Carbohydrate Polymers 88 (2012) 132–138

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Flocculation behavior of a new recyclable flocculant based on pH responsive tertiary amine starch ether

Yulin Shi, Benzhi Ju, Shufen Zhang*

State Key Lab of Fine Chemicals, Dalian University of Technology, Dalian 116024, PR China

ARTICLE INFO

Article history:
Received 29 September 2011
Received in revised form
18 November 2011
Accepted 23 November 2011
Available online 6 December 2011

Keywords:
Cationic starch
Flocculation
Regeneration
Anionic dye
pH responsive

ABSTRACT

We designed a new tertiary amine starch ether (2,4-bis(dimethylamino)-[1,3,5]-triazine-6-yl)-starch (BDATS) via etherification of starch with 2,4-bis(dimethylamino)-6-chloro-[1,3,5]-triazine (BDAT), which demonstrated a reversible pH response in aqueous solution. BDATS could be utilized as an effective flocculant because of its favorable interaction with anionic dyes. The flocculation was solution pH dependent and that color removal as high as 97% was possible at pH 2. BDATS shows high flocculation capacity, with the maximum flocculation capacity (DS = 0.63) at 1158 mg g^{-1} for C.I. Reactive Red 141, 873 mg g^{-1} for C.I. Acid Red 1 and 2296 mg g^{-1} for C.I. Acid Blue 324, respectively. The theoretical flocculation capacity was calculated, and the results showed that the experimental flocculation capacity was near to the theoretical one. At pH 8, the dye-loaded flocculant could be regenerated and the recovery ratio of the flocculant was 80%. After five cycles of flocculation/regeneration, color removal ratio was still above 94%. BDATS made it a good candidate for an effective re-cycled flocculant for the treatment of colored effluents.

1. Introduction

Dyestuff is present in waste effluents generated by various industries (e.g., dyeing, textiles, tannery and the paint industry). It has subsequently been identified as a pollutant of concern because of its potential toxic impact on the environment (Atia, Donia, & Al-Amrani, 2009; Kyzas & Lazaridis, 2009; Mishra & Bajpai, 2006). Hence, removal of dyes from such wastewater is a matter of great urgency, and significant efforts have been put into the development of efficient, simple and cheap decolorization methods.

Many methods including flocculation, membrane filtration, adsorption, photocatalysis, and advance oxidation have been used in wastewater treatment (Zhou, Gao, & Xu, 2010). Among them, flocculation is a very effective and economical technology for the treatment of wastewater containing dyes (Fang, Cheng, & Xu, 2010). Some commercially available flocculants, such as polyaluminum chloride, polyferric sulfate and polyacrylamides, have been widely used in water treatment (Chang, Zhang, & Wang, 2009; Golob, Vinder, & Simonic, 2005). However, the negative health and environmental issue of inorganic and synthetic polymer flocculants has been extensively reported (Krentz et al., 2006; You, Lu, Li, Qiao, & Yin, 2009). There is now a strong incentive to provide alternative, environmentally friendly flocculant in dye wastewater treatment.

Recently, numerous research articles have focused on the use of natural polysaccharides or their derivatives as replacements for conventional flocculants, which present considerable advantages including abundance, renewability, ecofriendliness and cost effectiveness (Jiang, Qi, Wang, & Tian, 2010; Mishra & Bajpai, 2005; Song, Zhang, Gan, Zhou, & Zhang, 2009). Special attention has been given to starch-based materials. Specifically, cationic starch derivatives have been shown to be particularly effective in carrying anionic dyes (Delval, Crini, Bertini, Filiatre, & Torri, 2005; Khalil & Aly, 2004; Klimaviciute, Riauka, & Zemaitaitis, 2007; Renault, Morin-Crini, Gimbert, Badot, & Crini, 2008). However, because of the high affinity between anionic dye molecules and cations, the regeneration of the cationic starch flocculant is difficult using conventional regenerants. The development of recyclable flocculant could minimize the costs of flocculation and could solve the problem of exhausted flocculant disposal (Kuo, 2008). For this purpose, it is desirable to regenerate the starch-based flocculant for use in multiple flocculation/regeneration cycles. As yet, there is little literature on this particular topic.

In this paper, a novel cationic starch (2,4-bis(dimethylamino)-[1,3,5]-triazine-6-yl)-starch (BDATS) was designed and synthesized by incorporating 2,4-bis(dimethylamino)-6-chloro-[1,3,5]-triazine (BDAT) into the starch structure. BDATS was found to be an effective flocculant for the removal of anionic dyes from aqueous solution. The flocculation of C.I. Reactive Red 141, C.I. Acid Red 1 and C.I. Acid Blue 324 were examined by the batch method with respect to pH, contact time, degree of substitution (DS) of the cationic starch derivatives and flocculant dose. In addition, the reusability of the

* Corresponding author. Tel.: +86 411 84986265; fax: +86 411 84986264.
E-mail address: zhangshf@dlut.edu.cn (S. Zhang).

0144-8617/$ – see front matter © 2011 Published by Elsevier Ltd.
doi:10.1016/j.carbpol.2011.11.076

flocculant was also examined in alternating cycles of flocculation and regeneration over five times.

