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Study on the Discoloration of Simulating Dye Effluemts with a Kind of Amphoteric Lignin-based Flocculant*

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Abstract: The calcium lignosulphonate was adopted as the raw material to prepare the amphoteric lignin-based flocculant, denoted as LSDC. Then the LSDC was adopted to flocculate the different simulating dye effluents, e. g., reactive blue X-BR, reactive yellow X-R, reactive violet K-3R and reactive black K-BR. And, different flocculation effectors were optimized. It can be concluded that the flocculation efficiency of LSDC has found to be effluent pH and flocculant dose dependent. The discoloring rate increases with an increase in the LSDC dose ranging from 0 to 150 mg/L. However, COD_{Cr} of the simulating dye effluents also increases by addition of the LSDC. Consequently, the LSDC should be limited to a permissible dose. The LSDC contains the anionic sulfonic group and cationic quaternary ammonium group. Consequently, the kinds and number of the function groups on the dye molecular chains also showed great effect on the discoloring efficiency. For the reactive dyes, the discoloring flocculation capacities decreased with an increase of the numbers of the functional groups of the dyes. Among the effluent pH ranging from 4 to 8, the discoloring rates of the reactive blue X-BR, reactive yellow X-R, reactive violet K-3R and reactive black K-BR could reach 83.78%, 99.39%, 98.25% and 82.13%, respectively.

Key words: Lignin; calcium lignosulphonate; flocculant; discoloration; dye effluent
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1 Introduction

Lignin is one of the most abundant natural renewable materials on the earth. Most of the industrial lignin is from the red liquors or black liquors in the pulping process[1]. And, for the large-scale pulp and paper mills, the black liquors were used to recycle the alkali liquor by the procedures of concentration, combustion and causticization. The lignin was combusted. Consequently, the silvola recovery process is only a good way to avoid the black-liquor pollution. It is not an economic method that causes the tremendous resources waste. For the medium and small pulp and paper mills, the black liquors from the pulping process were discharged directly without any treatments, which caused the severe environmental pollution. Therefore, how to prepare the lignin-based products that yield a high added value and thus to avoid the environmental pollution has aroused the increasing interests of the many chemists and technologists.

Presently, the lignin and its modified products have been used as the soil stabilizing agents, cement porphyrization assistants, water reducing agents of cements and concretes, cohesive amterials, dispersing agents of slurry in the oil drilling and cement retarding agents in the oil wells etc.[2] Moreover, they also can be used as emulsification stabilizers in such hydrophobic substances, e. g., bitumen emulsions. And, they have been successfully applied in the light industry as the additives of dyes, pigments, coatings, printing inks, tanning agents and rubber items etc.[2]

The lignin and its modified products have been reported as the flocculants in the waste-water treatment[3,4]. However, no satisfactory flocculation efficiency has been achieved, especially for the treatment of gourmet effluents, pharmaceutical effluents and dye effluents. In this paper, the calcium lignosulphonate was adopted as the raw material to prepare the amphoteric lignin-based flocculant (denoted as LSDC) by the graft copolymerization and methylamination. Then the discoloring flocculation was conducted to test the flocculation performance of LSDC

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with the different simulating dye effluents, e. g., reactive blue X-BR, reactive yellow X-R, reactive violet K-3R and reactive black K-BR.

2 Experimental

2.1 Material and reagents

The calcium lignosulphonate was kindly provided by the Guangzhou Paper Group Co, Ltd, Guangzhou, China. The acrylamide, potassium persulfate, sodium hydroxide, acetone, formaldehyde and dimethylamine etc. were chemically pure. The reactive dyes, e. g., reactive blue X-BR, reactive yellow X-R, reactive violet K-3R and reactive black K-BR were commercially pure.

2.2 Instrumentation

The analytical instruments used included a HI99721 COD determinator (Hanna Instrumental Co, Italy), a PHS-25 pH-meter (Shanghai Hongyi Instruments Co, Ltd, China), a UV-2201 ultraviolet-visible spectrophotometer (Shimadzu, Japan) and a Precisa XT 120A (Swiss).

