Synthesis, Characterization, and Flocculation Performance of a Sulfonated Polytriazine

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ABSTRACT: A novel sulfonated polytriazine (SP) is synthesized by the condensation polymerization reaction of 2-(4,6-dichloro-1,3,5-triazin-2-ylamino)benzene-1,4-disulfonic acid (Compound I) and 1,4-diaminobenzene. The structure of SP is characterized by FTIR spectroscopy, ^{1}H-NMR, and gel permeation chromatography (GPC). The flocculation performances for the cationic dyes are evaluated. The experimental results show that SP can efficiently remove the color of wastewater containing cationic dyes. The rates of color removal from C.I. Basic red 18 and C.I. Basic blue 9 reach as high as 99.6% and 98.5%, respectively. The synthesized SP shows high adsorption capacities of 1719 and 1988 mg/g for C.I. Basic blue 9 and C.I. Basic red 18, respectively. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39669.

INTRODUCTION

Cationic dyes are mainly used in the coloration of acrylic fibers,[1] paper,[2] and nylon.[3] However, these dyes cannot be completely fixed on the substrates, and the utilization ratio is only 60%.[4] Consequently, the dyeing procedure generates large quantities of wastewater containing cationic dyes. Wastewater treatment is very difficult because the dyes have a complex molecular structure, which makes them stable and difficult to be biodegraded.[5] To remove the color from wastewater, many chemical and physical treatment methods have been extensively used in dye wastewater treatment.[6] These methods include chemical oxidation and electrolysis, biodegradation, physical flocculation, or a combination of the above methods.[7] Among these treatments, physical flocculation has been widely applied in the decolorization of dye wastewater as a pretreatment procedure.[8–10]

Flocculation is a very well known process of precipitating soluble substances by charge neutralization and adsorption bridging.[11] The typical flocculating agents are classified into inorganic coagulants and organic polymeric flocculants. However, inorganic coagulants cannot be used to remove cationic coloring dyes because of the electropositivity and high residue of ions such as Fe^{2+}, Fe^{3+}, or Al^{3+}.[12] By contrast, the proper use of electronegative organic polymeric flocculants can successfully remove cationic dyes from wastewater produced by the

dyeing processes of acrylic fibers.[13,14] Anionic polymeric flocculants adsorb cationic dyes via opposite charge attraction and adsorption bridging.[15] So the anionic polymers containing carboxyl groups[16,17] or sulfonic groups[18,19] are mainly used to flocculate cationic dyes in acid condition. However, the polymers containing carboxyl groups would become less water soluble due to the low dissociation degree of carboxyl group in acid condition, especially in the presence of higher ionic environment. In contrast to carboxyl groups, the sulfonic groups have high dissociation degree in acid condition. The sulfonated polymers with high sulfonic group content are effective flocculating agents for the removal of cationic dyes from wastewater, but their simple synthesis is still a challenge. The sulfonated polymers were mainly obtained by copolymerization or polymer modification. However, the introduction of other copolymerization monomer would reduce the sulfonic group content. The polymer modification by sulfonation reaction could effectively increase the sulfonic group content, but this process would produce much waste acid, which was very difficult to treat.

The aim of this study is to synthesize novel sulfonated polymer with high charge density by the facile preparation route to resolve the above problems about the sulfonated polymers. So, one type of novel sulfonated polytriazine (SP) with high charge density was developed by the facile condensation polymerization process, in which the cyanuric chloride with a controllable

reactive temperature was introduced. Cyanuric chloride has three different active chlorines (reactive temperatures of 0–10, 40–50, and 90–100°C, respectively).[20,21] Therefore, the reaction of cyanuric chloride with aromatic amine can be very easily controlled, and large numbers of small molecular derivatives can be obtained.[22,23] Based on the controllable reactive characteristic, the higher sulfonic group content of SP can be easily obtained by the condensation polymerization of Compound I and 1,4-diaminobenzene (Scheme 1), because there are two sulfonic groups in Compound I, which is derived from condensation reaction of 2-amino-benzene-1, 4-disulphonic acid with cyanuric chloride. That is very important to improve the flocculating performance for cationic dyes due to the increase of charge neutralization. The flocculation performances of SP for the two cationic dyes C.I. Basic blue 9 (BB9) and C.I. Basic red 18 (BR18) were studied in detail. The high color removal rates and adsorption capacities can be attributed to the high charge density in the polymeric structure and chain elongation of SP in water.

