

Reusing salt of reactive dyeing wastewater for reactive dyeing

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Abstract: In order to reduce salt pollution and reuse reactive dyeing wastewater efficiently, the residual dye was removed by calcium hydroxide, and the residual liquid was purified to remove the excess calcium hydroxide. The liquid was reused for reactive dyeing after the pH value was adjusted and the salinity was measured. The influence of calcium hydroxide on decolorization of dyeing wastewater was studied, and the dyeing properties of fabrics treated with recycled water and pure water were compared. The results showed that the residual dyes in reactive dye wastewater could be removed by calcium hydroxide, and the spectral curve of the treatment fluid is basically the same as that of pure water of the same salt concentration. The reuse dyeing has no influence on the color parameters and shade of fabric. After three times of reuse, the dyeing fastness is basically the same as that of dyed fabrics with pure water. Treatment of the dyeing wastewater of reactive dyes was studied, the corresponding treatment method was established. It provided a reference for reusing salt and water for dyeing wastewater of reactive dyes in this paper.

Introduction

Reactive dyes are primary dyes in textile dyeing industries due to their superior fastness, high photolytic stability and high solubility^[1]. It is difficult to migrate negative dye anions from dyebath to the cotton due to negative charge at the surface of fiber in an aqueous medium. In order to offset such repulsion between fiber and dye, a large amount of salt (NaCl or Na₂SO₄) should be used in the dyebath. The quantities of salt can vary from 30~150g/L, therefore wastewater contains a significant quantity of salt, leading to serious environmental problem^[2].

For the printing and dyeing industry, the removal of inorganic salts from dyeing wastewater is still in the preliminary stage. Firstly, the existing desalination technologies mainly include ion exchange and membrane separation at home and abroad. Ion exchange desalting technology is mainly the removal of harmful ions in wastewater by ion exchange reaction between ions in an ion exchanger and ions in wastewater. However, when the salt content of wastewater is higher than a certain value, the exchange capacity of the resin will be quickly reached, and a large number of regeneration agents need to be consumed. The amount of washing water will be increased, the processing cost will increase, and the operation will be tedious^[3]. Membrane separation technology is a method of separating selectively some components in liquid by special film, but there are some problems such as higher cost and slow processing speed^[4]. Secondly, high salinity wastewater will affect the reuse of water. Some studies have shown that when the salt content of printing and dyeing water is greater than 2g/L, the salt easily produces traces on the fabric, affecting the quality of the product^[5]. Thirdly, high salinity will also have a bad effect on the biochemical treatment of wastewater, and even the sewage treatment system will be collapsed^[6]. Finally, the discharge of high salinity wastewater is also a great waste to the enterprise itself.

Through the analysis of dyeing process of cotton fabric, the dyeing wastewater mainly contains inorganic salts, reactive dyes, sodium carbonate^[7]. If the reactive dye and sodium carbonate can be removed, the treated wastewater becomes an inorganic salt solution, which is the ideal carrier for dyeing cellulose fiber with reactive dyes.

Calcium hydroxide is a kind of white powder solid, commonly known as slaked lime and

slaked lime. Calcium hydroxide dissolved in water, the formation of calcium ions and hydroxyl ions, which can precipitate calcium ions and anionic dyes. The calcium hydroxide was mainly used to remove color from dyeing wastewater. After the salt content of the solution was measured by the light index method, the dyeing wastewater was reused. It provided a reference for the effective treatment of dyeing wastewater containing salt.

Experimental

Materials

Woven, bleached, scoured cotton fabric(130 g/m²)was obtained from the Haihong Company (China).Reactive Red 3BS, Reactive Yellow 3RS and Reactive Blue M-2GE were purchased from Yide Chemical Ltd. Sulfuric acid, sodium sulfate and calcium hydroxide were all analytical reagents. Levelling agent peregol O was industrial product. Soaping agent 209 was purchased from Transfar Chemicals Ltd.

