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Synthesis of a Decolourising Agent and its Application

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Abstract
A type of cationic decolourising agent was prepared and applied to printing and dyeing wastewater treatment. The effects of the concentration of the decolourising agent, the pH value and stirring speed on decolourisation efficiency were studied. The results show that the optimum decolourisation process of the decolourising agent is determined as follows: at room temperature, a dosage of the decolourising agent of 7 mg/l, pH =7.0, and a stirring speed of 150 rpm. The decolourising agent applied to decolourise a direct dye, strong acid dye, weak acid dye and reactive dye in simulated wastewater showed high decolourisation efficiency in all cases. The range of decolourisation efficiency from the highest to lowest is as follows: direct dye, weak acid dye, strong acid dye, and reactive dye.

Key words: *decolourising agent, decolourisation efficiency, printing and dyeing wastewater.*

Introduction

At present, dye wastewater has become one of the important factors threatening water environment safety in China. In the next five years, energy conservation, pollution reduction, clean production and comprehensive treatment will become major issues affecting the development of industry. There are three kinds of dye wastewater treatment methods commonly used at present [1]. The physical method is often used as the pretreatment method for dye wastewater, which is convenient to recover dye molecules from wastewater, reduce salt and metal ion content, and improve its biodegradability [2, 3]. The physical methods used in the field of dye wastewater treatment include adsorption and membrane separation. Adsorption is a solid surface phenomenon. A porous solid adsorbent is used to treat gaseous pollutants so that one or several of the components on the surface of the solid adsorbent, under the action of molecular gravity or the chemical bond force, are adsorbed , so as to achieve the purpose of separation [4, 5]. The treatment of dye wastewater by membrane separation technology mainly uses the selective separation function of the membrane to pretreat dye wastewater. The separation of dye molecules from water molecules in dye wastewater is realised, and the recovery of dye molecules and salts as well as the improvement of biochemical properties of the wastewater are achieved [6]. The process is only a physical process and does not destroy the molecular structure of the dye. Chemical treatment mainly includes the traditional electrochemical method and advanced oxidation method [7, 8]. The main disadvantages of the electrochemical method are high energy consumption and cost. Advanced oxidation technology is used in the process, producing strong oxidising hydroxyl free radicals, which creates a lot of structure stability and even makes it hard for the microbial decomposition of organic molecules into harmless non-toxic biodegradable low molecular substances. The reactions end product is mostly carbon dioxide, water and inorganic ions, free of excess sludge and concentrate [9]. The biological method is characterised by low energy consumption and good economy, but the treatment cycle is long and the scope narrow. It is usually combined with a physicochemical method or chemical method to improve the treatment efficiency [10], which mainly include anaerobic biodegradation, aerobic biodegradation and the anaerobic – aerobic combination [11, 12].

Printing and dyeing wastewater is difficult to degrade and the traditional processing methods used are not ideal. In treatment by means of the decolourisation of printing and dyeing wastewater, the flocculation method is widely applied because of its low investment cost, large handling capacity and high decolourisation efficiency [13, 15]. The varieties of decolourising agent used mainly include the inorganic decolourising agent, organic polymer decolourising agent, microbial decolourising agent and composite decolourising agent. The organic cationic decolourising agent, in which negatively-charged colloidal particles and other pollutants are destabilised and removed through two mechanisms, namely adsorption charge neutralisation and adsorption bridging, provides good removal of turbidity and a decolouring function [16-20]. In addition, this type of decolourising agent has many advantages, such as a low dosage requirement, fast flocculation, small impact by coexisting salts and other environment materials, low quantity of sludge produced, and ease of handling, features which cannot be matched by any inorganic or polymer decolourising agent. Thus, it is especially suitable for the treatment of printing and dyeing wastewater [21-25]. Therefore, both domestic and foreign organisations are committed to the development of new organic decolouring decolourising agents [26-29]. A type of cationic decolourising agent was prepared and applied to printing and dyeing wastewater treatment. The effects of the concentration of the decolourising agent's, pH value and stirring speed on decolourisation efficiency were studied.

