

The Binding of Anionic Dyes by Cross-Linked Cationic Starches

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Abstract

Adsorption of anionic dyes on the cross-linked with epichlorohydrin starches containing quaternary ammonium groups (CCS) was investigated and compared with that of modified starches containing only quaternary ammonium groups (CS). The adsorption of anionic dyes on CS and CCS closely follows the Langmuir model of adsorption. The computed Langmuir saturation capacity Q_o increases with increasing degree of substitution (DS) of CS or CCS and has the value from 0.81 mol/kg to 3.22 mol/kg for CCS and from 0.88 mol/kg to 1.87 mol/kg for CS. The effectiveness of the cationic groups in dye binding was about 1 mol/equiv for CCS with DS from 0.47 to 0.62 and all the cationic groups had attached one anionic groups of the dye. Increasing DS of CS decreases the effectiveness of dye binding due to the increase in solubility of CS, and the soluble part of CS binds the dye as a typical soluble polyelectrolyte. CCS are more suitable than CS for the anionic dye adsorption from a textile dyeing solution. DS of CCS should be about 0.5–0.6. They adsorb the anionic dyes in few minutes and acts in the wide range of pH of the solutions. The Langmuir saturation capacity Q_o and the effectiveness of the cationic groups in dye binding increase with an increase of the adsorption temperature. The positive values of the enthalpy and entropy suggest that the adsorption is endothermic and during the adsorption of the anionic dye on CCS the randomness of the system increases.

Abbreviations: AB 25 : C. I. Acid Blue 25; AB 78 : C. I. Acid Blue 78; AO 7 : C. I. Acid Orange 7; AO 52 : C. I. Acid Orange 52; AR 151 : C. I. Acid Red 151; AY 36 : C. I. Acid Yellow 36; AGU : anhydroglucoside unit of starch; DS : degree of substitution; CS : cationic starch; CCS : cationic cross-linked starch; EF : effectiveness of the cationic groups; EPCH : epichlorohydrin; SCS : water-soluble cationic starch; Q_o : saturation capacity; ΔG° : the change in free energy; ΔH° : the change in enthalpy; ΔS° : the change in entropy

Introduction

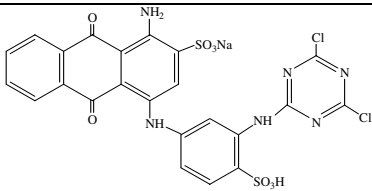
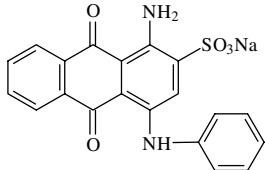
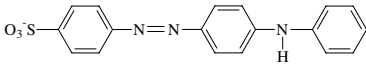
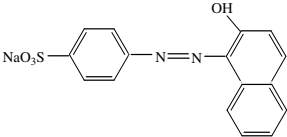
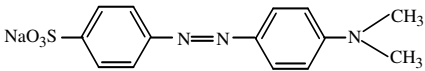
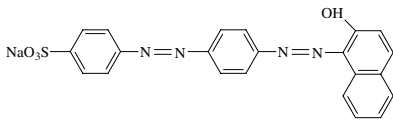
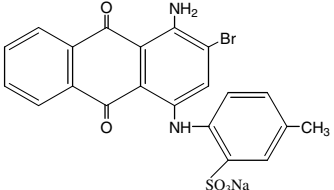
Textile wastewater is a complex medium containing a great variety of substances, many of which are hard to remove and slowly biodegradable. Besides, the wastewater from textile dye houses usually has a very intensive colour. Efficient and complete dye removal from wastewater is necessary, on the one hand, for water re-use in the textile finishing process, on the other hand, to prevent these harmful compounds from release into the environment.

Some different physical–chemical and biological processes have been proposed and used for treatment of coloured textile wastewater [1]. Inorganic salts such as ferrous sulphate [2], alum [3] or/and cationic flocculants [4] are used in a precipitation process. An oxidative [5] decolourization of the textile wastewater also was proposed. Adsorption technique is widely used to remove various classes of dyes from the wastewater [6–20]. The suitable adsorbent should have the high affinity and capacity for target compounds, tolerance for a wide range of wastewater parameters and should be inexpensive.

Studies on the removal of dyes by adsorption on various natural adsorbents, such as silica beads, glasses, alunite, perlite, zeolites [6], kaolinite and montmorillonite [7] agriculture wastes [8], activated sludge biomass [9] have been carried out. The activated carbon is the commonly used adsorbent [6, 10, 11]. It has a high degree of porosity, large surface area and is the effective adsorbent. Activation [12] is used to introduce polar groups and increase the sorption capacity of carbonaceous adsorbents. Adsorption capacities of the commercial activated carbons are from 8 to 1,179 mg/g [6]. However, the activated carbons are quite expensive. The low-cost activated carbons have been prepared from the wood and agriculture wastes, but the adsorption capacities depend on the source of a raw material and preparation [6].

