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Advanced treatment of spent acid dyebath and reuse of water, salt and surfactant therein

Chun-Hui Li [a,b], Jin-Xin He [c,*]

[a] College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, China
[b] Key Laboratory of Coordination Chemistry and Functional Materials in Universities of Shandong, Dezhou University, Dezhou 253023, China
[c] Key Laboratory of Textile Science & Technology, Ministry of Education, Shanghai 201620, China

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ABSTRACT

In this research, a facile process combined chitosan adsorption and UV-Fenton advanced oxidation process (CAAOP) has been developed for the treatment and reuse of spent acid dyebaths. The acid dyes in the spent dyebaths are completely removed through the adsorption column filled with chitosan, while most of sodium sulphate and Peregal O-25 (nonionic organic surfactant) can pass through the adsorption column with the water. Although the resulting recycled spent acid dyebaths are reused over ten times as new dyebaths for dyeing with C.I. Acid Red 1, the changes of the color differences and the relative unlevelness properties on dyed fabrics are still remained within the acceptable levels. That is also true for the other shade dye, namely C.I. Acid Yellow 11, in the 11th recycling cycle. As a result, an average saving of 87.4%, 91.7% and 50.1% for water, sodium sulphate and Peregal O-25, respectively, is achieved with the reuse process for the total eleven dyebaths. The exhausted chitosan can be easily recovered by dilute alkali as a desorbing agent, and the emissions from the two eluted concentrates treated with UV-Fenton are found to meet the most stringent emission standards for both COD and color in China. Results reveal that CAAOP is a promising process for the treatment and reuse of textile dyeing wastewaters, which can benefit the environment and reduce the operating cost.

1. Introduction

Textile dyeing is not only a significant consumer of water, dyes and chemical auxiliaries, but also a big producer of contaminated aqueous waste streams. A typical dyeing process consumes about 120–280 L of water for every kg of processed cloth averagely. As extensively used dyes for the protein fiber, about 10% of the applied acid dyes generally remains in the spent dyebaths. Besides dyes, there are also other chemical additives in the spent acid dyebaths, such as, sodium sulphate (as retarding agent), sulfuric acid (for pH control), and surfactant (as wetting and leveling agent). The spent acid dyebaths, of low volume compared with other baths coming from different washing operations, generate considerable pollution and contaminate other wastewaters that are generally less loaded with pollutants (Tahri et al., 2012). Therefore, the recycling of the spent acid dyebath will save operating cost and mitigate environmental pollution.

Burkinshaw et al. (1993) confirmed the residual dyes in the spent dyebaths can take dye-sites of the fibers and thereby influence the dyeing quality and the exhaustion of the freshly added dyes. Thus, the spent acid dyebaths must be treated to remove the residual dyes before being reused as reconstituted ones, while water and textile chemical auxiliaries therein had better be preserved and recycled.

Among the most common processes used for recycling spent dyebaths are membrane filtrations and advanced oxidation processes (AOPs). Membrane filtrations are preferable to remove color, and reclaim water and salts (Kim et al., 2005). Many related reports (Vishnu and Joseph, 2008; Lu et al., 2010; Vergili et al., 2012) have revealed that the dyeing with recycled water and electrolyte solution gives no differences from that using a fresh dyebath. However, a severe limitation for membrane filtration is the high cost, which presumably prevents its wider acceptance especially for the small and medium-size dyehouses. The flux decline, disposal of the concentrate stream, irreversible fouling and hardly selective separation for organic matters are the other concerns.

AOPs are considered to be very effective on decoloration and oxidative degradation of dyes. Some AOPs, such as ozone (Perkins et al., 1996; Chen et al., 1994; Muthukumar et al., 2005), electrochemical oxidation (Víctor et al., 2011), UV/H_2O_2 (Uygur, 2001), and Fenton reagent (Fe^{2+}/H_2O_2) (Gregon and Solvary, 1998), were

* Corresponding author. Tel.: +86 21 6779 2602; fax: +86 21 6779 2608.
E-mail address: jxhe@dhu.edu.cn (J.-X. He).

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employed for decoloration, and the reclaimed water and salts were used for new dyeing. However, there are some problems for the recycling of spent dyebath wastewater with AOPs. The residual oxidants and iron ions added during some AOPs have to be removed before the reuse of the resulting water. As AOPs are based on non-selective radical reactions, the organic chemical auxiliaries can also be oxidized, and they are hard to be reclaimed. More seriously, typical by-products for ozonation (0–20% reduction of chemical demand oxygen) are aldehydes (Gaehr et al., 1994; Perkowski et al., 1996), which may be more toxic than the parent compounds. Furthermore, for diversity of dyes and chemical auxiliaries applied in dyeing, their degradation products generated by AOPs are hard to be predicted and evaluated with safety, and may stick to the dyed fabric leading to some potential negative effect on dyeing quality, especially with the increasingly stringent eco-textile label requirements. Consequently, it is difficult to directly treat the spent dyebath for reuse with AOPs, especially for those with poor oxidation ability.

