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Decolorization of Dyeing Wastewater with Use of Chitosan Materials

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Abstract – More attention has been paid to the research on decolorization of dyeing wastewater nowadays. In this study, an investigation into the decolorization of dyeing wastewater was conducted using a combination of coagulant, carboxymethyl chitosan (NOCC) and coagulant aid, polyscrylamide (PAM). The factors influencing the decolorization efficiency, such as pH value, coagulant and the dosages of coagulant, were discussed. The results showed that using PAM as coagulant aid could reach a high decolorization efficiency compared with using NOCC alone. The optimal conditions were pH 2.3, 480 mg/L for NOCC, and 4-8 mg/L for PAM. Under the optimum conditions, the rate of decolorization could achieve 99%, and the removal of chemical oxygen demand (COD) could achieve 90%. In addition, the membrane processes with chitosan/rare-earth-metals could enhance the decolorization rate of Direct Black FF to 94.7%, and Indanthren Red F3B to 98.2%, respectively.

Key words – Carboxymethyl chitosan, PAM, Dyeing wastewater, Decolorization, Chitosan/rare-earth membrane

1. Introduction

No doubt that the textile industry is rather significant in Chinese economic development; however, the wastewater that it annually contributes is quite considerable, among of which dyeing wastewater accounts for as much as 80 percent. On the basis of the survey results, we noticed that the color concentration and chemical oxygen demand (COD) were the two major polluting indices of dyeing wastewater. As a matter of fact, decolorization is one of the most difficult processes in treating wastewater (Huang *et al.* 1987; Olcay *et al.* 1996). As a natural biological macromolecule, chitosan (CTS) has been universally used in decolorization research with its specialties for flocculation, adsorption, chelation, and membrane-making (Chen and Chen 2000; Chen *et al.* 2001; Wan and Du 2003; Long and Lu 2003; Xing *et al.* 2004; Gregorio 2005).

Because of its poor water-solubility, CTS has been frequently modified into carboxymethyl chitosan (NOCC) in the process of treating wastewater. Two research groups (Zhang and Tang 1995; Huang *et al.* 2002) tried dealing with dyeing wastewater that came from a towel factory by using CTS and NOCC. Surprisingly, they discovered that the effectiveness of decolorization and COD reduction was more obvious than were approaches using other coagulants, while NOCC was proved superior to CTS in this aspect.

It's not difficult for us to observe that membrane processes have been wildely used as a specialized technology for wastewater treatment research in the past decades. Owing to characteristics such as no phase-change, low energy-consumption, and environment-friendly separation, condensation and recycling have been classified in this technology. It has been demonstrated that the two major membrane processes for treating dyeing wastewater are ultrafiltration and reverse osmosis (Peng and Yang 2003). CTS has been recognized as a new clean functional macromolecular membrane material and has played an increasingly important role in color removing research (Barbara 2005). Feng *et al.* (1998) treated methyleneblue and Acid Red B dyeing wastewater with the use of CTS ultrafiltration membrane, and found the effect of decolorization was more apparent than other commercial ones. Yu (1999)

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*Corresponding author. E-mail: shl@scsio.ac.cn utilized CTS/activated carbon complex ultrafiltration membrane, and it proved to be effective for decolorizing Acid Red B water solutions.

Keeping pace with this present trend, we cautiously present further research on decolorization methods with two major raw materials°™ CTS and NOCC. According to Liu (2002) and our primary test, we learnt that NOCC as a coagulant alone could make the floccules too small to precipitate out, which ended up with unsatisfactory pellucidity. Hence, we considered combining PAM with NOCC in order to improve the effectiveness of decolorization. Then, as the next step, we focused our attention on the application of rare-earth-metals. As we all know, Chinese environmentalists have been striving to apply rare-earth-metals (one of Chinese abundant resources) to dyeing wastewater treating research for years. Bravely Wei *et al.* (2002) took the lead in this field. Here a bench-scale experiment of membrane processes performed with CTS/rare-earth-metals was conducted in our research. After careful experimentation we gained the following breakthrough: the complex membrane is far more capable of removing coloring materials than CTS membrane. It's still an open field, worldwide, the use of CTS and rare-earth-metals to handling dyeing wastewater. Although our research is still far from being perfect, our achievement will hopefully offer a somewhat unique perspective on broader application fields of CTS and rare-earth-metals in the long run. For further advancement, continuing efforts will be made to meet a higher expectation.