The development of adsorbents based on natural polymers is very attractive from the biodegradability point of view and their little cost. First of all, chitosan has been proposed as an adsorbent of anionic dyes with the high potential [13]. It contains a high amount of amino groups, which are ionized in an acid medium, hence, the electro-

Table 1. Structure and characteristics of the anionic dyes.

Anionic dye	Formula	λ_{\max}	Molecular weight	Supplier
C. I. Reactive Blue 4 C.I. 61205		598	659	Boruta, Poland
C. I. Acid Blue 25 (AB 25) C.I. 62055		602	416	Boruta, Poland
C. I. Acid Yellow 36 (AY 36) C.I. 13065		435	375	Boruta, Poland
C.I. Acid Orange 7 (AO 7) C.I. 11510		483	350	Boruta, Poland
C.I. Acid Orange 52 (AO 52) C.I. 13025		465	327	Acros Organics
C. I. Acid Red 151 (AR 151) C.I. 26900		512	454	Sigma-Aldrich
C. I. Acid Blue 78 (AB 78) C.I. 62105		567	509	Rubezhansk chemical plant, Ukraine

static attraction take place between chitosan and dyes. However, below pH 5.5 chitosan forms gels and is not suitable for the dye removal. The cross-linking of chitosan makes it insoluble in acid solutions. If pH value of the dye solution is from 3 to 4 chemically cross-linked chitosan beads have a very large value of the adsorption capacity (1,911–2,498 g/kg), but adsorption lasts from 3 to 8 h [14, 15]. It could be emphasized that most of the dyeing baths are alkaline or at least neutral, therefore the application of chitosan beads might be complicated.

Starch is another natural polysaccharide that can be modified and used for the dye adsorption. Cationized and both cationized and cross-linked starches are used for this purpose [16–20].

The nature of the cationic group in cationic starch derivatives plays an important role for the dye adsorption. The cationic starches containing primary, secondary and tertiary amino groups and quaternary ammonium salts of starch, prepared by etherification and grafting, were investigated as adsorbents for acid, hydrolyzed reactive and direct dyes by Khalil and Aly [16]. They found that the value of the dye sorption increased with the increasing amount of nitrogen in the cationic starch, reached the maximum value and then decreased. This phenomenon occurred with all types of investigated cationic starch derivatives. The cationic starch ethers were better adsorbents for dyes than the grafted cationic starch derivatives. The adsorption of all investigated dyes by the cationic

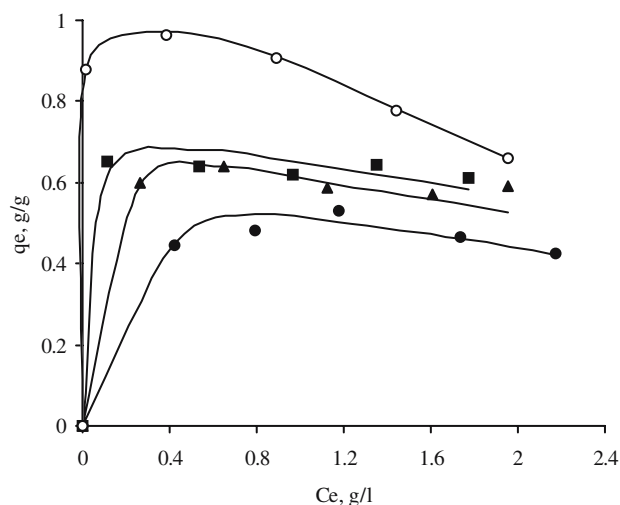


Figure 1. Experimental adsorption isotherms of AB 25 on CS with different DS: 0.2 (filled circle), 0.325 (filled triangle), 0.56 (filled square), 1.03 (open circle). The amount of CS in the solution was 1 g/l, adsorption time 30 min and temperature 30 °C.

starches with different groups increased in the following order: primary amino < secondary amino < tertiary amino < quaternary ammonium groups. The adsorption of the dyes by the cationic starches having primary, secondary and tertiary amino groups effectively proceeded only in the acid solution. Only quaternary ammonium groups can effectively work both in alkaline and acid solutions of dyes. In the work [17] the commercial products of cationic starch having a small amount of the quaternary ammonium groups (DS = 0.055) were evaluated as adsorbing materials for the decolorisation of the solution of hydrolyzed reactive dyes. But their sorption capacity was very low and decreased in the presence of an electrolyte in the dye solution.