The synthesis equipments included the thermostat and constant—rate reactors and the electric agitators.

2.3 Preparation of LSDC

The calculated amounts of the calcium lignosulphonate and water were mixed into the thermostat and constant-rate reactor for 10 min. Then 0.5×10^{-2} mol/L of the $K_2S_2O_8$ initiator was added into the above mixture. After initiation reaction for 30 min, 1.4 mol/L of acrylamide monomer was added into the reactor slowly and the N_2 was adopted as the shielding gas. Then the reaction temperature was raised to 50 ℃. The copolymer product was thus obtained after 2.5 h of the graft reaction.

The above ropy reaction solution was adjusted to pH =9.5 with 10% of the sodium hydroxide aqueous solution. Then 37% of the formaldehyde aqueous solution was fed into the reactor at 50 ℃. After 1 h, a calculated amount of the dimethylamine was added into the above solution, and the LSDC was obtained after 2 h of the methylamination.

2.4 Determination and characterization

The effluent pH, colourity and COD_{Cr} were determined with a PHS-25 pH-meter, a UV-2201 ultraviolet-visible spectrophotometer and a HI99721 COD determinator, respectively.

2.5 Discoloring flocculation experiments

The predetermined concentrations of the reactive dyes ranging from 0 to 70 mg/L were prepared. And, a UV-2201 ultraviolet-visible spectrophotometer was used to determine the corresponding the absorbance, denoted as A, at the corresponding predetermined wavelengths. Then the calibration curves of the reactive dyes were obtained.

The various LSDC doses were used to carry out the discoloring flocculationexperiments. The experiments were conducted under such conditions as 100 ml of the simulating dye effluent and 1 min of agitation. After stewing for 30 min, the colourity of the supernatant fluid was determined with a UV-2201 ultraviolet-visible spectrophotometer. The residual concentrations of the simulating dye effluents were calculated from the calibration curves. And, the discoloring rate, denoted as R, could be obtained by the following formula:

$$R(\%) = \left(1-\frac{C}{C_0}\right)\times 100\%$$

Where, C_0 and C are the initial and residual concentrations of the simulating dye effluent (mg/L).

The flocculation discoloring capacity, denoted as FD, could be calculated by the following formula[5]:

$$FD = \frac{V(C_0 - C)}{W}$$

Where, FD is the flocculation discoloring capacity (mg/mg); C_0 and C are the initial and residual concentrations of the simulating dye effluent (mg/L); V is effluent volume (L).

3 Results and discussion

3.1 Establishment of the calibration curves of various reactive dyes

The concentration-absorbance calibration curves were plotted by determinations of the absorbance of the simulating dye effluents with various concentrations. The curves are listed in Tab. 1.

Tab 1 The calibration curves of various reactive dyes

Simulating dye effluent	λ_{max}/nm	Calibration curve formula
Reactive blue X—BR	594.5	$A=0.0049C+0.0063$
Reactive yellow X—R	350.5	$A=0.0141C+0.0286$
Reactive violet K—3R	561.0	$A=0.0204C+0.027$
Reactive black K—BR	598.5	$A=0.0213C+0.0063$

Note: A is the absorbance; C is the concentration of the dye solution.

3.2 Effect of LSDC dose on the discoloring efficiency

The LSDC dose showed great effect on the discoloring efficiency. The results are shown in Fig. 1. Among the LSDC dose range of 0 and 150 mg/L, the discoloring rate increased with an increase of the LSDC dose. And, the discoloring rates were 83.78%, 99.39%, 98.25% and 66% for the reactive blue X-BR, reactive yellow X-R and reactive violet K-3R, respectively. For the reactive black K-BR, the maximum discoloring rate reached 82.13% when the 200 mg/L of LSDC dose was used. When the LSDC dose exceeded 150 mg/L, the discoloring rate remained constant for the reactive blue X-BR, reactive yellow

X-R and reactive violet K-3R. And for the reactive black K-BR, the discoloring rate only reached 82.5% when the LSDC dose exceeded 200 mg/L. Moreover, the excessive dose would cause the increase in the COD of the simulating dye effluents. Consequently, the LSDC dose should be adjusted in an ideal range.

