Interaction of Dis-azo Dyes with Quaternized Poly(dimethylaminoethyl methacrylate) as a Function of the Dye Structure and Polycation Charge Density

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ABSTRACT: Interactions between some dis-azo dyes, different by either the position of their sulfonic groups or their number (Ponceau SS, Crocein Scarlet MOO, Congo Red, and Direct Blue 1), and some strong polycations (PCs), with cationic centers in their side chains and dye removal from artificial wastewaters were systematically investigated in this study. PCs with variable charge densities (CDs) were prepared from poly(dimethylaminoethyl methacrylate) by controlled quaternization with benzyl chloride. Even when the main process in the dye removal was charge neutralization (coagulation) for all of the dyes, significant effects of the CD and dis-azo dye structure on the metachromatic behavior of the dyes in dilute aqueous solutions and on the dye removal efficiency were observed. The stability of the PC/azo dye complex and, connected with this, the flocculation window were higher when the PC with the highest CD was used. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 728–735, 2009

Key words: colloids; dyes/pigments; UV–vis spectroscopy; water-soluble polymers

INTRODUCTION

Water-soluble dyes are very injurious; their presence in water even at low concentrations is visible and undesirable.[1] The release of colored wastewaters in effluents can affect the photosynthetic activity of aquatic life because of reduced light penetration,[2] and therefore, their decontamination is urgently required.[1] Furthermore, more stringent regulations concerning effluents require the diminishment of the dye content in water or even the banning of some dyes.[3] Among organic dyes, azo dyes make up the majority of colorants used for dyeing processes because of their vast number of shades and their fastness properties. However, many azo dyes have been determined to be very dangerous for the human body because the nitrogen–nitrogen bridge can be cleaved under reducing conditions, which leads to aromatic amines, which have been proven as or are suspected to be carcinogenic.[2,3] Typically, dye wastewater treatment methods are coagulation/flocculation, oxidation, and adsorption in combination with biological treatments. Adsorption process would have the potential advantage of allowing recovery of the dyes in a concentrated form.[4–9] However, coagulation/flocculation processes are the most widely used as pretreatments to remove suspended particles and coloring materials before biological treatment. So far, numerous investigations have been done on the interaction between organic (synthetic and natural) flocculation agents and water-soluble pollutants.[4,10,11] Among synthetic flocculants, polycations (PCs) are the most used.[12–14] Chain flexibility, molar mass, and charge density (CD) are the main factors that determine the specific applications of PCs.[12] Different mechanisms have been postulated for their action, with practical significance being charge neutralization, including electrostatic patch effects, and bridging flocculation.[12,14]

Many scientists in the field have pointed out that the main driving force in the interaction between polyelectrolytes and ionic dyes is the Coulomb interaction, that is, the charge neutralization of the dye charges by oppositely charged polyions.[15–18] In our previous investigations, PCs containing quaternary ammonium groups in the backbone were synthesized[19,20] and used in the separation of montmorillonite[21] and in dye removal.[22] The stoichiometry of PC/azo dye complexes[23–25] and the formation of PC/dye/polyanion tricomponent complexes[26] have been also investigated. In this study, we focused on the interactions of some dis-azo dyes, different by either the position of sulfonic groups, with two isomers being selected [Ponceau SS (PSS) and Crocein Scarlet MOO (CSMOO)], or the number of anionic groups, with two benzidine-type azo dyes being used [Congo Red (CR) and Direct Blue 1 (DB1)],
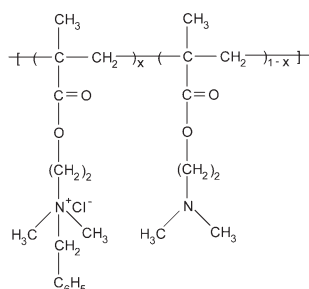
x = 0.45, polycation Q$_{45}$; x = 0.73, polycation Q$_{73,}$; x = 0.85, polycation Q$_{85}$

Chart 1 Chemical structure of the Q$_x$-type PCs. Q$_x$ means mol % of quaternary ammonium salt groups in PC.

with some PCs, having cationic centers in the side chain. PCs with variable CDs were derived from poly(dimethylaminoethyl methacrylate) (PDMAEM) by quaternization with benzyl chloride (BC Q$_x$ PCs). Unlike PCs containing N,N-dimethyl-2-hydroxypropylene ammonium chloride units in their backbone,[19,20] which are very hydrophilic, PCs derived from PDMAEM contain hydrophobic substituents in every repeat unit. Such PCs are often used as flocculants,[27–30] but no systematic investigation on the correlation between their CD and the dye structure, on the one hand, and dye removal efficiency, on the other hand, is available so far. Therefore, the main objective of our study was to identify the particularities of interactions between PCs of Q$_x$ type and the dis-azo dyes mentioned previously and to determine the applicability of PCs with variable CDs as effective agents for the removal of the dyes from water, with the stability of the PC/dye complex in the presence of PC in excess being correlated with the flocculation window.