2. Materials and Methods

CTS-PAM test

Firstly, put a certain amount of NOCC (supplied by Zhejiang Aoxing Biological Technology Company, China) into the solution of dyeing wastewater (50 ml 100 mg/L. Direct Black FF, Indanthren Red F3B, Reactive Orange X-G: water-soluble dyes supplied by Guangdong Sanshui Jinsheng Xinwei Dyeing Company, China, confected to be 100 mg/L single dyes simulated wastewater), then add 1 mol/L HCl for adjusting pH value. Later, stir this resultant solution at a relatively fast speed for 1 min, then add PAM (AR, 1‰water solution) to it and stir it slowly for another 1 min. When the steps above are finished, let the solution alone for 10 hours, and then measure the upper pellucid layer for absorbency and COD. Finally, the color-removing and COD-reducing rate are calculated.

CTS membrane and CTS/rare-earth-metals complex membrane test

Initially, place the shells of the shrimp into 3% (V/V) HCl for 20 h. Then wash them to be neutral and dip them in 5% (w/w) NaOH for 0.5 h. Later, wash the shells of shrimps to be neutral again, but this time they should be dried to afford chitin. Last but not least, put 5.0 g chitin in 50% (w/w) NaOH and subject it to the ultrasonic reaction to get CTS, which is to be washed to become neutral and dried.

Secondly, let 4.0 g CTS dissolve with 200 ml 0.1% HOAc, and then pour this mixture into a cultivated vessel where it extracted liquid membrane. After the membrane is dried at room temperature (r.t.), 5% (w/w) NaOH is added to separate the membrane from the vessel. Then the following process is to wash this CTS membrane to be neutral with distilled water and dry it again in r.t.

Last but not least, put the dried CTS membrane into 11.26% (w/w) $La(NO_3)_3$ (AR, supplied by Shanghai Chemical Reagent Company, China) for 6 h and 24 h respectively, and then dry it in r.t. Later, place the complex membrane into 50 ml 100 mg/L dyeing wastewater for a certain period of time. In the end, measure its absorbency and calculate its color-removing rate.

Measurement methods

Color-removing rate

$\eta(\%)=[(A_0-A)/A_0]\times 100\%$

A_0: absorbency before treatment

A: absorbency after treatment

Absorbency was measured by 722 visible spectrophotometer (Shanghai Compact Scientific Instrument Company, China). In addition, molecule weight and wave length of the tested dyes were listed in Table 1.

COD test

COD was measured by standard $K_2Cr_2O_7$ (State Environmental Protection Administration of China, 2002).

Table 1. Molecular weight and wavelength of the tested dyes

Dyes	M.W	Wavelength/nm
Direct Black FF	756	340
Indanthren Red F3B	512	480
Reactive Orange X-G	615	430

3. Results and Discussion

Effects of pH on flocculation and decolorization

Generally speaking, Dyeing wastewater is an electriferous colloid solution. According to the basic principles of colloid chemistry, the stability of colloid is closely related to ζ potential of colloid particles, and the latter one changed with the pH value of solution. In other words, the acidity directly affects the effectiveness of flocculation. To assure the accuracy of the experiment results, the effects of pH and dosage of PAM on decolorization of dyeing wastewater should be tightly controlled. Here we used the dosage of NOCC to 480 mg/L, and the color removing rate could be calculated later.

It can be clearly observed that the color-removing rate and pH value were closely related, the Indanthren Red F3B > Direct Black FF > Reactive Orange X-G. Color-removing rate increased as pH value ascended, and it reached a peak when pH=2.3, then it started to drop while pH value kept ascending. Respecting the course, we should not neglect the fact that Coagulant aid PAM was effectively bridging them when its dosage was 4-8mg/L. It's known that NOCC is amphoteric, and that is the reason for its solution being rather sensitive to pH value. While pH value stayed low, Ionization of acidic group was restricted, making NOCC a positive ion coagulant so that it played the role of neutralizing dyeing colloid particles with negative charge. However, when pH value was low enough, positive ion properties of NH_2 group of dyeing molecule would take the key role. As a result, the electronically repulse coagulant would come out with discouraging low treating effectiveness.

Dyes of varied types are fabricated with different molecular structures, and that is why different reactions appeared while the pH value changed. To summarize, besides pH value, ζ potential of colloid particles, the constitution and structure of the particles that form colloid are closely linked to each other.

