Flocculation Performance of Trimethyl Quaternary Ammonium Salt of Lignin-Sodium Alginate Polyampholyte

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In order to improve the molecular weight and application of a lignin byproduct, the trimethyl quaternary ammonium salt of lignin-sodium alginate polyampholyte (QL-SA) was prepared with trimethyl quaternary ammonium salt of lignin (QL) and sodium alginate (SA), using the cross-linker glutaraldehyde. Its structure was analyzed by FTIR, SEM, and analysis of nitrogen and carboxylic contents. Results showed that QL and SA were grafted successfully. The nitrogen content was diminished from 4.21% to 3.69% and its carboxyl content increased from 2.66 mmol/g to 6.47 mmol/g. The product behaved as flocculant by electrostatic interactions and bridging actions. The effects of QL-SA on the flocculation performance of dyes were investigated with methylene blue and acid black ATT water as the representative dyes. The maximum decolorization rate of acid black ATT was 94.91% and methylene blue was 97.11% under the corresponding optimal conditions (5 g/L of the flocculant at pH 3, 30 °C, and 8 g/L at pH 8, 30 °C). The effect of QL-SA was found to be markedly superior to SA and QL on the whole. The QL-SA showed promise for practical applications.

Keywords: Trimethyl quaternary ammonium salt of lignin (QL); Sodium alginate (SA); Polyampholyte; Flocculation

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INTRODUCTION

Dyeing effluents mainly contain the wastewater from all of the dyeing processes of various natural celluloses and synthetic celluloses (Liu *et al.* 2005; Suteu and Malutan 2012). The dyeing effluents have a high chromaticity, a high level of toxicity, and are generally non-biodegradable (Fang *et al.* 2010). As a result, dye wastewater represents a considerable source of environmental pollution (Mishra *et al.* 2006). The process for color removal from dyeing effluents includes biological treatment, flocculation, adsorption, oxidation, hyper-filtration, *etc.* (Chakrabarti *et al.* 2008; Raluca *et al.* 2012; Dinesh *et al.* 2006; Latif *et al.* 2010; Mohan *et al.* 2006; Suteu *et al.* 2009).

However, with the growing resource crisis and the human awareness of environmental protection, the qualities that exist in the source of the natural polymer, such as being abundant, cheap, renewable, biodegradable nature, *etc.*, makes studying the natural modified polyelectrolyte flocculant an increasing concern (Szygula *et al.* 2009; Akhtar *et al.* 2009). Most of those flocculants require rigorous reaction conditions or high cost (Bozlur *et al.* 2010). In this context, lignin, which is the second most abundant polymer in nature after cellulose, appears as a promising candidate. Lignin (Banoub *et al.* 2007;

Doherty *et al.* 2011) is an amorphous, highly branched polyphenolic macromolecule of complex structure.

To enhance the flocculation property of lignin, the most widespread method is to introduce a cationic group such as the quaternary ammonium group into lignin (Monteil-Rivera *et al.* 2013; Fang *et al.* 2003; Yang *et al.* 2008, Yang and Jiang 2007). The quaternary ammonium salt of lignin is a well-known, nontoxic, and biodegradable polymer with high positive charges; hence it will not bring secondary contamination when it is used to treat wastewater as a flocculant. However, its lower molecular weight and its amorphous state also affect its applications (Ahvazi *et al.* 2011; Panswad and Luangdilok 2000).

Sodium alginate contains numerous carboxyl and hydroxyl groups (Guo *et al.* 2011). This natural polyelectrolyte has been increasingly in the international spotlight because of its environment-friendly nature and low cost (Tripathya *et al.* 1999). However, both sodium alginate and lignosulfonate are water-soluble, which limits their ranges of application. The wide range of applications of both the anionic and cationic groups of polyampholyte can be used for processing different charges pollutants. Taking advantage of the smaller dosage, faster flocculating rate not only can reduce the agent dosage substantially but also improve the flocculating performance, especially in the removal of organic matter (Zhou *et al.* 2008; Wang *et al.* 2008; Gu and Ma 2009; Li *et al.* 2010).