EXPERIMENTAL

PCs

PDMAEM was synthesized by free-radical polymerization in the presence of 2,2′-azobisisobutyronitrile as the radical initiator. Size exclusion chromatography was performed in tetrahydrofuran + 2 wt % NEt$_3$ at 35°C, according to Dubois et al.,[31] with a Polymer Laboratories gel permeation chromatograph (Amherst, MA) equipped with a PL-EMD 950 evaporative mass detector. Two samples of PDMAEM were used: PDMAEM1 [weight-average molecular weight (M_w) = 42,340 g/mol, M_w/number-average molecular weight (M_n) = 1.98] and PDMAEM3 (M_w = 60,242 g/mol, M_w/M_n = 1.97). Copolymers of the Q$_x$ type with quaternary ammonium salt groups in the side chain, with controlled quaternization degrees (α's), were synthesized by the quaternization of PDMAEM1 with BC, as previously shown.[32] Typically, a volume of BC corre-

sponding to a certain α in 20 mL of dimethyl sulfoxide was added to 5 g of PDMAEM dissolved in 40 mL of dimethylformamide. The reaction was carried out at 50°C for 3 h. From the cold reaction mixture, the Q$_x$ PC was precipitated either with acetone, for α's higher than 50 mol %, or with diethyl ether, for α's lower than 50 mol %. Their general structure is presented in Chart 1.

The ionic chlorine content (Cl$_i$) was measured by potentiometric titration with 0.02N AgNO$_3$. α of the Q$_x$ copolymers was calculated with the following equation:

$$\alpha \text{ (mol \%)} = 100 \times Cl_i(\%) \times 157.21/[100 \times 35.45$$
$$- Cl_i(\%) \times 126.58] \quad (1)$$

where 157.21 is the molar mass of the repeat unit of PDMAEM and 126.58 is the molar mass of BC.

Cl$_i$ and the corresponding α, calculated with eq. (1), are included in Table I.

Dis-azo dyes

The azo dyes (PSS, CR, and DB1; Aldrich, St. Louis, MO, USA) and CSMOO (Fluka, Buchs, Switzerland) were used after they were recrystallized three times from an aqueous methanol solution (methanol/water = 70/30 v/v). The molecular structures of the dis-azo dyes used in this study are shown in Chart 2, and their main characteristics are collected in Table II.

PCs and azo dye solutions

All PC solutions were prepared at room temperature 1 day before use. The polymer concentrations were 0.1 wt%, unless another concentration is indicated. A stock solution of the PC with a concentration of 1 wt% was prepared first. The initial solution pH depended on the PC structure and was about 5.5–6.0 for the Q$_x$ PCs and about 7.5 for the PDMAEM solution. To check the influence of the PC solution pH on the dye removal efficiency, the pH of the PDMAEM3 solution was adjusted to about 5.0 by the addition of a 10^{-1} M HCl aqueous solution. The

TABLE I
α Values of Q$_x$-Type PCs

PC[a]	Cl$_i$ (%)	α (mol %)[b]
Q$_{45}$	7.5	45.43
Q$_{73}$	10.35	72.81
Q$_{86}$	11.45	85.89

