

# Starch-Cationic Polyelectrolyte Complexes and Their Interaction with Acid Dye

## Abstract

*The formation of polyelectrolyte complexes (PECs) by the interaction between poly(dimethyl-diallylammonium chloride) and native potato starch was investigated. PECs with optimal dye binding properties containing 0.015-0.02 mole cationic polymer/anhydroglucose residue were prepared. It was shown that the anionic (acid) dye was incorporated into PECs by electrostatic interaction with the free cationic groups of PECs. The principal role of the hydrophobicity of the PECs containing acid dye in their stability in water solutions was revealed. The precipitation occurred due to the minimum amount of free ionic groups.*

**Key words:** polyelectrolyte complex, cationized starch, acid dye, precipitation.

Various physico-chemical and biological processes have been proposed or used for treating coloured textile wastewater. In the precipitation process, inorganic salts such as ferrous sulphate [1] or alum [2] are used. The addition of synthetic flocculants can reduce the dosage of coagulant and improve the efficiency of colour and turbidity removal [2]. Furthermore, the microbial [3-5] and oxidative [6] decolorisation of textile wastewater has been proposed. Studies on the removal of dyes by absorption on various carbons [7], activated sludge biomass [8], kaolinite and montmorillonite [9] have been carried out with the aim of obtaining information on treating effluents from the dyeing industry. The commercial cationic starch products (DS=0.055) can be used as absorbing materials for decolourising reactive dyestuff hydrolysates [10]. For the sorption of various textile dyes from their aqueous solutions, crosslinked polysaccharides containing tertiary amino [11] or quaternary ammonium [12] groups were examined.

Most dyes in textile wastewater are anionic compounds, and can therefore be bound with cationic polyelectrolytes. Besides dyestuffs, textile wastes contain other negatively charged compounds such as thickeners, dispersing agents, anionic detergents, etc., which are able to facilitate the flocculation of ionic and disperse dyes [13]. Under controllable conditions, the polymer and the textile auxiliaries form polyelectrolyte complexes (PECs) which can incorporate the dyes, leading to a triple complex precipitation [13-15]. Electrostatic interactions are responsible for transferring anionic dye particles from the water environmental to the polymer chain. For effective binding, free, dissociated and easily accessible cationic groups in the

complexes must be preserved. Disperse dyes which are uncharged can also be bound by PECs [15]. In this case, anionic polyfunctional compounds with a proper chemical structure dispersed the dye carrier to cationic polymers.

The interaction between polyelectrolytes and dyes was also studied to assess the nature of the driving forces for dye binding by PECs, and the importance of both electrostatic and hydrophobic interactions has been emphasised. Buchhammer et al. [16] compared the sorption capability of preformed polyelectrolyte-micelle complexes and polycation-polyanion complexes for a p-nitrophenol or anionic dye model, bromocresol green. They showed that sorption capability strongly depends on the structure and net charge of complex particles, and increases with the increase in the molar mass and hydrophobic properties of the components used. However, the binding level of the ionic substance was higher than that of p-nitrophenol. Dragan et al. [17] examined the formation of the tricomponent complexes from preformed nonstoichiometric polycation-anionic dye complexes and polyanions added, and postulated the significance of the electrostatic interactions between the negative and the free residual positive charges in the former complexes. Ortel et al. [18] described the surface modification of finely dispersed silica materials by polyelectrolytes, and provided evidence that only nonstoichiometric polycomplexes with a great excess of cationic charge exhibit any enhanced adsorption of the anionic dyestuff. The minimum value observed at the molar ratio of polyanion/polycation was 1. Takagishi et al. [19] have provided evidence that insoluble polyion complexes of sodium poly(methacrylate) and piperidinium cationic polymers are capable of binding Methyl Orange and

## ■ Introduction

Textile plants use huge amounts of water. Wastewater polluted with auxiliaries and textile dyes is discharged into municipal outlets. Generally all these contaminants biodegrade only slowly. Furthermore, textile wastewater usually has a very intensive colour. Pre-treatment of textile wastewater before it reaches municipal outlets is necessary. The creation of universal and effective technologies for wastewater treatment is urgent, because solving environmental problems is one of the most important tasks for the survival and further development of textile companies in Lithuania.

its homologues in water solutions. The polycomplexes examined corresponded to 1:1 stoichiometry, thus this matrix, as supposed, should be electrically neutral. Interestingly, the significance of the electrostatic interactions that accompany the binding has been postulated. Such controversial results and their interpretation provide an area for further discussion.

