values of the correlation coefficient ($R^2 > 0.99$) showed that Langmuir, Dubinin–Radushkevich and Temkin adsorption equations can satisfactorily describe the adsorption of Cr(VI) onto different CCS. Slightly lower R^2 values were obtained in the case of
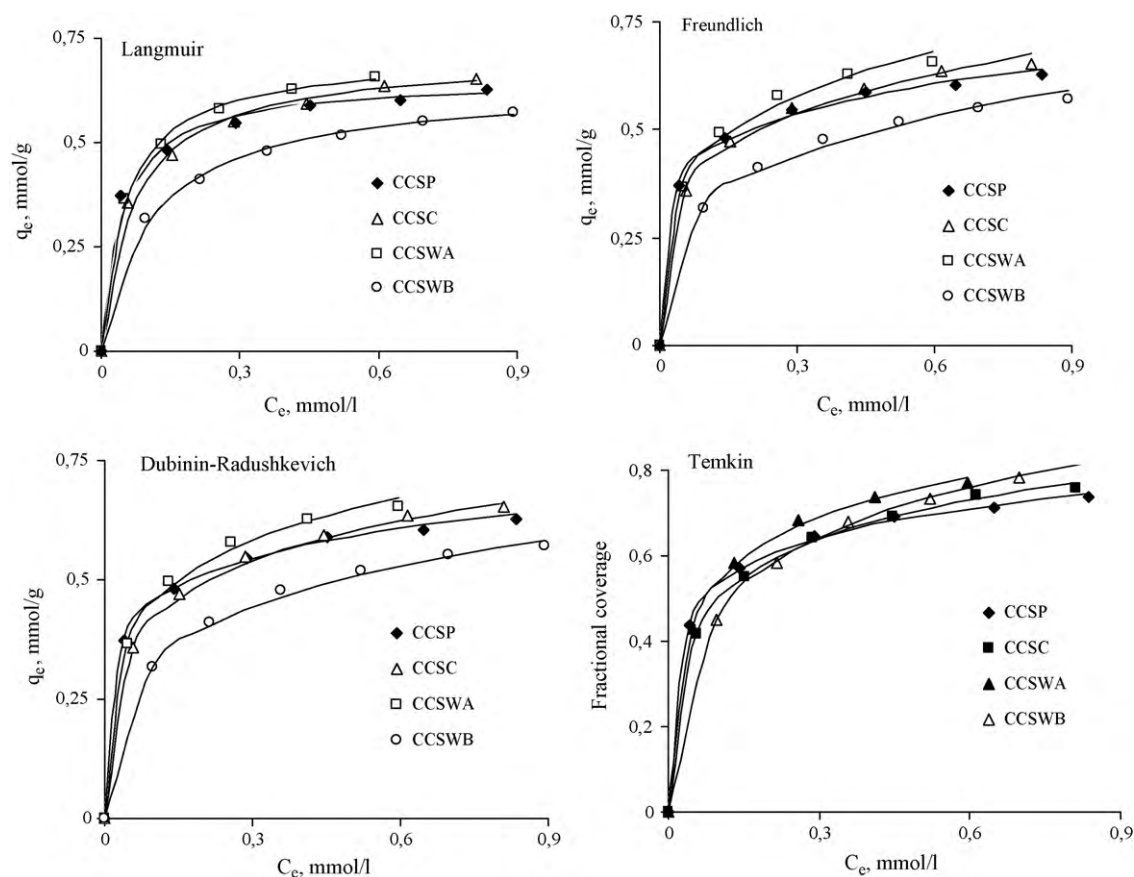
Fig. 1. Adsorption isotherms of Cr(VI) onto CCS obtained from different native starches. The symbols represent experimental data and the lines represent fitted curves of adsorption models. Adsorption temperature 20 °C.

using the Freundlich adsorption model. If to compare the values of *ARE* calculated for the Langmuir and Freundlich adsorption models, the values obtained for the Freundlich model are lower, i.e. the quality of the Freundlich model fits were better. However, the curves

Table 2
Parameters of adsorption models for adsorption of Cr(VI) onto CCS from different native starches at 20 °C.

