

Adsorption of Hexavalent Chromium on Cationic Starches with Different Degree of Crosslinking

D. Sidlauskienė, R. Klimaviciute, A. Zemaitaitis

Kaunas University of Technology, Radvilenu 19, LT-50254 Kaunas

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ABSTRACT: The influence of the degree of crosslinking in the association with the degree of cationization on the adsorption of Cr(VI) by crosslinked cationic starches (CCS) was examined. The amount of adsorbed Cr(VI) depends on the preparation of CCS before adsorption experiments (dry or preswollen CCS) and has a higher value when dry CCS are used. The amount of crosslinks in CCS needed to reach the maximum effectiveness of the cationic groups of CCS in the binding of Cr(VI) depends also on the form in which CCS are used. The adsorption capacity for Cr(VI) decreases both with dry and preswollen CCS when the adsorption temperature increases. The thermodynamic parameters are

calculated. The negative values of ΔG° and ΔH° indicated that the adsorption process in both cases was spontaneous and exothermic. If preswollen CCS is used, the entropy change has a positive value and indicates that the randomness of the system increases, whereas the negative value of entropy change when Cr(VI) species are adsorbed by dry CCS shows that in this case the order of the system increases like in the classical adsorption process. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3469–3475, 2008

Key words: cationic crosslinked starch; hexavalent chromium; adsorption

INTRODUCTION

One of the major toxic metal ions endangering human life is hexavalent chromium Cr(VI) which is released because of the extensive use of chromate and dichromate in metal plating. Thus, Cr(VI) removal from wastewater has become an important and widely studied area where a number of technologies have been developed. The conventional process used to remove Cr(VI) is its reduction and precipitation as chromium (III) hydroxide.^{1–3} This process 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 can remove and recover Cr(VI) economically.

Adsorption has been one of the methods used to remove chromium species from aqueous solutions. Cr(VI) species may be in the form of dichromate ($\text{Cr}_2\text{O}_7^{2-}$), hydrochromate (HCrO_4^-), or chromate (CrO_4^{2-}) in a solution of different pH values.⁴

There are many types of adsorbents, including activated carbons,^{5–7} biomaterials,^{8–10} wine processing¹¹ and distillery¹² sludge, residual lignin,¹³ formaldehyde-treated sawdust¹⁴ and amine-modified polyacrylamide-grafted coconut¹⁵ that have been studied for the adsorption of chromium from aqueous solutions. However, some of these adsorbents do not have high adsorption capacities, need a long adsorption equilibrium time or adsorb chromium only from strong acid solutions. The results¹⁶ show that significant amounts of Cr(III) or Cr(VI) species can be adsorbed by aminated polyacrylonitrile fibres, although the adsorption performances were greatly dependent upon the pH value of solution. Cr(III) species were adsorbed due to the formation of surface complexes with the nitrogen atom of fibre, and the adsorption increased with increasing solution pH values, while Cr(VI) species are adsorbed due to the formation of hydrogen bonds at high pH values of solution or both electrostatic attraction and surface complexation at low pH values of solution. It has been found⁴ that biopolymeric beads composed of crosslinked sodium alginate and crosslinked gelatine are an effective adsorbent for the removal of dichromate ions from aqueous solutions. The chemical composition of beads greatly influences their adsorption capacity. The adsorption of Cr(VI) increases with the increasing concentrations of sodium alginate, gelatine, and glutaraldehyde, it is quite sensitive to the pH of a suspension and shows an optimum uptake value at pH 8.9, which is identical to

Correspondence to: R. Klimaviciute (rimakli@ktu.lt).

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the isoelectric point of gelatine. Chitosan-based polymeric surfactants prepared by partial *N*-acylation of amine groups on chitosan with acid anhydrides were also used for the removal of Cr(VI) from wastewater.¹⁷ The removal efficiency depended on the pH and ionic strength of solution and the adsorbent dose. The maximum adsorption capacity of Cr(VI) was 180 mg/g at a final pH of 5.3.