Only few works [18–20] were found, in which the sorption of various anionic textile dyes from their aqueous solutions by cationic cross-linked starches had been investigated. The cross-linked starches having tertiary amino groups were prepared by the modification of the starch [18] or starch-enriched flour [19] with epichlorohydrin as a cross-linking agent in the presence of NH_4OH . Depending on the amount of cationic groups and concentration of the dye in the solution they adsorbed up to 65%–100% of the dye but only from acidic solutions. Simkovic [20] investigated the dye binding properties of the cross-linked cationic starches having both tertiary amino and quaternary ammonium groups. It was found that the dye binding properties were pH dependent for the derivatives containing both tertiary amino and quaternary ammonium groups and were close to pH-independent when containing only quaternary ammonium groups. Detailed studies of the adsorption of anionic dyes by the cross-linked starches having only quaternary ammonium groups are absent.

The aim of this work was to evaluate the adsorption of anionic dyes by the cross-linked starches containing quaternary ammonium groups and compare with that of starches containing only quaternary ammonium groups.

Materials and methods

Materials

The Antanavas Starch Plant (Lithuania) supplied a native potato starch (intrinsic viscosity $[\eta] = 0.39 \times 10^3 \text{ ml/g}$). Hydroxyethylated starch Kollotex 1250 ($[\eta] = 0.136 \times 10^3 \text{ ml/g}$) was supplied by Avebe, the Netherlands. 2,3-epoxypropyltrimethylammonium chloride and epichlorohydrin were purchased from Sigma-Aldrich.

The characteristics of anionic dyes used are listed in Table 1. The dyes (except of the reactive) were purified before use by the precipitation from solutions with HCl.

Preparation of cationic starches

Cationic starches were prepared by the etherification of the native potato or hydroxyethylated starch with 2,3-epoxypropyltrimethylammonium chloride in the presence of sodium hydroxide (the molar ratio of the reagents was starch/epoxide/NaOH = 1:(0.4–0.7):0.04) at 45 °C for 3–24 h.

During the cationization macromolecules of the starch were cross-linked with epichlorohydrin. The amount of epichlorohydrin was from 0.003 to 0.16 mol/AGU.

Obtained starch derivatives were washed with isopropanol and dried at 50 °C. The nitrogen content was estimated according to the Kjeldahl method after purification by Soxhlet extraction with methanol for 16 h. The degree of substitution (DS) was calculated from nitrogen content:

$$DS = \frac{(162 + b) \cdot N}{1400 - 151.5 \cdot N} \quad (1)$$

where N – nitrogen content, %; b – molecular weight of the substituent (for hydroxyethylated starch b is 3.22, in other cases $b = 0$).

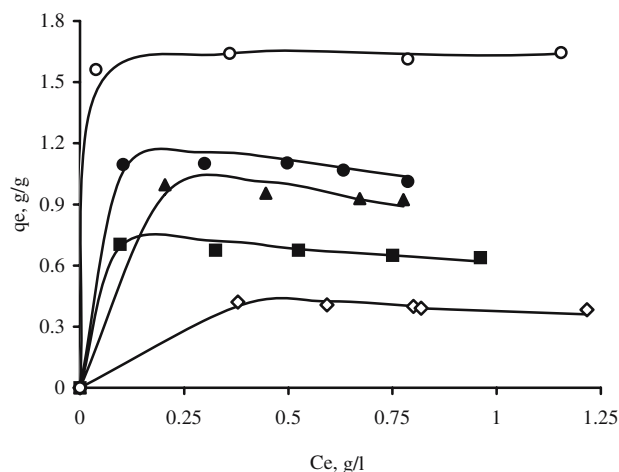


Figure 2. Experimental adsorption isotherms of AR 151 on CCS (the amount of EPCH 0.05 mol/AGU) with different DS: 0.19 (diamond), 0.32 (filled square), 0.47 (filled triangle), 0.54 (filled circle), 1.16 (open circle). The amount of CCS in the solution was 1 g/l, adsorption time 30 min and temperature 60 °C.

Table 2. The Langmuir saturation capacity Q_0 and the EF for AR 151 dye on CCS and AB 25 dye on CS.