Parameter	Type of CCS			
	CCSP	CCSC	CCSWA	CCSWB
Langmuir model (first linear equation)				
Q_L (mmol/g)	0.652	0.703	0.708	0.638
K_L (l/mol)	2.2050	1.4260	1.9020	8.890
R_L (C_o = 1 mmol/l)	0.043	0.066	0.050	0.101
EF (equiv./equiv.)	**0.77**	**0.82**	**0.835**	**0.91**
R^2	0.9989	0.9986	0.9994	0.9990
ARE (%)	4.11	3.59	2.32	2.22
Freundlich model				
n_F	**5.77**	**4.39**	**4.26**	**3.74**
K_F (l/mol)	0.0022	0.0034	0.0039	0.0039
R^2	0.9841	0.9869	0.9765	0.9862
ARE (%)	2.23	2.08	2.97	2.07
Dubinin–Radushkevich model				
E_{DR} (kJ/mol)	**17.15**	**14.74**	**14.74**	**13.36**
Q_{DR} (mmol/g)	1.06	1.32	1.43	1.32
R^2	0.9939	0.9950	0.9900	0.9938
ARE (%)	1.39	1.42	2.14	1.52
Temkin model				
f	9.99	7.61	7.25	5.90
ΔE_T (kJ/mol)	**24.30**	**18.50**	**17.70**	**14.40**
R^2	0.9953	0.9975	0.9937	0.9992
ARE (%)	1.02	0.72	1.46	0.66

of the Langmuir isotherms coincided with the experimental results better than in the case of applying Freundlich equation (Fig. 1). It seems likely that values of R^2 in this case can give more information about the suitability of adsorption model than the values of the *ARE*. For the Dubinin–Radushkevich and Temkin adsorption models both values of R^2 and *ARE* indicated the best fitting to the experimental data.

According to the Langmuir adsorption model Cr(VI) was adsorbed on the active centres of CCS, i.e. on quaternary ammonium groups. The driving forces of the adsorption were the electrostatic interactions between these groups and dichromate anions. The values of the Langmuir sorption capacity Q_L and equilibrium constant K_L depended on the kind of CCS used for Cr(VI) adsorption (see Table 2). The highest value of K_L was observed in the case of adsorption onto CCSP. With the decrease of native starch granule size the value of equilibrium constant K_L decreased and the smallest value of K_L was determined for CCSWB. It could be concluded that with the decrease of CCS granule size the difference between the adsorption and desorption rates decreases.

The values of the dimensionless factor R_L calculated from the values of K_L are very low (in the range from 0.043 to 0.101) and show that the adsorption of Cr(VI) onto all investigated CCS is favourable and it could be, also, irreversible.

The values of effectiveness of cationic groups in the binding of Cr(VI) *EF* (Table 2) calculated from the Langmuir sorption capacity Q_L confirmed that cationic groups of CCSWB existing as the smallest granules interact with dichromate anions more effectively. The value of *EF* increases in the following order: CCSP < CCSC < CCSWA < CCSWB.

The constants of other adsorption models threw some light on the Cr(VI) adsorption mechanism and different behaviours of

CCS obtained from different native starches. The mean free energy of adsorption E_{DR} calculated from the Dubinin–Radushkevich isotherm equation gives further information about the adsorption mechanism. The values of E_{DR} are in the range from 13.36 to 17.15 kJ/mol (Table 2) and indicate that the adsorption of Cr(VI) onto all CCS followed ion-exchange mechanism between chloride ion of CCS quaternary ammonium group and dichromate. The ion-exchange mechanism is more predominant than Cr(VI) is adsorbed by CCSP with large granules (E_{DR} = 17.15 kJ/mol). With the decrease of granule size the value of E_{DR} decreases to 13.36–14.74 kJ/mol so the ion-exchange proceeds to less extent. The values of Freundlich constant n_F confirm such presumption. Despite the fact that adsorption of Cr(VI) was favourable independent of the origin of native starch used to obtain the CCS (value of R_L), the adsorption of Cr(VI) onto CCSP was the most favourable (n_F = 5.77). The favourability of adsorption and ion-change increases in the following order: CCSWB < CCSWA ≈ CCSC < CCSP.