3.3 Effect of effluent pH on the discoloring efficiency

Under the otherwise identical conditions, the discoloring efficiency has found to be effluent pH dependent. The effluent pH affected the existing state and charge characteristics of the amphoteric lignin-based flocculant — LSDC, which would change the combination forms and degrees of the LSDC molecules with the dye molecules. Then the discoloring efficiency was thus affected. The experimental results indicated that the effect of the effluent pH on the discoloring rate varied with the dye variety. And, excellent discoloring efficiency could be achieved among the pH range of 4 and 8. Under the extreme conditions, i.e., the strong acidity or the strong basicity, about 10% of the discoloring rate would be reduced.

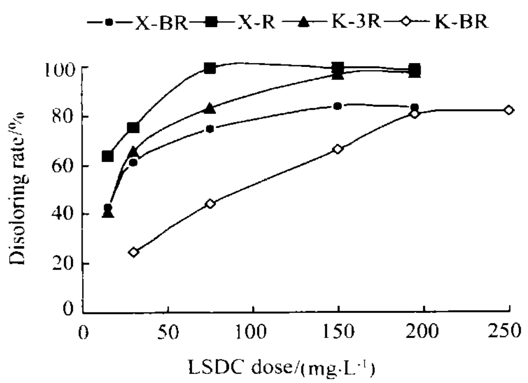

Fig 1 Effect of LSDC dose on the discoloring efficiency

3.4 Effect of LSDC on the effluent COD_{Cr}

The composition of the calcium lignosulphonate is very complex. And, it contains different aromatic compounds with various molecular weights. Therefore, excessive LSDC dose will cause the COD_{Cr} increase. It is necessary to conduct the studies on the relation between the LSDC dose and the simulating effluent COD_{Cr}. The results are shown in Fig. 2 and Tab. 2. The results showed that the COD_{Cr} increased with an increase of the LSDC dose. Furthermore, the COD_{Cr} was also reversely related to the discoloring rate. The satisfactory discoloring rate helped to reduce the COD_{Cr} efficiently, which would cause no secondary pollution. However, poor discoloring results would increase the COD_{Cr}, which would bring about the secondary pollution. It can be confirmed that the functional groups in the LSDC molecules can react with the corresponding functional groups in the dye molecules to form the salt bonds. Then the colourity of the simulating dye effluents can thus be removed. Nevertheless, the unreacted LSDC will cause the COD_{Cr} increase during the discoloring flocculation process, which will cause the secondary pollution. Hence, it is very important to adjust the LSDC dose to a permissible range.

Tab 2 variation of CODcr initial and final of dye treating

Simulating dye effluent	LSDC dose (mg·L⁻¹)	Discoloring rate/%	COD_{Cr} (mg·L⁻¹)
Reactive blue X—BR	150	83.78	+135
Reactive yellow X—R	75	99.39	−3
Reactive violet K—3R	150	98.25	+42
Reactive black K—BR	200	82.13	+266

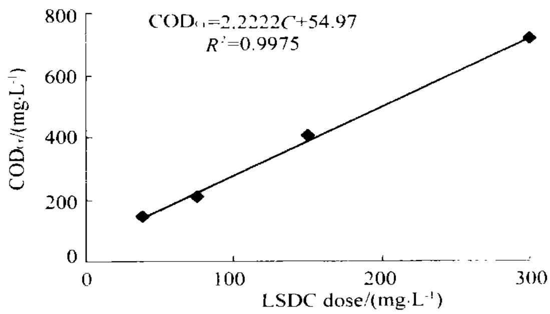

Fig 2 The relational curve of the LSDC dose and effluent COD_{Cr}

The discoloring experiments also indicated that the satisfactory discoloring efficiency could be achieved when the LSDC was adopted as the discoloring flocculant. Moreover, it could not cause the secondary pollution under the optimum conditions.