The electrostatically driven interactions between oppositely-charged macromolecules have long been known, but have attracted considerable interest in recent years because of the various industrial and environmental applications of PECs. Cationic quaternary polyelectrolytes such as poly(diallyldimethylammonium chloride) (PDADMAC) can form PECs with various anionic polymers. PECs prepared from PDADMAC and starch showed effective flocculating properties in the dewatering of paper pulps [20]. The composition and properties of such PECs depended on the molecular mass of components and on the reaction conditions (concentration of components, pH and the ionic strength of solution, the order in which the components are added).

The present work focuses on an investigation of the formation of polycomplexes between PDADMAC and starch in pastes, and their role in the acid dye binding process.

## Materials and Methods

The Antanavas Starch Plant, Lithuania, supplied potato starch. PDADMAC with

the average molecular weight of 2000 (manufactured by Reachim, Russia), sodium hydroxide, hydrochloric acid and urea were of analytical grade. C. I. Acid blue 78 (trade name 'kislотноj chisto goluboj antraquinonyj', produced by the Rubezhansk chemical plant, Ukraine) was a commercial product and used without purification.

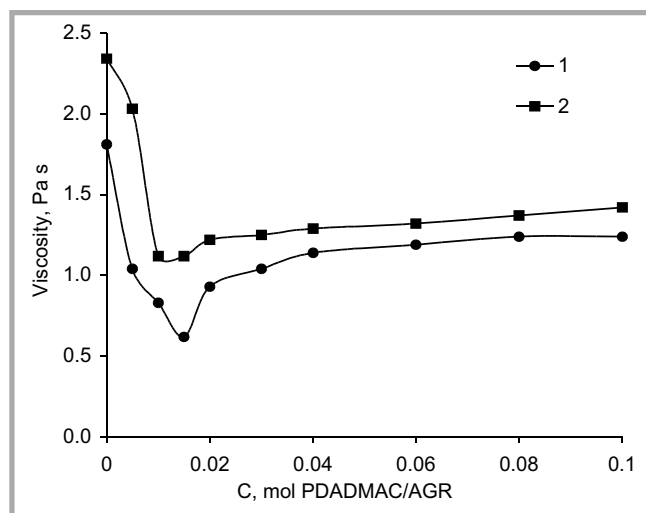
The PECs from potato starch and the PDADMAC were prepared as follows. A calculated amount of starch (4-6%) was suspended in cold water (100 cm<sup>3</sup>) containing a certain amount of PDADMAC, boiled for 15 min at 85°C using a mechanical stirrer, and then cooled down. The dynamic viscosity of the prepared PEC pastes and starch pastes alone was measured with RHEOTEST-2 (Germany) at 20°C using an S1 system.

The precipitation of dye was examined as follows. The dye was dissolved in water. 90 cm<sup>3</sup> of dye solution was transported to the flocculation tubes, and increasing amounts of PECs and decreasing amounts of distilled water were added. The total amount of the solutions was 100 cm<sup>3</sup>, the initial dye concentration being 0.1 g/l. The solutions were slowly mixed for 30 s and allowed to sediment for 24 h. Samples were taken for analysis from a layer 3-5 cm below the surface. After filtration through a paper filter, the absorbance at  $\lambda=567$  nm of the supernatant solutions was measured using a KFK-3 colorimeter (Russia). The residual dye D in % was evaluated as a ratio of light absorption before and