[a] The values of α, shown as subscripts, are rounded.
[b] Calculated with eq. (1).
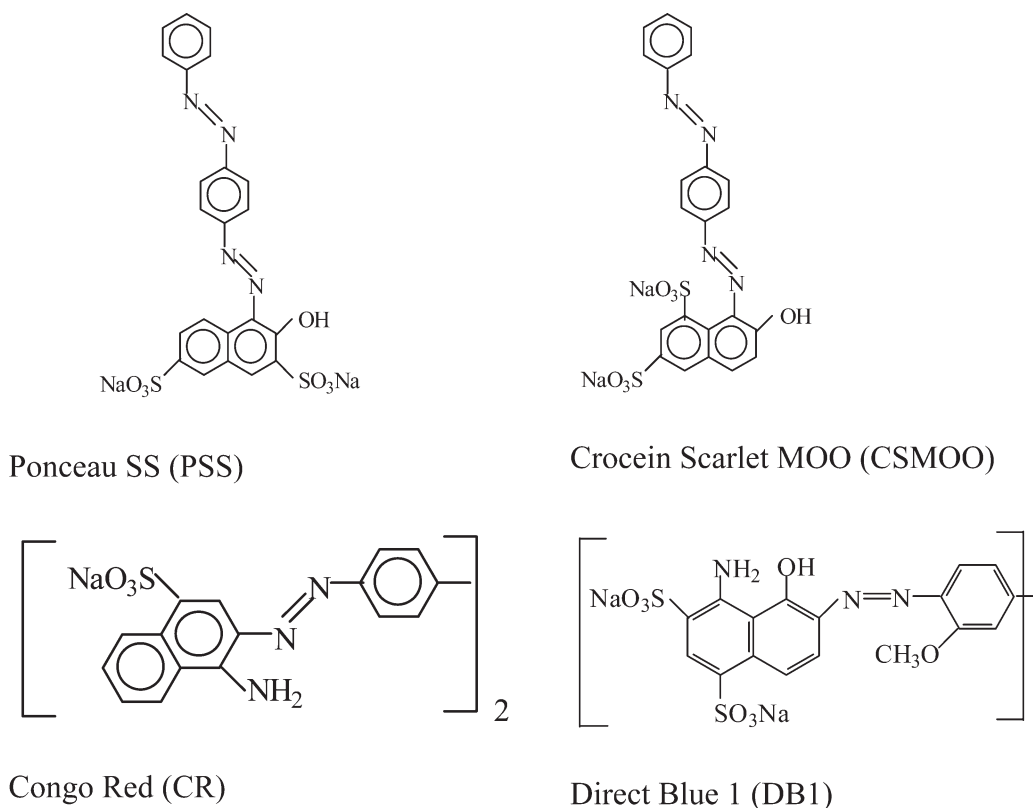
Chart 2   Molecular structures of the dis-azo dyes used in this study.

azo dyes (PSS, CSMOO, CR, and DB1) were dissolved in distilled water at concentrations of 2×10^{-4} M.

PC/azo dye complexation and dye removal

The ultraviolet–visible (UV–vis) spectra of the dyes in the presence of PCs in dilute aqueous solutions were recorded with a Specord M42 spectrophotometer (Jena, Germany). Increasing volumes of PC solution were added first to 50 mL of dye solution under stirring to determine the PC/azo dye complex stoichiometry. The stirring went on for 10 min, and the UV–vis spectra of the supernatant were recorded after 24 h, as already described.[23,24]

Jar tests were also performed to establish the dye removal efficiency. Typically, a standard jar-test apparatus equipped with stainless steel paddles and a stirrer was used for the coagulation and flocculation tests. Volumes of 400 mL of dye solution were transferred into 600-mL beakers. The sample was rapidly mixed at a paddle speed of around 180 rpm, and then, the polymer was added. The rapid mixing was continued for 3 min; this was followed by slow mixing for 15 min at about 50 rpm. After 24 h, the dye concentrations were determined by the measurement of the absorbance in the supernatant at the λ_{max} (characteristic wavelength) (Table II) of each dye.

RESULTS AND DISCUSSION

It is known that dyes aggregate as a consequence of their flat geometries. Aggregation level, and mode depend on the dye structure and the environmental characteristics. Maximum contact between the dye molecules results when the dye aggregation is

TABLE II
Main Characteristics of the Disazo Dyes

| Azo dye	Color index name	Color index number	Molar mass	λ_{max} (nm)
PSS	Acid Red 150	27,190	556.48	514
CSMOO	Acid Red 73	27,290	556.48	510
CR	Direct Red 28	22,120	696.66	497
Chicago Sky Blue 6B	DB1	24,410	992.80	620

mainly side by side, with a hypsochromic spectral shift being characteristic (H aggregation). Spectral shifts to longer wavelengths relative to the monomeric dye absorption are characteristic of the so-called J aggregates.[33–35] In dilute aqueous solutions, the azo dyes used in this study showed metachromatic behavior in the presence of both PDMAEM and the Q_x PCs. That is, some UV–vis spectral changes accompanied the ionic binding of the dye to the PC chain as a consequence of π–π interactions between adjacent dye molecules. As anionic dye molecules are attracted to oppositely charged sites on the PC chain, they came into close proximity of each other. As a result, spectral shifts were observed at longer wavelengths (bathochromic effect) or shorter wavelengths (hypsochromic effect); this depended on the mutual orientation of dipole moments.[35] Thus, characteristic wavelengths of non-aggregated dye molecules were found at 514 nm for PSS, 510 nm for CSMOO, 497 nm for CR, and 620 nm for DB1, but some spectral shifts appeared in the presence of PDMAEM and the Q_x PCs. A redshift from 514 nm to about 535 nm and a distinct shoulder at about 560–570 nm were found for PSS in the presence of PDMAEM1 [Fig. 1(a)]; the redshift was at about 520 nm, and the shoulder was at about 550–560 nm when Q_{45} [Fig. 1(b)] and Q_{85} [Fig. 1(c)] were added to the PSS solution.