Starch is a low-cost natural renewable polymer that can be highly crosslinked with epichlorohydrin or other agents to make them water-insoluble and modified with various reagents yields ionic products that can be used to remove heavy metal ions from wastewater. It has been indicated¹⁸ that water insoluble crosslinked amphoteric starch containing phosphate groups and tertiary amine groups can remove Cr(VI), Pb²⁺ 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 crosslinked starches with cationic quaternary ammonium and anionic carboxymethyl groups was also investigated.¹⁹ The adsorption process was found to follow the Langmuir isotherm, to be dependent on initial pH, Cr(VI) concentration, adsorbent dose, temperature, and was exothermic. The adsorption capacity decreased with increasing the degree of substitution of anionic groups.

From this point of view, crosslinked and only cationized starches are more favourable for the adsorption of Cr(VI) species. Chan and Ferng²⁰ investigated dynamic adsorption behaviors between Cr(VI) ion and water-insoluble cationic starches with tertiary amine groups and found the sorption process to proceed in two stages: the external mass transport occurs in the early stage and the intraparticle diffusion process in the long-time stage. The external mass transport is an endothermic process while the intraparticle diffusion is exothermic. The adsorption of Cr(VI) on crosslinked cationic starches with quaternary ammonium groups was investigated by Xu et al.²¹ 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 adsorbents and adsorption temperature. The adsorption reaches equilibrium in a short time and follows the Langmuir isotherm. The adsorption capacity increases with increasing the amount of cationic groups. An adsorption thermodynamics study shows that adsorption processes are exothermic and lower temperature favors the adsorption of Cr(VI).

There are some works to examine the adsorption behavior of crosslinked cationic or amphoteric starches; however, there is no evidence of the influence of crosslinking on the adsorption capacity of such derivatives. Crosslinking drastically reduces segment mobility in the polymer, and a three-dimensional

network is formed. If the degree of reticulation is sufficiently high, the matrix of the polymers becomes insoluble but swellable in water. The two most important factors controlling the extent of adsorption properties of polysaccharide-based materials are the hydrophilicity of the polymer and the crosslink density.²² After crosslinking materials become more resistant to shear, high temperature and low pH compared with their parent polysaccharide.²³ Crosslinking reduces the amount of crystalline domains in the polysaccharide and can change the crystalline nature of the raw polymer. This parameter significantly influences the sorption properties, because it may control the accessibility of sorption sites.²³

The present work examines the influence of the degree of crosslinking in association with the degree of cationization on the adsorption of hexavalent chromium by crosslinked cationic starches (CCS). In addition, the effect of the preparation of CCS before adsorption experiments and temperature on the adsorption capacity has been investigated.

MATERIALS AND METHODS

Materials

The Antanavas Starch Plant (Lithuania) supplied native potato starch (intrinsic viscosity $[\eta] = 0.39 \times 10^3$ mL/g). The reagents (2,3-epoxypropyltrimethylammonium chloride and epichlorohydrin) were purchased from Fluka.

Preparation of CCS or CS

The molecular mass of the anhydroglucoside unit (AGU) was taken as a mole of starch. The potato starch was crosslinked with different amounts (0.002–0.2 mol/AGU) of epichlorohydrin (EPCH) in the presence of sodium hydroxide, washed with cold water, and then cationized with 2,3-epoxypropyltrimethylammonium chloride in the presence of sodium hydroxide (the molar ratio AGU : epoxide : NaOH was 1 : (0.4–0.7) : 0.04) at 45°C for 3–24 h. Only cationized starch (CS) was obtained by the cationization of native potato starch in the same conditions.

The amount of cationic groups in CS or CCS was expressed as the degree of substitution (DS) that was calculated from the nitrogen content estimated by the Kjeldahl method after purification by Soxhlet extraction with methanol for 16 h.