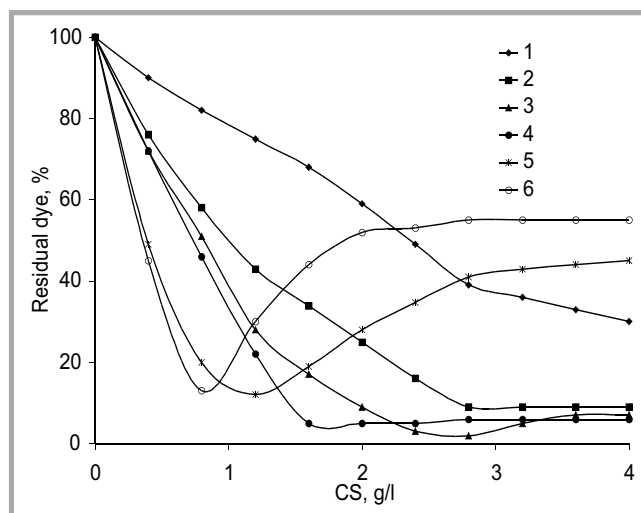
after treatment. The precipitation of dyes in the presence of HCl, NaOH and urea has been examined in a similar way. In some cases, PDADMAC and starch paste or PDAMAC alone was used instead of PECs. The light absorption spectra of dye solution were recorded using a SPECORD UV-VIS spectrophotometer (Carl Zeiss Jena, Germany).

## Results and Discussion

Potato starch is the only commercial starch that contains an appreciable amount of chemically bound phosphate ester groups. The phosphate substituents confer the properties of an anionic polyelectrolyte on potato starch amylopectin when dispersed into aqueous solutions. These anionic groups can interact with oppositely charged macromolecules of PDADMAC and form PECs. For determination of optimal molar relations of the PECs constituents, the dynamic viscosity of the PECs obtained from potato starch and PDADMAC was tested. The data in Figure 1 show that the viscosity of the PECs pastes depends on the amount of added cationic polyelectrolyte, and decreases in all cases. However, the viscosity of the PEC pastes has a minimum value when the amount of PDADMAC is 0.01-0.015 mol to anhydroglucose residue (mol/AGR). Further increases of the amount of cationic polyelectrolyte increase the viscosity only negligibly. Such behaviour at a certain concentration of the constituents is connected with the formation of compact and hydrophobic PECs, part of which is insoluble in water.



**Figure 1.** Viscosity of PECs pastes depending on amount of PDADMAC when concentration of starch in the pastes: 1 - 4% (shear rate 5.4 s<sup>-1</sup>); 2 - 6% (shear rate 27.0 s<sup>-1</sup>).



**Figure 2.** Residual C. I. Acid blue 78 v.s. concentration of CS in dye solution. Amount of PDADMAC in CS, mol/AGR: 1 - 0.005; 2 - 0.01; 3 - 0.015; 4 - 0.02; 5 - 0.03; 6 - 0.04. Initial concentration C. I. Acid blue 78 0.1 g/l. Amount of starch in CS pastes 4%.

The amount of phosphate groups in potato starch reaches 1 per 200 to 400 AGR. This corresponds to a degree of substitution of about 0.003 to 0.005 [21]. The optimal composition of PECs showed that all regularly distributed cationic groups of PDADMAC cannot react with unevenly distributed phosphate groups of starch. For this reason, the PECs have an appreciable amount of free quaternary ammonium groups. Such nonstoichiometric PECs can be designated as cationised starches (CS).

In [13] it is shown that the acid dyes can be removed from their water solutions with PECs formed from PDADMAC and various anionic compounds, such as sodium alginate, sodium carboxymethylstarch and others. However, excellent precipitation of acid dyes can be observed only within a narrow range of the molar ratios of both PEC reagents, and only when PECs are formed in the dye solution.