EXPERIMENTAL

Materials

The test cationic dyes BB9 (68.3% purity) and BR18 (88.97% purity) were procured from Shanghai Dyestuff Company. These dyes were further purified by the CH3COOK-CH3CH2OH method.[24,25] Cyanuric chloride was obtained from Sanzheng Chemical Factory, Liaoning, China. All other chemicals were analytical grade and purchased from Shenyang No. 1 Chemical Reagent Factory, Liaoning, China.

Synthesis of 2-(4,6-Dichloro-1,3,5-triazin-2-ylamino)benzene-1,4-disulfonic Acid (Compound I)

A solution of 2-amino-benzene-1, 4-disulphonic acid (5.0 g, 0.02 mol) in water (66 mL) was added to a suspension of cyanuric chloride (3.9 g, 0.021 mol) in a mixture of water (15 mL) and ice (20 g). The reaction mixture was stirred for 4 h at 0–5°C and pH 6–7. The reaction was monitored by thin-layer chromatography (TLC) using n-BuOH : n-PrOH : EtOAc : H$_2$O (2 : 4 : 1 : 3) as the eluent and silica gel TLC plates as the stationary phase. The synthesized Compound I (Scheme 1) was isolated by adding 10% CH3COOK (KOAc), collected by

filtration, washed with ethanol several times to remove KOAc, and dried in a vacuum to give 8.05 g (yield: 90.7%; purity: 99.5% by HPLC; R_f = 0.75; λ_{max} (H$_2$O) = 227 nm). ^{1}H-NMR (400 MHz, DMSO-d_6, δ): 11.0 (s, 1H, NH), 8.4 (s, 1H, Ar H), 7.6 (d, 1H, Ar H), 7.4 (d, 1H, Ar H); IR (KBr): v (cm^{-1}) 3450 (OH), 1544 (C≡N), 1404 (C≡N), 1221 (SO$_3$H), 1015 (SO$_3$H); APCIMS m/z: [M-H]$^-$ 398.9.

Synthesis of SP

1,4-Diaminobenzene (1.08 g, 0.01 mol), Compound I (4.44 g, 0.01 mol), DMSO (30.0 mL), and triethylamine (2.02 g) were mixed in a three-neck flask. The reaction mixture was stirred for 4 h at 40–45°C and pH 6–7. The reaction temperature was then increased to 90–95°C with continuous stirring for 48 h. N$_2$ gas was purged into the flask to isolate the oxygen during the entire reaction. Finally, SP solid was obtained by dialyzing, concentrating, and drying the reaction solution, and the solubility was 38 g/100 mL water at 25°C. The dialyzing process was determined by TLC and conductivity determination. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) of SP are determined by gel permeation chromatography (GPC), which is an Agilent Technologies 1200 with standard refractive index. The GPC separation is carried out by using UltrahydrogelTM 1000 columns at 40°C, and the water flow rate is 1 mL/min. The pH value was 6.32 when the concentration of SP was 75 mg/L at 25°C. ^{1}H-NMR (400 MHz, DMSO-d_6, δ): 9.6 (s, 1H, NH), 9.4 (s, 2H, NH), 8.8 (s, 1H, Ar H), 8.6 (s, 1H, Ar H), 8.0 (s, 1H, Ar H), 7.7 (s, 2H, Ar H), 7.3 (d, 2H, Ar H); IR (KBr): v (cm^{-1}) 3450 (OH), 1544 (C≡N), 1404 (C≡N), 1311(C—N—C), 1221 (SO$_3$H), 1015 (SO$_3$H).