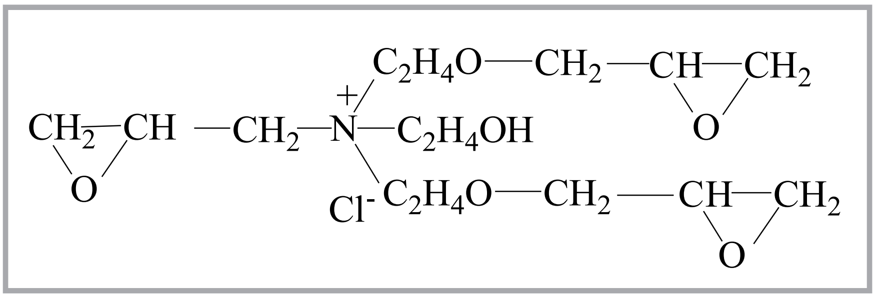

Figure 1. Structure of decolouriser.

Experimental

Main reagents

Epichlorohydrin and triethanolamine(analytically pure, Tianjin Hengxing chemical reagent manufacturing Co., Ltd.); sodium hydroxide (analytically pure, Tianjin Hengxing chemical reagent manufacturing Co., Ltd.), and hydrochloric acid (analytically pure, Tianjin Star Chemical reagent manufacturing Co., Ltd.). All the dyes: direct fast green 5GLL, weakly acidic yellow 3 GS, acid red AV, and reactive brilliant red M-2B (industrial products, Shanghai KELONG dyestuff Co., Ltd.).

Preparation process of the decolouriser

1. Two reagents were added, at a molar ratio n (triethanolamine): n (Epichlorohydrin) = 1:3, into a three-necked flask, and stirred for 10 minutes at a temperature of 50 °C.
2. Then, with stirring, a certain amount of sodium hydroxide solution was added dropwise. After the addition, the mixture was allowed to react for 8 hours at a temperature of 25 °C.
3. Vacuum distillation.

Structure characteristics and decolourisation mechanism of the decolouriser

The decolouriser is a cationic quaternary ammonium salt type crosslinking modification agent, which was prepared by our research group, and contains a plurality of epoxy ethane groups. It is a light yellow viscous liquid, and the main feature of its chemical structure is the presence of highly reactive epoxy ethane groups. These can react with amino (-NH2), carboxyl (COOH), hydroxyl (-OH), sulfhydryl (-SH) and other polar groups. The structure of the decolouriser is shown in ***Figure 1***. The mechanism of the dye and decolourising agent's reaction may be proposed as follows: Dye molecules commonly contain sulfonic acid groups, which are ionised in aqueous solution so that the dye ion is negatively charged, and the decolouring agent containing quaternary ammonium salt groups is positively charged. Thus, the decolouring agent combines with dye anions to form a salt, which is unstable in solution, giving rise to sedimentation and flocculation. In addition, direct dye and reactive dye may contain groups such as -OH and -NH_2, which can form hydrogen bonds with -OH groups on the decolourising agent molecule. Reactive dye molecules contain active groups, and they can react with -OH, -NH_2 in the decolouring agent to form a covalent bond and a more solid valence bond. Direct dyes are linear molecules, a feature that enhances the adsorption ability for the decolouring agent, so that the dyes in the wastewater and the decolouring agent react to form complexes with a large molecular size, which tend to flocculate and separate out.

Simulation of printing and dyeing wastewater and the decolourisation process

Simulated printing and dyeing wastewater was prepared. A certain amount of the decolouring agent was added into the simulated printing and dyeing wastewater and mixed rapidly for 2h with a magnetic stirrer at room temperature, leading to flocculation and sedimentation. Then, the decolourising rate was measured.

Test of decolourisation efficiency

The absorbance at the maximum absorption wavelength of the decolourisation liquid, after filtration with filter paper, was determined by spectrophotometry, and the decolourisation efficiency (R) of the decolourising agent was calculated according to the following formula:

$$R = (1 - nA_i/mA_0) \times 100\%$$

In the formula, A_0 is the absorbance at the maximum absorption wavelength of simulated wastewater after dilution n times. A_i is the absorbance at the maximum absorption wavelength of the supernatant after flocculation and decolourisation, and dilution m times.

Results and discussion

Infrared spectral analysis of decolourising agent

The infrared spectrum of the decolourising agent is shown in ***Figure 2***.