The flocculation behaviour of the preformed CS depends on their composition. The amount of the C. I. Acid blue 78 precipitated from its aqueous solutions by preformed CS was examined (Figure 2). The amount of the residual dye characterises the optimal dye removal level. From the data shown in Figure 2, it is clear that preformed CS can effectively remove acid dye from the water solution. The effectiveness of dye precipitation and the amount of CS needed for this purpose depend on the composition of CS. When the amount of PDADMAC in CS increases, the level of residual dye decreases. The

best precipitation of dye is achieved with CS containing 0.015-0.02 mol/AGR PDADMAC (Figure 2, curves 3 and 4). In this case only 3-5% of residual C. I. Acid blue 78 remains in solution, and the dye precipitates in a wide range of CS concentrations. A further increase in the amount of PDADMAC in CS changes the nature of the curves (Figure 2, curves 5 and 6). They become similar to that obtained with PDADMAC alone (Figure 3, curve 3), and CS precipitates the dyes at a narrow range of concentrations.

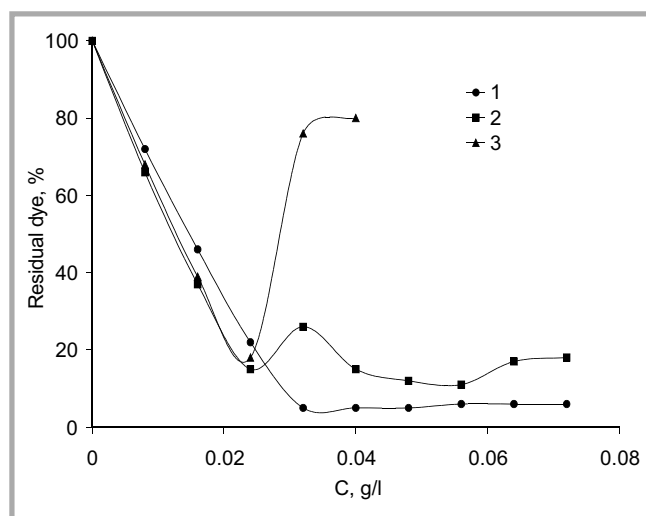
The flocculation results with the preformed CS and CS formed in dye solution by a separate dosing of PDADMAC and starch have been compared (Figure 3). This figure also shows the data obtained with PDADMAC alone. The results indicate that at lower concentrations of CS, the residual dye curves change in the same manner as with PDADMAC alone. When the concentration of PDADMAC alone becomes higher than needed to bind a maximum amount of dye, the character of the curves is different. PDADMAC precipitates dye only at its optimal concentration. Upon the overdosing of PDADMAC, restabilisation occurs. If PDADMAC is bonded in PECs, its action in dye precipitation depends less on the concentration of PECs, and the dye precipitates in a wide range of the concentrations. In all cases, preformed CS flocculates the dye more effectively than that formed in the dye solution.

**Table 1.** Dependence of residual C. I. Acid blue 78 on the composition and concentration of CS.

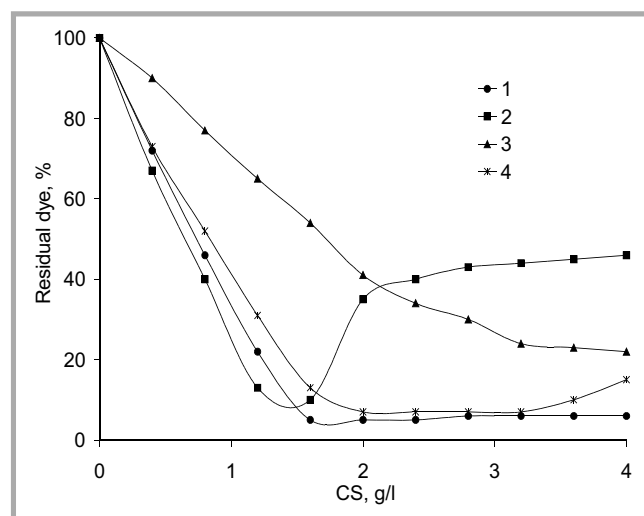
Amount of PDADMAC in preformed CS, mol/AGR	Concentration of CS in dye solution, g/l	Residual dye, %
0.005	4	30
0.01	2.8	4
0.015	2.4	2
0.02	1.6	5
0.03	1.2	12
0.04	0.8	13
Starch alone	4	70
PDADMAC alone	0.024	20

The data in Table 1 illustrate the flocculation results for dye/CS systems achieved by varying the composition of CS. As shown in Table 1, effective removal of the dye occurs with the CS whose composition corresponds to the optimal conditions of the formation of nonstoichiometric PECs, i.e. CS with 0.015 mol/AGR PDADMAC. In practice, it is more reasonable to use CS with 0.02 mol/AGR PDADMAC, because in this case the dye binding results are good enough (5%), but the concentration range to obtain optimal sedimentation is wider (Figure 2, curves 3 and 4). For this reason, the CS with 0.02 mol/AGR PDADMAC was used in the following investigations.