Adsorbent/dye	DS	Q_0 (mol/kg)	b (l/mol)	EF (mol/equiv)	R^2
CCS/AR 151	0.19	0.81	8.4	0.83	0.9996
	0.32	1.39	24.3	0.91	0.9992
	0.47	1.98	20.5	0.99	0.9999
	0.54	2.23	21.5	1	0.9991
	0.62	2.45	25.6	1	0.9995
	1.16	3.22	9.8	0.94	0.9965
CS/AB 25	0.2	0.88	2.9	0.84	0.9911
	0.325	1.38	13.7	0.90	0.998
	0.56	1.42	17.5	0.63	0.9934
	1.03	1.87	8.3	0.59	0.9903

The geometric mean value of CCS particles diameter in distillate water depended on the DS and was from 65.5–77.8 μm . The size distribution of CCS particles measured by Coulter LS 200 Particle Size Analyser equipped with the Coulter Fluid Module (Beckman Coulter, USA).

Adsorption investigations

The anionic dye solutions were prepared by dissolving the purified dye in the distilled water containing an equimolar amount of NaOH. The pH of the dye solutions was adjusted by adding 0.1 N solutions of NaOH or HCl.

In the experiments of the equilibrium dye adsorption the mixture of the cationic starch (containing 0.1 g of the dry material) and 100 cm^3 of the dye solution were shaken (70 rpm) until equilibrium in orbital shaker YBMT-12-250 (Russia) at the fixed temperature with the control of ± 1 $^\circ\text{C}$.

After filtration through a paper filter in the experiments with acid dyes or through a glass filter in a case of reactive dyes the absorbency at λ_{max} (presented in Table 1) of the supernatant solution was measured using a KFK colorimeter (Russia). The concentration of the dye in the supernatant solution was calculated from the calibration curves. The amount of the adsorbed dye q_e (g/g) was calculated according to the equation:

$$q_e = \frac{(C_0 - C)V}{W} \quad (2)$$

where C_0 – the initial dye concentration (g/l); C – the dye concentration at the equilibrium or at the time t in the supernatant solution (g/l); V – the volume of the solution (l); W – the weight of cationic starch (dry material; g).

In the experiments with the technical reactive dye the residual colour in % was calculated as a ratio of the light absorption before and after adsorption of the dye on the cationic starches.

The light absorption spectra of dye solutions were recorded using a SPECORD UV-VIS spectrophotometer (Carl Zeiss Jena, Germany).

Results and discussion

We have investigated the cationic starches with quaternary ammonium groups (CS), obtained from the native potato starch under conditions of heterogeneous reactions, preserving the morphologic structure of starch granules unchanged. CS with $\text{DS} \geq 0.2$ have the pasting temperature lower than the room temperature (18 $^\circ\text{C}$) and form a transparent colloidal dispersion in cold water. If during the cationization with 2,3-epoxypropyltrimethylammonium chloride macromolecules of potato starch polysaccharides are cross-linked with epichlorohydrin (EPCH), the cationic cross-linked starches (CCS) are obtained. CCS in cold water exists in the form of swelled particles.

The adsorption of anionic dyes by CS and CCS was investigated. Preliminary kinetic experiments had shown that 30 min contact time was sufficient for equilibrium to be reached.

Adsorption isotherms of the acid dye AB 25 on CS with different DS and the acid dye AR 151 on CCS (the amount of EPCH was 0.05 mol/AGU) with different DS have been obtained and are shown in Figure 1 and 2. A rectangular shape of the isotherms indicates that both CS and CCS have high adsorption density even at a low dye concentration. Data presented in the figures also show that the amount of cationic groups in the adsorbent plays an important role in dye adsorption. The amount of the adsorbed dye increases with increasing DS of CS or CCS. The amount of the adsorbed dye slightly decreases with the increase of the initial concentration of the anionic dye in solution. This decrease is more noticeable for the adsorption of AB 25 dye on CS, especially with increasing DS.

Adsorption isotherms reveal the way in which adsorbates interact with adsorbents. The Langmuir isotherm equation assumes that adsorption takes place at specific homogeneous sites within the adsorbent and that once a