Instrument and equipment

Salinity refractometer BGBG-213ATC, Tianjin Baosteel Optical Instrument Co. Ltd.; Beijing LG10-2.4A high-speed centrifuge, centrifuge Co. Ltd; pH HQ11d, Shanghai Li Hai Industrial Co. Ltd.; color matching system Datacolor 600, Datacolor, L-12C/L-24A-1C; Oscillating dyeing machine, Xiamen ruibi Pml Precision Mechanism Ltd

Dyeing conditions

All dyeings were carried out using a liquor ratio of 30:1.The dyebath was prepared by adding dye (1% o.w.f.) to distilled water at 60°C. Wet fabric was added to the dyebath and left for 15 min, and then suitable mount of electrolyte was added into the dyebath. Temperature was rised subsequently to 80°C, and fixation was conducted using sodium carbonate (10g /L), and left for 30min.The dyed fabrics were rinsed thoroughly in hot water and soaped in a soap solution (5g/L soap power, 15 min) at 95°C, then rinsed thoroughly in hot tap water and air-dried.

Salinity determination

The salinity meter uses two glass mirrors with the same contact surface, and the solution is sandwiched between the two surfaces to form a film of parallel sides. The principle of liquid refractive index measurement is as follows:

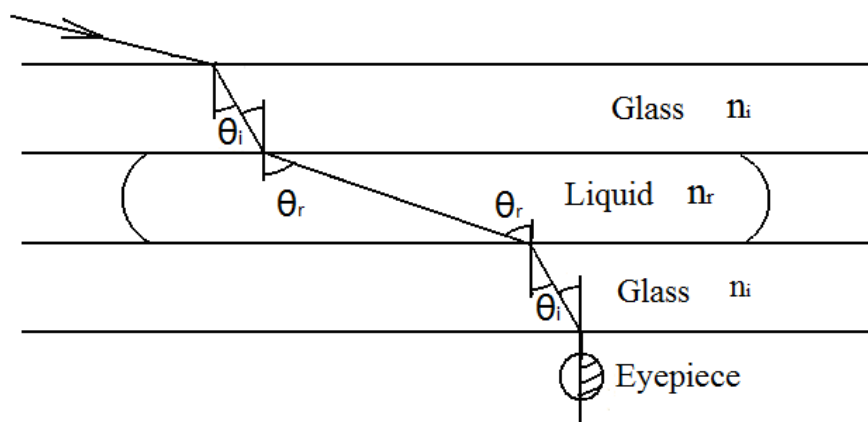


Fig. 1 Schematic diagram of salinity meter

A light ray passes from the more dense medium into the less dense medium. when the incident angle increases to a certain angle, the refraction angle reaches 90 degrees. It is a total reflection phenomenon that refraction of light completely disappeared, leaving only the reflected light. The

incident angle is called the critical angle.

The critical angle is the θ_i that gives a θ_r value of 90 degrees. If this information is substituted into Snell's Law equation, a generic equation for predicting the critical angle can be derived. The derivation is shown below.

$$n_i \cdot \text{sine}(\theta_i) = n_r \cdot \text{sine}(\theta_r)$$

$$n_i \cdot \text{sine}(\theta_{\text{crit}}) = n_r \cdot \text{sine}(90 \text{ degrees})$$

$$n_i \cdot \text{sine}(\theta_{\text{crit}}) = n_r$$

It is shown by the diagram that the region($\theta_i > \theta_{\text{crit}}$) forms the dark area, and the region($\theta_i < \theta_{\text{crit}}$) forms a bright area. The n_i is the refractive index of the glass. As long as the critical angle is obtained, the refractive index of the liquid can be obtained.

The refractive index of a liquid is directly proportional to the concentration of a liquid and thus the concentration of a liquid is obtained^[8].

Decolorization of dyeing wastewater

At room temperature, a certain amount of calcium hydroxide add into the dyeing wastewater (50mL), fully mixing, keep for a while until the upper liquid is clarified. The upper liquid centrifuge separate(1000r/min,3min) to obtain the clear liquid.