The PAM became a more effective media for flocculation as long as its dosage arrived to be 4-8 mg/L, shaping floccules large enough to precipitate out rapidly. Oddly enough, once the dosage was excessive, PAM switched to protect the colloid by making it suspend again. As a consequence, a cloudy solution was formed and a minus color-removing rate was calculated. Inevitably, the effectiveness of decolorization could not be shown appropriately in this situation.

Effects of dosage of NOCC and PAM

The effects of dosage of NOCC and PAM on decolorization of three tested dyeing wastewater can be observed in Table 3 (pH value was fixed to 2.3).

Upon consideration of the information in Table 3, we could draw the conclusion that the dosage of coagulant and effectiveness of the three tested dyes' decolorization were closely related. Due to a sustainable increase in the dosage of coagulant, the color-removing rate kept on climbing; it would reach its peak while the dosage was 480 mg/L. After that, the rate commenced to drop if the dosage of coagulant maintained a rise. This result almost

Table 2. Effects of pH and dosage of PAM on decolorization

Dyes	pH	PAM/mg·L^{-1}					
		0	4	8	12	16	20
Direct Black FF	2.0	75.5	60	21.8	-----	-----	-----
	2.3	83.1	99.1	98.1	86.3	65.9	51.1
	2.6	61.2	41.5	44.4	78.6	64.9	49.0
	3.0	60.8	40.3	45.1	75.2	64.1	47.3
Indanthren Red F3B	2.0	75.5	60	21.8	-----	-----	-----
	2.3	83.1	99.1	98.1	86.3	65.9	51.1
	2.6	61.2	41.5	44.4	78.6	64.9	49.0
	3.0	60.8	40.3	45.1	75.2	64.1	47.3
Reactive Orange X-G	2.0	75.5	60	21.8	-----	-----	-----
	2.3	83.1	99.1	98.1	86.3	65.9	51.1
	2.6	61.2	41.5	44.4	78.6	64.9	49.0
	3.0	60.8	40.3	45.1	75.2	64.1	47.3

Note: "----" represents minus values.

Table 3. Effects of dosage of NOCC and PAM on decolorization

Dyes	NOCC/ mg·L^{-1}	PAM/mg·L^{-1}				
		0	4	8	12	16
Direct Black FF	224	47.3	61.0	68.6	36.6	19.1
	480	83.1	99.1	98.1	86.3	65.9
	720	78.7	85.5	80.3	81.1	80.6
	960	78.5	79.1	79.2	78.8	79.6
Indanthren Red F3B	224	0.87	0.73	0.54	0.27	0.22
	480	87.3	96.5	99.0	91.8	84.2
	720	97.1	97.5	98.1	97.4	92.6
	960	96.7	94.1	95.3	94.6	93.7
Reactive Orange X-G	224	80.9	84.5	77.1	73.9	73.4
	480	97.2	99.1	96.3	96.7	95.9
	720	96.2	96.9	96.6	95.7	96.2
	960	95.6	95.0	96.6	94.2	89.8

coincided exactly with the general flocculation phenomenon.

In addition, colloid particles could not be neutralized completely by the insufficient coagulant, while an adequate amount of coagulant decreased the static repulse among dyeing colloid particles and accelerated them to absorb together. NOCC is a macromolecule with linear structure; therefore, it can easily cooperate with another dyeing molecule to conduct the bridging function and congregate a great number of floccule sediment. The NOCC tended to be excessive as it continued to be added, and then the neutralized particles could be made bear positive charge again and head to multiply their ζ potential. On the other hand, when the coagulant became superabundant, the quantity of dyeing particles would turn to be relatively small. Due to the failure of integrating with the second particle, the stretching portion of macromolecular polymer would be attached to other parts of the macromolecule by the original one, causing a reduction in the adsorbing points on the surface of floccules, and end up with poor effectiveness of flocculation.

It would highlight the function of coagulant aid PAM when the condensation of NOCC was below 720 mg/L. Probably because when the quantity of floccules was small, the dimension of floccules would become relative slight in the NOCC. In this way, the PAM could assist remarkably in bridging the floccules and optimizing their structures, enabling them to be compacted and big enough to precipitate out. As coagulant continued to be added, the dimension of floccules could be large enough to precipitate out without the help of PAM.