To improve the molecular weight and applied rage of lignin, in this study, a trimethyl quaternary ammonium salt of lignin-sodium alginate polyampholyte (QL-SA) was prepared and the flocculation performance on two different types of dyes, which were acid black ATT and methylene blue, was investigated according to major influencing factors. This was aimed to provide further exploration and research for the alkali lignin in its application as a water treatment agent.

EXPERIMENTAL

Materials

Alkaline lignin (Quanlin Paper Co., Shandong, China) was purified in our laboratory. Sodium alginate (SA) was purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). Trimethylamine (33 wt% in aqueous solution) was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Methylene blue and Acid Black ATT were commercial dyes and used without further purification. The grade of epoxy chloropropane, ammonium persulfate, glutaraldehyde, sodium hydroxide, hydrochloric acid, and other reagents were analytical.

Synthesis

*Synthesis of trimethyl quaternary ammonium salt of lignin (QL) (*Fang *et al. 2003)*

The synthetic route is shown in Fig. 1. The product was a dark brown viscous liquid, in which there was about 36 wt% of solid content.

Synthesis of QL-SA

2:1 mass ratio of the trimethyl quaternary ammonium salt of lignin to sodium alginate was added in a three-necked flask with a reflux condensing set. The pH of the

reaction system was adjusted between 8 to 10, which was placed in 70 °C water bath to heat up. The 4-wt% glutaraldehyde was added in the reaction system after the initial reactant had dissolved. The new reaction system was cooled down to room temperature after it had been stirring at 500 revs/min for 4 h. Finally, the polyelectrolyte was a dark brown powder after the intermediate had been centrifuged, repetitively washed, and dried under vacuum.

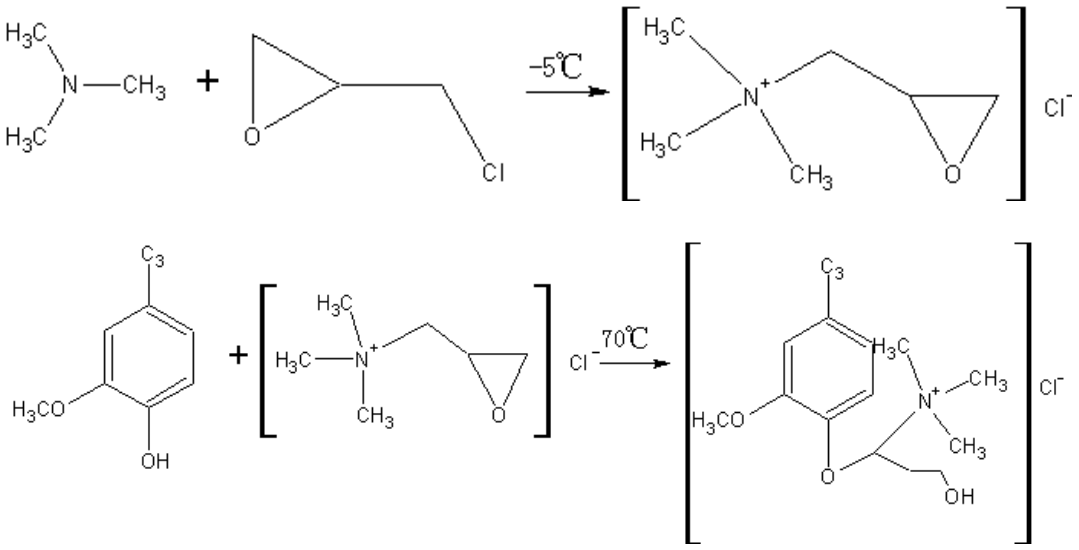

Fig. 1. The synthetic route of QL

Flocculation in Dyeing Wastewater

The initial concentration of the dye was 0.1g/L. The target pH was adjusted by adding 1 mol/L HCl or 1 mol/L NaOH solution into the dye solutions. The required dose of the flocculant was added into a 20 mL tube, in which there had been the water sample of 20 mL. The flocs settled down and went undisturbed for 2 h after shaking. The three dyes were measured with a UV spectrophotometer (Tu-1800PC, Beijing, China) at the maximum absorption wavelength (λ_{max}).

The color removal efficiency (R%) was defined as,

$$R\% = (1\text{-}c/q)*100\% \quad (1)$$

where q and c are the concentration of dye solution before and after treatment (g/L), respectively.

