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Preparation of a Kind of Non-Woven Viscose Colour Absorbing Material and Research of its Colour Absorption Properties

DOI: 10.5604/01.3001.0013.0745

Abstract

A non-woven viscose material was modified with self-made cationic gelatin protein auxiliary by the padding process. The material prepared was then used as an environmentally friendly colour absorbent for the decolourisation of dye wastewater. The effects of the sodium hydroxide swelling pretreatment process and cationic padding modification process on the colour absorption and decolourisation rate were discussed. Moreover an optimal preparation process for the colour-absorbing material was determined. This was as follows: In order to make the non-woven viscose material swell and improve the subsequent modification effect, first the non-woven viscose material was pretreated with an aqueous solution containing 50 g/l of sodium hydroxide, at room temperature, for 5 min. Then the material was padded in a mixed aqueous solution containing 80 g/l of cationic gelatin and 18 g/l of sodium hydroxide by means of a laboratory padder with two dips and two nips. After treatment, the material was dried and steamed for 4 min. Lastly the material was washed with water and dried. The results show that the colour-absorbing material prepared by this process has the advantages of a high colour absorption rate and high decolourisation percentage. And it could be applied to the decolourisation of printing and dyeing wastewater, or to prevent washed off dyestuff staining on light colour clothes in the process of laundry.

Key words: non-woven viscose material, decolourisation, colour-absorbing material, cationic gelatin, padding modification.

Introduction

It is very important to decolourise dye wastewater, which can not only reduce the colour pollution of dyeing wastewater but also remove the floating colour of the dyed fabric surface, and decrease the staining of dropped dyes on fabric after dyed fabric clearing treatment [1-4]. Colour absorbing material can remove colour effectively, thus it has wide application. The number of washings of dyed fabric and the staining of dropped dyes on materials should be effectively reduced by the application of colour absorbing material. At the same time, the recovery of waste dyes and the reuse of dyeing wastewater are expected so as to protect our environment [5-6]. In addition, it is possible to use colour absorbing materials to avoid staining when dark coloured and light coloured clothes are washed together in the daily laundry process. There are many kinds of colour absorbing materials in the world. It has obvious advantages to select large-surface-area, porous and biodegradable fiber materials, which contain more groups that can combine with dyes, acting as colour absorbing materials [7-9]. Fibre materials have better adsorption performance for the dye and are chemically modified easily. If such materials are modified properly, more groups which can combine with dyes can be introduced onto the materials to improve their colour absorption properties further [10-11]. Therefore environmental modified fiber-based colour absorbing materials acting as the water treatment agent have attracted the great attention of researchers [12-14]. At present, people are paying more attention to the modification of waste materials and the preparation of environmentally friendly colour absorbing materials [15-17]. This kind of colour-absorbing material can effectively remove the coloured substances from the wastewater, achieving the purpose of purifying water, saving energy and reducing water pollution. It can be seen that the development of fiber-based colour absorbing materials have great practical significance and development prospects due to their low toxicity, low energy consumption, adequate raw materials and high efficiency. A viscose non-woven fabric was modified with self-made cationic gelatin protein auxiliary by the padding method in the study. Cationic and protein structural groups were introduced onto modified viscose materials so that the adsorption properties of the modified material for anionic dyes increased significantly. Consequently the eco-friendly colour-absorbing material prepared by this research can remove colour pollution in wastewater effectively, with the added advantage of the cost of decolourisation being low. This is a meaningful study that accords with environmental protection.