2. Materials and methods

2.1. Materials and instrumentations

Cornstarch, food grade quality, was obtained from Huanglong Food Company (Changchun, PR China). Tertiary amine cationic etherifying agent 2,4-bis(dimethylamino)-6-chloro-[1,3,5]-triazine (BDAT) (purity 98%) was prepared according to literature procedures (Baliani et al., 2005). Three commercially available dyes, C.I. Reactive Red 141 (RR 141; purity 71%; M_w = 1772 g mol^{-1}; λ_{max} = 541 nm), C.I. Acid Blue 324 (AB 324; purity 75.6%; M_w = 473 g mol^{-1}; λ_{max} = 600 nm) and C.I. Acid Red 1 (AR 1; purity 77.2%; M_w = 509 g mol^{-1}; λ_{max} = 506 nm), were obtained from Shangyu Guangming Chemical Co. Ltd. and were used without further purification. The detailed structures of the dyes are given in Fig. 1. All the reagents were used without undergoing further purification unless otherwise stated. Tap water was used throughout the dye flocculation/regeneration experiments.

The IR spectra of cornstarch and BDATS were recorded with the KBr dispersion method on an FT-IR spectrometer (JASCO IR-430, Japan). The absorbency of the dye solution was measured using UV–visible spectrophotometry (HP 8453, USA) at λ_{max}. Nitrogen content was determined by nitrogen elemental analysis (Elemental Analyzer Vario EL, Germany). Flocculation and regeneration experiments were investigated as batch tests in a series of 1 L beakers (MY3000-6, China).

2.2. Preparation of (2,4-bis(dimethylamino)-[1,3,5]-triazine-6-yl)-starch (BDATS)

BDATS was prepared via an etherifying reaction between starch and BDAT in dimethyl sulfoxide. Briefly, dry starch (8.1 g, 0.05 mol) and solid sodium hydroxide (2.8 g, 0.07 mol) were dissolved in 120 g dimethyl sulfoxide and heated to 70 °C for 30 min. Subsequently, BDAT (10.3 g, 0.05 mol) was added, and the reaction mixture was allowed to stir at 120 °C for 10 h. After cooling, the reaction solution was neutralized with HCl (1 M) to pH 7, and the product was isolated by precipitation in water. The precipitate was washed with acetone to obtain the pure product. TLC (THF:hexyl hydride = 1:3) was used to monitor the content of residue BDAT. The crude product was washed until the BDAT spot disappeared on the TLC plate. IR (KBr): 3426 (s, OH), 2928 (CH), 1154, 1082, 1022 (starch backbone), 1583, 1397 (s-triazine ring) cm^{-1}.

The degree of substitution (DS) of the cationic starch was calculated from the nitrogen content according to Eq. (1).

$$DS = \frac{162 \times N(\%)/5}{1400 - 166 \times N(\%)/5} \quad (1)$$

where N is nitrogen content (%), 162 is the molar quantity of anhydroglucose units in starch, and 166 is the molar quantity of substituted groups. Four samples of BDATS with DS 0.23, 0.48, 0.63 and 1.01 were synthesized and used as flocculants in the experiments.

2.3. Flocculation/regeneration cycles

Flocculation experiments were run as batch tests in a series of six 1 L beakers at 24.5 ± 0.5 °C. An accurately weighed quantity of the BDATS powder was dissolved in dilute hydrochloric acid solution (0.5 wt%) to prepare a flocculant solution (20 g L^{-1}). Volumes of 10–100 mL of flocculant solution were added into 500 mL of dye solution, after which water was added to a volume of 1 L. The final concentration of dye was then 350 mg L^{-1}. The initial pH of the solution was adjusted to the required value with 1 M hydrochloric acid or sodium hydroxide after mixing the flocculant and dye solutions. The resulting mixture was stirred at a constant speed of 150 rpm for 10 min and then at a speed of 50 rpm for 20 min. Subsequently, the flocs were allowed to settle for 30 min. After flocculation of dyes, the flocs were separated by filtration through filter paper (0.45 μm). The filtrate was then adjusted to a pH level of 7.0 using HCl or NaOH solutions and measured using UV–visible spectrophotometry at the maximum absorbance wavelength. Color removal (R%) and the amount of dye flocculation capacity (q; mg g^{-1}) were calculated according to Eqs. (2) and (3).

$$R\% = \frac{C_0 - Ce}{C_0} \times 100 \quad (2)$$

$$q = \frac{V(C_0 - C_e)}{m} \quad (3)$$

where C_0 and C_e denote the dye concentration in the solution before and after flocculation (mg L^{-1}), respectively, V is the volume of the dye solution (L) and m is the weight of the flocculant used (dry material, g).

For flocculant regeneration experiments, the dye-loaded flocculant was mixed with 50 mL of water at pH 8. The suspensions were then shaken for 30 min at 25 °C. Finally, the regenerated flocculant was separated by filtration through filter paper (0.45 μm) and then collected and dried to a constant weight in vacuum-dried at 50 °C for 8 h. Flocculant recovery ratio could be obtained as follows:

$$\text{Recovery ratio}(\%) = \frac{\text{mass of regeneration flocculant}}{\text{total mass of flocculant}} \times 100 \quad (4)$$

The flocculation/regeneration processes has been carried out for five cycles.