Colour measurements

The reflectance of dyed samples was measured with the Reflectance Spectrophotometer (Spectra Flash SF600, Data Color) under the illuminant D65 using 10° standard observer. The color strength of dyed samples was expressed with K/S value calculated by the Kubelka–Munk equation.

Determination of UV Vis spectrophotometric curve

The ultraviolet visible spectrum curve of the solution was obtained by scanning the 200-800nm wavelength range with UV-2450 spectrophotometer.

Fastness testing

The rubbing fastness and the washing fastness of dyed samples were tested according to ISO 105-X12 (2001) and ISO 105-C10 (2006), respectively.

Results and Discussion

Decoloration of reactive red 3bs by calcium hydroxide

At room temperature, a certain amount of calcium hydroxide is add into the dyeing wastewater (50mL), fully mixing, keep for a while until the upper liquid is clarified. The upper liquid centrifuge separate(1000r/min,3min) to obtain the clear liquid. the clear liquid, raw dyeing wastewater and pure water was tested for their spectral curves using UV-2450 spectrophotometer to test the decoloration effect of calcium hydroxide on dyeing wastewater. The result was shown in fig. 2.

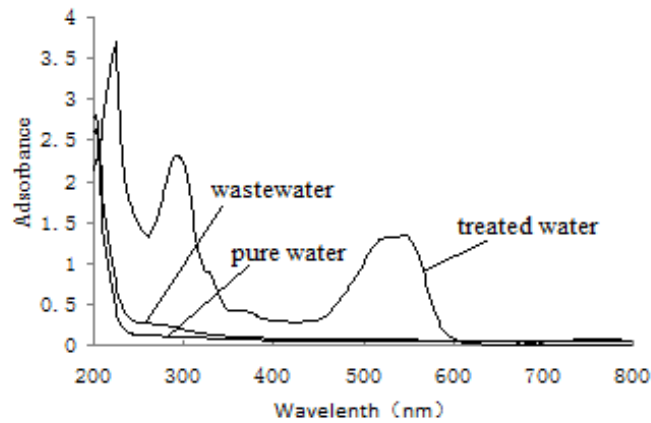


Fig. 2 Spectral curves of wastewater, treated water and pure water

It can be seen from Fig. 2 that the spectral curve of dyeing wastewater had obvious absorption peak in both UV and visible light region. The spectral curve of treated liquid basically coincided with the spectral curve of pure water. Not only the absorption peak of the visible light region disappeared, but also the absorption peak in the ultraviolet region disappeared. It was concluded that the dye in the residual liquid precipitated with calcium hydroxide and was almost completely removed.

The treated liquid should be used as a reuse water. Theoretically, the treated water should contain a certain amount of inorganic salt. The salinity of the treated water was measured by a salinity meter. The spectral curves of treated water and the pure water of the same salinity were tested and compared. The result was shown in Fig. 3.

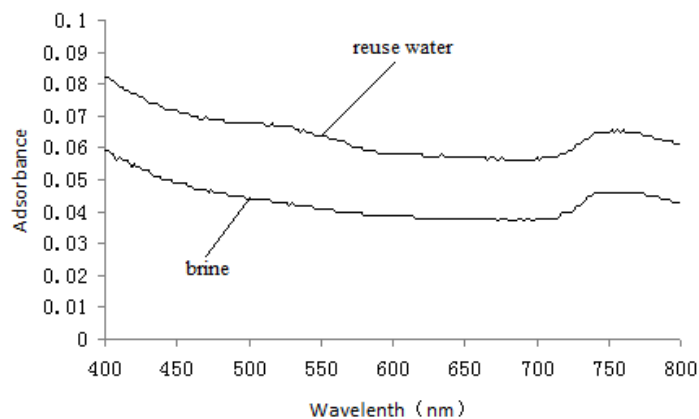


Fig.3 Spectral curves of treated water and pure water of the same salinity

It can be seen from figure 3. The two spectral curves were very close, and the absorbance of treated liquid was slightly higher than that of the same salinity pure water. Mainly due to there are a small amount of calcium hydroxide and other insoluble or slightly soluble impurities in treated liquid. In our opinion, the treated liquid can be used as a salt solution for reactive dyeing after proper purification.