Dye Removal

The flocculation test was carried out using a standard jar test apparatus (MY 3000-6) at 50 rpm. The effect of SP dosage on the color removal was carried out in the 200 mL of dye solutions (68 mg/L) with 5–30 mg of SP (M_n 914,000) at room temperature for 30 min, and the pH value was adjusted to 3 by using the 0.1 mol/L HCl solution, and the corresponding concentration ranged from 25 to 150 mg/L. The original dye solutions were obtained by dissolving 68 mg dye into 1000 mL deionized water. The effect of pH value of SP on the color
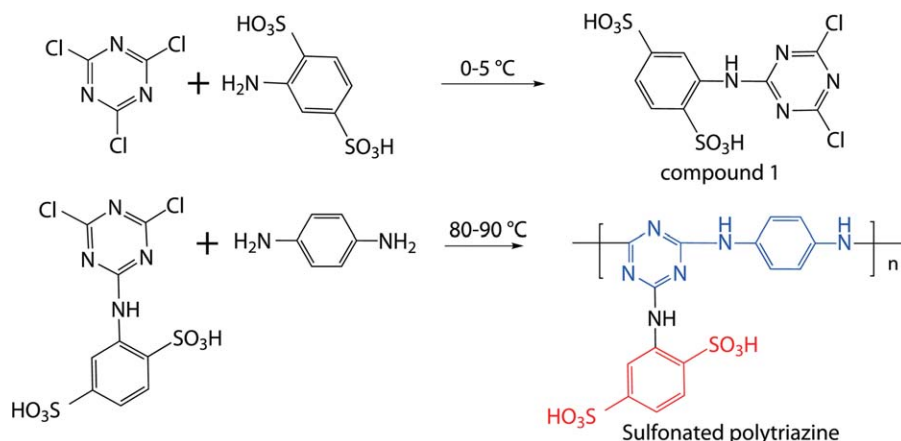
Scheme 1. Synthesis of the novel SP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

removal of cationic dye was carried out in the 200 mL of dye solutions (68 mg/L) with 15 mg of SP (M_n 914,000) at room temperature for 30 min, and the pH value was adjusted from 1 to 10 by using the 0.1 mol/L HCl solution or 0.1 mol/L Na_2CO_3 solution. The effects of salt dosage on the color removal of the cationic dye was carried out in the 200 mL of dye solutions (68 mg/L) with 15 mg of SP (M_n 914,000) at pH 3 and room temperature for 30 min, and the salt (Na_2SO_4) concentration was added from 0 to 0.13 mol/L. The effect of the molecular weight of SP on the color removal of the cationic dye was carried out in the 200 mL of dye solutions (68 mg/L) with 15 mg of SP at room temperature for 30 min. The adsorption capacity was obtained by the batch equilibrium adsorption experiments, which were carried out by agitating 200 mL various concentrations of BB9 or BR18 solutions at pH 3.0 with 15 mg of SP at room temperature until equilibrium was established. In all flocculation tests, the samples were withdrawn from the shaker when the stir ended. And the dye flcos was separated from the solution by centrifugation at 8000 rpm for 10 min. The absorbencies of samples were measured using a UV–vis spectrophotometer (HP8453) at wavelength 664 nm, 486 nm for BB9 and BR18, respectively. Then the concentrations of the residual dye in the solution were determined by using linear regression equation ($Y = 175.9250x$ (g/L) $+ 0.0048$, $R^2 = 0.9996$, for BB9; $Y = 61.5025x$ (g/L) $+ 0.0008$, $R^2 = 0.9999$ for BR18). The removal amounts of BB9 or BR18 were calculated by subtracting the final solution concentration from the initial concentration of dye solutions.

RESULTS AND DISCUSSION

Synthesis and Characterization of SP

SP was synthesized by the condensation polymerization reaction between the soluble Compound I and 1,4-diaminobenzene (Scheme 1). The number-average molecular weight (M_n), weight-average molecular weight (M_w), and PDI of SP are obtained from the GPC results, which are summarized in Table I. The yield of SP and the structures of SP and the cationic dyes are also shown in the same table.