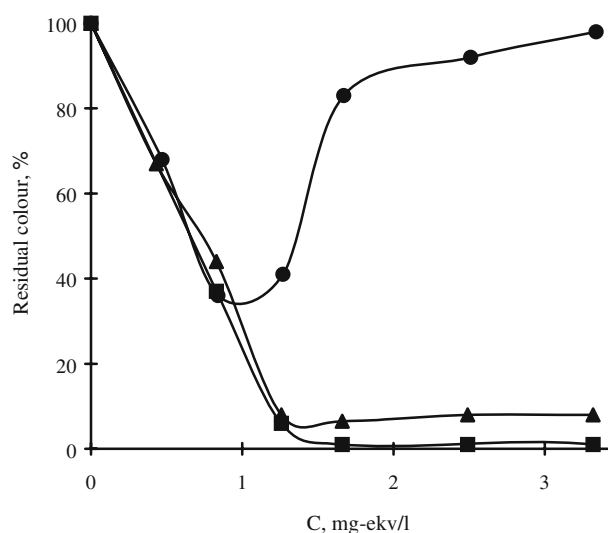


Figure 3. The influence of the amount of adsorbent on the colour removal from the solution of C.I. Reactive Blue 4 when using: SCS with $\text{DS} = 0.37$ (filled circle), CC with $\text{DS} = 0.36$ (filled triangle), CCS with $\text{DS} = 0.36$ (filled square). The amount of dye and adsorbent in solution was 1 g/l, adsorption time 30 min and temperature 30 $^\circ\text{C}$.

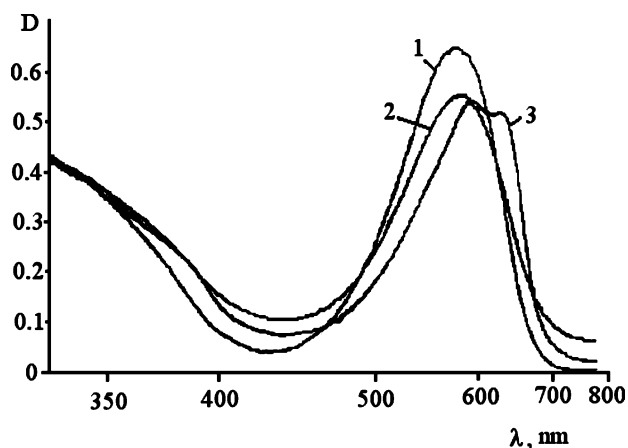


Figure 4. The spectra of light absorption by the solution of AB 78 (curve 1) and the mixture of the soluble part of CS with DS = 1.14 and AB 78: 2 – the amount of CS less than optimal; 3 – the amount of CS higher than optimal.

dye molecule occupies a site, no further adsorption can take place at that site. Moreover, the Langmuir equation is based on the assumption of the structurally homogeneous adsorbent, where all sorption sites are identical and energetically equivalent. Theoretically, the adsorbent has a finite capacity for the adsorbate. The saturated or monolayer capacity is represented by the equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_o \cdot b} + \frac{C_e}{Q_o} \quad (3)$$

where Q_o (g/g or mol/kg) is the maximum amount of the adsorbate per unit weight of the adsorbent to form a complete monolayer coverage on the surface (saturation capacity) at a high equilibrium concentration of adsorbate C_e , q_e is the amount of the adsorbate adsorbed by the adsorbent at the equilibrium and b (l/g or l/mol) is the Langmuir constant related to the affinity of binding sites.

The Q_o and b values were calculated from the slope and intercept of the linear plots of C_e/q_e vs C_e .

The linear Langmuir equation was applied to the adsorption curves presented in Figure 1 and 2, and the saturation capacity and the affinity of binding sites were calculated and shown in Table 2. Values of the correlation coefficients presented in this table show that the Langmuir isotherm equation fits quite well with the experimental adsorption data and according to the Langmuir model the adsorption of the anionic dyes on CS and CCS occurs due to the electrostatic interaction between the cationic groups of the modified starches and anionic groups of the dyes.

The calculated Langmuir saturation capacity Q_o increases with increasing DS of CS or CCS and has the value from 0.81 mol/kg for CCS with DS = 0.19 to 3.22 mol/kg for CCS with DS = 1.16 and from 0.88 mol/kg for CS with DS = 0.2 to 1.87 mol/kg for CS with DS = 1.03 (Table 2). Results (data not shown) indicated that the degree of cross-linking of CCS did not influence the amount of the adsorbed dye. Thus, CCS obtained with 0.05 mol/AGU of epichlorohydrin and having the different amount of cationic groups were used in the experiments of the dye adsorption.

Some differences between CS and CCS were observed when the effectiveness of the cationic groups in dye binding (EF), expressed as mole of dye *per* equivalent of cationic groups, was calculated from values of the saturation capacity Q_o (Table 2). If all cationic groups of the modified starch take part in the adsorption of an anionic dye, the EF is 1 mol/equiv. CSS with DS from 0.47 to 0.62 have such the EF suggesting that each cationic group has bond one anionic group of the dye. CCS with DS = 1.16 has the slightly lower EF (0.94 mol/equiv). It is possible that when the amount of cationic groups in CCS is high, the attraction of another dye molecules by the cationic groups already containing dye molecules attached side by side is restricted and some of the cationic groups do not take part in the dye attraction.