The Temkin adsorption model assumes that adsorption sites in the adsorbent are unequal and possess different adsorption coefficients and adsorption energies [32]. If the adsorption sites to arrange according to the decrease in adsorption energy the change of the Temkin adsorption energy ΔE_T will be proportional to the difference of the adsorption energy between two neighbouring active sites. From the chemistry point of view all quaternary ammonium groups in CCS are equal. Consequently the differences in the adsorption energy could be only related with their different locations in the polysaccharides molecule or granule of CCS. When the DS of CCS is the same the increase in the CCS granules size could cause uneven distribution of the quaternary ammonium groups and, subsequently, higher differences in their adsorption energy. The values of ΔE_T given in Table 2 confirm this presumption. The minimal value of ΔE_T was obtained when Cr(VI) was adsorbed on CCSWB and the amount of adsorbed chromium ions was the largest. Therefore it could be concluded that the more equal is the distribution of the adsorption energy of the quaternary ammonium groups in CCS granule (the less value of ΔE_T) the greater is the amount of Cr(VI) adsorbed onto CCS.

4.2. Influence of cationization catalyst on adsorption properties of CCS

Cationization reaction of starch using EPTMAC could be catalyzed both with inorganic and organic bases. When organic bases were used as catalysts in the reaction of cellulose with epoxy compounds the area of amorphous sites in the modified cellulose
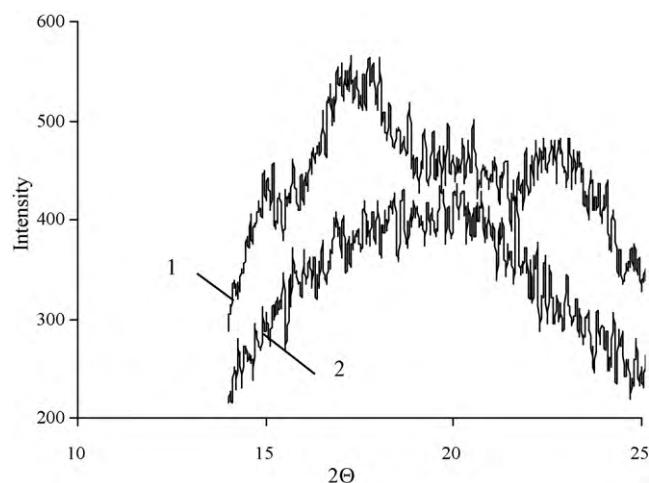

Fig. 2. X-ray diffraction spectra of CCS samples obtained by using different catalysts: 1 – CCSP, DS = 0.37 (NaOH as catalyst); 2 – CCSPO, DS = 0.39 (BTMAOH as catalyst).

increased compared to that obtained by the use of NaOH as catalyst [34]. BTMAOH has been used as catalyst in cationization reaction of cross-linked potato starch with EPTMAC. Obtained cationic starch derivative with DS = 0.39 was named as CCSPO. The X-ray diffraction spectra can give information about the changes in the quantity of the amorphous parts in modified polysaccharide granules. As could be seen from Fig. 2 in the X-ray diffraction spectra of CCSPO there were no peaks at 2θ about 17–18° and 23° associated with the crystalline regions of starch granules as distinct from the X-ray diffraction spectra of CCSP obtained by using NaOH as catalyst. Therefore the differences in the amount of amorphous sites in modified starch granules could have an influence on the adsorption properties of CCS.

