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Impacts of operating parameters on oxidation–reduction potential and pretreatment efficacy in the pretreatment of printing and dyeing wastewater by Fenton process

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HIGHLIGHTS

- A real printing and dyeing wastewater was pretreated by Fenton process.
- We investigated impacts of operating parameters on ORP and pretreatment efficacy.
- Relationship among ORP, operating parameters and treatment efficacy was established.
- Pretreatment efficacy was in proportion to the exponent of temperature reciprocal.
- We investigated kinetics of color and COD removal and BOD_5/COD ratio in solution.

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ABSTRACT

An experiment was conducted in a batch reactor for a real printing and dyeing wastewater pretreatment using Fenton process in this study. The results showed that original pH, hydrogen peroxide concentration and ferrous sulfate concentration affected ORP value and pretreatment efficacy greatly. Under experimental conditions, the optimal original pH was 6.61, and the optimal hydrogen peroxide and ferrous sulfate concentrations were 1.50 and 0.75 g L^{-1}, respectively. The relationship among ORP, original pH, hydrogen peroxide concentration, ferrous sulfate concentration, and color (COD or BOD_5/COD) was established, which would be instructive in on-line monitoring and control of Fenton process using ORP. In addition, the effects of wastewater temperature and oxidation time on pretreatment efficacy were also investigated. With an increase of temperature, color and COD removal efficiencies and BOD_5/COD ratio increased, and they were in proportion to the exponent of temperature reciprocal. Similarly, color and COD removal efficiencies increased with increasing oxidation time, and both color and COD removal obeyed the first-order kinetics. The BOD_5/COD ratio could be expressed by a second-degree polynomial with respect to oxidation time, and the best biodegradability of wastewater was present at the oxidation time of 6.10 h.

1. Introduction

A large numbers of synthetic dyes are produced worldwide every year for printing and dyeing and a portion is discharged with wastewater [1]. There are some dyestuff, slurry, dyeing aid, acid or alkali, fiber and inorganic compound in printing and dyeing wastewater. Furthermore, some dyestuff contains nitryl, amidocyanogen and heavy metals, such as copper, chrome, zinc and arsenic and so on. Besides, the components will be changed because of different dyestuff category, dyeing process, dye concentration and equipment scale [2]. Generally, the printing and dyeing wastewater is characterized by strong color, high pH, high chemical oxygen demand (COD), and low biodegradability [3]. Thus, such wastewater is difficult to treat, especially for color removal, using conventional wastewater processes [4], and the quality of effluent from biological wastewater process has often exceeded the discharge criterion.

Recently, advanced oxidation processes using ozone [5], titanium dioxide [6], ultra violet [7], and Fenton's reagent [8] have received considerable attention as effective pretreatment processes of less biodegradable wastewater [9]. Among them, Fenton's reagent is a mixture of hydrogen peroxide and ferrous ion, which generates hydroxyl radicals [10–12]. The highly reactive hydroxyl

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radicals (oxidation potential 2.8 V [13]) attack and destroy the organic pollutants in wastewater, and accordingly improve the biodegradability of refractory wastewater. Compared with other advanced oxidation processes, the Fenton's reaction has a shorter reaction time [14] and the faster degradation rate. Esplugas et al. [15] reported that Fenton's reagent showed the fastest degradation rate, 40 times higher than UV process and photocatalysis and five times higher than ozonation for phenol degradation. The shorter reaction time and faster degradation rate imply a lower capital cost than other advanced oxidation processes [15–17]. In addition, the Fenton's reagent is relatively cheap, easy to handle compared with other advanced oxidation processes [18], reacts well with organic compounds and does not produce toxic compounds during oxidation [19], Fenton process has been widely applied to treat various types of industrial wastewater [14,20–22,17]. The investigators have found that Fenton oxidation is effective in decolorizing and degrading organic compounds of the wastewater that contains various types of dyes [23–26]. In addition, the combined process of Fenton oxidation-biological process has been used to treat dye wastewater, in which Fenton process fills the role of improving the biodegradability of wastewater [27,18,28]. Thus, the fluctuation of effluent quality of Fenton oxidation process would cause on decrease of the overall process performance. However, according to the mechanisms of Fenton oxidation, the operational conditions including original pH level of wastewater, the dosages of hydrogen peroxide and ferrous ion, temperature and oxidation time play important roles in the removal of color and COD from wastewater and improvement of the biodegradability. In addition, the characteristics of printing and dyeing wastewater vary widely. So in order to attain better pretreatment efficacy and economization of reagents including hydrogen peroxide and ferrous sulfate simultaneously, the best operational conditions should be ascertained, and accordingly Fenton dosages should be adjusted dynamically according to influent qualities, treatment targets and operational conditions. However, the related on-line monitoring and control techniques are rarely discussed in the literature.