Infrared Spectroscopy

FT-IR spectra of reactants and products were obtained by using a FT-IR spectrophotometer (FTIR-650, Tianjin, China). The dry samples were mixed with KBr and pressed into a tablet form.

SEM Analysis

The reactants and products were observed by scanning electron microscope (SEM) (QUANTA 200, FEI).

Measurement on Nitrogen Content and Carboxyl Content

Measurement on nitrogen content

The nitrogen content of the product was measured by Kjeldahl's device (KDY-9810, Beijing, China).

Measurement on carboxyl content

Lignin, 40 to 60 mg, and 20 mL of 0.4 N solution of calcium acetate were mixed and added in a 25 mL volumetric flask at 85 °C for 0.5 h. The mixture was then cooled, and distilled water was added to the mark. Twenty milliliters of filtrate was filtered and potentiometrically titrated with 0.05 N NaOH standard solution, the same as for a blank experiment (Ren *et al.* 2008). The carboxyl content was determined by the amount of OH^- consumed, using Eq. 2,

$$[OH] = \frac{(a - a_0) f \times 1.25 \times 0.85}{A} \times 100\% \quad (2)$$

where a is the volume samples consumed by 0.05 N NaOH, mL, a_0 is the volume blank consumed by 0.05 N NaOH, mL, f is a correction factor, 1.25 is a reduction factor, 0.85 is equal to the carboxyl content of samples corresponding to 1 mL 0.05 N NaOH (mg), and A is the quality of lignin excluding water (mg).

RESULTS AND DISCUSSION

Characterization of QL-SA

FTIR

The FT-IR spectra of QL, SA, and QL-SA are shown in Fig. 2.

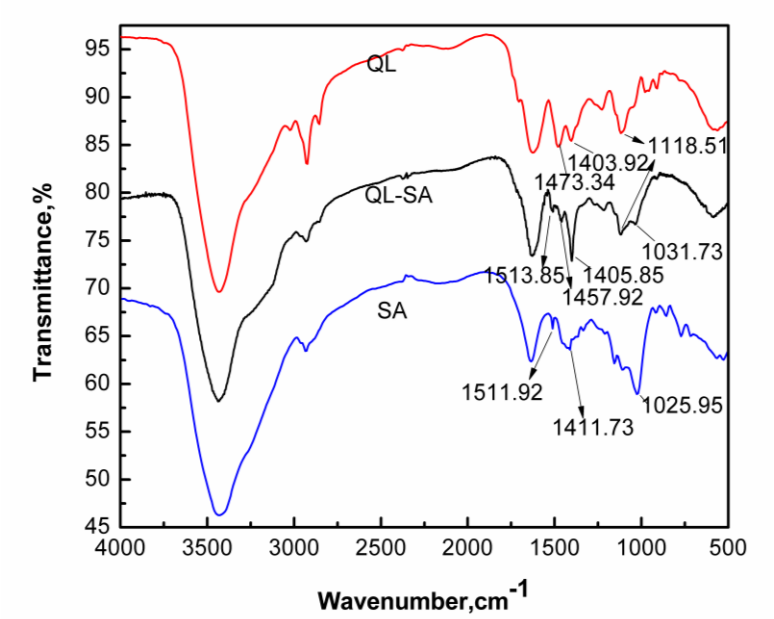

Fig. 2. FT-IR spectrum of QL (top), QL-SA (middle), and SA (bottom)

It is obvious that a characteristic peak at 1511 cm^{-1} for the –COO- group appears in QL-SA, which cannot be observed in QL. A new peak at 1031 cm^{-1} in QL-SA is due to the stretching vibration adsorption peak for the C-O group that is generated during the synthesis. A stretching vibration adsorption peak appeared at 1118 cm^{-1} for the C-N group in both QL and QL-SA. There was a new peak at 1457 cm^{-1} in QL-SA instead of the peak at 1473 cm^{-1} in QL, which is attributed to the characteristic peak of the N-H bend vibration of the quaternary ammonium group. This observation indicates that SA was synthesized successfully on QL, thus leading to the disappearance of -OH groups that had become connected with the quaternary ammonium and to a blue-shifting of the characteristic absorption peak of the quaternary ammonium group.