Table I shows that SP has a yield of 91.7%, M_n of 9.14×10^5, and PDI of 1.02. These results indicated that the condensation polymerization easily occurred by changing the reaction temper-
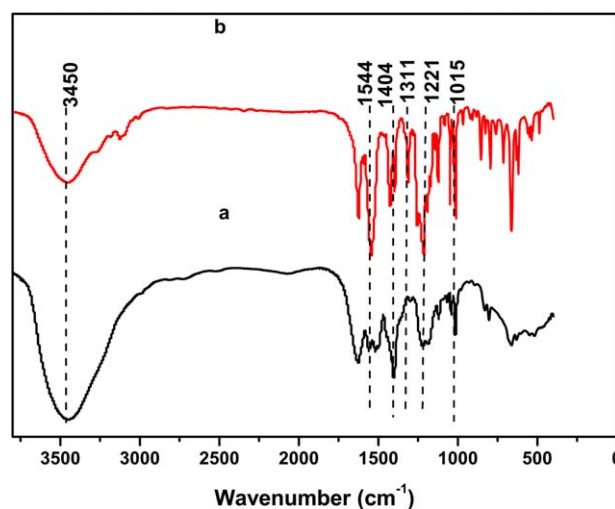

Figure 1. FTIR spectra of Compound I (a) and SP (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ature, because cyanuric chloride had three different active chlorines.[20,21] At the same time, the SP would have good flocculating performance for cationic dyes due to the increase of charge neutralization, because there were two sulfonic groups in one polymer segment.

Figure 1 shows the FTIR spectra (KBr) of Compound I [Figure 1(a)] and SP [Figure 1(b)]. The broad peak at 3450 cm^{-1} was assigned to the O—H vibration from the sulfonic acid groups in SP [Figure 1(a,b)]. The absorptions at 1221 and 1015 cm^{-1} were assigned to the sulfonic acid groups[26] in Compound I and SP. The spectrum of SP showed characteristic peaks of the s-triazine ring at 1544 and 1404 cm^{-1} [Figure 1(b)].[27] In contrast to the spectrum of Compound I [Figure 1(a)], a C—N—C stretching peak at 1311 cm^{-1} appeared in the spectrum of SP.[28] This finding indicated that the condensation polymerization between Compound I and 1,4-diaminobenzene had occurred.

Figure 2 shows the ^{1}H-NMR spectra (400 MHz, DMSO-d_6) of SP [Figure 2(a)] and Compound I [Figure 2(b)]. The peaks at 7.4, 7.6, and 8.4 ppm are ascribed to the protons at the 1, 2, and 3 sites of Compound I, respectively. However, the chemical

Table I. Structural Parameters of SP and the Dyes

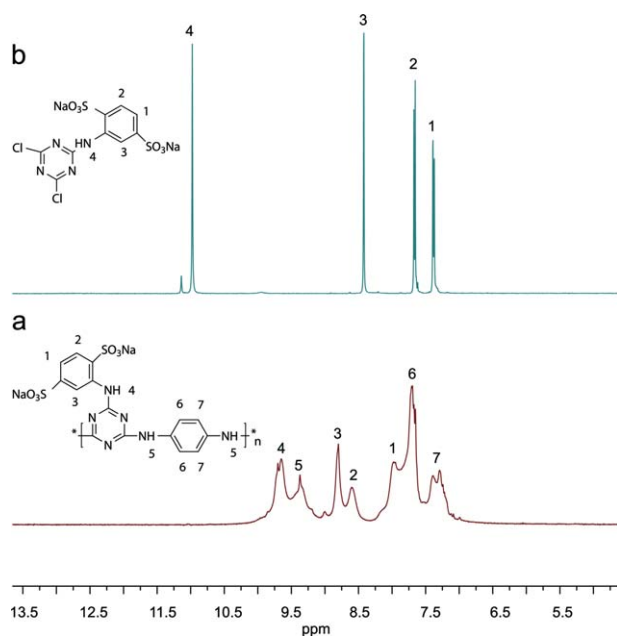| Samples	Structure	λ_{max} (H$_2$O) (nm)	Yield (%)	M_n	M_w	PDI
SP		280	91.7	9.14×10^5	9.35×10^5	1.02
BB9		664	–	–	319.8	–
BR18		486	–	–	426.3	–

Figure 2. ^{1}H-NMR spectra of Compound I and SP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shifts of the protons at the 1, 2, and 3 sites of SP appeared downfield (peaks at 8.0, 8.6, and 8.8 ppm, respectively) due to the deshielding effect of the neighboring benzene rings.[29] The peaks were also broadened due to the SP aggregation in solution because of the π–π interactions between aromatic rings.[30,31]

The GPC, IR, and ^{1}H-NMR analyses showed that SP with a high molecular weight was obtained by the condensation polymerization.