A redshift of the characteristic maximum from 510 nm to about 520 nm and a shoulder at about 550–560 nm were observed in the CSMOO spectra in the presence of PDMAEM1 [Fig. 2(a)]; the redshift was at about 515 nm, and the shoulder was at about 550–560 nm when Q_{45} [Fig. 2(b)] and Q_{85} [Fig. 2(c)] were added to the CSMOO solution.

The definite redshift of the maximum in the case of PSS and CSMOO showed that a J aggregation of the dye molecules occurred by interaction with the Q_x PC. No significant changes took place with the maximum at 350 nm, which was present in the UV–vis spectra of both PSS and CSMOO.

The UV–vis spectra corresponding to CR after the addition of increasing amounts of PC are collected in Figure 3(a,b) for PDMAEM3 and Q_{73}, respectively.

As shown in Figure 3(a), the addition of PDMAEM3 at pH 7.5 caused the decrease of the absorbance at the characteristic wavelength (497 nm) and a distinct shoulder at about 550 nm; the greater the amount of PC was, the higher the shoulder was. This showed that an aggregation of the dye molecules happened, but this process was not accompanied by the corresponding neutralization of the dye charges. Therefore, the absorbance remained high enough even at a high quantity of PC (the spectrum corresponding to 140 mg of the PDMAEM3/liter (L) CR aqueous solution). With a further increase in the
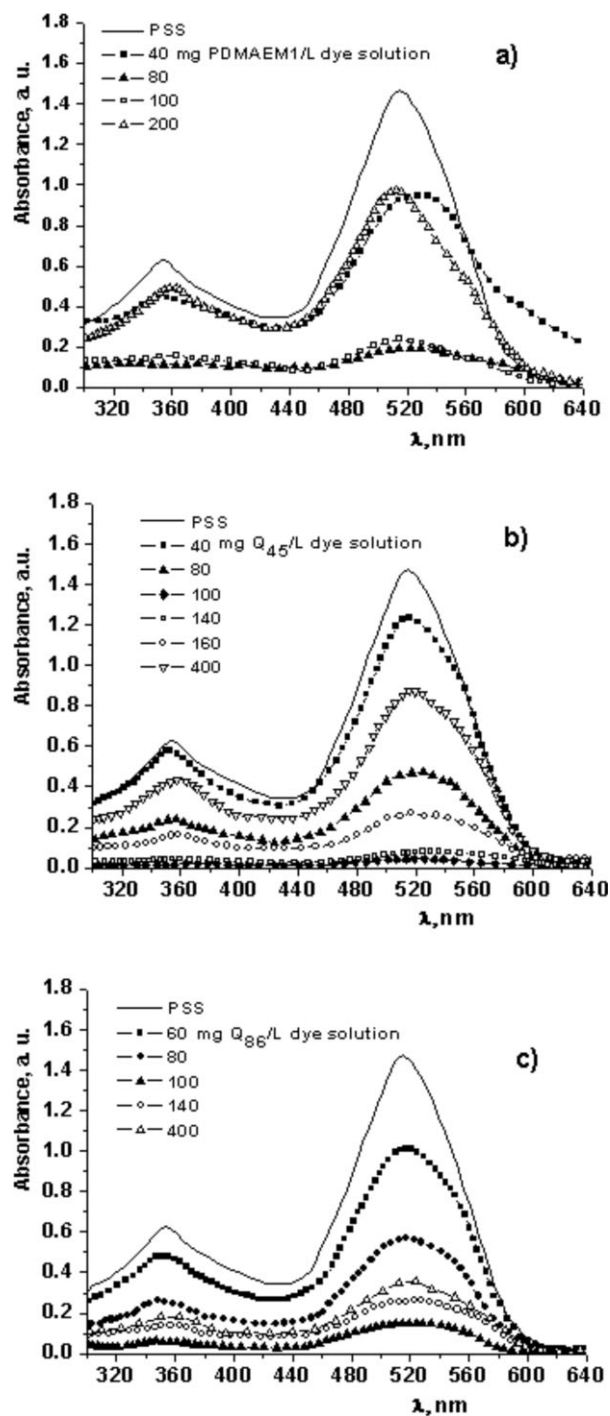
Figure 1 Absorbance (au) as a function of the amount of PC added to the PSS solution.