Experiments

Materials and instruments

The weight of each square metre of Spunlaced non-woven viscose material used in the study was 72 g/m². Reactive Black B133, Reactive Orange KGN, Lan-

asol Yellow CE, Direct Brown RVN, Disperse Orange S-4RL, Cationic Light Yellow 7GL, and Acid Lake Blue A were supplied by Shanghai Kelong Dyestuff Industry Co. Ltd. (Shanghai, China). Sodium chloride and anhydrous sodium carbonate were provided by Tianjin Hongyan Chemical Reagent Factory and Sodium hydroxide by Tianjin Hengxing Chemical Reagent Factory (Tianjin, China). All reagents were of analytical grade. Cationic gelatin was made by us. A 722 type spectrophotometer was provided by Shanghai Third Analytical Instrument Factory (Shanghai, China) and an X-Rite Colori7 spectrophotometer by Shanghai Jia’en Technology Co. Ltd. (Shenyang, China). An HHS-24 electronic constant temperature water bath pot was provided by Shanghai East Star Building Material Experiment Equipment Co. Ltd. (Shanghai, China). The HHS-24 high temperature program-controlled dyeing machine used was made by Nantong Hongda Ex-
Technological process

Swelling pretreatment of non-woven viscose material → Cationic padding modification treatment → Decolourisation → Test.

Alkali swelling pretreatment process

Non-woven viscose material was put into an aqueous solution of sodium hydroxide at a certain concentration. The material was then pretreated in an HHS-24 electronic constant temperature water bath pot while keeping the material-to-liquor ratio at 1:25 at a certain temperature for a certain time.

Cationic padding modification treatment

The swelling pretreatment non-woven viscose material was immersed in a mixed solution containing sodium hydroxide and cationic gelatin, then passed through a laboratory padder with two dips and two nips, where the wet pick-up was approximately 150% and the pressure 0.1 KPa, afterwards dried at 90 °C for 10 min, and finally steamed for some time in a CH-8156 high temperature steam oven. Then the cationic modified material was rinsed with water and dried at 40 °C in an oven.

Decolourisation process

The preparation of 0.1 g/l Reactive Black B133acted as simulated dye wastewater. Then the modified material was added to the dye solution and treated at room temperature for 10 min. Finally the material was taken out and dried, and the decolourisation rate and colour absorption degree of the modified material (expressed as K/S values) of the non-woven material viscose were determined.

Measurement index

Decolourisation rate determination

The absorbance value of simulated waste dye solution was determined before and after dye absorption with the 722 type spectrophotometer at the maximum absorption wavelength (λmax) of the dye.

The decolourisation rate (R) is calculated as follows:

\[ R (\%) = \left(1 - \frac{nA_i}{mA_0}\right) \times 100 \]

Where, \( A_i \) is the absorbance of simulated waste dye solution diluted \( n \) times after absorbing. \( A_0 \) is the absorbance of dye solution diluted \( m \) times before absorbing.

Colour depth (K/S value) determination

The reflectance values of the cationic modified non-woven viscose material after absorbing dye were measured under D65 illuminant at 10° observer using a X-Rite Color7 spectrophotometer. The colour absorption degree of the modified material (expressed as K/S values) was calculated from the reflectance \( R \) of each colour absorbed material at the maximum absorption wavelength of the dye using the Kubelka-Munk function, shown below. Each colour absorbed material was folded into two layers, then the K/S value measured at any 6 points, and an average value taken. The bigger the K/S, the better the colour absorption degree of the modified material.

\[ K/S = (1-R)^{2/2R} \]

Where, \( K \) is the coefficient of absorption, and \( S \) is the coefficient of scattering.

Results and discussion

Optimisation of alkali swelling pretreatment process

Effect of sodium hydroxide concentration on colour absorption of the materials

Non-woven viscose material was swelling treated for 4 min at room temperature according to the process described in “Alkali swelling pretreatment process”, in which the sodium hydroxide concentration was changed. Then the swelling pretreated non-woven viscose material was modified with cationic gelatin auxiliary according to the process described in “Cationic padding modification treatment”. The amount of cationic gelatin auxiliary was fixed at 80 g/l, that of sodium hydroxide at 18 g/l, and the steaming time was 4 min. The material was not washed. Lastly the material was used to absorb Reactive Black B133 according to the process described in “Decolourisation process”. The colour absorption properties are shown in Figure 1.