It can be seen from ***Figure 2*** that there are peaks characteristic of ternary ethylene oxide at 850 cm^{-1}, a stretching vibration of C-O-C in the range 1100 cm^{-1}~1030 cm^{-1}, a stretching vibration absorption peak of -OH near 3350 cm^{-1}, and an absorption peak of C-N at 1280 cm^{-1}. Primary hydroxyl groups have two absorption peaks at 1085 cm^{-1} and 1064 cm^{-1}, which are the stretching vibration absorption peaks of C-O. A characteristic absorption peak of quaternary ammonium salt is at 980 cm^{-1}, while at 920 cm^{-1}, there is a weak absorption peak, which is consistent with the stretching absorption peak of C-N in quaternary ammonium salt. Absorption in the range 2700 cm^{-1}~3000 cm^{-1} is due to the methylene (CH_2) stretching vibration peak. It is thus proved that the structure of the product referred to as a decolourising agent contains epoxy groups, quaternary ammonium salt and polar hydroxyl groups.

Study on the decolourising process of the decolourising agent in dyeing and printing wastewater

Effect of the concentration of the decolourising agent on decolourisation efficiency

Under the conditions of ambient temperature and a pH value of 7.0, wastewater was prepared using reactive brilliant red M-2B at a concentration of 100 mg/l. The processing of water samples was carried out by changing the dosage of the decolourising agent, with flocculation and decolourisation experiments conducted according to the method described in 2.3. The relationship between the dosage of the decolourising agent and decolourisation efficiency is shown in ***Figure 3***.