Nitrogen content and carboxyl content

The nitrogen content and the carboxyl content of QL with QL-SA was compared, and it was concluded that the nitrogen content by chemical modification of products is decreased and its carboxyl groups are increased, thus proving the QL has been introduced on the SA (see Tables 1 and 2). Infrared analysis of the product structure and the introduction of a quantitative analysis of the functional groups, as described above, all of characterization structure mutual support the grafting successful of QL and SA.

Table 1. Nitrogen content of QL and QL-SA

Sample	QL (%)	QL-SA (%)
Nitrogen content	4.21	3.29

Table 2. Carboxylic content of QL and QL-SA

Sample	QL (mmol/g)	QL-SA (mmol/g)
Carboxylic content	2.66	6.47

Scanning electron microscopy

The SEM photographs of SA, QL, and QL-SA are shown in Fig. 3. It is clear from the micrographs that the morphologies of SA and QL were entirely different from those of the QL-SA, exhibiting homogenous morphology of the QL-SA.

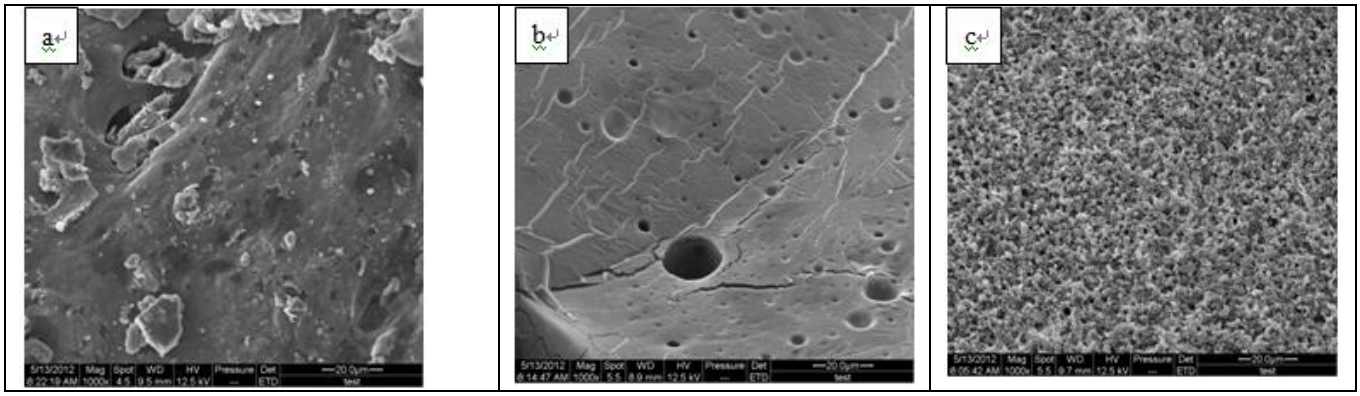

Fig. 3. SEM photographs of SA(a, 1000×), QL(b, 1000×), and QL-SA(c, 1000×)

It was also observed that the property of QL-SA was superior to both QL and SA, which is consistent with the data obtained from the analysis of their color removal rate. A rough surface can be expected to increase the surface area of flocculant material to obtain a better flocculation performance on dye small molecules by adsorption bridging action, and precipitate dyes *via* netting-sweeping action.

Flocculation Property of QL-SA

Establishment of linear equation of dyes

The effects of factors in flocculation, such as solution pH value, dose of flocculant, and settling temperature on the decolorization efficiency of QL-SA were investigated because these factors could affect the mechanisms of the removal process of dyes using QL-SA.

Table 3 shows that a linear equation is made for acid black ATT and methylene blue at their absorbance maximum wavelengths (λ_{max}).

Table 3. The Maximum Absorption Wavelength of Dyes and Calibration Curves

Kinds of Dye	λ_{max} (nm)	Calibration Curves
Acid black ATT	315	y = 16.167x
Methylene blue	663	y = 139.96x

In this table *y* is the absorbency and *x* is the concentration of the dye solutions.