Figure 1 showed that the decolourisation rate and K/S value of the absorbing material were increased with an increase in sodium hydroxide concentration. When the sodium hydroxide concentration was 50 g/l, the decolourisation rate and K/S value of the material reached the maximum. The concentration of sodium hydroxide was increased further, and the decolourisation rate and K/S value of the material was decreased. It was indicated that the appropriate concentration of sodium hydroxide is beneficial to the swelling of viscose materials and to increasing the accessibility of cellulose viscose materials. In addition, it is beneficial to the reaction between the cationic gelatin auxiliary and viscose material in the subsequent modification process, which leads to increasing the degree of cationic modification of the material. Thus the modified material can provide more capacity for the adsorption of anionic dyes, and consequently the colour absorption effect of the modified material increases. However, when the concentration of sodium hydroxide was too high, damage to the viscose material increased, and the number of dissolved and dropped fiber fragments increased as well as the weight loss of the viscose material. The mass used to colour the absorbing material was reduced (Because the mass of the colour absorbing material was measured before the material was modified). As a result, the total number of positive charges decreased, as well as the K/S value of the material and the decolourisation rate . Therefore the optimal mass concentration of sodium hydroxide is determined to be 50 g/l.

Effect of alkali treatment temperature on the colour absorption of the materials

Non-woven viscose material was treated at different temperature for 4 min. according to the process described in “Alkali swelling pretreatment process”, in which the concentration of sodium hydroxide solution was fixed at 50 g/l. Then the swelling pretreated non-woven viscose material was modified with cationic gelatin according to the process described in “Cationic padding modification treatment”. The conditions of cationic modification were the same as described in “Effect of sodium hydroxide concentration on the colour absorption of materials”. Lastly the material was used to absorb Reactive Black B133 according to the process described in “Decolourisation process”. The colour absorption properties are shown in Figure 2.
Figure 2 shows that the decolourisation rate and K/S value of the material decreased slowly with an increase in the alkali treatment temperature. This is due to the alkalisation of cellulose being an exothermic reaction. The reaction activity between alkali and fiber is decreased with an increase in the alkali treatment temperature, which leads to a decrease in the swelling degree of viscose material. Hence the modified degree of the materials is weakened. In addition, the damage and weight loss rate of the treated viscose material increases with an increase in temperature. The mass of viscose material used to adsorb dyes is reduced, leading to a decrease in the colour absorption properties of the material. Thus the alkali treatment temperature is determined to be 20 °C.

Effect of alkali treatment time on the colour absorption of the materials

The effect of the alkali treatment time on the colour absorption of the material is listed in Figure 3, from which it can be seen that the decolourisation rate and K/S value of the material increased with an increase in the alkali treatment time. This is due to the swelling degree and accessibility of the viscose material increasing with an increase in the treatment time, which is beneficial to the subsequent reaction between the cationic gelatin auxiliary and fiber, and the cationic modified degree of the material is enhanced. Thus the colour absorption properties of the material for anionic dye are increased. However, when the alkali treatment time was over 5 min, the mass of dissolved and fallen off material increased significantly, leading to decreased colour absorption properties. Thereby, the alkali treatment time is determined to be 5 min.

To summarise, the optimum process for alkali swelling pretreatment of non-woven viscose material is as follows: The viscose material is put into an aqueous solution containing 50 g/l of sodium hydroxide and then treated at room temperature for 5 min.

Optimisation of cationic padding modification technology

Effect of the amount of cationic gelatin auxiliary on the colour absorption of the material

Non-woven viscose material was treated according to an optimised alkali swelling process, then the swelling pretreated material was modified with cationic gelatin auxiliary. The effect of the amount of cationic gelatin auxiliary on the colour absorption of the material is shown in Figure 4.