3. Results and discussion

The completed BDATS has a heterocyclic ring (s-triazine ring) at the end of the tertiary amine group, which can accept and donate protons in response to environmental change in pH. At low pH, the polymer formed a more extended conformation and was molecularly dissolved in water because of the high ionizability of cationic groups (Schepelina & Zharov, 2008). As the pH of the BDATS solution was increased, the BDAT segments in the starch are progressively deprotonated and neutralized. The BDAT segment changes from a hydrophilic part into a hydrophobic one and thus forms aggregates as a result of the formation of hydrophobic microdomains. The obtained polymer exhibited pH responsive characteristics, and this behavior was entirely reversible by changing the solution pH without apparent loss of responsiveness. Therefore, a pH-sensitive trigger can be used to bind and release dye molecules. A simple schematic of the cyclic flocculation/regeneration procedure is shown in Fig. 2.

Azo and anthraquinone dyes approximately share in industrial application amounts to 80% of the synthetic dyestuff production, some of them are known to be very toxic and mutagenic to living organisms (Singh, Sharma, Tripathi, & Sanghi, 2009). Therefore, three widely used azo or anthraquinone type dyes, namely, RR 141, AR 1 and AB 324 were selected in our flocculation experiment.

3.1. Effect of pH on flocculation

The pH of the aqueous solution is an important controlling parameter in the dye flocculation process. The influence of pH on the color removal was observed over a pH range of 1–10 with fixed dosage of BDATS ($C_{f-RR\ 141}$ = 0.3 g L^{-1}; $C_{f-AB\ 324}$ = 0.15 g L^{-1}; $C_{f-AR\ 1}$ = 0.4 g L^{-1}) with DS 0.63. As can be seen from Fig. 3, dye

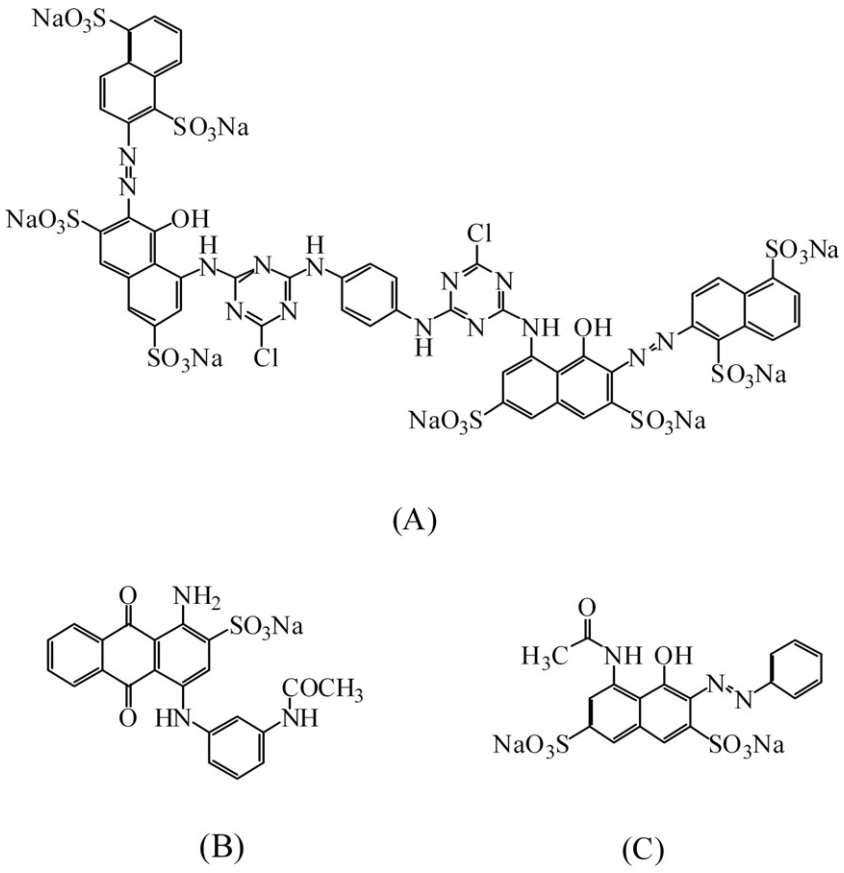

Fig. 1. Chemical structures of the dyes used in this study: (A) RR 141; (B) AB 324; and (C) AR 1.