Crosslinked starch obtained in the reaction of starch with EPCH contains only glucose units and hydroxyalkyl groups and it is very difficult to determine the amount of formed crosslinks. In works²⁴ it is shown that the bigger amount of EPCH added during the synthesis, the more extensive crosslinking reaction is taking place. For this reason the degree of

CCS crosslinking was expressed as the amount of EPCH used in the crosslinking reaction.^{25,26}

Equilibrium adsorption studies

Cr(VI) solutions were prepared from the fixanal of K₂Cr₂O₇ by dilution with distilled water to required concentrations. The pH of Cr(VI) solutions was from 5.3 to 5.4 in all experiments.

In experiments with dry CS or CCS, 0.1 g dry basis of material was placed in an Erlenmeyer flask, poured over with 100 cm³ Cr(VI) solution of a desired concentration, stoppered, and shaken for 60 min at a desired temperature (with temperature control ± 1°C) in a thermostating water bath with fixed shaking (Memmert GmbH, Germany). After that the mixture was filtered through paper filter and the residual concentration of Cr(VI) was determined.

In experiments with preswollen CS or CCS, 20 mL of suspension containing 0.1 g dry basis of material was added to 100 cm³ Cr(VI) solution of a desired concentration and after that the experiment was carried out in the same manner as above. Suspension of CS or CCS were prepared by stirring for 60 min at room temperature and used after 24 h.

Determination of Cr(VI) content

The Cr(VI) content was determined spectrophotometrically at 540 nm, following the 1,5-diphenyl-carbazide method accredited in Lithuania.²⁷

Measurement of particles size

The size distribution of CCS or CS particles was measured with a COULTER LS200 Particle Size Analyzer equipped with a Coulter Fluid Module (Beckman Coulter, USA). The results were expressed as a geometric mean value of the particle diameter.

Determination of water or solution retention

The precisely weighed amount of CCS or CS (0.25 g of dry basis) was suspended in 20 mL of distilled water and for 30 min stirred at room temperature (20°C). In another experiment, a solution of 50 mmol/L NaCl or 25 mmol/L dichromate was used instead of distilled water. After that, the samples were centrifuged at 3000 × g for 10 min. The supernatant was removed carefully and a sample of CCS or CS with adsorbed water or solution was weighed. The retention of a liquid (RS, g/g) was calculated according to the equation:

$$RS = \frac{(W_2 - W_1)}{W_1}, \quad (1)$$

where W₂ is the weight of a starch sample after supernatant removal, g, and W₁ is the weight of dry starch, g.

RESULTS AND DISCUSSION

Influence of the preparation of cationic starches before adsorption experiments

Chromium adsorption by cationic crosslinked starch (CCS) was examined from aqueous solutions containing Cr(VI) as potassium dichromate. Adsorption experiments were made with CCS having different DS according to cationic groups and a different degree of crosslinking, expressed as the amount of EPCH, mol/AGU, used in the crosslinking reaction. In some experiments only CS was used.

From the practical and economical points of view, dry CCS is more suitable as an adsorbent. But in cold water CCS exists in the form of swollen particles, and it is possible that these swollen particles may adsorb Cr(VI) more easily. For this reason, the influence of the preparation of CCS before adsorption experiments (dry or preswollen) on Cr(VI) adsorption on CCS was examined. The adsorption isotherms were obtained and shown in Figure 1. In this figure, adsorption isotherms obtained with dry and preswollen CS are also presented. It may be noted that the amount of adsorbed Cr(VI) has a higher value when dry cationic starches are used, especially with CS or CCS with a smaller amount of crosslinks. When the degree of crosslinking increases, the difference between the amounts of Cr(VI) adsorbed by dry and preswollen CCS decreases.