COD reduction test

COD values before and after treating have been listed in Table 4.

The study results conveyed that a combination of NOCC and PAM could successfully achieve the high COD reduction rate of three tested dyeing wastewaters. Therefore, there is sufficient evidence to support the conclusion that this treatment could significantly reduce the quantity of the coloring materials in dyeing wastewater. The color of floccules was almost the same as the tested dyes, that is to say, decolorization could be fulfilled without destroying the structure of dyeing molecules.

CTS/rare-earth-metals complex membrane test

In accordance with **1.2**, Complex membranes were

Table 4. COD-removal of dyeing wastewater after flocculation processes

Dyes	Before treatment COD/mg·L^{-1}	NOCC/mg·L^{-1}	PAM/mg·L^{-1}	pH	After treatment COD/mg·L^{-1}	COD reduction rate/%
Direct Black FF	504	480	4	2.3	46	90.9
Indanthren Red F3B	497	480	8	2.3	52	89.5
Reactive Orange X-G	950	480	4	2.3	38	96.0

Table 5. Decolorization with CTS and CTS/ La$(NO_3)_3$ membrane processes

Dyes	Treating time/h	Type of Membrane		
		CTS	CTS/ La$(NO_3)_3$ 6 h	CTS/ La$(NO_3)_3$ 24 h
Direct Black FF	9	3.6	46.2	73.9
	15	9.2	71.6	82.8
	24	18.7	94.3	91.5
	33	19.4	92.1	94.7
Indanthren Red F3B	9	3.2	84.2	93.1
	15	3.4	92.9	94.8
	24	4.1	95.6	96.8
	33	17.4	96.2	98.2
Reactive Orange X-G	9	87.6	59.8	64.7
	15	99.5	60.3	79.5
	24	99.2	62.7	96.1
	33	99.4	84.3	98.2

prepared and the decolorization test was performed, then the absorbency was measured during certain lengths of time; more introductions were listed in Table 5, including the color-removing rate

Although the CTS membrane achieved 99% color-removing rate for Reactive Orange, it didn't work for Direct Black and Indanthren Red, while CTS/rare-earth-metals complex membrane could apparently improve the effectiveness of decolorization for the latter two dyeing wastewaters.

This remains to be seen, however, since the decolorization mechanism of the CTS/rare-earth-metals complex membrane hasn't been completed yet. We can make only these initial suggestions in light of the structure of rare-earth-metals RE^{3+}:4f$^{0\text{-}14}$5d$^{0\text{-}1}$6s^{2}6p^0. With huge charge and large semidiameter (usually 0.1 mm), RE^{3+} chelateds with cluster by electrovalent bond; because of its empty (n-2)f orbit, this compound possesses an active internal function. Besides, RE^{3+} can enlarge the molecules by hydrolysis and polymerization in water solution. Therefore, three concepts about decolorization mechanism can be provided: (1) CTS and rare-earth-metals are cooperative on exercising the flocculating function. (2) rare-earth-metals hydrolyze and polymerize on the surface of complex membrane, working as a coagulant aid. (3) rare-earth-metals form a covalent or electrovalent bond with -SO^{3-}, -SO^{3-}, and OH of the dyeing molecule, and absorb dyeing molecule by static effect.

Based on the resulting data, we recognized that after the color-removing rate reached the top for a certain length of time, it would remain unchanged or would fall slightly. Obviously, it further illustrated that the interaction between the complex membrane and dyeing molecule was a process of absorption-desorption dynamic equilibrium.

4. Conclusions

The effectiveness of a treatment system for the decolorization of dyeing wastewater was investigated. It was discovered that a combination of coagulant (NOCC) and a coagulant aid (PAM) yielded an effective treatment for wastewater because almost complete decolorization was achieved and 90% of COD was reduced. The optimum pH value and dosage for treatment were found to be pH=2.3, 480 mg/L for NOCC and 4-8 mg/L for PAM respectively. Finally, a bench-scale experiment of membrane processes performed with CTS/rare-earth-metals was conducted. This breakthrough study indicated that complex membrane was capable of removing 94.7% of Direct Black FF and 98.2% of Indanthren Red F3B without adjusting the pH value. Although our research is still far from being perfect, our achievement will hopefully offer a somewhat unique perspective on broader application fields of CTS and rare-earth-metals in the long run. For further advancement, continuing efforts will be made to meet ever-rising expectations.

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