Oxidation–reduction potential (ORP) has been used as a tool for monitoring, control and optimization of biological treatment systems since 1980s [29–31], and has been proven to be economical and an effective technique for process control in many wastewater treatment systems, such as alternating aerobic-anoxic system [32], sequencing batch reactor [33], extended aeration treatment system [34] and sulfide oxidizing bioreactor [35]. For Fenton process, the hydroxyl radical is the major oxidizing species, however, on-line monitoring the hydroxyl radical is difficult. The ORP value in the oxidation stage should be high to be a controlling parameter for the Fenton process. Furthermore, ORP has been used as a control parameter for textile wastewater treatment in the Fenton process [19,36]. In the two literatures, one literature obtained the relationship among ORP value, Fenton's reagent concentration and COD, and ORP was used to control the COD removal; while another one obtained the relationship among ORP value, Fenton's reagent concentration, pH value and color, and ORP was used to control the color removal. However, as a pretreatment process, besides COD and color removal efficiencies, the BOD_5/COD ratio is also a key parameter to indicate the biodegradability of wastewater, but at present no literature, which published the relationship among ORP value, BOD_5/COD ratio and Fenton's reagent concentration, was searched.

In this study, the Fenton process was used to pretreat a real printing and dyeing wastewater, and the impacts of operating parameters such as original pH of wastewater, hydrogen peroxide concentration, ferrous sulfate concentration, temperature, and oxidation time on the pretreatment efficacy were investigated. In addition, we obtained the relationship among ORP, original pH, hydrogen peroxide concentration, ferrous sulfate concentration, and color or COD or BOD_5/COD ratio according to the results. The findings of this study may provide useful messages in the pretreatment of printing and dyeing wastewater using Fenton process, and may be instructive in on-line monitoring and control of Fenton process using ORP.

2. Experimental

2.1. Materials

Raw wastewater was a combination of printing and dyeing wastewater from certain printing and dyeing corporation, Nanjing city, PR China. The characteristics of wastewater were as follows: color concentration of 200 times, pH value of 12.77, COD of 1240 mg L^{-1}, BOD_5 of 397 mg L^{-1} and BOD_5/COD ratio of 0.320.

All chemicals were reagent-grade and were used as received, and all solutions were prepared with distilled water. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and hydrogen peroxide (30%, w/v) were used, and pH of the solution was adjusted by using the 0.5 M H_2SO_4. All chemicals were provided by Shanghai Chemicals Reagent Ltd.

2.2. Experiments

The experiments were conducted in a 300 mL batch reactor filled with 100 mL of sample, continuously mixed at 200 rpm with magnetic stirred bar. The whole set-up was placed in a water bath to control reaction temperature. Oxidation was carried out with the following steps: pH was adjusted to target value by using the 0.5 M H_2SO_4; the temperature was raised to target temperature with the water bath; $FeSO_4 \cdot 7H_2O$ was added in reactor and dissolved; and then the solution was slowly mixed with H_2O_2. At schedule time, the ORP values of the solution were determined, and the samples were collected and centrifuged for 10 min at 4000 × g. The supernatant was recovered and properly diluted for the measures of COD, BOD_5 and color.

We calculated the removal efficiency of color or COD using the following equation:

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where R is the removal efficiency of color or COD by the Fenton process, in %; and C_0 and C_t are the original concentration and the residual concentration of color or COD in solution, respectively, in times for color and mg L^{-1} for COD.

2.3. Analyses

According to the standard methods of China, COD was determined by the dichromate method (GB 11914-89 Water quality-Determination of the chemical oxygen demand-Dichromate method); BOD_5 was determined by the dilution and seeding method (HJ 505-2009 Water quality-Determination of biochemical oxygen demand after 5 days for dilution and seeding method); and color concentration was determined by the double dilution method (GB 11903-89 Water quality-Determination of colority). pH was measured by a MODEL PHS-3C pH meter. ORP was measured using a MODEL 250A pocket ORP meter.

3. Results and discussion

3.1. Effect of original pH

3.1.1. ORP variation

Under the conditions of temperature of 30 °C, hydrogen peroxide concentration of 0.60 g L^{-1}, and ferrous sulfate concentration of 0.50 g L^{-1}, ORP of solution at different original pH levels are showed