3.5 Effect of the kinds and number of the functional groups in the dye molecules

The LSDC molecular chain contains the sulfonic groups and cationic quaternary ammonium salt groups. The sulfonic groups and cationic quaternary ammonium salt groups in the LSDC molecules can combine with the amino groups and anionic groups, i.e., $-NO_2$ and $-Cl$ etc., in the reactive dyes, respectively. And, the salt bonds are thus formed to produce the aggregation substances by the charge neutralization and bridging action. The bigger flocculation substances are further formed and shaped by the van de Waals attractive forces. Then the soluble dyes are thus discolored with the LSDC.

The kinds and numbers of the functional groups on the dye molecular chains have a strong impact on the discoloring efficiency. The effect results are listed in Table 3. Tab. 3 indicated that the flocculation discoloring capacity decreased with an increase of the numbers of the functional groups of the dyes.

Tab 3 The influence of group category and quantity dye contained on decolorization rate

Reactive	dye category and quantity of group					FD/$mg \cdot mg^{-1}$
	$-SO_3Na$	$-NO_2$	$-NH-$	$-Cl$	$-NH_2$	
Active brilliant blue X—BR		2	3	2	11 40	
Active yellow X—R	2		1	2		3. 31
Active purple K—3R	4		2	1	0. 98	
Active black K—BR	2	1	1	1	1	0. 82

4 Conclusions

(1) The amphoteric lignin-based flocculant prepared with the calcium lignosulphonate could be adopted as the discoloring flocculant. And, it showed satisfactory discoloring efficiency in the discoloring flocculation process. Under the optimum conditions, the discoloring rates of the reactive blue X-BR, reactive yellow X-R, reactive violet K-3R and reactive black K-BR could reach 83. 78%, 99. 39%, 98. 25% and 82. 13%, respectively.

(2) Excessive LSDC dose could cause the increase of the effluent COD_{Cr}, which would cause the secondary pollution. Consequently, permissible LSDC dose should be adjusted to avoid the secondary pollution and to achieve the excellent discoloring efficiency.

(3) The LSDC contains the anionic sulfonic group and cationic quaternary ammonium group. Consequently, the kinds and numbers of the function groups on the dye molecular chains also show great effect on the flocculation efficiency. For the reactive dyes, the discoloring flocculation capacities decreased with an increase of the numbers of the functional groups of the dyes.

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两性木素絮凝剂用于模拟染料废水的脱色处理研究

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摘　要：以木质素磺酸钙为原料制备了两性木素絮凝剂 LSDC，并将 LSDC 用于活性艳蓝 X-BR、活性黄 X-R、活性紫 K-3R、活性黑 K-BR 等多种模拟染料废水的脱色处理。讨论了 LSDC 投加量和溶液 pH 值对不同染料脱色效果的影响。实验结果说明，LSDC 对各染料的脱色率在投加量 0 ~ 150 mg/L 范围内脱色率随投加量增大而增大，同时投加量增加可能引起废水 COD_{Cr}的提高，需控制适当的投加量范围，在投加量不大时不会造成二次污染。染料所含活性基因数目和种类对脱色效果也有较大影响，对实验中涉及的几种活性染料，活性基团数目越多，絮凝脱色量越小。在 pH 4 ~ 8 的范围内，活性艳蓝 X-BR、活性黄 X-R、活性紫 K-3R、活性黑 K-BR 的脱色率分别可达 83. 7%，99. 39%，98. 25% 和 82. 13%。

关键词：木素；木素磺酸钙；絮凝剂；脱色；染料废水
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