As can be seen from Figure 4, the decolorisation rate and K/S value of the material increased significantly with an increase in the amount of cationic gelatin auxiliary. When the mass concentration of the cationic gelatin auxiliary was 80 g/l, the decolorization rate and K/S value of the material reached the maximum. But the mass concentration of the cationic gelatin auxiliary exceeded 80 g/l, and the colour absorption of the material decreased slightly. This is
because the cationic modified degree of the material increases with an increase in the amount of cationic gelatin auxiliary, as well as the adsorption capacity of the material for anionic dyes. This leads to an increased decolourisation rate and K/S value of the material. However, when the amount of cationic gelatin auxiliary is too much, the excess can only be gathered on the surface of the material and cannot be combined with the material firmly. In the process of material colour absorption, excess cationic gelatin auxiliary falls from the material surface but can combine with anionic dye in the dyeing liquid, which hinders dye adsorption onto the material surface, resulting in a reduction in colour absorption properties. Therefore the optimal dosage of cationic gelatin auxiliary is determined to be 80 g/l.

Effect of the amount of alkali agent on the colour absorption of the material in cationic modification

The effect of the amount of alkali agent on the colour absorption of the materials in cationic modification is shown in Figure 5. As can be seen, the decolourisation rate and K/S value of the material increased with an increase in the amount of sodium hydroxide. When the sodium hydroxide dosage was 18 g/l, the decolourisation rate and K/S value of the material reached the maximum. The amount of sodium hydroxide continued to increase, and the decolourisation rate and K/S value of the material decreased. It shows that the proper amount of sodium hydroxide is beneficial to the reaction between hydroxyl groups in cellulose viscose materials and ethylene epoxide active contained in the cationic gelatin auxiliary, as well as for the improvement of the cationic modified degree of the material and enhanced colour absorbing ability of the material. However, when the dosage of sodium hydroxide was more than 18 g/l, the hydrolysis degree of the cationic gelatin auxiliary increased, which led to a decrease in the cationic modified degree and in the colour absorption properties of the material. Thus the optimal amount of sodium hydroxide is determined to be 18 g/l.

Effect of the amount of alkali agent on the colour absorption of the material in cationic modification

Effect of steaming time on colour absorption of the materials

Alkali swelling and cationic modification of nonwoven viscose material was conducted according to the optimum conditions above. The steaming time was changed. The effect of the steaming time on the colour (Reactive Black B133) absorption of the material is shown in Figure 6 and 7. As can be seen from Figure 6 and 7, the decolourisation rate and K/S value of the washed material after steaming is higher than those of the un-washed material, indicating that the washed material has better colour absorption properties after steaming. The reasons are that there is a large amount of alkali on the unwashed material. Alkali dissipates during the decolorisation process, which promotes...
the dissociation of hydroxyl on cellulose viscose material, and the negative charge of the material increases. This is not conducive to the adsorption of anionic dyes. The decolourisation rate and K/S value of the material are decreased. In addition, cationic gelatin auxiliary bonded to viscose materials unfirmly fall into the dyebath during the decolourisation process, which reacts with the dye and affects the adsorption of dye on the material surface. The colour absorption properties are reduced if the modified material is not washed after steaming. Therefore the material must be washed after steaming. As can be seen from Figure 7, the decolourisation rate and K/S value of the material increased with an increase in the steaming time. When the steaming time was 4 min., the decolourisation rate and K/S value of the material reached the maximum. The steaming time continued to be extended, and the decolourisation rate and K/S value of the material increased, which indicates that the steaming time is beneficial to the reaction between the cationic gelatin auxiliary and the material, for the improvement of the cationic modified degree of the material, for the adsorption of anionic dyes, and for the improvement of colour absorption properties. But when the steaming time is too long, the hydrolysis degree of cationic gelatin auxiliary on the material increases, and the covalent bond between the cationic gelatin auxiliary and the material may be broken, which leads to a decrease in the cationic modified degree of the material. Moreover the material damage degree increases, and the weight loss rate of the material increases with an increase in the steaming time. The combined effects of these factors will eventually lead to a decrease in colour absorption properties. Hence the steaming time is determined to be 4 min. And after steaming, the material needs to be washed.