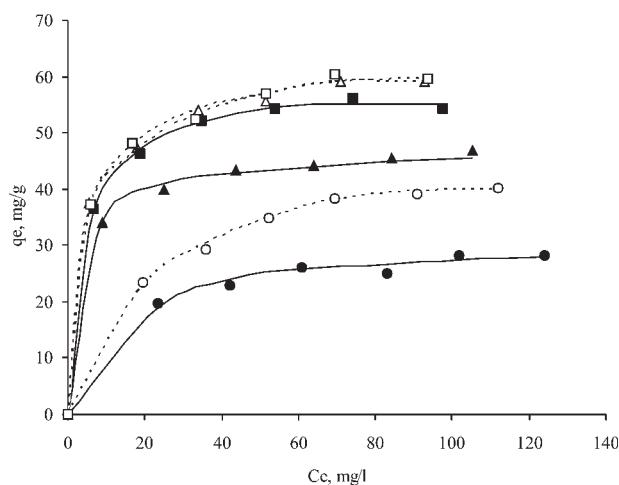


Figure 1 Experimental adsorption isotherms of Cr(VI) on modified starch with DS = 0.36: (●) and (○)—CS; (▲) and (△)—CCS (0.02 mol EPCH/AGU); (■) and (□)—CCS (0.05 mol EPCH/AGU). Solid line represents preswollen and dotted line dry CCS. Temperature 20°C.

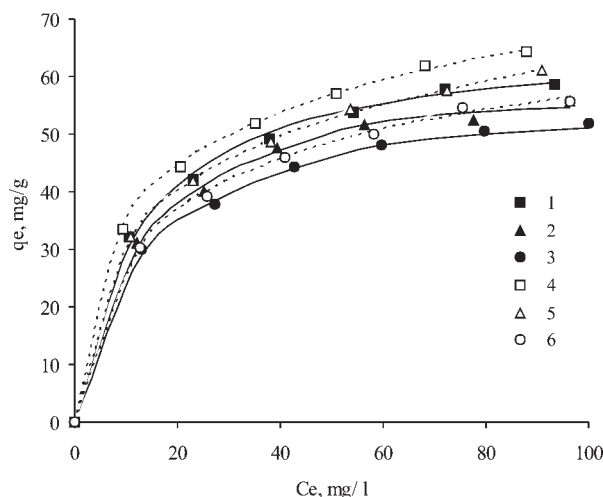


Figure 2 Adsorption isotherms of Cr(VI) on CCS when preswollen (1–3) and dry (4–6) CCS are used: 1, 4—at 20°C; 2, 5—at 40°C; 3, 6—at 60°C. DS of CCS is 0.36; amount of EPCH used for crosslinking is 0.02 mol EPCH/AGU.

One of the factors that can explain the differences in the adsorption capacity of dry and preswollen CCS is the adsorption temperature. Figure 2 displays the adsorption isotherms of Cr(VI) on CCS obtained at the different temperatures and shows that the adsorption of Cr(VI) by CCS decreases with an increase in adsorption temperature. But amount of adsorbed Cr(VI) by dry CCS is higher at all investigated temperatures.

Xu et al.²¹ have shown that adsorption of Cr(VI) by CCS follows the Langmuir adsorption model. The Langmuir linear eq. (2) was applied to the experimental adsorption isotherms:

$$\frac{C_e}{q_e} = \frac{1}{Q_o \cdot b} + \frac{C_e}{Q_o}, \quad (2)$$

where Q_o (g/kg or mol/kg) is the maximum amount of Cr(VI) adsorbed per unit weight of cationic starch (Langmuir adsorption capacity) at a high equilibrium Cr(VI) concentration C_e , q_e is the amount of Cr(VI) adsorbed by cationic starch at equilibrium, and b is the Langmuir constant related to the affinity of the binding sites. Q_o values were calculated from

the slope of the linear plots of C_e/q_e versus C_e with a correlation coefficient more than 0.99 and are presented in Table I. The results have shown that the adsorption capacity Q_o decreases both with dry and preswollen CCS when the adsorption temperature increases from 20 to 60°C. But at all temperatures the adsorption capacities obtained with dry CCS have higher values.

To gain an insight into the thermodynamic nature of the adsorption process, changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined using the following equations:

$$K_C = \frac{C_{Ae}}{C_e}, \quad (3)$$

$$\Delta G^\circ = -RT \ln K_C, \quad (4)$$

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}, \quad (5)$$

where K_C is the thermodynamic equilibrium constant, C_{Ae} is the amount of Cr(VI) adsorbed on CCS per dm³ of the solution at equilibrium, C_e is the equilibrium concentration of Cr(VI) in solution, T is the solution temperature in K.