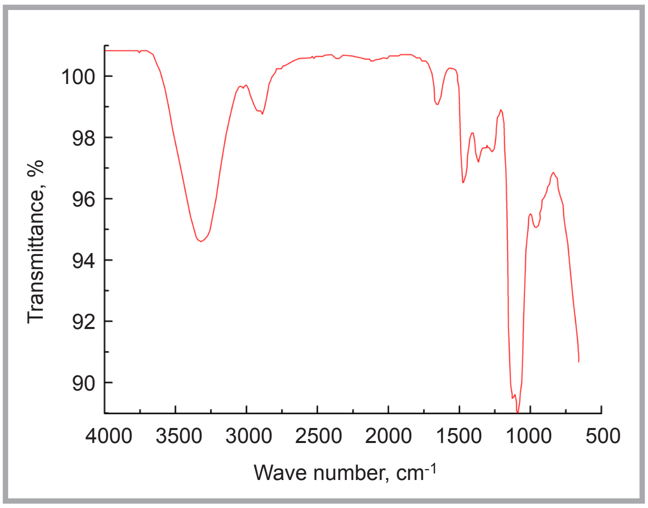

Figure 2. *Infrared spectrum of decolourising agent.*

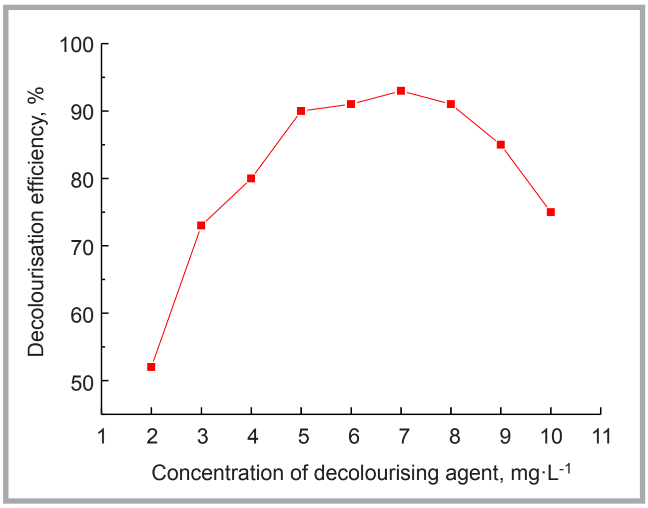

Figure 3. *Effect of decolourising agent dosage on decolourisation efficiency.*

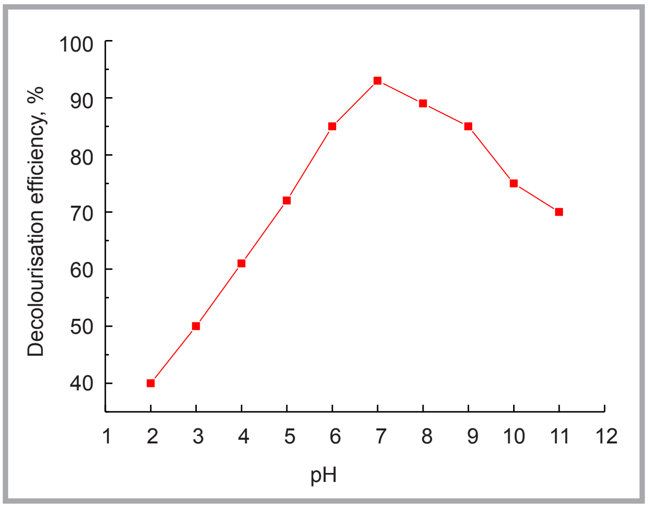

Figure 4. *Effect of pH value on decolourisation efficiency.*

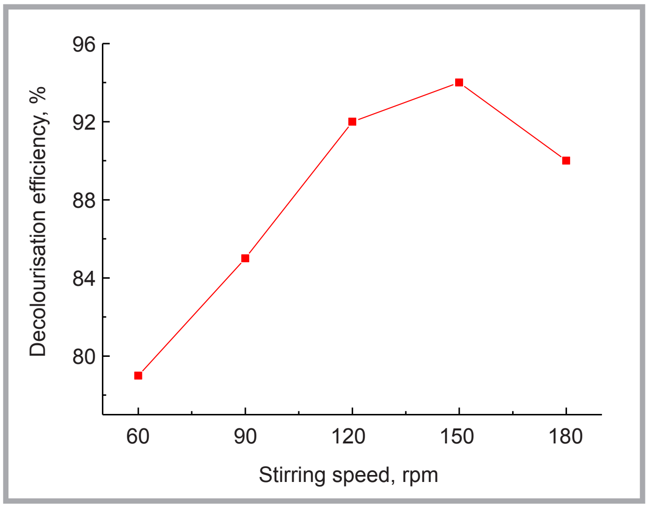

Figure 5. *Effect of the stirring speed on decolourisation efficiency.*

As is shown in ***Figure 3***, the decolourising agent is effective in its processing effect on printing and dyeing wastewater. The decolourisation efficiency continuously improves with an increase in the dosage of the decolourising agent when the concentration is in the 2 to 7 mg/l range. The decolouring effect is best when the concentration is 7 mg/l. However, the decolouring effect declines with an increase in the decolourising agent dosage when the concentration is greater than 7 mg/l. This is because when the decolourising agent is added, due to a reduction in the surface potential of the particles and a decrease in the surface repulsion between them, the particles in the wastewater begin to flocculate; with an increase in the concentration of the decolourising agent, the surface potential of particles gradually decreases to a minimum value, and the particles in the wastewater flocculate rapidly. Adding more of the decolourising agent continually causes the particles in the wastewater to be surrounded by an excess of the decolourising agent, thus inhibiting the chance of combining with other particles. In consequence, their surface potential starts to rise again and the repulsion increases, reaching a stable state, where agglomeration is not easy. At the same time, the decolourising agent also plays a role in facilitating dispersion, and thus the flocculation effect becomes poor .

Effect of the pH value on decolourisation efficiency

The pH value of wastewater was adjusted with dilute hydrochloric acid and sodium hydroxide solution under conditions of ambient temperature and a concentration of the decolourising agent of 7 mg/l, and the effect of the pH value on flocculation was investigated. The experimental results are shown in ***Figure 4***.

As shown in ***Figure 4***, the decolourising agent has a good flocculating and decontaminating effect when the pH value ranges from 5 to 11; thus, it is suitable for weakly acidic, neutral or weakly alkaline conditions. This is mainly because the decolourising agent contains quaternary ammonium groups, conferring a high cationic character and strong electropositivity; and thus it has a good electrical neutralisation capacity, whereby it can absorb negatively charged species to form particles that are unstable by compressing the electric double layer. In addition, the poly quaternary ammonium salt graft copolymer is of a polymer structure and has a strong absorption and bridging effect. In addition, the methylene groups in the decolourising agent are so hydrophobic that, once extended towards the