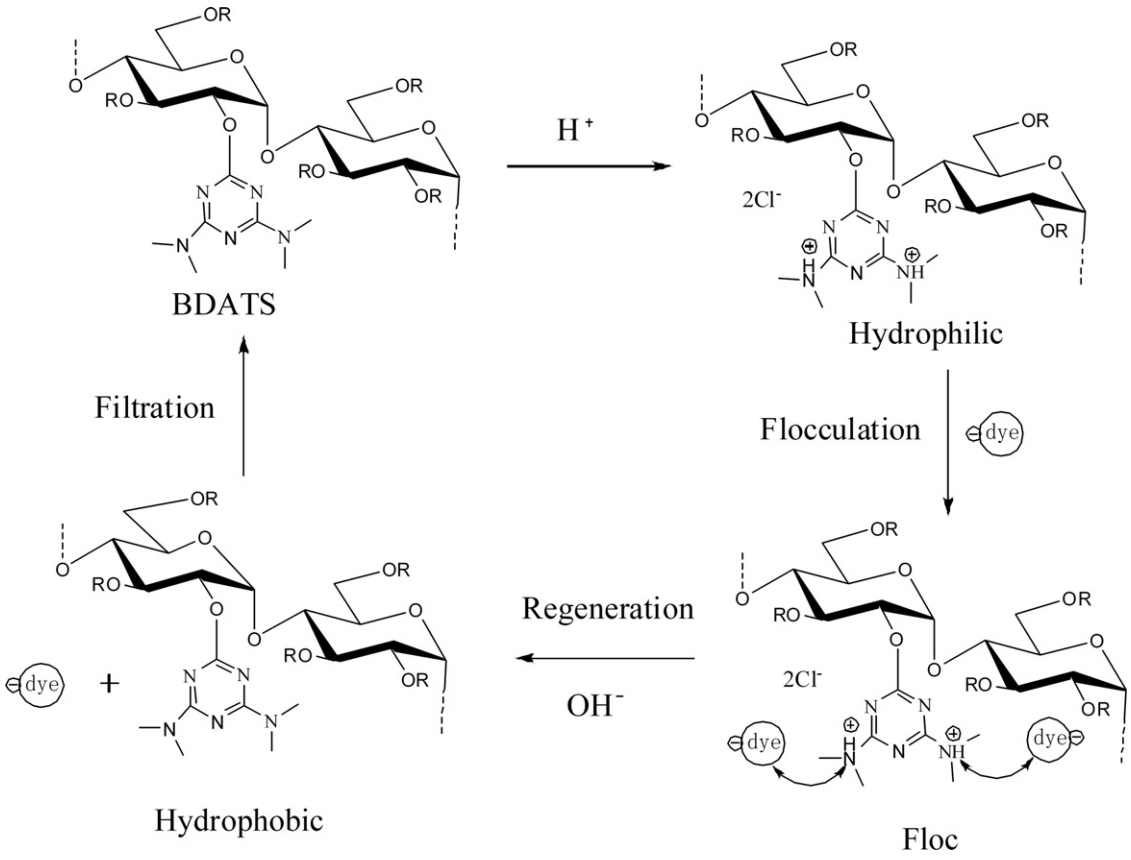

Fig. 2. Schematic of the cyclic flocculation/regeneration procedure.

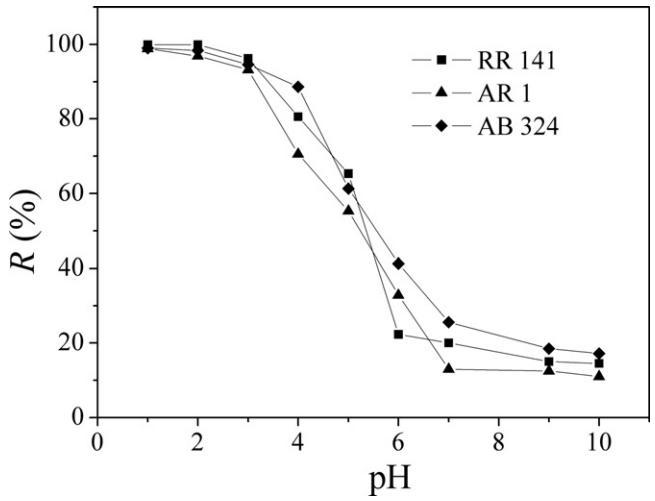

Fig. 3. Effect of pH on % color removal for RR 141, AB 324 and AR 1 with fixed flocculant dose.

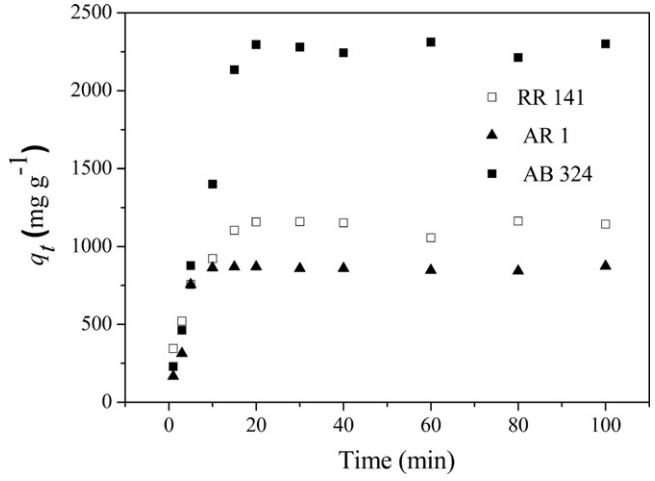

Fig. 4. Effect of contact time on % color removal.

flocculation was pH dependent, and excellent flocculation performance could be observed at pH < 3. The color removal for RR141, AR 1 and AB 324 was 99.5%, 97.9% and 98.4%, respectively, at an initial pH 2. Then, the color removal of all tested dyes decreased significantly as the solution pH increased from 3 to 10. At a lower pH solution, more amine residues of the BDATS were protonated and positively charged. The ionized cationic groups strongly attracted anionic dye ions ($-SO_3^-$) via electrostatic interactions, causing an increase in color removal (Chen & Chen, 2009). At high pH, color removal decreased because the polymeric chain was not positively charged and did not interact with the negative charges of the dye. Therefore, by choosing the right pH conditions, a platform may be found with properties that are advantageous for flocculating and releasing dye molecules in aqueous solution.