The adsorption technology has been considered as one of the most efficient and economic processes for removing dyes and other pollutants as complete molecules from aqueous streams (Sathishkumar et al., 2012). Activated carbon, which is widely used as adsorbent for the removal of pollutants from wastewaters, is generally considered to be nonselective and difficult to be recovered (Wang et al., 2010), so many investigators have turned their attention to alternative materials. Chitosan, as a natural biopolymer adsorbent, has outstanding adsorbability for various kinds of dyes (Wong et al., 2003; Kyzas George et al., 2011). The regeneration of exhausted chitosan for non-covalent adsorption can be easily obtained by using acidic solution, or alkaline solution, or organic solvents as desorbing agent, while the adsorbability remains unchanged after the treatment (Chatterjee et al., 2005; Hu et al., 2006; Crini et al., 2008). An interesting advantage of using chitosan for the treatment of spent acid dyebaths towards reuse is that there are no new compounds to be introduced into the resulting recycled liquor. However, few studies focus on the reuse feasibility of dyeing wastewater only by adsorption processes, especially that of surfactant therein.

The fate of the eluted concentrates produced from the regeneration of exhausted adsorbents must be considered. AOPs can be apparently applied to treat the eluted concentrates in order to meet emission standards. Many studies have demonstrated that UV-Fenton oxidation is superior to other AOPs for treatment of effluents containing dyes by comparing the decoloration rate, COD removal rate, electrical energy consumption, oxidant utilization rate, and initial dye concentration (Arslan and Akmehmet Balcioglu, 1999; Xu, 2001; Neamtu et al., 2004; Muruganandham et al., 2007; Muruganandham and Swaminathan, 2006). So, the separation between physical removal (adsorption technology) and chemical oxidative degradation for treatment and reuse of the spent acid dyebaths by the combined adsorption and advanced oxidation process (CAAOP) is expected to avoid secondary pollution to the recycled water and solve other problems as mentioned above.

This study concerns the application of CAAOP (as depicted in Fig. 1) to the recycling of spent acid dyebaths on laboratory scale. In CAAOP, chitosan and UV-Fenton were employed in adsorption and advanced oxidation process, respectively. The two acid dyes, namely C.I. Acid Red 1 and C.I. Acid Yellow 11, were selected as targets. The spent acid dyebath was fed into the fixed column filled with chitosan for removing dye molecules through adsorption. The resulting recycled spent acid dyebath was reused over eleven times as a reconstituted dyebath. Dilute alkali was employed as the desorbing agent for the recovery of exhausted chitosan, and the resulting eluted concentrates underwent oxidative degradation by

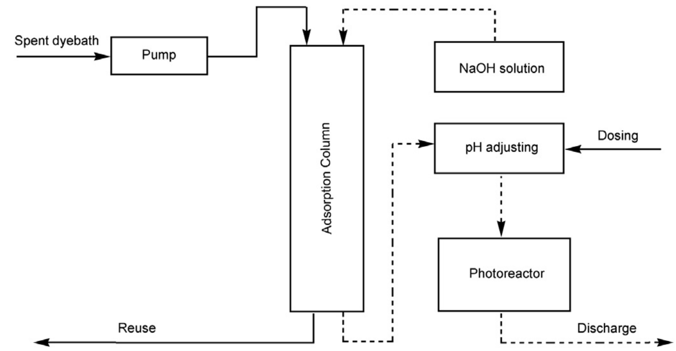

Fig. 1. Flow chart of CAAOP.

UV-Fenton before discharge. The quality measurements of the recycled spent acid dyebath, the dyed fabrics, and the eluted concentrates before and after oxidation were done to evaluate the feasibility of CAAOP.

2. Experimental

2.1. Materials

The fabric used is 100% wool woven fabric (Shandong Ruyi Group, Shandong, China), and its specification is 23S/2 × 22S/2 97 × 61. The two commercial acid dyes, C.I. Acid Red 1 and C.I. Acid Yellow 11, were supplied by Shendaruitai Chemical Co., Ltd (Tianjin, China) and used as received, and their structures are shown in Fig. 2. Chitosan biopolymer (M_w = 100 kDa) with approximately 96.2% of deacetylation and 150–200 mesh was obtained from Yongyue Ocean Biology Co., Ltd (Zhejiang, China). All other chemical reagents used in the experiments are of analytical grade except for Peregal O-25 (chemical pure). Deionized water was used throughout this study.

2.2. Dyeing procedure

Two grams of wool fabric were dyed to get 1% shade on weight of fiber (owf) with the selected dye in a mass ratio of 1:80 (fabric to dyebath). The dyebath was prepared by adding 4% owf of sulfuric acid (98%), 0.5% owf of Peregal O-25 (nonionic surfactant as wetting

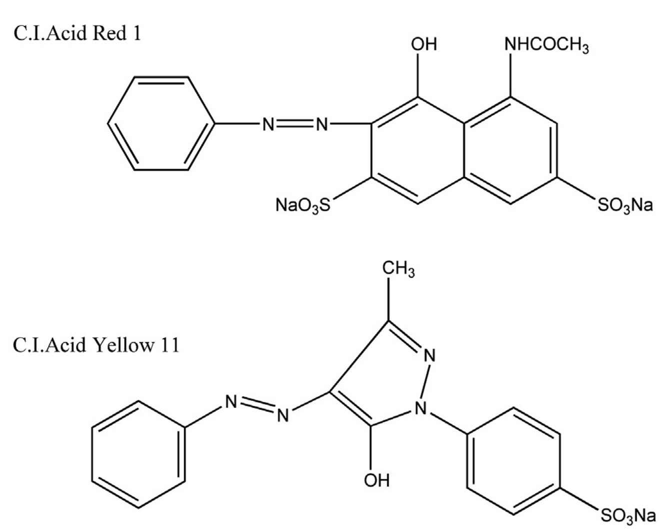

Fig. 2. Chemical structures of the two acid dyes.