The experimental adsorption isotherms of Cr(VI) onto the CCSPO were obtained (see Fig. 3). Alongside the parameters of adsorption models were calculated and presented in Table 3. By comparing the values of adsorption models parameters calculated for the adsorption of Cr(VI) onto CCSPO (Table 3) and CCSP (Table 2) the remarkable differences were observed. The Langmuir adsorption model describes the adsorption of Cr(VI) on CCSPO particularly well. The fits of Freundlich and Dubinin–Radushkevich models were much worse when comparing with the adsorption of Cr(VI) onto CCSP. Meanwhile the Temkin adsorption model described the adsorption of Cr(VI) on both CCSP and CCSPO with the same approximation.
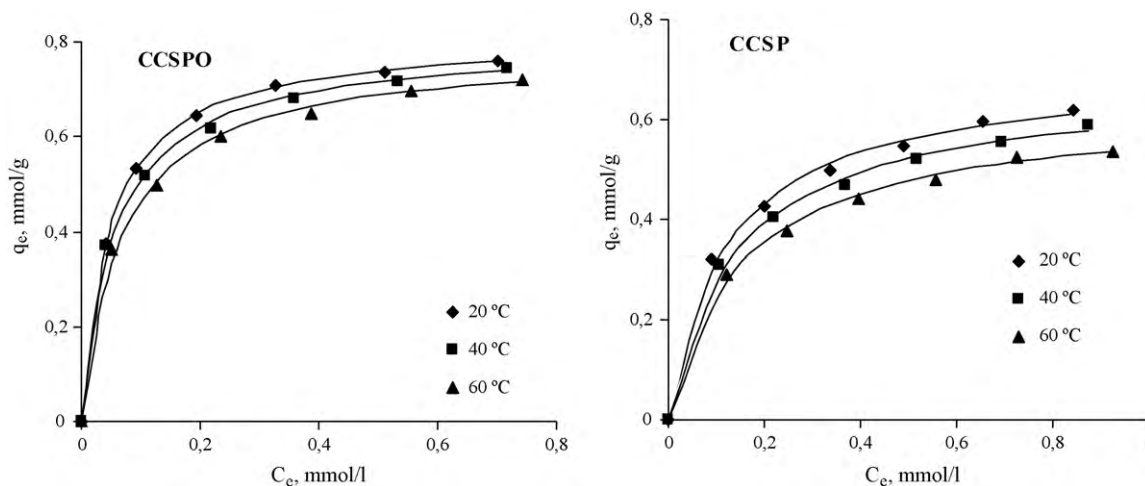

Fig. 3. Adsorption isotherms of Cr(VI) onto CCSPO (DS = 0.39) and CCSP (DS = 0.37) at different temperatures. The symbols represent experimental data and the lines represent fitted curves of the Langmuir model.

Table 3
Parameters of adsorption models for adsorption of Cr(VI) onto CCSPO (DS = 0.39) at 20 °C.

Langmuir					Freundlich		Dubinin–Radushkevich		Temkin	
Q_L (mmol/g)	K_L (l/mol)	EF (equiv./equiv)	R^2	ARE (%)	n_F	R^2	E_{DR} (kJ/mol)	R^2	ΔE_T (kJ/mol)	R^2
0.81	20460	0.92	1	0.4	3.74	0.9288	14.43	0.9508	13.20	0.9919

Although the values of Langmuir equilibrium constant K_L were similar for Cr(VI) adsorption onto both CCSPO and CCSP, the Langmuir sorption capacity Q_L and effectiveness of cationic groups EF values were much higher in the case of Cr(VI) adsorption onto the CCSPO. From lower values of the Dubinin–Radushkevich adsorption energy E_{DR} and the Freundlich constant n_F it could be predicted that adsorption and ion-exchange proceeded with difficulties when Cr(VI) was adsorbed onto CCSPO. ΔE_T value was 13.2 kJ/mol for the adsorption of Cr(VI) onto the CCSPO and 17.15 kJ/mol in the case of adsorption onto the CCSP. It is obvious that the differences in adsorption energy of quaternary ammonium groups in the amorphous granule of CCSPO are smaller.

These data confirmed the presumption that the more evenly quaternary ammonium groups are distributed in the granule of CCS according to their adsorption energy as indicated by Temkin adsorption model, the more effectively they participate in the adsorption of Cr(VI). One of the ways to increase sorption capacity of CCS is to increase the number of amorphous sites in modified starch granules; another way is to produce the adsorbents by modifying the native starch with smaller granules.

4.3. Adsorption thermodynamics

Essential factor that could give the information about adsorption process is the temperature. The adsorption isotherms of Cr(VI) onto CCSP and CCSPO at different temperatures are presented in Fig. 3 and show that with the increase of temperature the amount of Cr(VI) adsorbed at equilibrium onto both CCS decreases. However, the amount of Cr(VI) adsorbed onto CCSPO is higher compared to that adsorbed onto CCSP. The same tendency at all investigated temperatures was observed. The decrease of adsorption capacity with the increase of temperature is due to enhancement of the mobility of interacting species and as a consequence the equilibrium is shifted towards desorption. Such kind of adsorption is especially typical for the chemosorption.

The changes in free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were determined using the following equations:

$$K_C = \frac{C_{Ae}}{C_e}, \tag{4.1}$$

$$\Delta G° = -RT \ln K_C, \tag{4.2}$$

$$\ln K_C = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT}, \tag{4.3}$$

where K_C is the thermodynamic distribution constant, C_{Ae} is the amount of Cr(VI) adsorbed on CCS per dm^3 of the solution at equilibrium (mol/l), C_e is the equilibrium concentration of Cr(VI) in solution and T is the solution temperature in K.