PC added (the spectrum corresponding to 200 mg of the PDMAEM3/L CR aqueous solution), the absorbance increased again, and this demonstrated weak interaction between PDMAEM and CR at pH 7.5. On the other side, the addition of Q_{73} led to the complete removal of the dye, with the absorbance at 497 nm about zero at 100 mg of PC/L CR aqueous solution; this slowly increased with increasing PC addition [Fig. 3(b)].
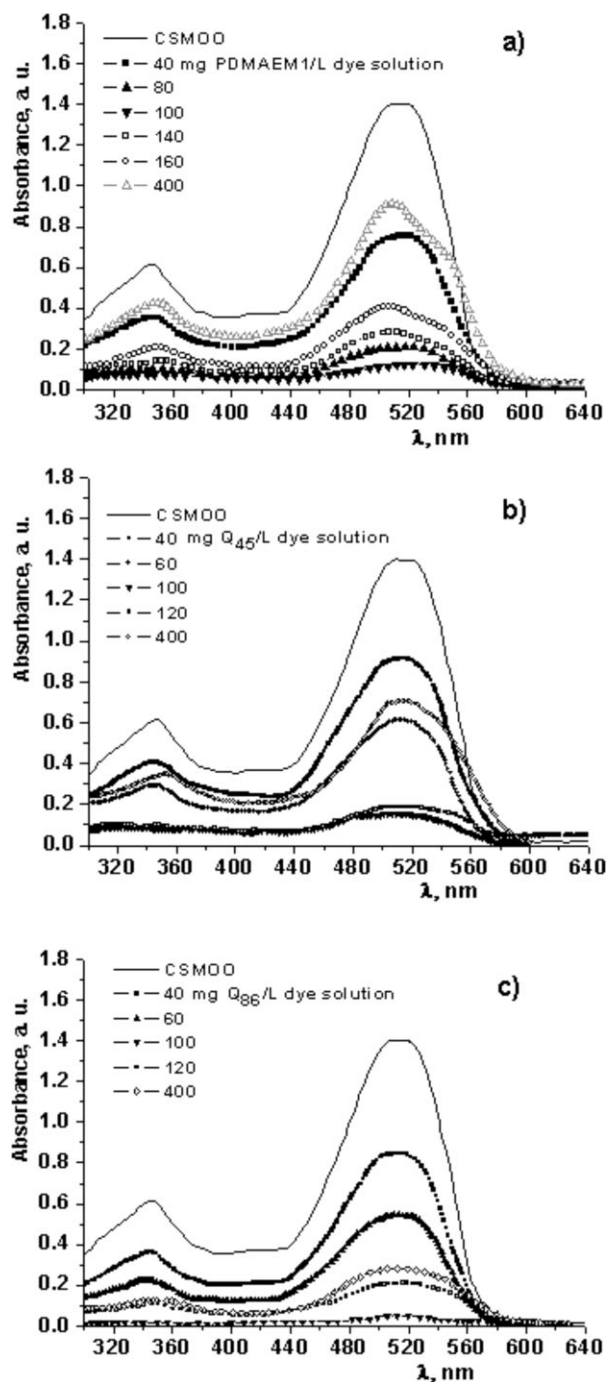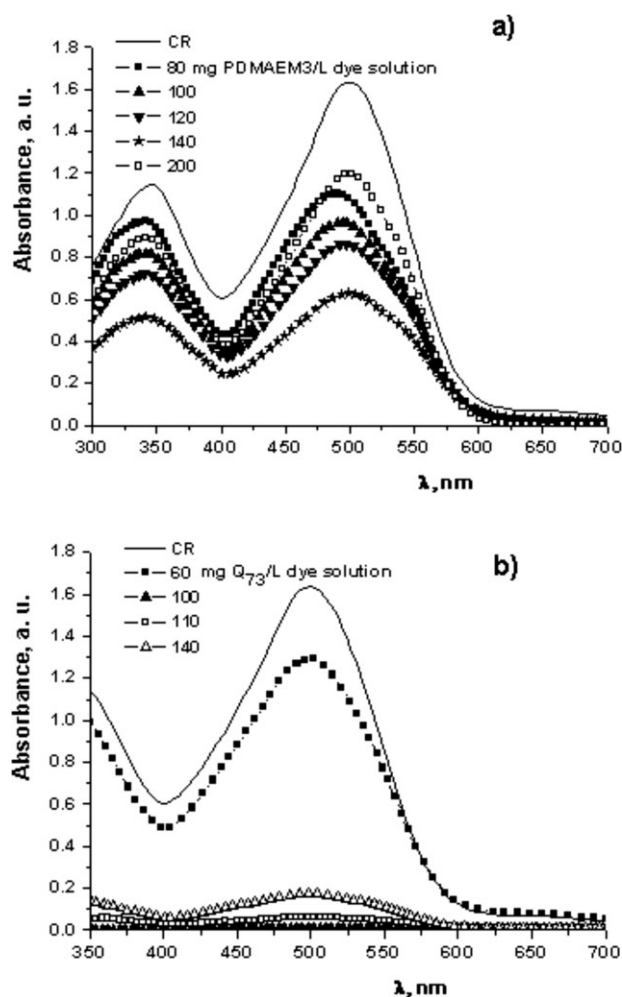
Figure 2 Absorbance (au) as a function of the amount of PC added to the CSMOO solution.