3.2. Effect of contact time on flocculation

Fig. 4 shows the amount of dye flocculation capacity (mg g^{-1}) at different time (min) with the optimum flocculant dose ($C_{f^-\text{RR 141}} = 0.3$ g L^{-1}; $C_{f^-\text{AB 324}} = 0.15$ g L^{-1}; $C_{f^-\text{AR 1}} = 0.4$ g L^{-1}) for cationic starch with DS 0.63 at pH 2. As expected, the overall trend was an increase in flocculation capacity with increasing contact time for all three dyes. The flocculation process was very fast initially, indicating that there were plenty of readily accessible sites, so electrostatic attractions rapidly took place between the ammonium groups on the flocculant and the sulfonate groups of the dye (Rosa, Laranjeira, Riela, & Favere, 2008). This fast initial phase was followed by a slow increase to equilibrium, where the concentration of dye in the liquid phase remained almost constant. Twenty minutes proved to be enough to reach flocculation equilibrium, at which point the saturated flocculation capacity was 1158 mg g^{-1} for RR 141, 873 mg g^{-1} for AR 1 and 2296 mg g^{-1} for AB 324, respectively. The reason for this enhancement in flocculation rate may be attributed to complex coagulation mechanisms that involves polymer bridging and formation of a net-like structure, which does not need a very long contact time (Beltran-Heredia, Sanchez-Martin, Delgado-Regalado, & Jurado-Bustos, 2009; Yu, Wang, Ge, Yan, & Yang, 2006). On the other hand, introduction of hydrophobic units into the starch structure dramatically enhanced the hydrophobicity of flocs, which improved the flocs structure and consequently sped up phase separation process (Shang, Liu, Zheng, & Wang, 2009). These results were a great improvement over other processes like sorption, in which contact time is usually much longer.

3.3. Effects of DS and flocculant dose on flocculation

To evaluate the effects of flocculant dose and DS on color removal, four cationic starch products of different DS (0.23–1.01) and flocculant dose (0.02–4 g L^{-1}) were exposed to a fixed initial dye concentration (350 mg L^{-1}). The results are shown in Fig. 5. It can be seen that the color removal increased with increasing dose of flocculant up to the optimal value, followed by a decreasing trend in color removal with further increases in dose level. These curves are a typical flocculation system controlled by a charge neutralization mechanism (Szygula, Guibal, Palacin, Ruiza, & Sastre, 2009). Specifically, when the amount of cationic charges was sufficient for complete neutralization of anionic charges, the color removal had reached its maximum. An excess of cationic charges on the overdosing of the flocculant induced a dispersion re-stabilization phenomenon and a subsequent decrease in the efficiency of the flocculation process (Bratskaya et al., 2005a; Bratskaya, Schwarz, Liebert, & Heinze, 2005b).

DS also had a large influence on optimum dose of flocculant. For highly substituted cationic starches, the lower flocculant dose should be used to reach the same color removal effect. For example, with an increase in DS from 0.23 to 0.63, the optimum dose of flocculant decreased from 1.8 g L^{-1} to 0.3 g L^{-1} for RR 141, 0.8 g L^{-1} to 0.15 g L^{-1} for AB 324 and 2.0 g L^{-1} to 0.4 g L^{-1} for AR 1, respectively. The decrease in the dose of flocculant was due to the increase in the available sorption sites in the starch chain. In addition, the higher DS of BDATS could help to improve the hydrophilicity of flocculant in water, which allowing increasing its reactivity for dye binding due to higher accessibility and better availability of amine groups (Guibal & Roussy, 2007).

Fig. 6 illustrates the effect of DS on the dye flocculation capacity at the optimal flocculant dose. The flocculation capacity increased with increasing DS because of the increasing amine content of the cationic starch. Additionally, we found that BDATS possess exceptionally large dye flocculation capacity. Specifically, the maximum dye flocculation capacity (q_{max}, mg g^{-1}) was found to be 1158 mg g^{-1} for RR 141, 873 mg g^{-1} for AR 1 and 2296 mg g^{-1} for AB 324 for cationic starch with DS 0.63. Because there are two tertiary amine groups per glucose unit of BDATS, two sulfonic acid groups of dyes can be absorbed into such a glucose unit at the same time in theory. As a result, the theoretical flocculation capacity of flocculant with DS 0.63 is 1047 mg g^{-1} for RR 141, 1116 mg g^{-1} for AR 1 and 2406 mg g^{-1} for AB 324. The results showed that the experimental flocculation capacity was near to the theoretical one.

The maximum dye flocculation capacity (q_{max}, mg g^{-1}) of BDATS with DS 1.01 was found to be 1763 mg g^{-1} for RR 141, 1125 mg g^{-1}