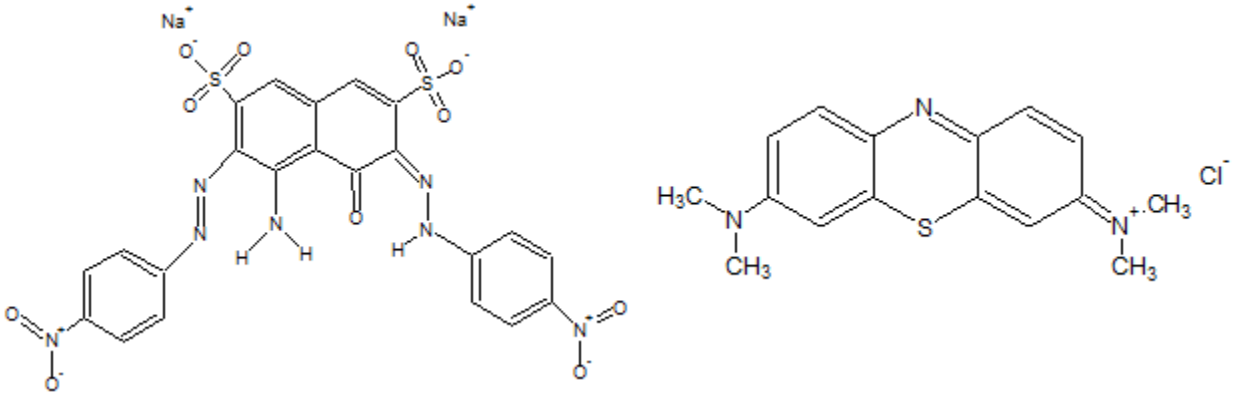

Fig. 4. Molecular structure of acid black (left) and methylene blue (right)

Electrostatic interactions are also the most important behavior between dye molecules and the polymer, excluding bridging actions (Szygula *et al.* 2008). The Acid ATT molecular structure (Fig. 4, left) contains a sulfonic group, which can react with a quaternary ammonium group in QL-SA.

The characteristic functional group in the methylene blue molecule (Fig. 4, right) is able to neutralize the carboxylate radical in QL-SA. In conclusion, flocculation of QL-SA results from the synergism of surface morphology (Fig. 3) and chemistry (Fig. 4).