Flocculation Study

The performance of SP was investigated by conducting tests using cationic dye solutions. The results are shown in Figures 3–7.
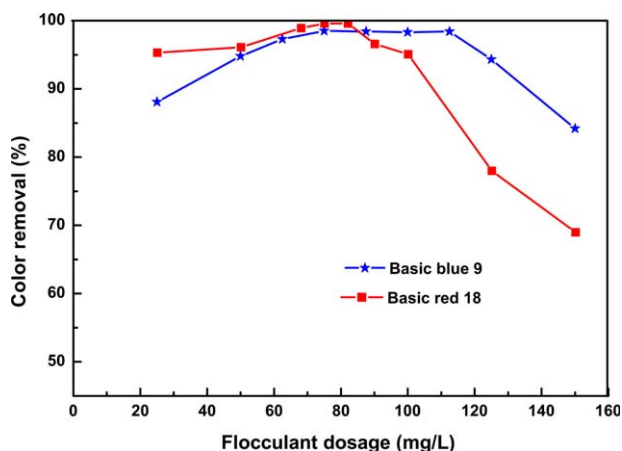
Effect of SP Dosage on the Color Removal. The effects of different dosages of SP (25–150 mg/L) on the color removal of BB9 and BR18 were examined at pH 3 and room temperature. The effect of SP dosage on the color removal at 68 mg/L of dye at pH 3 and room temperature is shown in Figure 3. SP provided SO_3^- ion to adsorb cationic dyes. So, the color removal efficiencies of the cationic dye solutions increased with SP dosage due to the improvement in charge-neutralization. The highest color removal rate of BB9 was more than 98.5% when the concentrations of SP were within the range of 75–112.5 mg/L. For the flocculation of BR18, the preferable concentrations of SP were 75–90 mg/L, and the highest color removal rate was 99.6%. For the two dyes, when the concentration of SP was higher than the preferable concentration range, the color removal rate decreased because the superfluous flocculant changed the electric charges on the surfaces. Consequently, the electrostatic attraction between the dye molecules and flocculants decreased.[12]

Effect of pH of SP on the Color Removal of Cationic Dyes. pH plays an important role in the color removal of dye from solution.[32,33] So, the effect of pH on the dye removal was evaluated at an SP concentration of 75 mg/L and room temperature, and the results are shown in Figure 4. And the original pH values of BB9 and BR18 solutions (68 mg/L) were 7.56 and 7.07 at room temperature, respectively. The pH value was adjusted to the assumed value according to different flocculation conditions. The results showed that the better dye removal ratio was obtained within the range of pH 1–3.0 for BB9 and pH 3–6 for BR18 (Figure 4). The reason is the moderate electro-ionization degree of the SO_3H group under acidic or weakly acidic conditions. The cationic dye was adsorbed on the flocculant by the electrostatic force between SO_3^- and the positively charged dye (Scheme 2). The association behavior of the hydrophobic groups of the flocculant chain accelerated the floc development.[12] However, SO_3Na had a high electro-ionization degree under alkaline conditions,[34] the $SO_3^-Dye^+$ easily dissociated under the attack of OH^-, thus, floc development was difficult.

