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DECOLORIZATION OF AZO DYES BY MODIFIED FENTON PROCESS

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ABSTRACT: In the present study, the decolorization of C.I. Reactive Orange 127 (RO 127) and C.I. Reactive Yellow 145 (RY 145) by modified-Fenton process (Fe^0/H_2O_2) was investigated. The experiments were carried out to determine the process's optimal operational conditions: pH, Fe0 and H_2O_2 concentrations. This study shows that modified Fenton process is an efficient process for the decolorization of synthetic textile wastewater including azo dye and polyvynil alcohol (PVA). The optimal conditions experimentally determined was found to be initial pH = 3.5, [H_2O_2] = 20 mg/L, [Fe^0]= 80 mg/L for RO 127 and pH = 4.0, [H_2O_2] = 20 mg/L, [Fe^0] = 60 mg/L for RY 145. Under the optimal conditions, 92% and 80% decolorization were achieved after 60 min of reaction for RO 127 and RY 145, respectively.

Key Words: *Decolorization, Fenton's process, iron powder, RY 145, RO 127.*

Modifiye Fenton Prosesi ile Azo Boyaların Dekolorizasyonu

ÖZET: Bu çalışmada C.I. Reaktif Orange 127 (RO 127) ve C.I. Reaktif Yellow 145 (RY 145) boyalarının modifiye edilmiş Fenton prosesi (Fe^0/H_2O_2) ile renk giderimi araştırılmıştır. Deneylerde optimum çalışma koşullarının belirlenmesi için pH, Fe^0 ve H_2O_2 konsantrasyonu için çalışma yürütülmüştür. Bu çalışmada azo boya ve polivinil alkol (PVA) içeren sentetik tekstil atıksuyunun renksizleştirilmesinde modifiye edilmiş Fenton prosesinin verimli bir uygulama olduğunu göstermektedir. Optimum çalışma koşullarının belirlenmesi için yapılan deneylerde RO 127 için pH=3.5, [H_2O_2] = 20 mg/L, [Fe^0]= 80 mg/L ve RY 145 için ise pH = 4.0, [H_2O_2] = 20 mg/L, [Fe^0] = 60 mg/L tespit edildi. Belirlenen optimum şartlar altında 60 dakikalık temas süresinde RO 127 ve RY 145 için sırasıyla %92 ve %80 oranında renk giderimi sağlanmıştır.

Anahtar Kelimeler: *Renk giderimi, Fenton prosesi, Demir tozu, RY 145, RO 127.*

1. INTRODUCTION

Textile industry is one of the most important industrial area in developing countries. The colored wastewater of textile industry including adjuvant chemicals such as azo dyes and PVA (Grau, 1992) is an environmental threat risk for aquatic life in receiving medium. This type of wastewater causes colorization of aquatic life with its color, prevents sunlight to be spread in aquatic medium, and moreover, decreases oxygenation capacity of aquatic medium. In addition to this, azo dyes in the effluents have risk with their cancerogenic and toxic structures (Nillson *et al*., 1993).

In previously published literatures, there have been studies related with the methods such as chemical precipitation (Tünay *et al*., 1996), adsorption (Al-Degs *et al*., 2000; Morais *et al*., 1999), photo-catalytic oxidation (Arslan *et al*., 1999), ozonation (Lin and Lai, 2000), Fenton oxidation (Kang *et al*., 2002) and acoustic cavitation (Zang *et al*., 2009) for the removal of dyestuff. Among these methods, coagulation and adsorption have been based on the phase transfer of pollutants from liquid to solid phase. However, phase transfer is not the accurate solution for this problem. Another method used for the removal of dyestuff is oxidation. Recently, advanced oxidation processes (AOPs) have been used for the treatment of wastewater in textile industry and the removal of dyestuff. Fenton process, the most commonly known AOP, has been based on the production of $OH^{\bullet}$ as a result of the reaction between Fe^{+2} and H_2O_2 under acidic conditions (Walling, 1975). The process has been improved by using different sources of iron such as iron powder (Ozdemir *et al.*, 2008). The reaction of Fenton process in which Fe^0 is used can be carried out mainly in two ways: (i) oxidation of pollutant as a result of the reaction with H_2O_2 on the surface of iron and (ii) oxidation of pollutant as a result of the reaction of H_2O_2 with Fe^{+2} which is transferred to the liquid phase by dissolving on the surface of the iron.

In the present study, Reactive Orange 127 (RO 127) and Reactive Yellow 145 (RY145) were selected which have not been attained in the literature till now. It was aimed to remove dyestuff by Fenton type process in which zero valent iron was used. Optimizations of pH, dosages of Fe^0 and H_2O_2 as well as kinetic studies were performed for the removal of both dyes.