In the case of CS, when DS exceeds 0.32 the EF begins to decrease. When DS of CS is more than 0.56, only about 60% of the cationic groups take part in the dye adsorption. The same dependences are also noted in the work [16] but no reasons of such behaviour are explained.

The decreasing of the EF of CS can be associated with the increasing solubility of CS at increased DS. The water-soluble part of CS binds the dye as a soluble polyelectrolyte, when insoluble complexes with the dye are formed at a certain concentration of the components [4, 21]. A water-soluble cationic starch (SCS) was obtained from hydroxyethylated starch ($[\eta] = 0.136 \times 10^3 \text{ ml/g}$). SCS, CS and CCS with approximately the same DS were compared for their potential to adsorb an anionic reactive dye. From the data shown in Figure 3 it can be seen that SCS acts as a typical soluble polyelectrolyte and forms an insoluble complex with the dye only at the optimal concentration. CS and CCS adsorb all the dye present in the solution if their amount is sufficient.

It seems likely that soluble complexes of dye-CS are formed but a part of them remains in the solution. To confirm this assumption a colloidal dispersion of CS with

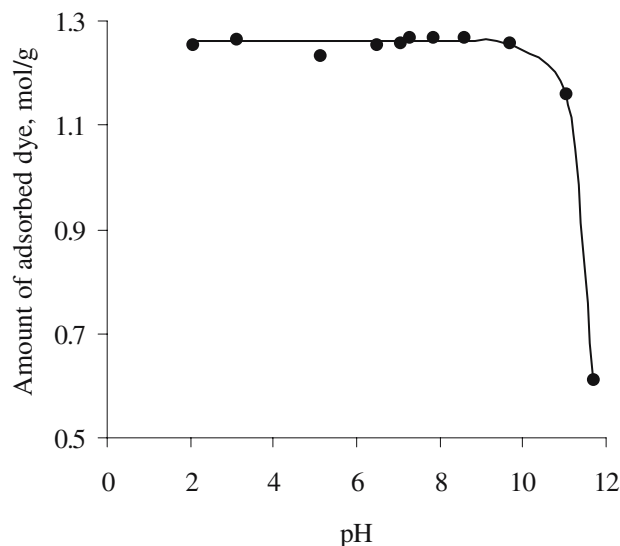


Figure 5. The effect of the pH on the amount of AO 7 dye adsorbed by CCS (the amount of EPCH 0.05 mol/AGU) with DS = 0.32 at equilibrium. The amount of CCS and the initial concentration of dye in solution was 1 g/l, adsorption time 30 min and temperature 60 °C.

Table 3. The Langmuir saturation capacity Q_o and the EF for AR 151, AY 36 and AO 52 dyes adsorbed on CCS (DS = 0.32, the amount of EPCH 0.05 mol/AGU) at different temperatures.

Temperature, °C	Q_o (mol/kg)	b (l/mol)	EF (mol/equiv)	R^2
AR 151				
35	1.27	12	0.84	0.9976
60	1.39	24	0.92	0.9992
75	1.46	28	0.99	0.9986
AY 36				
16	1.39	221	0.94	0.9997
30	1.42	147	0.96	0.9997
60	1.45	146	0.98	0.9961
AO 52				
11	1.48	121	1	1
30	1.49	29	1.01	0.9967
60	1.66	29	1.12	0.998

DS = 1.14 was filtered and the interaction of AB 78 with the soluble part of CS presented in the supernatant was examined. This anionic dye can be used as an optical probe, because the changes in its colour strongly depend on the ionisation of the dye. In the acid medium the dye solution is blue with a red tint, while in the alkali medium the colour of the dye solution becomes sky-blue. In the first case the light absorption spectra of the dye solution have one maximum, in the latter case two-absorption maxima shifted to the longer waves are noticed. Such changes in the colour were observed when AB 78 was precipitated with polydiallyldimethylammonium chloride or its poly-complexes with potato starch at the neutral pH values of solutions [21]. When the soluble part of CS was mixed with the solution of AB 78, some part of the dye-CS precipitated and the colour of the mixture depended on the amount of CS solution added. Up to the optimal concentration of CS required to precipitate the dye, the colour of the mixture was reddish blue and the spectra of light absorption had one maximum as the solution containing only the dye (Figure 4, curves 1 and 2). If the amount of CS was high enough to bind the dye, the colour of the mixture became sky-blue and the two maxima were seen in the spectra (Figure 4, curve 3). The sky-blue colour of the mixture of dye and CS solutions showed that the soluble complex of the dye-CS exists in the solution. The soluble part of the dye-CS complex decreases the EF of CS as the adsorbent and is responsible for the configuration of the adsorption isotherms of AB 25 on CS (Figure 1).