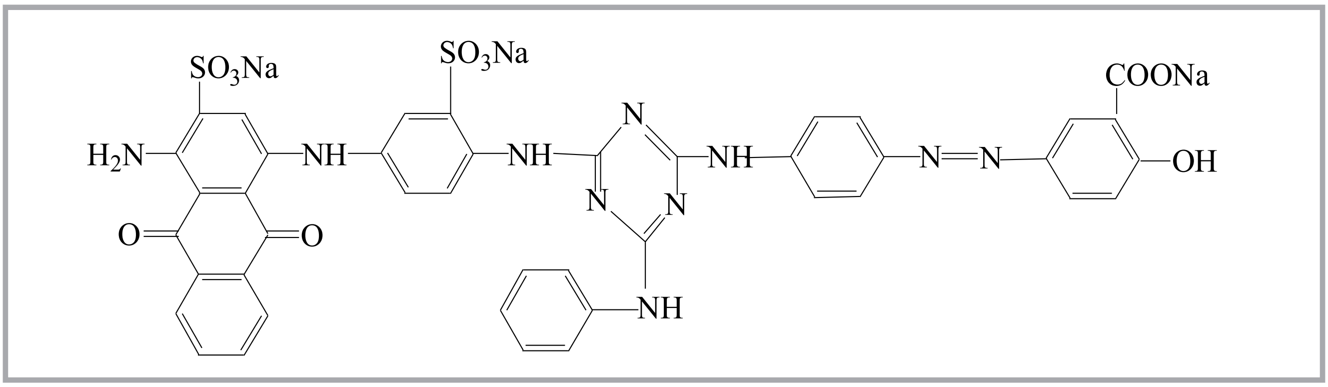

Figure 6. *Molecular structure of direct fast green 5GLL.*

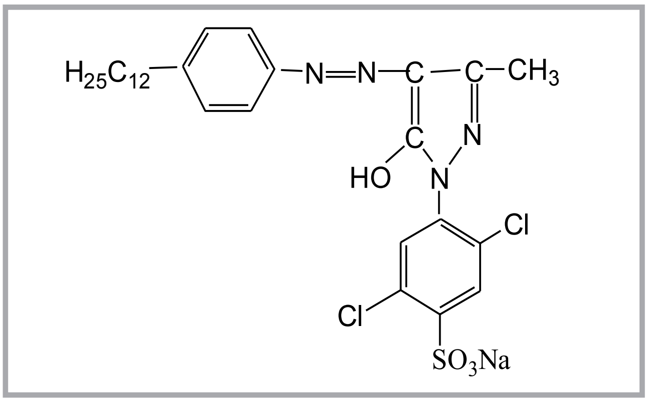

Figure 7. *Molecular structure of weakly acidic yellow 3 GS.*

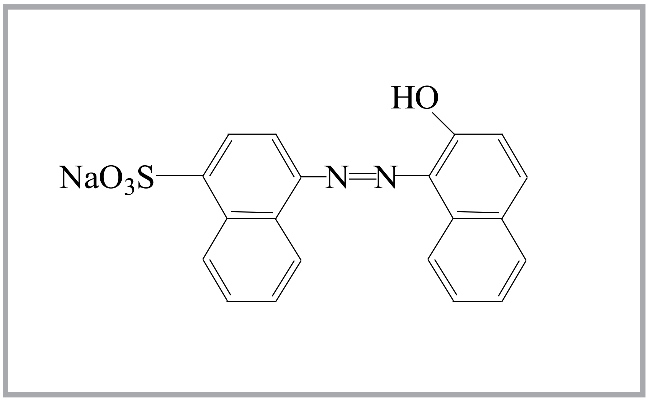

Figure 8. *Molecular structure of acid red AV.*

surrounding water molecules, the solid-liquid interfacial tension will increase. Consequently, the repulsion forces and contact angles with water will increase, thus strengthening the flocculation effect. Therefore, the decolourising agent has an enhanced flocculation effect.

Effect of the stirring speed on decolourisation efficiency

The effect of the stirring speed on the decolourisation efficiency of the decolourising agent is shown in ***Figure 5***.

As is shown in ***Figure 5***, the faster the stirring speed, the better the decolourisation effect. The decolourisation efficiency is maximum when the speed is 150 rpm, because this provides sufficient agitation to ensure that the decolourising agent mixes fully with the wastewater, which is beneficial to the dispersion of the decolourising agent and the formation of floccules. However, the decolourisation efficiency declines when the speed is more than 150 rpm. When the stirring speed is too fast, it will lead to some breaking of the floccules formed; and then the decolourising agent will detach from the surface of the solid particles, thus opening up new spaces, which t will absorb more of the decolourising agent, unfavourable for flocculation.