Figure 4 illustrates the interaction between two PCs of Q_x type (Q_{45} and Q_{73}) and the DB1 dye. A bathochromic shift of the characteristic maximum of the dye and a shoulder at about 660 nm were observed in the presence of both PCs. The increase in the PC amount after stoichiometry led to a decrease in the aggregation level of the dye, which was reflected in the increase of the absorbance, but, for the same amount of PC, the absorbance was

higher in the case of Q_{45}. That is, the complex stability was lower when the CD of PC was lower.

As Figures 1–4 show, with increasing amount of PC, the intensity of the characteristic maximum of the dyes increased again because the distance between the bound dye molecules increased, and therefore, their interaction possibilities diminished, but the metachromatic effect was still observed for all of the dyes.

Ionic dye molecules are water-soluble organic matter, which consist of low-molar-mass species that aggregate at high concentrations but still remain much smaller than the fine particles present in water at a colloidal level. It could be assumed that, similar to the removal of dissolved natural organic matter in surface waters, such as humic acids,[14] the optimum dose to correspond closely with charge neutralization and stoichiometry between the dye charges and the charges of the added polyelectrolyte could be found. Figures 5–8 show the variation of the relative absorbance (A_c/A_i, where A_c and A_i are the

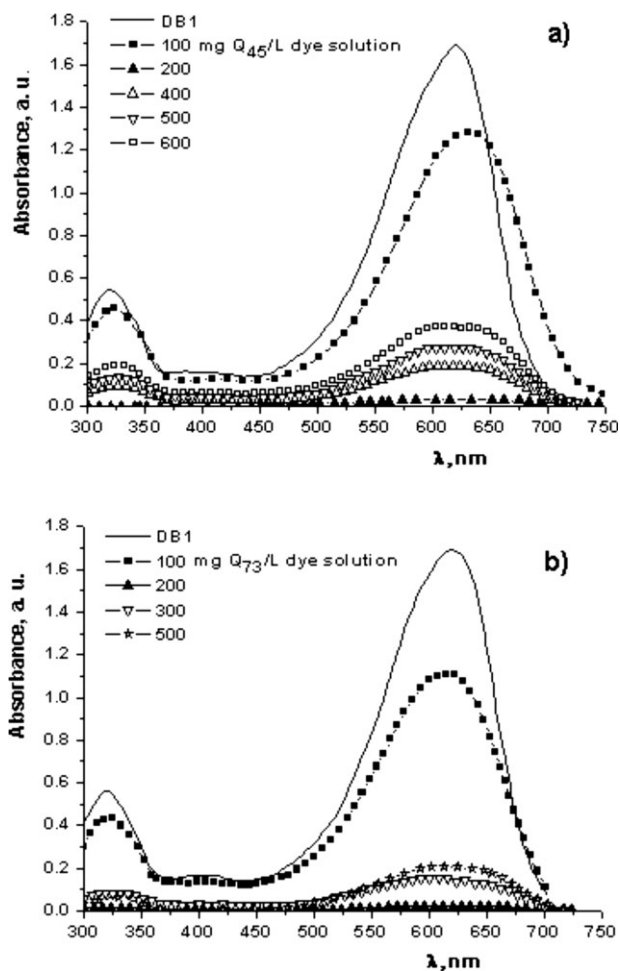**Figure 3** Absorbance (au) as a function of the amount of PC added to the CR solution.

Figure 4 Absorbance (au) as a function of the amount of PC added to the DB1 solution.

absorbances after and before the addition of PC, respectively) as a function of the molar ratio of PC with different CDs to the azo dyes ([P]/[D]).

As a general trend, the intensity of the characteristic maximum and, consequently, A_c/A_i decreased with the increase of [P]/[D]; only the position of the minimum was a function of CD and the dye structure. Thus, for the dyes having two sulfonic groups, the value of [P]/[D] corresponding to the stoichiometry of the PC/dye complex when Q_x's with a high CD were used (Q_{73} and Q_{86}) was about 2 [Figs. 5(a), 6, and 7], and it was a little higher (ca. 2.4–2.5) when Q_{45} was used [Figs. 5(a) and 6]. Another difference was in the complex stability reflected in the larger flocculation window in the case of Q_{73} and Q_{86} compared with Q_{45}; that is, a higher [P]/[D] was necessary to increase A_c/A_i after the complex stoichiometry [Figs. 5(a) and 6].