The thermodynamic equilibrium constant K_C for the adsorption process was determined by linear regression analysis of $\ln q_e/C_e$ vs. q_e .²⁸ The intersection of the straight lines with the vertical axis gives the value of $\ln K_C$. ΔH° and ΔS° were calculated from the slope and intercept of plots of $\ln K_C$ vs. $1/T$ (a correlation coefficient more than 0.99). The calculated thermodynamic parameters are presented in Table I and might shed some light on the differences in Cr(VI) adsorption by dry and preswollen CCS. The negative values of ΔG° indicate that the adsorption process in both cases is spontaneous. The change in the enthalpy is negative in both cases also and shows that adsorption of Cr(VI) by CCS is exothermic. But the absolute value of ΔH° calculated for preswollen particles of CCS is twice as low as that obtained with dry particles of CCS. Moreover, if preswollen CCS is used for Cr(VI) adsorption, the en-

TABLE I
Thermodynamic Parameters for Cr(VI) Adsorption by Dry and Preswollen CCS with DS 0.36

T , (°C)	Dry				Preswollen			
	Q_o , (mg/g)	ΔG° , (kJ/mol)	ΔH° , (kJ/mol)	ΔS° , [J/(mol K)]	Q_o , mg/g	ΔG° , (kJ/mol)	ΔH° , (kJ/mol)	ΔS° , [J/(mol K)]
20	73.5	-7.2			67.1	-7.2		
40	70	-7.1	-10.1	-9.8	62.5	-7.3	-5.2	+6.6
60	65.4	-6.8			58.5	-7.4		

The amount of EPCH was 0.02 mol/AGU.

TABLE II
Influence of the Amount of EPCH used in Crosslinking Reaction on the Size of CCS Particles in Water

Amount of EPCH, mol/AGU	Particle diameter (geometric mean value), μm , measured according to			
	Volume		Number	
	DS = 0.22	DS = 0.36	DS = 0.22	DS = 0.36
0.002	185	194	17	21
0.02	151	163	11	7.8
0.05	94	99	5.4	5.2
0.1	75	80	3.3	3.3
0.15	64	79	3.8	2.8
0.2	82	75	3.0	2.8

tropy change has a positive value and indicates that the randomness of the system increases, whereas the negative value of the entropy change when Cr(VI) species are adsorbed by dry CCS shows that in this case the order of the system increases. The presented thermodynamic parameters unambiguously indicate that Cr(VI) adsorption by dry CCS particles is more efficient than by preswollen ones.

As in Ref. 21, we have noted that the adsorption of dichromate by CCS occurs very quickly. During the first 5 min the maximum adsorption occurred (data not shown). As one might expect, the cationic groups in the large preswollen particles of CCS are hydrated, and it is difficult for dichromate anions to approach them. When dry CCS is used for adsorption, dichromate anions do not compete with water molecules and adsorption occurs more easily. This might explain the difference in the change of enthalpy (Table I). In the case of preswollen CCS it is less than in the case of dry CCS, therefore Cr(VI) adsorption by dry CCS is preferable.

On the other hand, adsorption of dichromate anions on large swollen CCS particles could release great amounts of water molecules and disturb their order in the environment. This can explain the positive changes of entropy (Table I) in the case of Cr(VI) adsorption by preswollen CCS particles. When Cr(VI) is adsorbed by dry CCS, the order of the system, as in the classical adsorption process increases, and the change of entropy is negative.

Influence of crosslinking degree on CCS particle size in water, liquids retention, and dichromate adsorption

One of the reasons for the different adsorption behavior might be the different particle size of dry and preswollen CCS in initial stages of adsorption. On the other hand, the particle size of CCS in water depends on the amount of crosslinks. The size distribution of CCS particles in water according to the volume and number of particles was measured and expressed as a geometric mean value of the particle

diameter. The obtained results are presented in Table II. The particle diameter measured according to the volume characterizes the size of the large particles, while the particle size measured according to the number of particles characterizes the size of the small ones. As one can see in Table II, with increasing the amount of the crosslinks the size of both large and small swollen particles of CCS decreases.