From the technological point of view, the valuation of dye binding in the solutions containing substances that destroy PECs was a matter of great importance. The influence of the additions of alkali,



**Figure 3.** Residual C. I. Acid blue 78 v. s. concentration of PDADMAC (used alone or in CS) in dye solution: 1 - preformed CS; 2 - CS formed in dye solution; 3 - PDADMAC. Initial concentration C. I. Acid blue 78 0.1 g/l. Amount of PDADMAC in CS 0.02 mol/AGR, amount of starch in CS - 4%.

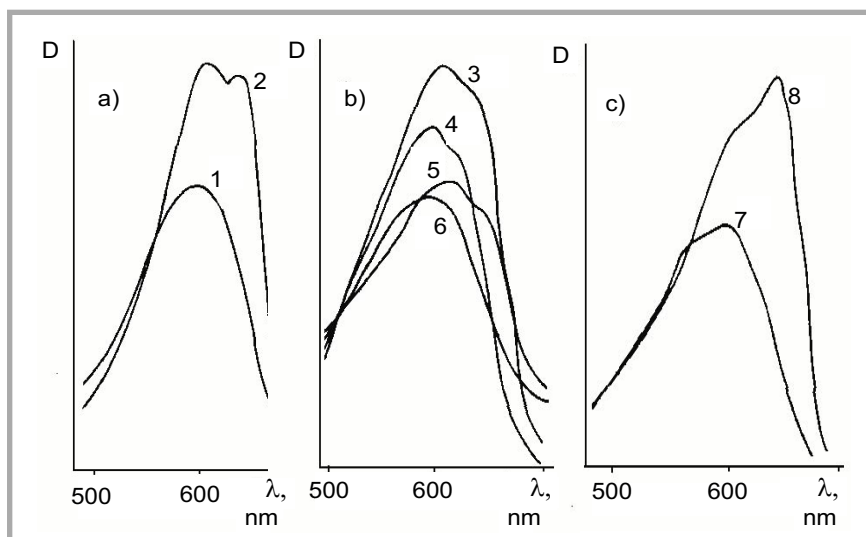


**Figure 4.** Residual C. I. Acid blue 78 v. s. concentration of CS in dye solution: 1 - in dist. water; 2 - in 0.01 N HCl; 3 - in 0.01 N NaOH; 4 - in 0.01 N urea. Initial concentration C. I. Acid blue 78 0.1 g/l. Amount of PDADMAC in CS 0.02 mol/AGR, amount of starch in CS paste - 4%.

acid and urea on the precipitation of C. I. Acid blue 78 by preformed CS with 0.02 mol/AGR PDADMAC has been examined, and the data are shown in Figure 4. The acid dye is better bound by CS in the absence of an alkali or acid. Obviously in the alkaline solution, the ionisation of sulphate groups of the acid dye occurs, the dye itself becomes more soluble, which in turn causes a worsening of the dye binding. In the acidic solution, the ionisation of the anionic phosphate groups of starch in CS is suppressed, and the CS is destroyed. Surprisingly, the binding of the dye in the presence of urea does not change.

It can be concluded that cationic nonstoichiometric PECs of starch and PDADMAC effectively remove the acid dye from the solution in the absence of an acid or alkali. On the contrary, for other PECs described in [13-15], CS can be used preformed. At a suitable molar ratio of CS components, acid dye can be precipitated without the negative influence of CS concentration excess, but this data is insufficient to explain the mechanism of the incorporation of acid dye into the PECs.