The thermodynamic distribution constant K_C was determined by linear regression analysis of $\ln q_e/C_e$ versus q_e [35]. The intersection of the straight lines (data not shown) with the vertical axis gives the value of $\ln K_C$. $\Delta H°$ and $\Delta S°$ were calculated from the slope and intercept of plots of $\ln K_C$ versus $1/T$. The calculated thermodynamic parameters along with the values of correlation coefficients are presented in Table 4.

Values of change in free energy $\Delta G°$ give some information about affinity of adsorbate to adsorbent and driving forces of adsorption. The more the negative value of $\Delta G°$ the larger is the affinity and more spontaneously the adsorption proceeds. Presented data (Table 4) indicate that the distribution constant K_C values were 4.5–8.5 times higher and $\Delta G°$ values were 1.6–1.7 times higher for dichromate anions adsorption onto CCSPO compared to those for CCSP. Consequently, the affinity of dichromate anions increases when Cr(VI) is adsorbed onto modified starch granules with a higher number of amorphous regions. Also, adsorption of Cr(VI) onto CCSPO is more exothermic as witnessed by higher negative value of $\Delta H°$ and the order of system undergoes the major changes during adsorption as indicated by higher negative value of $\Delta S°$. For this reason the CCSPO obtained using BTMAOH as catalyst had higher adsorption capacity for Cr(VI) ions. However, BTMAOH is more expensive comparing with NaOH and the price of starch adsorbents would be higher.

4.4. Removal and recovery of Cr(VI) from wastewater of plating bath

Unlike the modelling solutions containing only potassium dichromate, real plating wastewater contains both Cr(VI) and Cr(III) ions and some other additives. Besides that, both concentration of Cr(VI) and acidity of plating wastewater is very high. For laboratory scale experiments the wastewater of plating baths from kinescope producer "Panevezio Ekranas" (Lithuania) was obtained. The concentration of Cr(VI) in wastewater was 2788 mg/l, meanwhile, the pH was 1.75. For the removal of such a huge amount of Cr(VI) the larger amount of CCSP (DS = 0.33) should be used. For comparison the adsorption of Cr(VI) from the model solution of potassium dichromate was performed. The data presented in Table 5 show that about 95% of Cr(VI), i.e. 2632 mg from one litre of wastewater could be adsorbed onto CCSP from the plating waste but effectiveness of cationic groups in Cr(VI) binding is lower compared to adsorption from the model dichromate solution.

Table 4
Thermodynamic parameters of Cr(VI) adsorption onto CCSP and CCSPO.

Temperature (°C)	$\ln K_C$	K_C	R^2	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol K)	R^2
CCSP (DS = 0.37)							
20	2.99	20.0	0.9961	−7.3			
40	2.75	15.6	0.9980	−7.15	−10.2	−9.9	0.9981
60	2.49	12.1	0.9872	−6.95			
CCSPO (DS = 0.39)							
20	5.15	173	0.9593	−12.6			
40	4.38	80	0.9781	−11.4	−23.3	−37.0	0.9736
60	4.01	55	0.9755	−11.1			

Table 5
Adsorption of Cr(VI) onto CCSP (DS = 0.33) from plating wastewater and model dichromate solution.

Parameter	The source of Cr(VI)	
	Model dichromate solution	Wastewater of plating bath
Amount of CCSP (g/l)	1	50
Initial amount of Cr(VI) in solution (mg/l)	88	2788
Amount of Cr(VI) in solution after adsorption (mg/l)	22	156
Adsorbed amount of Cr(VI) (%)	75	94
Adsorbed amount of Cr(VI) (mg/g)	66	53
EF (equiv./equiv.)	0.84	0.65

Table 6
Quantities of recovered Cr(VI) using different recovery methods.