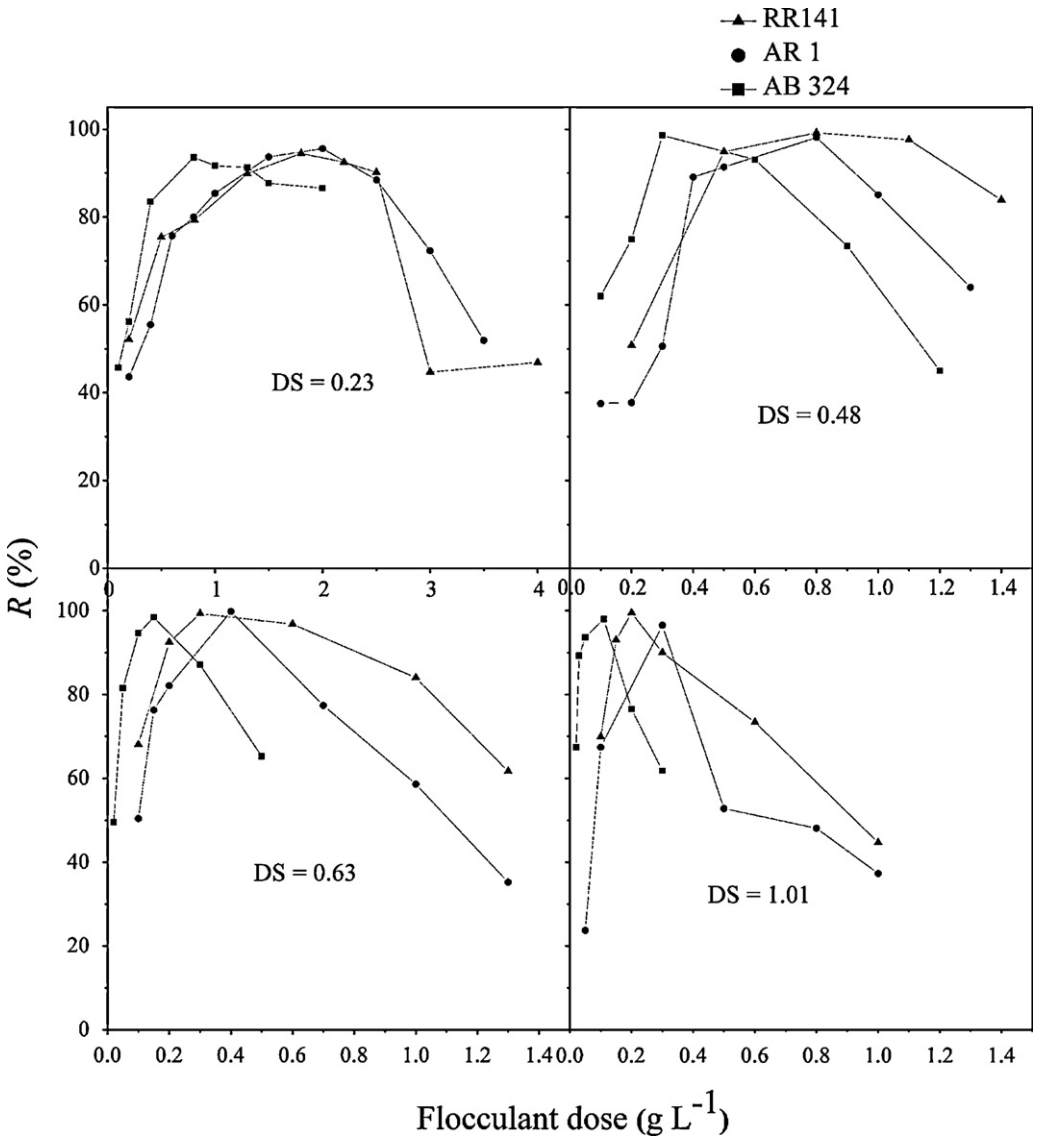

Fig. 5. Effects of DS and dose on % color removal.

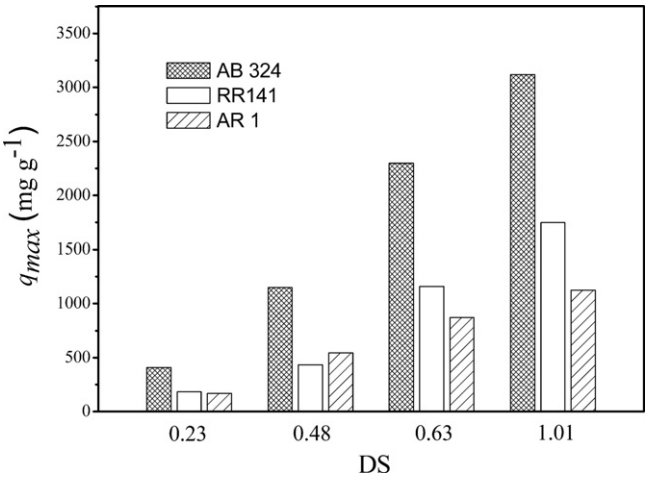

Fig. 6. Effect of DS on the maximum dye flocculation capacity.

for AR 1 and 3118 mg g^{-1} for AB 324. Although the higher DS of cationic starch, the larger dye flocculation capacity, increasing DS is not always a good method to decrease amounts of flocculant because of the higher cost for obtaining a higher substitution degree on starch. Moreover, it was previously shown that higher DS also contributed to mismatch in charge spacing, the efficiency of flocculation performance increased slower than DS of cationic starch (Bratskaya et al., 2005a). Therefore, BDATS with DS up to 0.63 are efficient and relevant to industrial applications because of the higher dye flocculation capacity.

3.4. Cycles of flocculation/regeneration

The regeneration capability of the flocculant is very important in practical applications. Since the interactions between the anionic dyes and BDATS were driven mainly by electrostatic adsorption in the present work, NaOH was good candidate for the regeneration of the flocculant. Therefore, the regeneration conditions had an initial pH of 8 from the NaOH solution. Five cycles of flocculation/regeneration were conducted to investigate the regeneration

Table 1
Effect of regeneration times on color removal ratio.