Figure 3. Effect of SP dosage on the color removal (dye solution 68 mg/L, SP M_n 914,000, room temperature, 30 min, pH value 3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
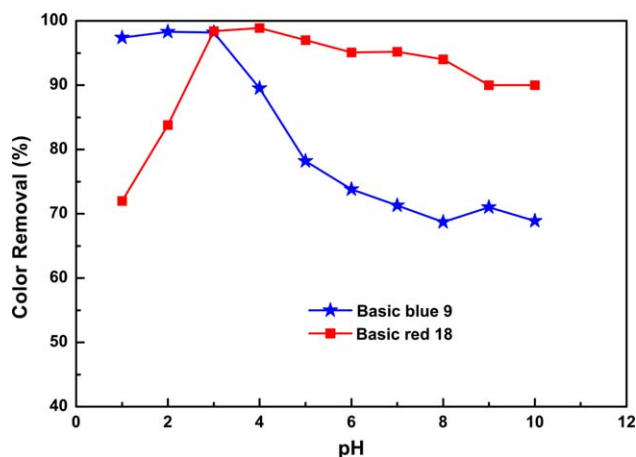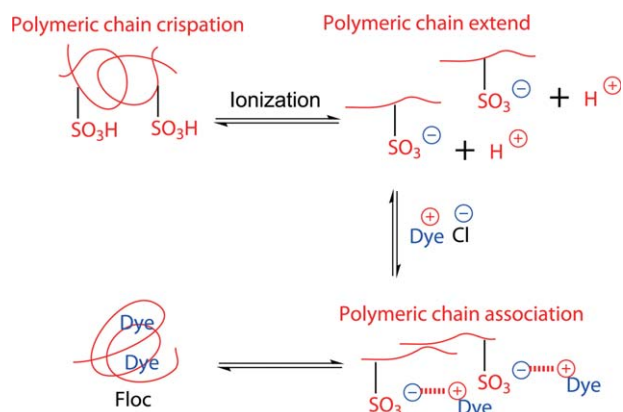

Figure 4. Effect of pH of SP on the color removal of cationic dyes (dye solution 68 mg/L, 15 mg of SP, SP M_n 914,000, room temperature, 30 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 2. Schematic diagram of the dye removal from solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Therefore, SP can be used to remove cationic dyes in acidic or weakly acidic conditions (pH ≤ 6).

Effects of Salt Dosage on the Color Removal of the Cationic Dye Solutions. Electrolytes play important roles in the application of dyes.[35] Usually, electrolytes can either accelerate or retard the dye adsorption process[36] by the "salting out" or "retarding ionization" effects.[37] And during the dyeing process of fiber, Na_2SO_4 can influence the migration power of cationic dye. So, the dyeing procedure generates large quantities of wastewater containing Na_2SO_4. Thus, the commonly used Na_2SO_4 in fiber dyeing was employed to study the effect of electrolytes on the color removal of cationic dyes at pH 3, concentration of 68.3 mg/L, and room temperature, and the results are shown in Figure 5. The removal ratio remained unchanged with increased Na_2SO_4 concentration. Hence, the SP had anti-electrolyte properties that met the requirements of practical application. The reason is that the sulfonic groups in the SP
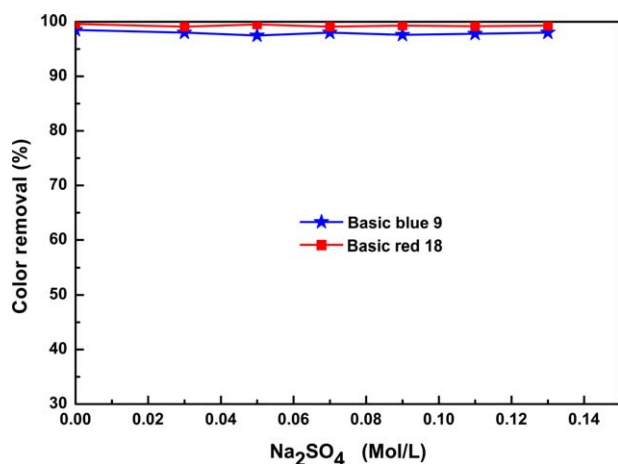
have high dissociation degree in acid condition and higher ionic strength environment.