The use of PDMAEM1 at pH 7.5 for the removal of PSS [Fig. 5(a)] and CSMOO (Fig. 6) showed different behavior manifested by the shift to the right of [P]/[D] corresponding to the minimum A_c/A_i, with a higher value of A_c/A_i corresponding to the mini-
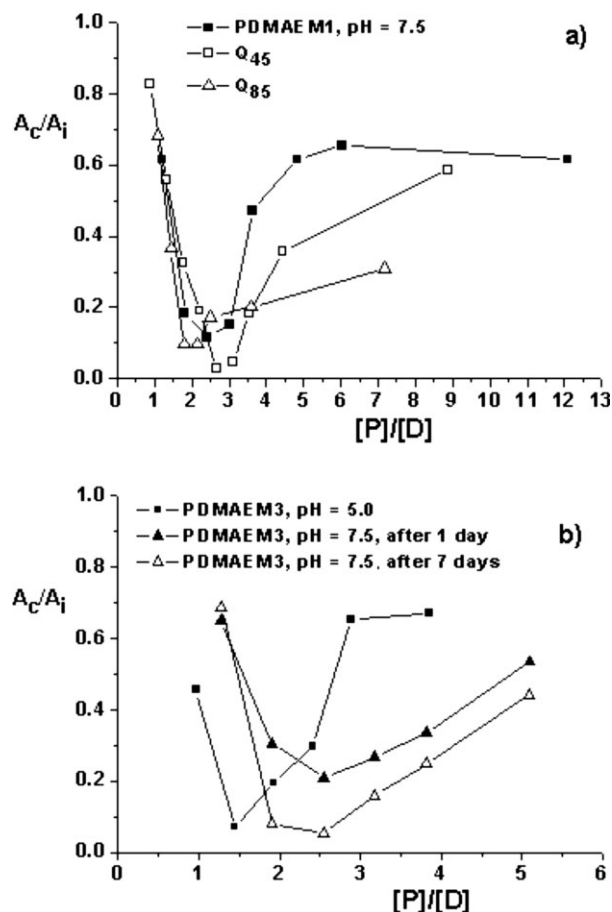

Figure 5 A_c/A_i as a function of [P]/[D] with different PCs added to PSS solutions.

mum and a narrow flocculation window. The use of PDMAEM3, with a higher molar mass, did not significantly improve the dye removal [PSS, Fig. 5(b)]. The increase of the settling time from 24 h up to 7 days led to an increase in the dye removal [PSS, Fig. 5(b); CR, Fig. 7]. A lower [P]/[D], corresponding
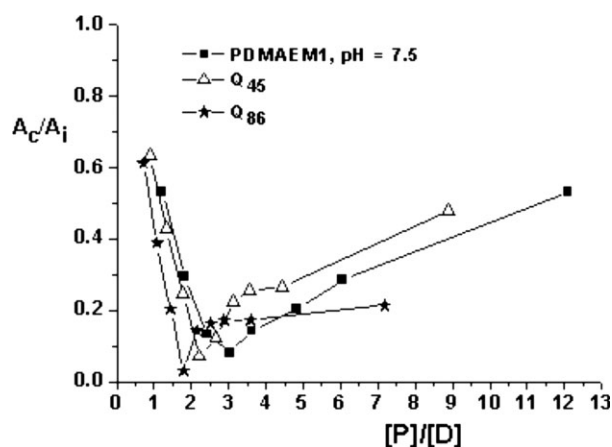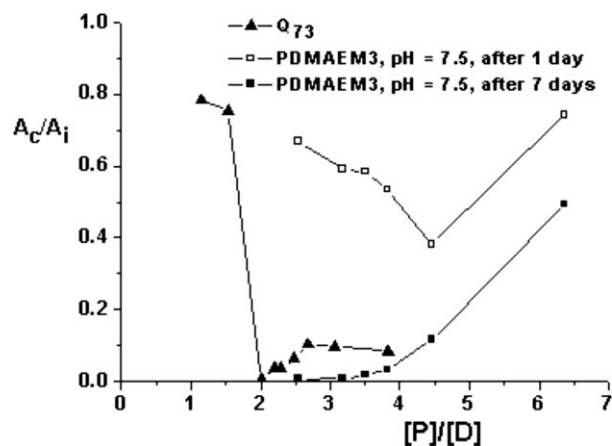