Recovery method	The source of Cr(VI)	Adsorbed amount of Cr(VI) (mg/g)	Recovered amount (mg)		Recovered amount (%)	
			Cr(VI)	Cr(III)	Cr(VI)	Cr(III)
Concentrated H_2SO_4	Model solution	66	0.7	26	1	39
	Plating wastewater	53	0.7	39	1	74
Incineration at 800 °C	Model solution	66	55	11	83	14
	Plating wastewater	53	51	2	95	4

The price of adsorbent markedly depends on the possibility to regenerate it. Meanwhile Cr(VI) is extremely toxic and exhibits carcinogenic effects on biological systems. For this reason, regeneration of Cr(VI) is more attractive comparing with the regeneration of the adsorbent. Some attempts were done to regenerate the Cr(VI) after adsorption onto CCSP. Two different recovery methods were used. By using the first one, CCSP with adsorbed Cr(VI) was degraded by boiling in concentrated sulphuric acid. In the second method CCSP was incinerated at 800 °C temperature. In the latter case CCSP was degraded to carbon, hydrogen and nitrogen oxides and Cr(VI) anhydride was left in the dry rest. The amount of recovered Cr(VI) and Cr(III) was determined either in the solution of sulphuric acid or after the dissolution of dry content in distilled water.

The amount of recovered Cr(VI) depends on the recovery method and the solution (model or plating waste) from which it was adsorbed by CCSP (see Table 6). Cr(VI) was regenerated more effectively by mineralization method following the adsorption of heavy metal ions from the plating wastewater. In this case the amount of 95% of Cr(VI) was regenerated, 4% of chromium was reduced to Cr(III) and only 1% was lost.

5. Conclusions

The influence of cationic cross-linked starch (CCS) granule size and the amount of amorphous sites in CCS granule on the adsorption of Cr(VI) onto CCS have been investigated. CCS granule size depended on the botanical source of starch used in the cationic modification. Potato, corn, type A and type B wheat starches have been used to obtain CCS. Number of amorphous sites in CCS granule depended on the type of catalyst used in cationization. By the use of organic base – benzyltrimethylammonium hydroxide (BTMAOH) as catalyst the number of amorphous sites in CCS increased in comparison with CCS obtained using NaOH as catalyst.

The Langmuir, Freundlich, Dubinin–Radushkevich and Temkin models have been used to describe the equilibrium adsorption of Cr(VI) onto CCS. The Langmuir, Dubinin–Radushkevich and Temkin models indicated the best fitting to the experimental data. Meanwhile the quality of the fits of Freundlich adsorption model was lower.

According to the increase of granule size and, thus, favour the adsorption of Cr(VI) and ion-exchange to proceed, CCS could be arranged in the following order: obtained from type B wheat starch < obtained from type A wheat starch ≈ CCS obtained from corn starch < CCS obtained from potato starch. According to the increase of effectiveness of CCS cationic groups in the binding of dichromate anions (*EF*), expressed as an equivalent of dichromate per equivalent of cationic groups and calculated from the Langmuir sorption capacity data, CCS could be arranged in the following order: CCS obtained from potato starch < CCS obtained from type A wheat starch < CCS obtained from corn starch < CCS obtained from type B wheat starch.

The more equal is the adsorption energy of the quaternary ammonium groups in CCS granules as indicated by low value of change of Temkin adsorption energy ΔE_T the greater is the amount of Cr(VI) adsorbed onto CCS. From the chemistry point of view all quaternary ammonium groups in CCS are equal. The differences in the adsorption energy could be related to their location in the polysaccharides molecules or CCS granules. The increase in CCS granule size could cause uneven distribution of the quaternary ammonium groups and higher differences in their adsorption energy.

The more equal distribution of quaternary ammonium groups according to their adsorption energy was achieved by the increase of content of amorphous parts in CCS granule and the sorption capacity and *EF* of CCS has been increased. At the same time the affinity of dichromate anions to CCS increased and the adsorption of Cr(VI) proceeded more spontaneously as indicated by the higher negative value of $\Delta G°$. The adsorption of Cr(VI) onto amorphous granules CCS was more exothermic as witnessed by higher negative value of $\Delta H°$ and the order of system undergoes the major changes during adsorption as indicated by higher negative value of $\Delta S°$.

In laboratory scale experiments Cr(VI) was adsorbed onto CCS from wastewater of plating bath and regenerated by using two methods: boiling of CCS with adsorbed Cr(VI) in concentrated sulphuric acid and incineration at 800 °C temperature. After incineration the amount of 95% of Cr(VI) was regenerated as chromium anhydride, 4% of chromium was reduced to Cr(III) and only 1% was lost.

Acknowledgement

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