C.I. Acid blue 78 has polar and non-polar groups. Due to the hydrophobic hydration of these groups, the dye molecules draw closer to one another or to other hydrophobic particles. However, the addition of urea, known in terms of classical interpretations as a 'destroyer' of the hydrophobic bond, has no influence on the dye binding by CS (Figure 4, curves 1 and 4). So the hydrophobic interaction



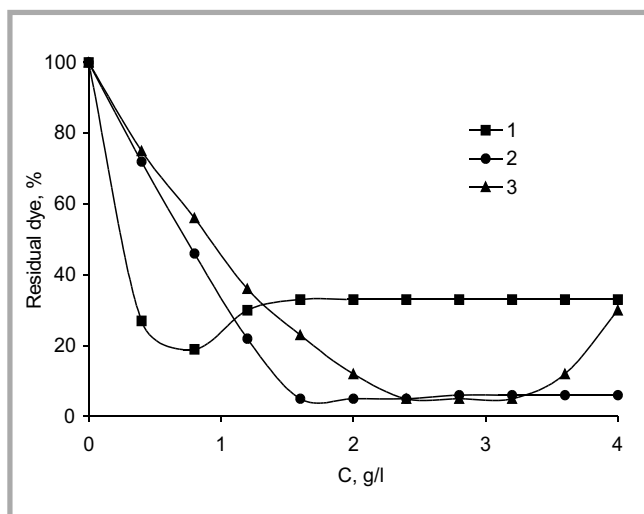
**Figure 5.** Spectra of light absorption of solution of C. I. Acid blue 78 before (a) and after precipitation in distilled water (b) and HCl solution (c): 1 - 0.01 N HCl; 2 - 0.01 N NaOH; 3 - 0.032 g/l PDADMAC; 4 - 0.008 g/l PDADMAC; 5 - 0.16 g/l CS; 6 - 0.04 g/l CS; 7 - 0.08 g/l CS; 8 - 0.32 g/l CS. Amount of PDADMAC in CS 0.02 mol/AGR, amount of starch in CS paste - 4%.

is not a decisive determinant in dye binding by CS.

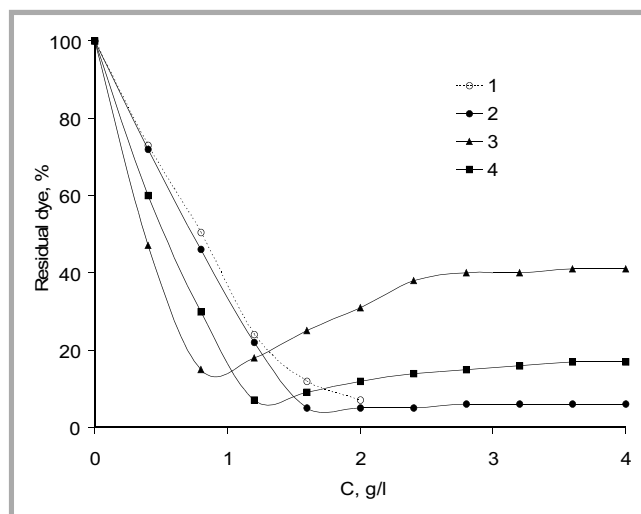
More information can be obtained by investigating the light absorption of the solutions of C. I. Acid blue 78. This dye can be used as an optical probe, because the changes in its colour strongly depend on the ionisation of the dye. The pH value of the commercial dye solution is 4-5. In the presence of alkali, ionisation of the dye occurs, electron-donating properties of dye molecules increase [23], and the light absorption of dye solution increases (Figure 5a). In the light absorption spectra, two absorption maximum shifted to the longer waves were noted. These light

absorption changes are seen even visually. In the acid medium the dye solution is blue with a red tint, and in the alkali medium the colour of the dye solution becomes sky-blue.