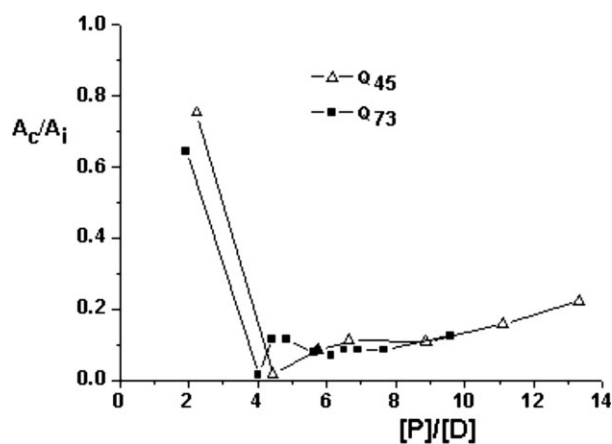**Figure 6** A_c/A_i as a function of [P]/[D] with different PCs added to CSMOO solutions.

Figure 7 A_c/A_i as a function of [P]/[D] with different PCs added to CR solutions.

TABLE III
Results of the Jar Test with Q_{73} as a PC for Dye Removal

Disazo dye	[P]/[D]	A_c/A_i	CRE (%)[a]
PSS	1.8081	0.2206	77.94
	2.009	0.0759	92.41
	2.4108	0.2414	75.86
CSMOO	1.6072	0.2043	79.57
	1.8081	0.1137	88.63
	2.009	0.0264	97.36
CR	2.009	0.094	90.6
	2.4108	0.1035	89.65
	2.8126	0.1517	84.83
DB1	4.018	0	100
	4.8216	0.0798	92.02
	6.027	0.1191	88.09

[a] CRE = color removal efficiency [CRE = $(1 - A_c/A_i) \times 100$].

to the minimum A_c/A_i, was found when the solution pH of PDMAEM decreased to 5.0 [Fig. 5(b)], but the flocculation window was much narrower compared with that found at pH 7.5.

The [P]/[D]'s needed to achieve the minimum A_c/A_i were 4.0 and about 4.2 in the cases of the interaction of DB1 with Q_{73} and Q_{45}, respectively (Fig. 8). The higher amount of Q_{45} necessary to reach the minimum A_c/A_i could be explained by the difficulties in the compensation of charges, similar with the other three dis-azo dyes. The particularity of this dye was the time necessary to get a good separation of the PC/DB1 complexes, which was much longer than for the other dyes (ca. 40 h compared with 24 h for the dyes with only two sulfonic groups).

Some of the results obtained in the process of dye removal under the conditions of the jar test are collected in Table III.

PC Q_{73} was used for all jar tests. As shown in Table III, the jar experiments confirmed the stoichiometry of each PC/azo dye complex and demonstrated

a high efficiency in the dye removal, as high as the number of sulfonic groups was higher. A special comment is necessary for the dye CR: the lower efficiency observed in the jar test was due to its structure, with the distance between sulfonic groups being higher than in the case of the other two disulfonic azo dyes. The compensation of opposite charges could be more difficult in the case of CR. To demonstrate this was the reason, a different experiment was performed with a lower addition rate of PC corresponding to a [P]/[D] of about 2 and vigorous stirring of the dye solution for 10 min. As a result, the dye removal efficiency was almost 100%.

CONCLUSIONS

Dye removal by PCs of Q_x type obtained by the quaternization of PDMAEM1 with BC (Q_x, with $x = 0$, 45, 73, and 86) was investigated for four pure disazo dyes (PSS, CSMOO, CR, and DB1). It was demonstrated that the interaction between Q_x-type PCs and all the dyes led to almost stoichiometric PC/azo dye complexes, and this showed that charge neutralization (coagulation) was the main process of dye removal. It was shown that not only the number of sulfonic groups, that is, the charge of the azo dye, but also the position of the anionic charges and the whole structure of the dye determined the most effective PC in dye removal and PC/dye complex stability (the flocculation window). The highest stability of the PC/dye complex, for PSS and CSMOO, when PC was added in excess (a larger flocculation window), was found with Q_{86}, that is, with the PC characterized by the highest CD, and this demonstrated a higher order in compensation of charges in the PC/dye complex formation. CR was difficult to remove with PDMAEM but very easy with Q_{73}, where a large flocculation window was found. The highest stability of PC/azo dye complex (the largest

Figure 8 A_c/A_i as a function of [P]/[D] with two PCs added to DB1 solutions.

flocculation window) was found in the case of DB1; that is, the higher the number of sulfonic groups was, the stronger the interaction between the PC and this direct azo dye. The removal efficiency of the dyes with PDMAEM was sensitive to pH and was lower in basic pH, when this PC became deprotonated.

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