Effect of the Molecular Weight of SP on the Color Removal of the Cationic Dye Solutions. The effect of the molecular weight of SP on the color removal of the cationic dye was carried out in the 200 mL of dye solutions (68 mg/L) with 15 mg of SP at room temperature, and the results are shown in Figure 6. The removal ratios almost remain unchanged with increased M_n, which was controlled by condensation polymerization time. The condensation polymerization times of SP with M_n 4.9 × 10^5, 6.4 × 10^5, 9.14 × 10^5, 1.55 × 10^6 were 24 h, 28 h, 48 h, 77 h, respectively. Flocculation is a very well known process of precipitating soluble substances by charge neutralization, adsorption bridging, or combination of them. If the adsorption bridging was the main factor for flocculation, the removal ratios should increase when the molecular weight increased. Hence, the flocculation performance of SP mainly depended on charge neutralization and the bridge effect was not significant.[38]

Comparison of SP with Other Flocculants. The adsorption capacity q_c is a well-known parameter that can explain the adsorption process, and it is defined as[39]

$$q_c = (C_0 - C_1)V/W$$

where q_c is the amount of dye adsorbed (mg/g), C_0 and C_1 are the concentrations of the dye in the wastewater before and after the adsorption period (mg/L), V is the volume of the wastewater (L) and W is the amount of SP used (g).

To obtain the q_c values for the sorption of BB9 and BR18 onto SP, the effect of the initial dye concentration was determined, and the results are shown in Figure 7(a) (pH 3.0 with 15 mg of SP at room temperature). The dye removal first increased, and then decreased when the initial dye concentration increased. When the dye concentration was low, the dye could be completely adsorbed by SP because of charge neutralization. The
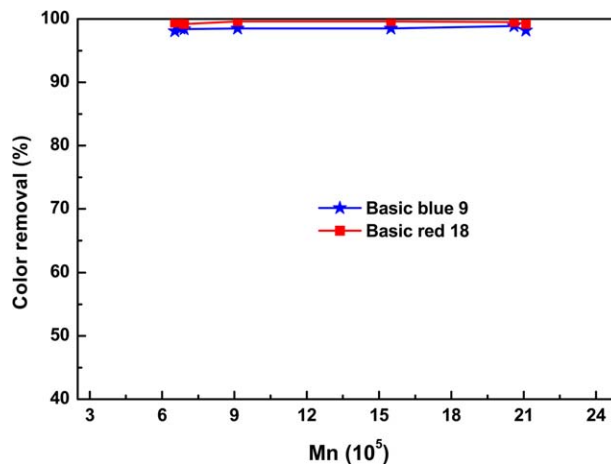

Figure 5. Effect of salt dosage on the color removal of cationic dyes (dye solution 68 mg/L, 15 mg of SP, SP M_n 914,000, room temperature, 30 min, pH value 3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. Effect of the SP molecular weight on the color removal of cationic dyes (dye solution 68 mg/L, 15 mg of SP, room temperature, 30 min, pH value 3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
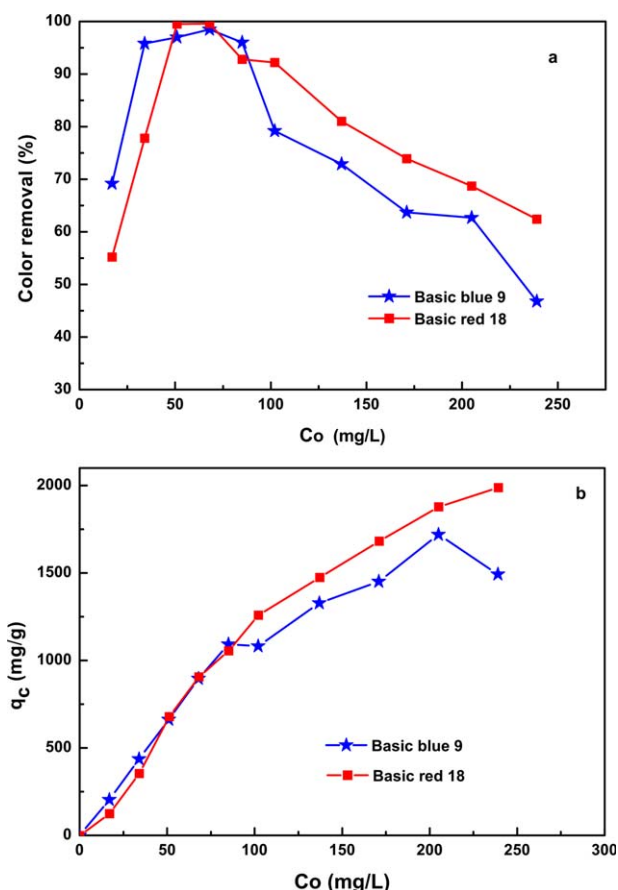
Figure 7. Effect of the initial dye concentration of SP on the color removal of cationic dyes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