Purification of reuse water and its influence on fabric dyeing

After the decolorization of the dyeing wastewater, there is a small amount of calcium hydroxide in the residue, which does not react with the dye molecule. If the treatment solution is

used directly for dyeing, calcium hydroxide will precipitate with reactive dyes. It will result in dye waste and dyeing defects, so it is necessary to remove the excess calcium hydroxide before the water is reused. In order to remove the residual calcium hydroxide, a small amount of sodium carbonate (Na_2CO_3) is added to the liquid, and the precipitate is removed by centrifugation. The liquid pH is adjusted to 7 by sulfuric acid, and then the excess sodium carbonate is converted into sodium sulfate. After the salinity of the liquid is measured by a salinity meter, the liquid is reused for reactive dyeing.

A certain amount of sodium sulfate is added to the pure water according to the salinity of the reuse water, so that both of them have the same salinity. Dyeing effects of pure water was compared with that of reuse water on cotton fabrics. The results are shown in Tab. 1.

Tab. 1 Influence of reuse water on color of dyed fabric

	L	a	b	C	h	CMC ΔE
Reactive red 3BS	52.00	54.082	-7.53	55.33	352.18	0.51
Reuse water	51.32	54.02	-8.01	54.61	351.56	
Reactive blue M-2GE	26.36	-3.95	-19.53	19.93	258.57	0.11
Reuse water	26.47	-4.03	-19.49	19.90	258.31	
Reactive yellow 3RS	73.45	28.38	61.59	67.82	65.26	0.75
Reuse water	73.78	27.59	59.60	65.67	65.16	

It can be seen from Tab. 1 that reuse water has less influence on fabric shade, and the color difference is between 0.11~0.75.

Effect of multiple reuse on the fastness of dyed fabrics

With the above method, the dyeing fastness of each dyed fabric was determined after reuse for three times. The result is shown in Tab. 2.

Tab. 2 Effects of repeated reuse on color fastness

	Washing fastness		Dry rubbing fastness		Wet rubbing fastness	
	Fading	Staining	Wrap	Weft	Wrap	Weft
Pure water	4	3-4	5	5	4-5	4
Primary reuse	4	3-4	5	5	4-5	4-5
Two times reuse	4	3-4	5	5	4-5	4-5
Three times reuse	4	3-4	5	5	4-5	4-5

The comparison of the fastness between running water dyed fabrics and reuse water dyed fabrics are showed in Tab. 2 that the water fastness and dry and wet rubbing fastness of the three dyed fabrics were not affected.

Conclusions

calcium hydroxide was used to remove the dyeing residue of reactive dyes, and the treatment solution was compared with the same salinity brine. Finally, the dyeing properties of the recycled dyed fabrics were studied in this paper. Results show:

- 1) calcium hydroxide can be used to remove residual dyes in reactive dyeing wastewater. The

spectral curve shows that the treated solution is basically the same as pure water.

2) The residual calcium hydroxide in the liquid was removed by sodium carbonate. After centrifugation, the liquid pH was adjusted to by sulfuric acid. The liquid salinity was determined and could be used for reactive dye dyeing. Compared with pure water, the color difference of dyed fabrics is below 0.75, and the reflectance curves of them are basically the same. The reuse dyeing has no influence on the color of dyed fabric.

3) the dyeing residue of reactive dye can be reused many times by this method. In the three reuse dyeing, the reuse water has no influence on the washing fastness and dry and wet rubbing fastness of dyed fabrics.

The decolorization of dyeing wastewater by calcium hydroxide, after removal of excess calcium hydroxide, using sulfuric acid to adjust the pH value, refractive index determination of salt concentration dyeing wastewater, dye additives added after the required for reuse of dyeing. It provides a reference for reusing the salt in dyeing wastewater and reducing salt pollution.

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