Dye	Regeneration time	Recovery of flocculant/%	Color removal ratio/%
AB 324	0	–	98.1
	1	81	98.2
	2	83	98.6
	3	82	97.5
	4	78	97.1
RR 141	0	–	99.4
	1	87	99.1
	2	88	97.9
	3	83	97.1
	4	85	98.3
AR 1	0	–	97.0
	1	85	96.2
	2	84	96.0
	3	80	95.7
	4	82	94.7

Table 2
The concentration of dye solution after two cycles of flocculation/desorption processes.

Dye	Times	Initial dye concentration ($g L^{-1}$)	Color removal ratio (%)	Dye concentration of desorption solution ($g L^{-1}$)
RR 141	1	0.35	99.4	6.93
	2	6.93	97.6	135.3
AB 324	1	0.35	98.1	6.86
	2	6.86	95.0	130.3
AR 1	1	0.35	97.2	6.79
	2	6.79	93.0	126.3

and re-flocculation of BDATS. The concentration of dyes and flocculant were kept unchanged, the results are shown in Table 1. It can be seen that the color removal ratio was kept between 94% and 98% for the three dyes. The recovery of BDATS was located in the range of 78–87% after the regeneration. When amine groups were deprotonated and electrostatic interactions disappeared within the polymer network, hydrophobic properties dominated, introducing hydrophobic group (s-triazine ring) effects that caused aggregation of the polymer chains and dissolution of the dye in water. Therefore, binding and releasing anionic dye may be realized by choosing the right pH conditions.

After two continuous cycles of flocculation/desorption processes, the desorption solution could increase 400 times compared to that of the original dye concentration (Table 2). The solid-state dye was obtained by rotary evaporation of water. Thus, our flocculant not only resolved the water pollution problem, but also recycled and reused dye for many times, promising its great potential in real applications.

4. Conclusion

We synthesized a new cationic starch (2,4-bis(dimethylamino)-[1,3,5]-triazine-6-yl)-starch (BDATS) by an etherifying reaction between starch and 2,4-bis(dimethylamino)-6-chloro-[1,3,5]-triazine (BDAT). We found that BDATS exhibited pH responsive behavior that was entirely reversible in aqueous medium because of the protonation and deprotonation of the amine groups. The data revealed that BDATS could be used as an effective flocculant for the removal of anionic dyes from aqueous solutions. Maximum color removal rates of 99.5% for RR141, 97.9% for AR 1 and 98.4% for AB 324 were observed at pH 2 for an initial dye concentration of 350 $mg L^{-1}$. The flocculation capacity increased with increasing DS because of the increasing amine content of the cationic starch. The maximum flocculation capacity was 1158 $mg g^{-1}$ for RR 141, 873 $mg g^{-1}$ for AR 1 and 2296 $mg g^{-1}$ for AB 324 for cationic starch with DS 0.63. The experimental flocculation capacity was near to the theoretical one. In addition, basic treatment was attempted for the regeneration of the spent flocculant at pH 8. The flocculant retained high flocculation capacity even after five cycles of flocculation/regeneration. Therefore, the high flocculation capacity and good regeneration ability make BDATS an important candidate for removing anionic dyes from aqueous solutions.

Acknowledgements

We thank the Natural Science Foundation of China (20836001) and National Science and Technology Support Foundation of China (2011BAE07B01) for financial support of this research.