The sky-blue colour characteristic of the ionising C. I. Acid blue 78 was observed at the initial moment of CS or PDADMAC addition. When the dye interacts with the cationic polymer, the colour can change. Up to the optimal concentration of CS or PDADMAC required to precipitate the dye, the colour of dye solution after sedimentation was reddish blue. When the concentration of CS or PDADMAC was high enough to bind



**Figure 6.** Residual C. I. Acid blue 78 vs. amount of CS in dye solution. Concentration of dye: 1 - 0.05 g/l; 2 - 0.1 g/l; 3 - 0.15 g/l. Amount of PDADMAC in CS 0.02 mol/AGR, amount of starch in CS paste - 4%.



**Figure 7.** Residual C.I. Acid blue 78 vs. amount of CS in dye solution. Amount of starch in CS pastes: 1 - 2%; 2 - 4%; 3, 4 - 6%. Amount of PDADMAC in CS: 1-3 - 0.02 mol/AGR; 4 - 0.015 mol/AGR.

the dye, the colour of the dye solution after sedimentation becomes sky-blue. The visible colour changes in the C. I. Acid blue 78 solution coincide with the changing of the absorption maximum in the absorption spectra of the dye solution after sedimentation (Figure 5b). It has been pointed out that these changes of colour are not related to the pH value of the dye solution; the pH value of the dye solutions varied from 4.6 to 5.6. However, the same changes of colour occurred when the dye was precipitated by CS from a solution with a strongly acidic medium (the pH value of dye solution in 0.01 N HCl was about 2). Until the optimal concentration of CS, the colour of the dye solution was reddish-blue (Figure 5c, curve 7), and when the optimal concentration of CS was exceeded, the colour was sky-blue (Figure 5c, curve 8).

It is reasonable that the changes in the colour of the dye solution after precipitation with CS are related to the changes of dye ionisation. So, the interaction of CS with dye seems to be electrostatic. The fact that the amount of CS needed for the precipitation of the dye depends on the dye's concentration in the solution (Figure 6) confirms the importance of the free cationic groups of CS for dye binding.

Electrostatic interaction cannot explain all the experimental results. In many cases, the curves of dye precipitation have a minimum. Nor is it clear why CS with completely realised ionic bonds, and therefore with a minimum amount of the free cationic groups, shows the best precipitation of acid dye. An important role may be played by the affinity of the triple PECs including dyestuff to water, i.e. their hydrophilicity and the conformation of macromolecules in the PECs. Only when these parameters are optimal can dye removal from its solution be effective. This conclusion is supported by the observations illustrated in Figure 7. In this series of experiments, the dye was precipitated by CS in whose pastes the concentration of starch was 2, 4 and 6%, while the concentration of PDADMAC was constant (0.02 mol/AGR). When the amount of starch in CS increased to 6%, the residual concentration of acid dye in solution increased, probably due to the increase in the hydrophilicity of the triple polycomplex. More acid dye can be bound into a triple complex by a CS with 6% of starch, but only when the amount of PDADMAC, the other hydrophilic

component of CS, decreases (Figure 7, curve 3 and 4).

The experimental data shows that non-stoichiometric PECs can be formed in the solution of starch and PDADMAC. The composition and properties of these PECs depend on the molar ratio of ionogenic groups in the initial polymers. In the formation of PECs with native potato starch, 0.015–0.02 mol PDADMAC/AGR was needed. Even at the optimal composition, PECs contains free and dissociated cationic groups. In the solution of C. I. Acid blue 78, such PECs react with acid dye, and more hydrophobic and compact triple starch-PDADMAC-dye polycomplexes are formed. The acid dye is bound due to the electrostatic interaction between the dye and free cationic groups of PECs. Only when PECs with an incorporated acid dye contain a minimised amount of ionogenic hydrophilic groups they can aggregate and precipitate. This condition is indispensable for an effective clarification of textile wastewater with PECs.

## Conclusions

During the interaction of poly(diallyldimethylammonium chloride) (PDADMAC) and potato starch, non-stoichiometric polycomplexes (PECs) are formed. The optimal composition of preformed PEC was 0.01–0.015 mol PDADMAC to anhydroglucose residue. Such PECs contain an appreciable amount of free quaternary ammonium groups, and are called cationized starches (CS).