The results presented above show that CCS are more suitable for the anionic dye adsorption from a textile dyeing solution. For the effective adsorption of the anionic dyes the DS of CCS should be about 0.5–0.6.

Comparing the effectiveness of chitosan in dye binding [14, 15] with the effectiveness of CCS, it can be concluded that CCS and chitosan as adsorbents are in the same level. Moreover, the adsorption of anionic dyes by chitosan lasts for at least 8 h [14, 15], whereas CCS adsorbs the anionic dyes in few minutes (data not shown). Another important feature of CCS as an adsorbent is that they act in the wide

range of the pH of dye solutions, i.e., from pH 2 to 10 (Figure 5). Only when the pH of the dye solution exceeds 11, the amount of the dye adsorbed by CCS drastically decreases.

Investigations of the influence of the temperature on the adsorption of anionic dyes on CCS also offered interesting results. The linear Langmuir isotherm equation was applied for the experimental data of the adsorption of several anionic dyes on CCS (DS = 0.32, the amount of EPCH 0.05 mol/AGU) at different temperatures. The estimated Langmuir saturation capacity Q_o , together with the EF of CCS at the different temperatures for dyes AR 151, AY 36 and AO 52 is presented in Table 3. For all three dyes the Q_o and EF increase with the increase of the adsorption temperature. The EF for AO 52 that has the lowest molecule weight becomes more than 1 with the increasing temperature.

The thermodynamic parameters such as the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined according to the commonly used equations [22]. The results are listed in Table 4.

The negative values of ΔG° indicate spontaneous overall adsorption process. More negative values of ΔG° at higher temperatures imply the greater driving force of the adsorption in high temperatures than in low. The unexpected positive values of the enthalpy and entropy suggest that the process is endothermic and the randomness of the analyzed system during the adsorption of the anionic dye on CCS increases.

An analysis of works on adsorption thermodynamics revealed that the positive changes of enthalpy for binding of the ions are not a rare exception, but a rather typical fact for polysaccharides. That was detected for the adsorption of chromium by wine processing waste sludge [23], Japanese cedar bark [24], cross-linked alginate and gelatine [25], Cu (II) ions by the cross-linked amphoteric starch [22]. However, the adsorption of Cr (VI) by the cross-linked starch with only quaternary ammonium groups was found to be exothermic [26]. Changes of the enthalpy and entropy calculated from the kinetic data of the dye adsorption by the cross-linked chitosan also were negative [14, 15].

Table 4. The thermodynamic parameters for the adsorption of anionic dyes on CCS (DS = 0.32, the amount of EPCH 0.05 mol/AGU) when the initial concentration of dyes was 2 mol/m³.

Temperature, °C	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol·K)	R^2
AR 151				
35	-1.42	19.2	74.1	0.9914
60	-2.30			
75	-2.89			
AY 36				
16	-1.99	6.3	37.6	0.9974
30	-2.24			
60	-2.71			
AO 52				
11	-2.81	35.6	149	0.9675
30	-4.44			
60	-6.01			

One of the reasons for the positive changes of the enthalpy and entropy in the case of the adsorption of anionic dyes on CCS could be the release of the great amount of water molecules. Beyond a doubt, the adsorption of the large hydrated anions onto a hydrophilic polymer matrix inevitably disturbs the order of water molecules in the nearest environment and releases them to the external liquid. On the other hand, it is reasonable to consider that adsorbed anions are attracted probably due to the long distance electrostatic interaction between oppositely charged groups. During the formation of the ionic bonds between the dye and the active sites of the polymer, the counter-ions should gain a higher degree of freedom and increase the entropy.

Conclusion

The adsorption of anionic dyes on the cross-linked with epichlorohydrin starches containing quaternary ammonium groups (CCS) was investigated and compared with that of modified starches containing only quaternary ammonium groups (CS).

The high values of the correlation coefficients strongly support the fact that the adsorption of the anionic dyes on CS and CCS closely follows the Langmuir model of adsorption. The adsorption occurs first of all due to an electrostatic interaction between the cationic groups of the modified starch and the anionic groups of the dyes. The computed Langmuir saturation capacity Q_0 increases with increasing DS of CS or CCS and has the value from 0.81 mol/kg to 3.22 mol/kg for CCS and from 0.88 mol/kg to 1.87 mol/kg for CS investigated.