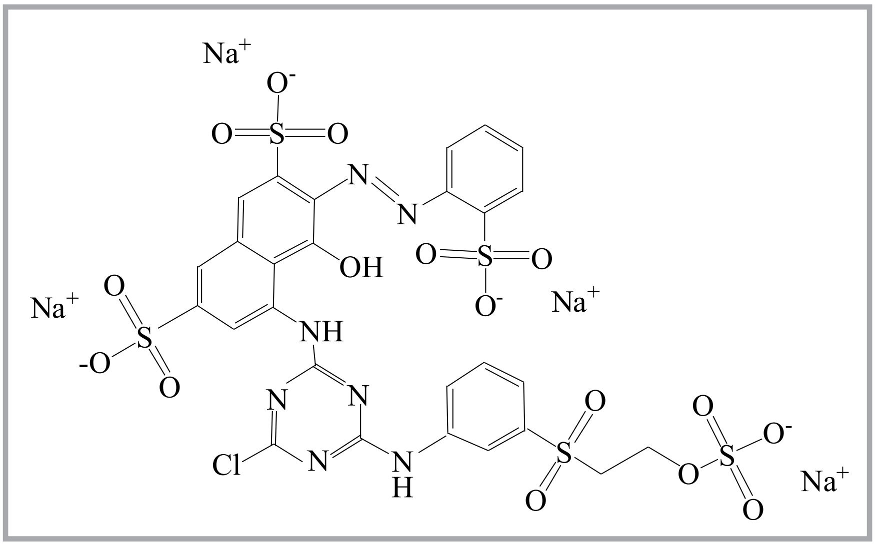

Figure 9. *Molecular structure of reactive Brilliant Red M-2B.*

Decolourisation efficiency of the decolourising agent with other types of dye

The structure of the following four different kinds of dyes: direct fast green 5GLL, weakly acidic yellow 3 GS, acid red AV, reactive brilliant red M-2B is shown in ***Figures 6-9***. The decolourisation effect of the decolourising agent on the types of dye is shown in ***Figure 10***.

Figure 10 shows that under the same conditions, the decolourising agent has a good decolourisation effect on the above dyes. For comparison, the dyes are arranged from high to low decolour-

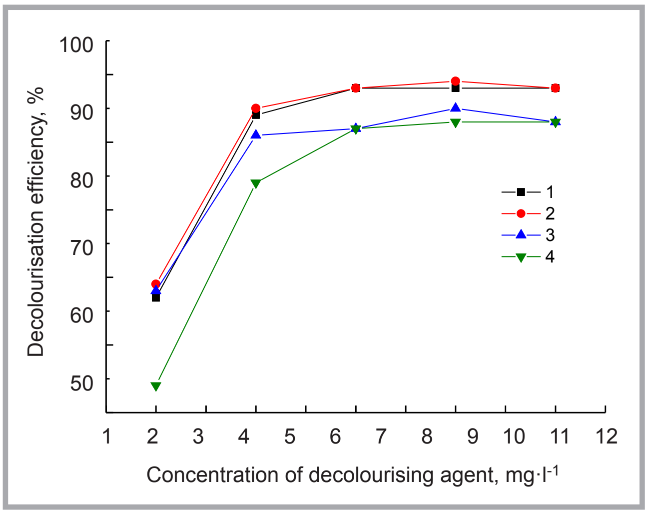

Figure10. *Effect of types of dye on decolourisation efficiency: 1 – direct fast green 5GLL, 2 – weakly acidic yellow 3 GS, 3 – acid red AV, 4 – reactive brilliant red M-2B.*

isation efficiency as follows: direct dye, weak acid dye, strong acid dye, reactive dye. When the direct dye (with the most complicated structure, containing an extended conjugated system, and good molecular planarity) and weak acid dyes are dissolved in water, there are a large number of anionic groups. They react with an appropriate amount of the decolourising agent, which has a good synergistic decolouration effect, causing destabilisation and precipitation of the dyes in printing and dyeing wastewater. Thus, the decolourisation effect is obvious. The molecular weight of the strongly acidic dye is small and its structure is simple. The force between the dye and decolourising agent is small, resulting in a poorer decolourisation effect. The number of anionic groups in reactive dyes (whose matrix structure is similar to the structure of strong acid dyes) is less than that of the other dyes; thus the decolourisation effect is relatively poor.

Conclusions

The optimum decolourisation process of a decolourising agent is determined as follows: at room temperature, a dosage of the decolourising agent of 7 mg/l, pH = 7.0, and a stirring speed of 150 rpm. Under the same conditions, the decolourising agent applied to decolourise a direct dye, strong acid dye, weak acid dye and reactive dye in simulated wastewater showed high decolourisation efficiency in all cases. The decolourisation efficiency arranged from the highest to lowest is direct dye, weak acid dye, strong acid dye and, reactive dye.

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