A preformed CS can effectively eliminate acid dye from the water solution. The best precipitation of C. I. Acid blue 78 is achieved with a CS containing 0.015–0.02 mol/AGR PDADMAC. In this case, only 3–5% residual dye remains in solution, and the dye precipitates in a wide range of CS concentrations.

Investigations of light absorption of C. I. Acid blue 78 solutions showed that dye precipitation with CS is related to changes in dye ionisation. The dye was incorporated into PECs by electrostatic interaction with the free cationic groups of CS, and more hydrophobic and compact triple starch-PDADMAC-dye polycomplexes were formed. Only when PECs with incorporated acid dye contain the minimised amount of ionogenic hid-

rophilic groups they can aggregate and precipitate. Such CS can be used for the clarification of textile wastewater.

## References

1. G. Carvalho et al., *Coloration technology*, 2002, vol. 118, No 5, pp. 215–219.
2. J. H. Choi et al., *Separation Science and technology*, 2001, vol. 36, No 13, pp. 2945–2958.
3. N. Hatvani, J. Mecs, *Enzyme and microbial technology*, 2002, vol. 30, No 3, pp. 381–386.
4. C. O'Neil et al., *Water Research*, 2000, vol. 34, No 6, pp. 2355–2361.
5. S. Chinwekitvanich, M. Tuntoolvest, T. Panswad, *Water Research*, 2000, vol. 34, No 6, pp. 2223–2232.
6. C. G. Namboodi, W. K. Walsh, *Amer. Dyestuff Rep.*, 1996, vol. 3, pp. 15–25.
7. N. Kannan, H. M. Sundaram, *Fresenius Environmental Bulletin*, 2001, vol. 10, No 11, pp. 814–822.
8. H. C. Chu, K. M. Chen, *Process Biochemistry*, 2002, vol. 37, No 6, pp. 595–600.
9. O. Yavuz, A. H. Aydin, *Fresenius Environmental Bulletin*, 2002, vol. 11, No 7, pp. 377–383.
10. A. Nechwatal, M. Nicolai, K. P. Mieck, *Starch*, 1999, vol. 51, No 8–9, pp. 286–293.
11. F. Delval et al., *Dyes and Pigments*, 2002, vol. 53, No 1, pp. 79–92.
12. I. Simkovich, *Carbohydrate Polymers*, 1996, vol. 31, No 1, pp. 47–51.
13. A. Jemaitaitis et al., *Melliand Textilber.*, 1994, vol. 75, pp. 312–314.
14. A. Jemaitaitis et al., *Melliand Textilber.*, 1997, vol. 77, Pp. 255–259.
15. R. J. Zemaitaitienė, E. Zliobaitė, R. Klimavičiūtė, A. Zemaitaitis, *Colloids and Surfaces A: Eng. Aspects*, 2003, vol. 214, pp. 37–47.
16. T. Takagishi, T. Sugimoto, A. Hayashi, *J. Polym. Sci. Polym. Chem.*, 1983, vol. 21, pp. 2311–2322.
17. H. M. Buchhammer, G. Petzold, K. Lunkwitz, *Colloid. Polym. Sci.*, 2000, vol. 278, pp. 841–847.
18. S. Dragan et al., *J. Polym. Sci. Part A - Polym. Chem.*, 1999, vol. 37, pp. 409–418.
19. U. Ortel et al., *Angew. Makromol. Chem.*, 1993, vol. 20, pp. 203–213.
20. T. Takagishi, H. Kozuka, N. Kuroki, *J. Polym. Sci. Polym. Chem.*, 1981, vol. 19, pp. 3237–3246.
21. M. G. Chausser, T. V. Samsonova, V. V. Lanin; *Bumazhnaya promishlennost'*, 1990, No 3, cc. 12–13.
22. Ir. J. J. M. Swinkels. *Industrial Starch Chemistry*, AVEBE, pp. 1–48.
23. B. I. Stepanov, *Vvedenie v khimiju i tekhnologiju organicheskikh krasitelej*. Moskva: Khimiya, 1984, pp. 69–72.

Received 20.08.2003 Reviewed 04.02.2004