The effectiveness of the cationic groups in dye binding, expressed as mole of dye per equivalent of cationic groups, was about 1 mol/equiv for CSS with DS from 0.47 to 0.62 and in this case all the cationic groups had attached one anionic group of the dye. Increasing DS of CS decreases the effectiveness of dye binding. When DS of CS is more than 0.56, only about 60% of cationic groups take part in the adsorption of the dye. These results are associated with the increased solubility of CS with increasing DS, and the soluble part of CS binds the dye as a typical soluble polyelectrolyte. The soluble part of dye-CS complexes diminishes the effectiveness of CS as the adsorbent.

It was shown that CCS are more suitable for the anionic dye adsorption from a textile dyeing solution. For the

effective dye adsorption the DS of CCS should be about 0.5–0.6. CCS adsorb anionic dyes in few minutes and act in the wide range of the solution pH.

The Langmuir saturation capacity Q_0 and the effectiveness of the cationic groups in dye binding increase with an increase of the adsorption temperature. The negative values of estimated ΔG° indicate spontaneous overall processes of the adsorption. The positive values of the enthalpy and entropy suggest that the adsorption is endothermic and during the adsorption of the anionic dye on CCS the randomness of the system increases.

References

1. E. Forgacs, T. Cserhati and G. Oros, *Environ. Int.*, **30**, 953 (2004).
2. G. Carvalho, W. Delee, J. M. Novais and H. M. Pinheiro, *Color. Technol.*, **118**, 215 (2002).
3. J. H. Choi, W. S. Shin, S. H. Lee, D. J. Joo, J. D. Lee, S. J. Choi and L. S. Park, *Separ. Sci. Technol.*, **36**, 2945 (2001).
4. R. J. Zemaitaitiene, E. Zliobaite, R. Klimaviciute and A. Zemaitaitis, *Colloid Surf. A*, **214**, 37 (2003).
5. J. N. Wu and T. W. Wang, *Environ. Sci. Health, Part A*, **36**, 1335 (2001).
6. G. Crini, *Bioresour. Technol.*, **97**, 1061 (2006).
7. O. Yavuz and A. H. Aydin, *Fresenius Environ. Bull.*, **11**, 377 (2002).
8. M. M. Davila-Jimenez, M. P. Elizalde-Gonzalez and A. A. Palaez-Cid, *Colloid Surf. A*, **254**, 107 (2005).
9. H. C. Chu and K. M. Chen, *Process. Biochem.*, **37**, 595 (2002).
10. C. Namasivayam and D. Kavitha, *Dyes Pigm.*, **54**, 47 (2002).
11. K. Nakagawa, A. Namba, S. R. Mukai, M. Tamon, P. Ariyadejwanich and W. Tanthapanichakoon, *Water Res.*, **38**, 1791 (2004).
12. P. C. C. Faria, J. J. M. Orfava and F. R. M. Pereira, *Water Res.*, **38**, 2043 (2004).
13. F. C. Wu, R. L. Tseng and R. S. Juang, *J. Hazard Mater.*, **373**, 63 (2000).
14. M. S. Chiou and H. Y. Li, *Chemosphere*, **50**, 1095 (2003).
15. M. S. Chiou, P. Y. Ho and H. Y. Li, *Dyes Pigm.*, **60**, 69 (2004).
16. M. I. Khalil and A. A. Aly, *J. Appl. Polym. Sci.*, **93**, 227 (2004).
17. A. Nechwatal, M. Nikolai and K. P. Miecek, *Starch*, **51**, 286 (1999).
18. I. Simkovic, J. A. Laszlo and A. R. Thompson, *Carbohydr. Polym.*, **30**, 25 (1996).
19. F. Delval, G. Crini, N. Morin, J. Vebrel, S. Bertini and G. Torri, *Dyes Pigm.*, **53**, 79 (2002).
20. I. Simkovic, *Carbohydr. Polym.*, **31**, 47 (1996).
21. R. Klimaviciute, *Fibres Text. East. Eur.*, **12**, 74 (2004).
22. S. M. Xu, S. Feng, F. Yue and J. D. Wang, *J. Appl. Polym. Sci.*, **92**, 728 (2004).
23. Y. S. Li, C. C. Liu and C. S. Chiou, *J. Colloid Interface Sci.*, **237**, 95 (2004).
24. M. Aoyama, M. Kishino and T. S. Jo, *Separ. Sci. Technol.*, **3**, 1149 (2004).
25. J. Bajpai, R. Shrivastava and A. K. Bajpai, *Colloids Surf.*, **236**, 81 (2004).
26. S. M. Xu, J. Wei, S. Feng, J. D. Wang and X. S. Li, *J. Polym. Res.*, **11**, 211 (2004).