2. MATERIAL AND METHOD

RO 127 and RY145 together with polyvinyl alcohol (PVA) were obtained commercially. Fe^0 (iron powder, 10 μm) and H_2O_2 were purchased from Merck. Additional purification was not carried out for the chemicals used in the experiments. Synthetic wastewater was prepared by using Reactive Orange 127 and Reactive Yellow 145 dyestuff and PVA. This prepared textile wastewater was included 50 mg/L dyestuff and 100 mg/L PVA (Sahinkaya *et al.*, 2008).

Oxidation experiments with iron powder were carried out in jar-test equipment (Velp, FC6S) at room temperature. First of all, pH was adjusted to the desired value and then it was accepted that oxidation reaction was started by addition of Fe^0 and H_2O_2 in desired amounts. At the end of 1-hour reaction period, pH was adjusted to 7.5 and the solution was recreated for 30 minutes under steady-state conditions for the precipitation of iron flocks. After that, 25 mL of samples were taken for color analysis.

MnO_2 was used for the quenching of unreacted H_2O_2 in the samples (Azbar *et al.*, 2004). Being no residual H_2O_2 in the sample was confirmed with Merckoquant H_2O_2 test strips (Ozdemir *et al.*, 2008). Then the samples were filtered through 0.45 um membrane filter papers and removal of MnO_2 and ferric hydroxyl compounds was provided. In color analysis, λ_{max} for RY 145 and RO 127 was measured as 480 and 497 nm, respectively. The concentration of residual dyestuff in the filtrates was determined by the spectrophotometer at maximum wavelength.

3. RESULT AND DISCUSSION

3.1. Effect of the initial pH on decolorization

pH of the solution affects iron concentration in Fenton type process where Fe^0 is used and therefore, also affects the amount of $OH^{\bullet}$ produced and oxidation efficiency of the system. In this study, pH optimization was performed in the range of 2.0-4.5. The results are shown in Figure 1. When initial pH was lower than 2.5, the efficiency decreased in accordance with Eq. 1 due to radical scavenging effect of H^+ ions (Kwon *et al.*, 1999). Moreover, H_2O_2 was stabilized as $H_3O_2^+$ (Eq. 2) at low pH values and its reaction with Fe^{+2} in the solution was retarded (Gallard *et al.*, 1998). At pH 4.5, the efficiency decreased since the solubility of iron in the solution also decreased. Optimum pH values for RO 127 and RY 145 were determined as 3.5 and 4.0, respectively.

$$OH^{\bullet} + H^+ + e^- \rightarrow H_2O \tag{1}$$

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \tag{2}$$

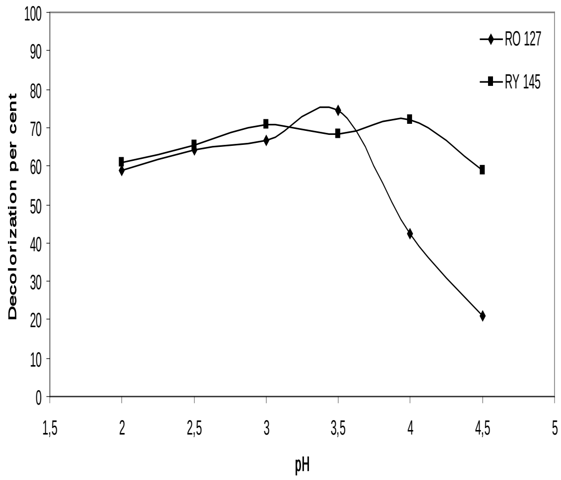

Figure 1. Effect of initial pH on decolorization

3.2. Effect of mixing speed on decolorization

The mixing speed of the solution affects the solubility speed of iron and rate of reaction. The optimization of mixing speed was carried out in the range of 50-200 rpm. Decolorization increased for RO 127 with increasing of mixing speed till 200 rpm, while no significant changes were being observed for RY 145.