In conclusion, the optimum preparation process of non-woven viscose absorbing material is as follows: first the viscose material is put into aqueous solution containing 50 g/l of sodium hydroxide for swelling pretreatment at room temperature for 5 min. Then the swelling pretreated material is modified with cationic gelatin auxiliary by the padding method. The modification solution contains 80 g/l of cationic gelatin and 18 g/l of sodium hydroxide. The material is dipped in the aqueous solution and passed through a laboratory padder with two dips and two nips, then dried at 90 ℃ for 10 min, and afterwards steamed 4 times. Lastly the cationic modified material is rinsed with water and dried at 40 ℃ in an oven. The modified material is used as a color absorbing material.

**Evaluation of the colour absorption effect of the modified nonwoven viscose material**

**Effect of the amount of the material on colour absorption**

A different mass of colour absorbing material was put into 10 ml of dye liquor containing Reactive Black B133 with a mass concentration of 0.1 g/l. The decolourisation rate of the modified material was measured after stirring at room temperature for different times and compared with the unmodified material. The results are shown in Figure 8.

As can be seen from Figure 8, the decolourization rate increased with an increase in the amount of colour absorbing material. When the dosage of the material was over 0.15 g, the decolourisation rate was enhanced little. The main reason is that the total number of positive charges of the material is increased with an increase in the amount of the material. The adsorption seats for anionic dye are also increased. Consequently the decolourisation rate is increased. When the amount of the modified material was 0.15 g, the anionic dyes in the dye solution were basically exhausted, and thus the decolourisation rate hardly increased while continuing to increase the amount of the material. In addition, it can be also seen that the decolourisation rate of 0.2 g unmodified materials was only 27.83% under same decolourisation conditions. The results show that the adsorption ability and decolourisation properties of the cationically modified material for anionic dyes can be improved significantly.

**Colour absorption rate of the material**

The 0.2 g colour absorbing material was put into 10ml of dye liquor containing Reactive Black B133 with a mass concentration of 0.1 g/l. The decolourisation rate of the modified material was measured after stirring at room temperature for different times and compared with the unmodified material. The results are shown in Figure 9.

As can be seen from Figure 9, the modified material prepared exhibited a higher decolourisation rate than that of the unmodified material. When the decolourisation time was 10 min., the decolourisation rate of the modified material prepared reached 92.13%. The decolourisation rate of the unmodified material was only 27.87% under same decolourisation conditions. The results show that...
the modified material prepared by this study has characteristics of a high colour absorption and high decolouration rate. Its colour absorbing effect is much better than that of unmodified materials.

**Decolourisation rate of differently treated materials with different concentration of dye**

The colour absorbing material was modified and decolourisation applied according to optimised technological conditions. The decolourisation rate of the material in alkali and cationic combined treatment with different concentrations of dye was measured and compared with that after only alkali swelling pretreatment, after only cationic modification and that of the unmodified non-woven viscose material. The results are shown in Figure 10.