Effect of different conditions on the removal of Acid black ATT

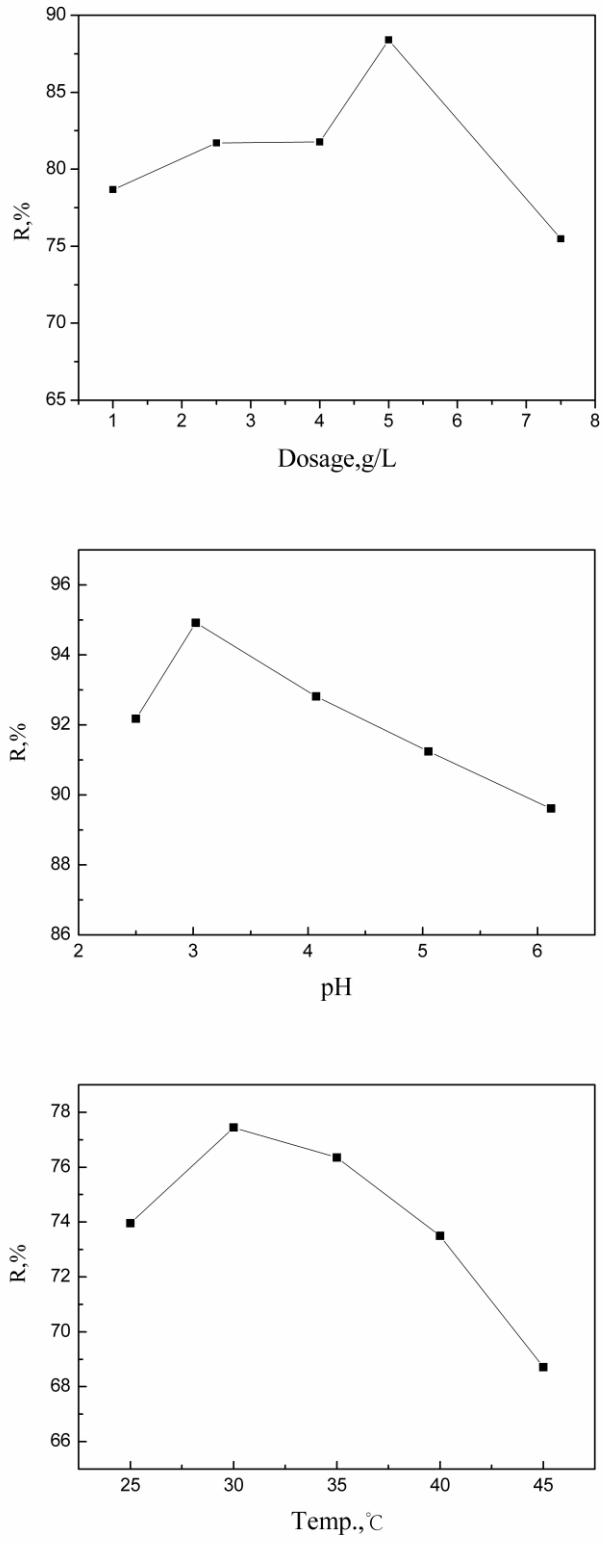

Fig. 5. Effect of different conditions on the removal of Acid black ATT

The effect of different conditions on the removal of Acid black ATT is seen in Fig. 5. It is shown that the flocculation performance on acid black ATT was best when the dosage of QL-SA was 5 g/L, the pH value of solution system was 3, and its temperature was 30 ^{o}C. Electrostatic interactions and bridging actions play an important role in controlling the flocculation of dye molecules on the polymer surfaces. In addition, -OH and COO-, which are presented in QL-SA, may also enhance the flocculation performance, which acts on strong electronegative oxygen atoms in acid black ATT, thus, to a certain extent, causing it to lose most of the electron cloud and form hydrogen bonds. With the increasing of dosage, electrostatic adherence is enhanced correspondingly. In contrast, the excessive flocculant may convert the initially flocculated system to a stable colloid. The removal of dyes is directly affected by the strength and the availability of positive charges that are influenced by the solution system. This theory is supported by Somasundaran and Runkana (2005), who concluded that the pH value of the dye solution influences the electrochemical property of the particles as well as the dissociation of the polyelectrolytes and affects their conformation in solution. Therefore, under acidic conditions, QL-SA exists in a stretched from which enhances the availability of the positive charges and the bridging capability of the flocculant. As shown in Fig. 4, the best decolorization temperature is at 30 ^{o}C. With increasing temperature, the increasing of flocculation performance may be due to the enhanced rate of dyes' intraparticle diffusion and change the size of the pores in the flocculant (Tan *et al.* 2012). As the temperature continues to rise, it leads to a decline in flocculation performance, because high temperature increases the probability of collision of the inter-polyampholyte.

Effect of different conditions on the removal of methylene blue

The effects of different conditions on the removal of methylene blue are seen in Fig. 6. It is shown that the flocculation performance on methylene blue was best when the dosage of QL-SA was 8 g/L, the pH value of solution system was 8, and its temperature was 30 ^{o}C. This flocculation mechanism on methylene blue is mainly attributed to the bridging action of QL-SA (Kavitha and Namasivayam 2007). It depends on the electrostatic repulsion among anionic groups, so as to stretch a molecular chain and absorb methylene blue molecules easier in this stretched state. Therefore, pH is the main factor affecting the flocculation performance. When the solution is alkaline, the negative electrostatic charge on the QL-SA surface is enhanced, leading to electrostatic repulsion; it easily forms a large floc through a bridging action with the chain cyclic adsorption of QL-SA. From this figure, the best pH value is 8, and the repulsion between methylene blue and QL-SA increases with increasing pH value. The increasing repulsion means that it becomes difficult to achieve contact between the molecules, thus weakening the flocculation performance. As an ionic flocculant, the effects of dosage and temperature were similar to those observed in the case of acid black ATT.

Comparison of the removal rate of QL-SA, QL and SA in the best condition

From Table 4 the optimal condition of the two different dyes can be seen. As shown, the flocculation performance of QL-SA was markedly superior to QL and SA. It is also conclusive that the synthesis of QL-SA expands its application ranges.