References

Atia, A. A., Donia, A. M., & Al-Amrani, W. A. (2009). Adsorption/desorption behavior of acid orange 10 on magnetic silica modified with amine groups. *Chemical Engineering Journal*, *150*(1), 55–62.
Baliani, A., Bueno, G. J., Stewart, M. L., Yardley, V., Brun, R., Barrett, M. P., & Gilbert, I. H. (2005). Design and synthesis of a series of melamine-based nitroheterocycles with activity against trypanosomatid parasites. *Journal of Medicinal Chemistry*, *48*(17), 5570–5579.
Beltran-Heredia, J., Sanchez-Martin, J., Delgado-Regalado, A., & Jurado-Bustos, C. (2009). Removal of Alizarin Violet 3R (anthraquinonic dye) from aqueous solutions by natural coagulants. *Journal of Hazardous Materials*, *170*(1), 43–50.
Bratskaya, S., Schwarz, S., Laube, J., Liebert, T., Heinze, T., Krentz, O., Lohmann, C., & Kulicke, W.-M. (2005). Effect of polyelectrolyte structural features on flocculation behavior: Cationic polysaccharides vs synthetic polycations. *Macromolecular Materials and Engineering*, *290*(8), 778–785.
Bratskaya, S., Schwarz, S., Liebert, T., & Heinze, T. (2005). Starch derivatives of high degree of functionalization: 10 Flocculation of kaolin dispersions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *254*(1-3), 75–80.
Chang, Q., Zhang, M., & Wang, J. (2009). Removal of Cu^{2+} and turbidity from wastewater by mercaptoacetyl chitosan. *Journal of Hazardous Materials*, *169*(1-3), 621–625.
Chen, A.-H., & Chen, S.-M. (2009). Biosorption of azo dyes from aqueous solution by glutaraldehyde-crosslinked chitosans. *Journal of Hazardous Materials*, *172*(2-3), 1111–1121.
Delval, F., Crini, G., Bertini, S., Filiatre, C., & Torri, G. (2005). Preparation, characterization and sorption properties of crosslinked starch-based exchangers. *Carbohydrate Polymers*, *60*(1), 67–75.
Fang, R., Cheng, X. S., & Xu, X. R. (2010). Synthesis of lignin-base cationic flocculant and its application in removing anionic azo-dyes from simulated wastewater. *Bioresource Technology*, *101*(19), 7323–7329.
Golob, V., Vinder, A., & Simonic, M. (2005). Efficiency of the coagulation/flocculation method for the treatment of dyebath effluents. *Dyes and Pigments*, *67*(2), 93–97.
Guibal, E., & Roussy, J. (2007). Coagulation and flocculation of dye-containing solutions using a biopolymer (chitosan). *Reactive & Functional Polymers*, *67*(1), 33–42.
Jiang, X., Qi, Y., Wang, S., & Tian, X. (2010). New amphoteric flocculant containing beta-cyclodextrin, synthesis, charaterization and decolorization properties. *Journal of Hazardous Materials*, *173*(1–3), 298–304.
Khalil, M. I., & Aly, A. A. (2004). Use of cationic starch derivatives for the removal of anionic dyes from textile effluents. *Journal of Applied Polymer Science*, *93*(1), 227–234.
Klimaviciute, R., Riauka, A., & Zemaitaitis, A. (2007). The binding of anionic dyes by cross-linked cationic starches. *Journal of Polymer Research*, *14*(1), 67–73.
Krentz, D.-O., Lohmann, C., Schwarz, S., Bratskaya, S., Liebert, T., Laube, J., Heinze, T., & Kulicke, W.-M. (2006). Properties and flocculation efficiency of highly cationized starch Derivatives. *Starch - Stärke*, *58*(3-4), 161–169.
Kuo, C. Y. (2008). Desorption and re-adsorption of carbon nanotubes: Comparisons of sodium hydroxide and microwave irradiation processes. *Journal of Hazardous Materials*, *152*(3), 949–954.
Kyzas, G. Z., & Lazaridis, N. K. (2009). Reactive and basic dyes removal by sorption onto chitosan derivatives. *Journal of Colloid and Interface Science*, *331*(1), 32–39.
Mishra, A., & Bajpai, M. (2005). Flocculation behaviour of model textile wastewater treated with a food grade polysaccharide. *Journal of Hazardous Materials*, *118*(1-3), 213–217.
Mishra, A., & Bajpai, M. (2006). The flocculation performance of *Tamarindus* mucilage in relation to removal of vat and direct dyes. *Bioresource Technology*, *97*(8), 1055–1059.
Renault, F., Morin-Crini, N., Gimbert, F., Badot, P.-M., & Crini, G. (2008). Cationized starch-based material as a new ion-exchanger adsorbent for the removal of C.I. Acid Blue 25 from aqueous solutions. *Bioresource Technology*, *99*(16), 7573–7586.
Rosa, S., Laranjeira, M. C. M., Riela, H. G., & Favere, V. T. (2008). Cross-linked quaternary chitosan as an adsorbent for the removal of the reactive dye from aqueous solutions. *Journal of Hazardous Materials*, *155*(1-2), 253–260.

Schepelina, O., & Zharov, I. (2008). Poly(2-(dimethylamino)ethyl methacrylate)-modified nanoporous colloidal films with pH and ion response. *Langmuir*, *24*(24), 14188–14194.

Shang, H., Liu, J., Zheng, Y., & Wang, L. (2009). Synthesis, characterization, and flocculation properties of poly(acrylamide-methacryloxyethyltrimethyl ammonium chloride-methacryloxypropyltrimethoxy silane). *Journal of Applied Polymer Science*, *111*(3), 1594–1599.

Singh, V., Sharma, A. K., Tripathi, D. N., & Sanghi, R. (2009). Poly(methylmethacrylate) grafted chitosan: An efficient adsorbent for anionic azo dyes. *Journal of Hazardous Materials*, *161*(2-3), 955–966.

Song, Y., Zhang, J., Gan, W., Zhou, J., & Zhang, L. (2009). Flocculation properties and antimicrobial activities of quaternized celluloses synthesized in NaOH/Urea aqueous solution. *Industrial & Engineering Chemistry Research*, *49*(3), 1242–1246.

Szygula, A., Guibal, E., Palacin, M. A., Ruiza, M., & Sastre, A. M. (2009). Removal of an anionic dye (Acid Blue 92) by coagulation–flocculation using chitosan. *Journal of Environmental Management*, *90*(10), 2979–2986.

You, L., Lu, F., Li, D., Qiao, Z., & Yin, Y. (2009). Preparation and flocculation properties of cationic starch/chitosan crosslinking-copolymer. *Journal of Hazardous Materials*, *172*(1), 38–45.

Yu, J., Wang, D., Ge, X., Yan, M., & Yang, M. (2006). Flocculation of kaolin particles by two typical polyelectrolytes: A comparative study on the kinetics and floc structures. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *290*(1–3), 288–294.

Zhou, L., Gao, C., & Xu, W. (2010). Magnetic dendritic materials for highly efficient adsorption of dyes and drugs. *ACS Applied Materials & Interfaces*, *2*(5), 1483–1491.