curve of q_c vs. C_0 was obtained [Figure 7(b)], and the q_c values are shown in Table II. The comparative analysis of SP with other current flocculants is also shown in Table II. The q_c values of SP reached 1719 mg/g for BB9 and 1988 mg/g for BR18, which were obviously higher than those in literature[17][40–45] containing a commercial agent.[32] The main reason is that the anionic polymers containing sulfonic group are used to flocculate cationic dyes in acid condition by opposite charge attraction. The high charge density and chain elongation were favorable to flocculate more cationic dyes from the waste water. In contrast to other materials used for the removal of cationic dyes, the SP has high charge density and its chain extends in water because it has two sulfonic groups in one polymer segment, so the flocculating performances of SP for cationic dyes are very excellent due to the increase of charge neutralization. Although the q_c values of chitosan-g-poly(acrylic acid)/montmorillonite [46] and chitosan-g-poly(acrylic acid)/attapulgite[47] from the *in situ* intercalated polymerization were 1859 mg/g and 1848 mg/g for BB9, the structure was complex and chitosan was more expensive. Thus, SP has a very wide application prospect in the field of the treatment of wastewater containing basic dyes due to the facile condensation polymerization reaction of Compound I and 1,4-diaminobenzene.

CONCLUSIONS

A novel SP flocculant with high charge density was prepared by a facile condensation polymerization reaction between soluble Compound I and 1,4-diaminobenzene. The highest color removal rates for the basic blue liquor and basic red liquor were 98.5% and 99.6%, respectively. The absorption capacity q_c values reached 1719 and 1988 mg/g, respectively, which were

Table II. Adsorption Capacity of SP and the Comparative Results

Material	Adsorbate	q_c (mg/g)	Color removal (%)	Source
SP	Basic blue 9	1719	98.5	Present paper
	Basic red	1988	99.6	
Commercial Jalshakti containing COOH	Safranin T	181.8	93	Ref. 32
	Basic blue 9	172.4	98	
	Crystal violet	12.9	84	
Commercial Active carbon	Basic blue 9	104.2	/	Ref. 32
Natural clay	Nile blue	25	/	Ref. 40
	Brilliant cresyl blue	42		
Rice straw bearing carboxyl groups	Basic blue 9	256.4	99.1	Ref. 17
	Basic green 4	238.1	97.3	
Rice straw bearing phosphoric acid	Basic blue 9	208.33	98.4	Ref. 41
	Basic red 5	188.68	97.9	
Carboxymethyl cellulose	Basic blue 9	331.5	/	Ref. 42
Anionic poly-γ-glutamic acid-based adsorbent	Basic blue 9	352.76	93.9	Ref. 43
	Basic green 4	293.32	91.8	
Chitosan bearing sulfonic acid	Basic blue 9	74.3	/	Ref. 44
Cation-exchange resin bearing sulfonic acid	Basic fuchsine	38.0	/	Ref. 45
	Crystal violet	18.0		
Chitosan-g-poly (acrylic acid)/MMT	Basic blue 9	1859		Ref. 46
Chitosan-g-poly (acrylic acid)/APT	Basic blue 9	1848	/	Ref. 47

attributed to the high charge density in the polymeric structure and chain elongation of SP in water. The Na_2SO_4 had no effect on the flocculation performance of SP, which further met the requirements of practical application.

ACKNOWLEDGMENTS

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