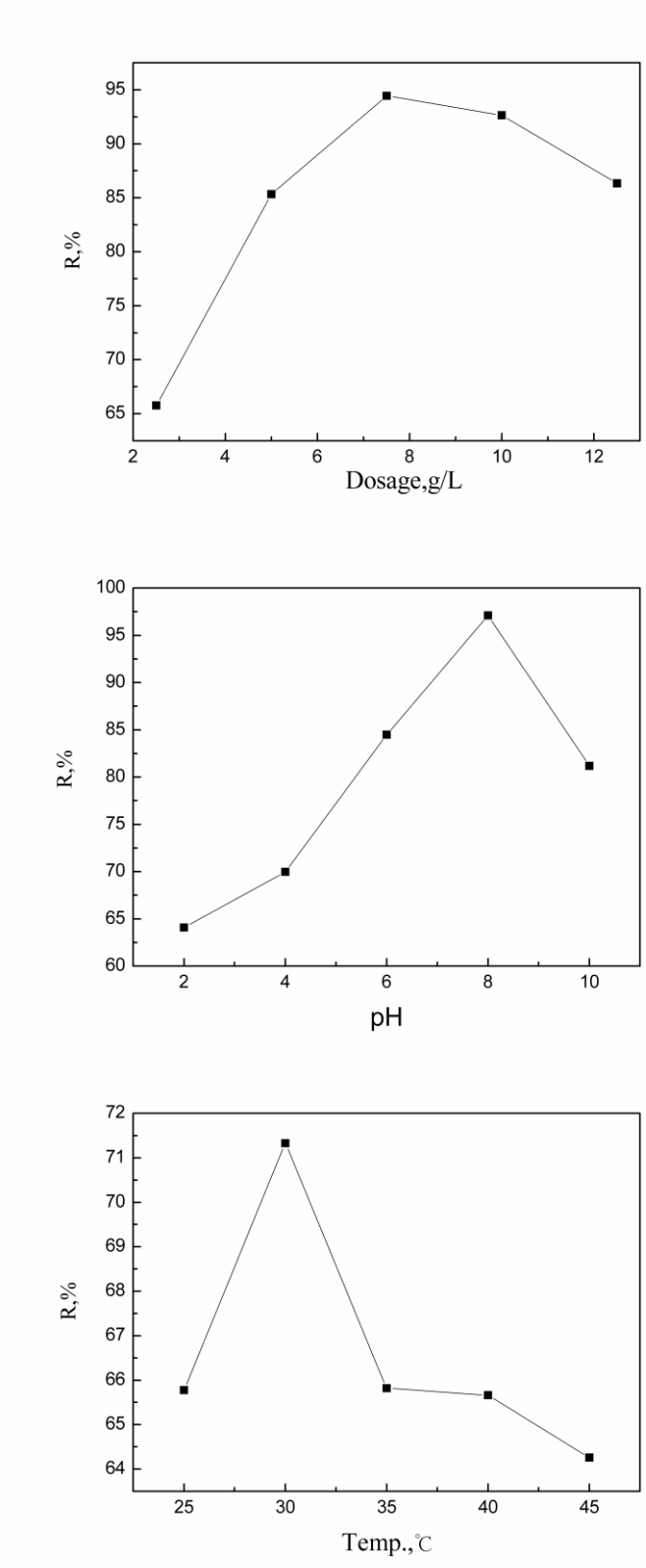

Fig. 6. Effect of different conditions on the removal of methylene blue

Table 4. The Removal Rate of QL-SA, QL, and SA in the Best Condition

	Methylene Blue %	Acid Black ATT %
QL-SA	97.11	94.91
QL	—	80.18
SA	62.61	—

CONCLUSIONS

1. QL-SA was analyzed by FTIR and SEM and its effects of QL-SA on the flocculation performance of dyes were investigated with methylene blue and acid black ATT water as the simulate dye. Results are as follows: the optimum flocculation temperature of acid black ATT was 30 ^{o}C; the best pH value of acid black ATT was 3, and the flocs dose was 5 g/L, while that of methylene blue was 30 ^{o}C, pH value of 8, and the flocs dose was 8 g/L.
2. In optimal conditions, the maximum decolorization rate of acid black ATT was 94.91% and methylene blue was 97.11%. The effect of QL-SA is markedly superior to SA and QL on the whole.
3. The advantages of QL-SA lies in its wide range of applications, which can handle different polarities of industrial wastewater, fast flocculation rates, clear stratification, and ease of recycling. Therefore, the QL-SA exhibits a good practical prospect.

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