The influence of the amount of EPCH used in the crosslinking reaction on the retention of water or dichromate or sodium chloride solution by CCS with DS = 0.36 was determined (Fig. 3). The results show that with increasing amount of crosslinks, CCS particles swell less and can contain a less amount of water or electrolyte solution. The retention of water by CCS is stronger than the retention of the dichromate solution, but this difference decreases with an increase of crosslinks in CCS. The retention of dichromate and NaCl solutions is similar. Both dichromate and NaCl act as an electrolyte causing contraction of swollen CCS particles. However, dif-

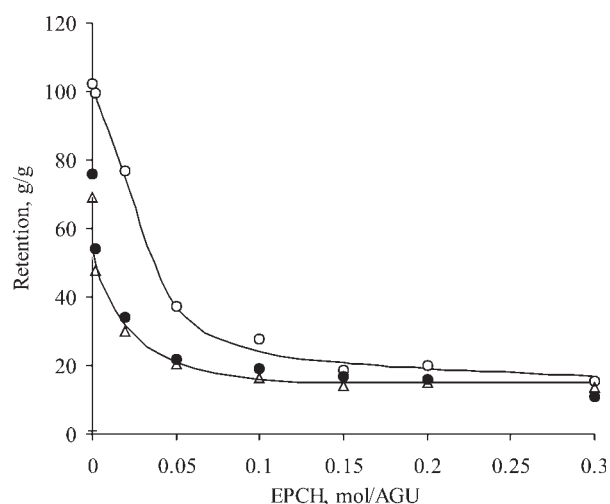


Figure 3 Influence of the amount of EPCH used in the crosslinking reaction on the retention of water (○) and dichromate (●) or NaCl (△) solutions by CCS with DS = 0.36. Temperature 20°C.

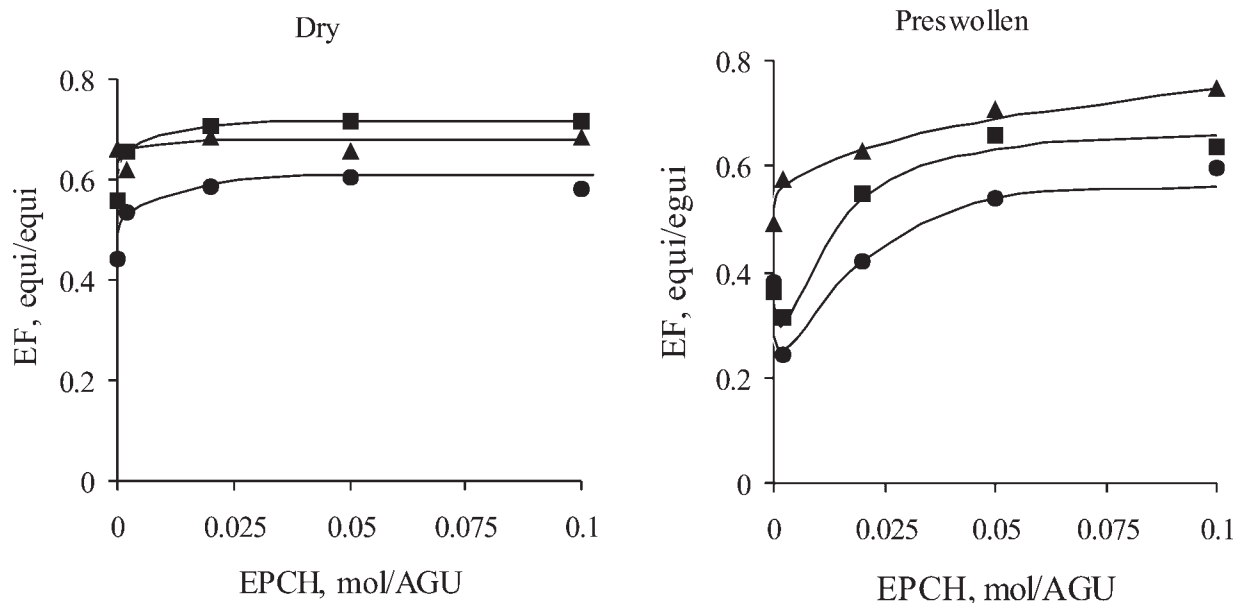


Figure 4 Influence of the amount of cross-linking agent on the effectiveness (EF) of CCS with DS: (●)—0.2; (■)—0.36; (▲)—0.47. Adsorption temperature 20°C.