As can be seen from Figure 10, the decolourisation rate of all the differently treated materials decreased with an increase in dye concentration. However, the decolourisation rate of the differently treated materials was different under the same dye concentration and decolourisation conditions. The decolourisation rate of the combination of alkali swelling pretreatment and cationic modification is the highest among the four kinds of materials. The decolourisation rate of the cationic modified only material is bigger than that of the untreated material. The decolourisation rate of the material only alkali swelling pretreated is the lowest among the four differently treated materials. This is due to the different structure of the differently treated materials. The surface of untreated non-woven viscose material has a negative charge in the dye liquor. Electrostatic repulsion exists between anionic dye and negative charge material, thus untreated non-woven viscose material has a lower decolourisation rate. However, the alkali swelling pretreated non-woven viscose material has more negative charges than the untreated non-woven viscose material in dye liquor. This is due to the formation of alkali cellulose or oxidized cellulose when non-woven viscose material is treated with alkali. Thus electrostatic repulsion between anionic dyes and the alkali swelling pretreated non-woven viscose material is the biggest, and hence the alkali swelling pretreated non-woven viscose material has the lowest decolourisation rate among the four differently treated materials. For the material modified with only a cationic gelatin agent, the electrostatic attraction between the material and anionic dye is enhanced, and the decolourisation rate is higher. For the material treated by a combination of alkali swelling pretreatment and cationic modification, the cationic modified degree is enhanced and the colour absorbing effect is improved further due to the swelling of alkali. Therefore the decolourisation rate of the combined treated materials is the highest, indicating that the material prepared by this study has excellent colour absorbing properties.

**Effect of differently treated materials on the decolourisation rate with different kinds of dyes**

The colour absorbing material was modified and decolourisation applied according to optimised technological conditions. And the decolourisation rate of the material treated by a combination of alkali swelling pretreatment and cationic modification with different kinds of dyes was measured and compared with that after alkali swelling pretreatment only, after only cationic modification, and with that of the unmodified non-woven viscose material. The results are shown in Figure 11.

As can be seen from Figure 11, the decolourisation rate of the differently treated materials was different under the same decolourisation conditions for various kinds of dyes. This is due to the different force between the various kinds of dyes and the differently treated materials, leading to various colour absorption effects. The order of the colour absorption effect of the differently treated materials for different kinds of anionic dyes is the same as that of the differently treated materials for various concentrations of dyes (see “Decolourisation rate of differently treated materials with various concentrations of dye”). The decolourisation rate of the material treated with a combination of alkali swelling pretreatment and cationic modification is the highest among the four differently treated materials for the four experimentally selected anionic dyes: Reactive Orange KGN, Lasanol Yellow CE, Direct Brown RVN and Acid Lake Blue A. The results show that the material treated with a combination of alkali swelling pretreatment and cationic modification has the best colour absorption effect for anionic dyes. However, the effects of the combined treatment material on the nonionic disperse dyes and cationic dyes were poor. Therefore the colour absorbing material prepared by this experiment is only suitable for the decolourisation of anionic dyes and is not suitable for the decolourisation of nonionic and cationic dyes.

### Conclusions

An optimised preparation process for non-woven viscose absorbing material was determined as follows: first the viscose material is put into an aqueous solution containing 50 g/l of sodium hydroxide for 5 min for swelling pretreatment at room temperature. Then the swelling pretreated material is modified with cationic gelatin auxiliary by the padding method. The modification bath contains 80 g/l of the cationic gelatin auxiliary and 18 g/l...
of sodium hydroxide. The material is dipped in the aqueous solution and passed through a laboratory padder with two dips and two nips, then dried at 90 °C for 10 min, and finally steamed 4 times. Lastly the cationic modified material is rinsed with water and dried at 40 °C in an oven.

The non-woven viscose material prepared by us has excellent colour absorption properties for anionic dye. The material has characteristics of fast colour absorption and a high colour absorption rate. The decolourisation rate of the 0.2 g materials prepared was 92.32% for 10 ml of dye liquor of Reactive Black B133 with a mass concentration of 0.1 g/l, when decolourisation was carried out at room temperature (about 25 °C) for 10 min. Compared with untreated materials under the same decolourisation conditions, the decolourisation rate of the materials prepared increased by 64.49%. It indicates that the colour absorbing material prepared has good color absorption properties for anionic dyes. It can act as a colour absorbing material for anionic dye decolourisation, but it is not suitable for the decolourisation of nonionic disperse and cationic dyes.

References


Received 13.10.2017 Reviewed 18.11.2018