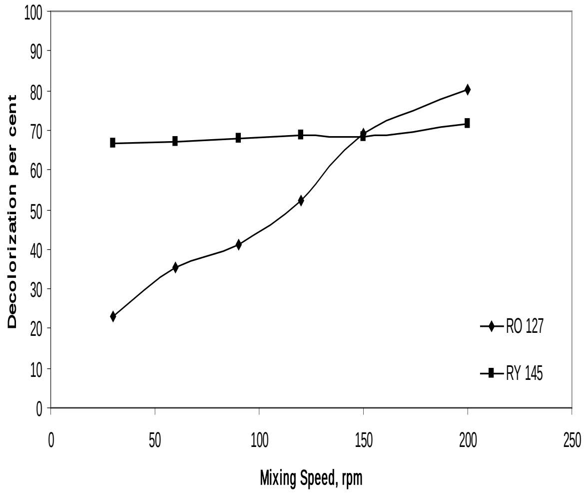

Figure2. Effect of mixing speed on decolorization

3.3. Effect of Fe^0 concentration on decolorization

Optimization of Fe^0 which is used as a catalyst in Fenton process is very important in terms of process efficiency. When excess iron is used, the amount of sludge and the cost of treatment increase. Fe^0 optimization was performed in the range of 5-100 mg/L. While decolorization efficiency increased with the increase in iron dosage until 80 mg/L for RO 127 in accordance with Eq. 1 (Walling, 1975), for RY 145, decolorization efficiency increased until 60 mg/L. Negligible change was observed in decolorization for both dyes with increasing iron concentration. Optimum Fe^0 dosages were selected as 80 and 60 mg/L for RO 127 and RY 145

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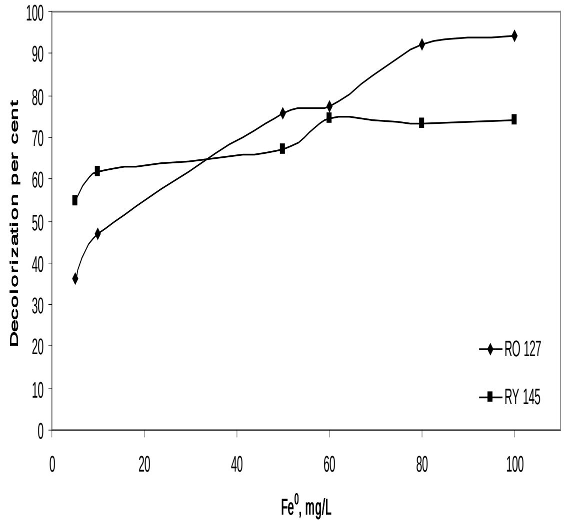

Figure 3. Effect of iron powder (Fe^0) dosage on decolorization.

3.4. Effect of H_2O_2 concentration on decolorization

The optimization for the concentration of H_2O_2 is important in decolorization process since H_2O_2 is the source of OH- which is produced in Fenton process. Its optimization study was carried out in the range of 5–30 mg/L and decolorization efficiencies of both dyes increased with increasing the dosage until 20 mg/L in accordance with Eq. 3 (Walling, 1975). With increasing high dosages, on the other hand, efficiency decreased because of the radical scavenging effect of excess H_2O_2 for RO 127 as shown in Eq. 4, while a negligible increase in efficiency was observed for RY 145. Optimum concentration was selected as 20 mg/L for decolorization of both dyes.

$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^{\bullet} + OH^{-} \quad (3)$$

$$H_2O_2 + OH^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad (4)$$

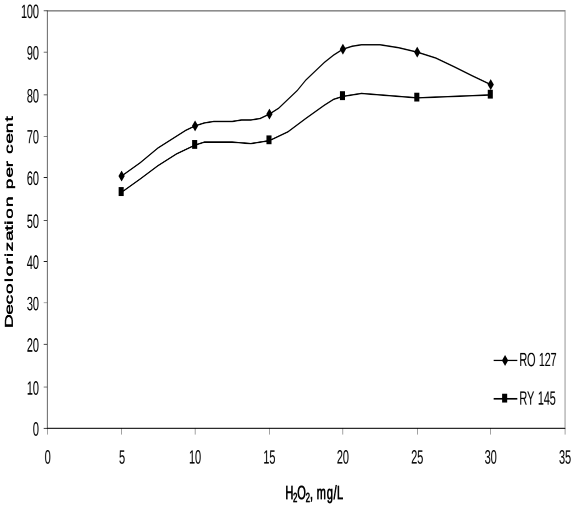

Figure 4. Effect of H_2O_2 dosage on decolorization.

4. CONCLUSION

In this present study, decolorization of RO 127 and RY 145 from aqueous solutions was investigated. Optimum conditions for RO 127 were determined as 90 rpm at pH 3.5 with 80 mg/L Fe^0 and 20 mg/L H_2O_2 and they were determined as 200 rpm at pH 4.0 with 60 mg/L Fe^0 and 20 mg/L H_2O_2 for RY 145. According to this, optimum molar ratios $[Fe^0]/[H_2O_2]$ were determined as 2.4/1 and 1.8/1 for RO 127 and RY 145, respectively. It was also concluded that Fenton type process in which zero valent iron was used was an effective process for decolorization of both dyes.

5. ACKNOWLEDGE

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