ferently from NaCl, dichromate anions are adsorbed by cationic groups of CCS immediately.

Experiments of adsorption of dichromate anions by dry and preswollen CCS with different DS and a different degree of crosslinking were made and the adsorption isotherms were obtained from which the Langmuir adsorption capacities were determined. The effectiveness (EF) of cationic groups in the binding of Cr(VI), expressed as an equivalent of dichromate per equivalent of cationic groups, was calculated from Q_0 values and presented in Figure 4.

A comparison of Figure 3 and curve represented the Cr(VI) adsorption by preswollen CCS with DS = 0.36 in Figure 4 indicates that cationic starches with a low reticulation soak much more dichromate anions than can be adsorbed. With an increase of the crosslinks, the adsorbed amount of dichromate is much higher than the soaked one and indicates that chemisorption prevails.

The amount of crosslinks in CCS needed to reach the maximum EF of CCS in the binding of dichromate anions depends on the form in which CCS are used. In the case of dry CCS, 0.02 mol/AGU of EPCH is enough to reach the best adsorption of Cr(IV) by CCS. When preswollen CCS is added to dichromate solution, a higher degree of crosslinking (0.05 mol/AGU of EPCH) is necessary to reach the maximum adsorption.

Another important indication of Figure 4 is that in the case of preswollen CCS with the same reticulation, EF increases with increasing the amount of cationic groups, whereas with dry CCS used for adsorption, CCS with DS = 0.36 is most effective.

CONCLUSIONS

1. The amount of adsorbed Cr(VI) depends on the preparation of crosslinked cationic starch (CCS) before adsorption experiments (dry or preswollen CCS) and is a higher when dry CCS is used, especially with only CS or CCS with a small amount of cross-links. When the degree of crosslinking increases, the difference between the amounts of Cr(VI) adsorbed by dry and preswollen CCS decreases.
2. With increasing the amount of cross-links, the size of CCS particles in water and the retention of water and dichromate solution decreases, but the amount of adsorbed dichromate anions increases.
3. The amount of crosslinks in CCS, indispensable for reaching the maximum effectiveness of the cationic groups of CCS in Cr(VI) binding, expressed as dichromate equivalent per the equivalent of cationic groups, depends on the form in which CCS are used. In the case of dry CCS, 0.02 mol/AGU of EPCH is enough for the best adsorption properties of CCS to exhibit. When preswollen CCS is added to dichromate solution, a higher degree of crosslinking (0.05 mol/AGU of EPCH) is necessary to reach the maximum adsorption.
4. The Cr(VI) adsorption capacity decreases both with dry and preswollen CCS when the temperature increases from 20 to 60°C. However, the adsorption capacities obtained with dry CCS are higher at all temperatures.

5. The thermodynamic parameters of Cr(VI) adsorption by dry and preswollen CCS have been calculated. The negative values of ΔG° indicate that the adsorption process in both cases is spontaneous. The change in the enthalpy is also negative in both cases and shows that Cr(VI) adsorption is exothermic. However, the absolute value of ΔH° calculated for preswollen CCS is twice as low as that obtained with dry CCS. If preswollen CCS is used for Cr(VI) adsorption, the entropy change has a positive value and indicates that the randomness of the system increases, whereas the negative value of the entropy change when Cr(VI) species are adsorbed by dry CCS shows that in this case the order of the system increases. The presented thermodynamic parameters unambiguously indicate that Cr(VI) adsorption by dry CCS particles is more efficient than by preswollen ones.

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