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Photo-fenton process: Optimization and decolourization and mineralization of reactive blue 222 dye

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Dye house effluents of textile industries leads to severe environmental problems when disposed to aquatic bodies without proper treatment. This work was carried out to optimize the Photo-Fenton process for decolorization and mineralization of a commercial textile dye, Reactive Blue 222. The effect of different process parameters on decolorization efficiency of Photo-Fenton process was investigated. The optimal conditions for process were observed as; pH level 3.5, \( \text{H}_2\text{O}_2 \) concentration \( 1 \times 10^{-2} \text{M} \), \( \text{FeSO}_4 \) concentration \( 3.5 \times 10^{-5} \text{mol L}^{-1} \), temperature 50°C and process time 50 min. The maximum 95% dye decolorization was achieved along with a significant (\( P< 0.05 \)) reduction of chemical oxygen demand and total organic. The degradation products were characterized by UV–visible and FTIR spectral techniques. The results provide evidence that Photo-Fenton process was able to oxidize and mineralize the selected azo dye into non-toxic metabolites.

Key words: Reactive blue 222, optimization, decolorization, photo-fenton process, water quality parameters, spectral analysis.

INTRODUCTION

Textile industries are found in most of the countries using synthetic complex organic dyes as the coloring material. Reactive dyes form a covalent bond with fabric on which they are applied. The release of azo dyes not only causes a negative aesthetic effect but also some dyes are toxic or even carcinogenic (McCurdy et al., 1992). The discharge of dye house wastewater into the environment damages the quality of the receiving streams and is toxic to aquatic life (Meyer, 1981). Therefore, treatment of industrial effluent having azo dyes is deemed necessary before their discharge into wastewater bodies.

As the characteristics of dye wastewater are very variable, many different physical, chemical and biological treatment methods are in use for its treatment; which one is effective treatment depend upon the type of dye wastewater.

One major drawback with physical methods is that they are non-destructive and unable to remove the recalcitrant azo dyes and/or their organic metabolites, generating a significant amount of sludge that may cause secondary pollution problems (Zhang et al., 2004). Therefore, new and different type of pollution is faced and further treatments are required. Chemical oxidation methods include a family of processes that may be appropriate for treating organic pollutants.

They are based on generation of highly potent oxidants such as hydroxyl radical (OH), a powerful non-selective chemical oxidant, which has a strong potential and acts very effectively with most organic pollutants. The high reactivity of radicals in driving oxidation processes is suitable for achieving the complete abatement and often mineralization of the pollutants (Malato et al., 2002; Ksibs, 2006). Photo-Fenton's oxidation is a
homogeneous catalytic oxidation process using a mixture of hydrogen peroxide and ferrous ions. The addition of UV or artificial light to Fenton's process could be an interesting allied in dye decolorization due to its capacity to influence the direct formation of *OH radicals (Feng et al., 2003). The main objective of this study was to analyze the feasibility of decolorization and mineralization of Reactive dye 222 by Photo- Fenton's process. The influence of different operational parameters (pH, H₂O₂ dosage, Fe²⁺ dosage, dye concentration and temperature which affect the efficiency of Photo-Fenton's reactions, in Reactive dye 222 oxidation was investigated. The efficiency of the oxidation process was evaluated by the spectral analysis.

**EXPERIMENTAL PROCEDURE**

**Materials**

The azo dye, Reactive dye 222 was kindly provided by Sandal dyestuffs, Pakistan and used as received without further purification. FeSO₄.7H₂O and H₂O₂ (30% w/w) were used as reagent grade. UV-Visible lamp (of 1500Lux light intensity) was used as a source of radiations to carry out Photo-Fenton process. For the photo bleaching process, 1% stock solution of reactive dye 222 (RD 222) was prepared in distilled water and diluted as required. The desired pH of the solution was adjusted by the addition of previously standardized 1M H₂SO₄/1M NaOH solutions. All laboratory reagents were of analytical grade (Sigma Aldrich Fluka, USA).

**Experimental procedure**

A 1% stock solution of Reactive dye 222 was prepared. 0.04% dye solution was prepared from the 1% stock solution. The FeSO₄ solutions of 3.5×10⁻⁵ mol L⁻¹ and H₂O₂ solution of 1×10⁻⁴ M were also prepared. The reaction started with the mixing of 70 mL of each solution (i.e. dye, H₂O₂ and FeSO₄ solution) in a reaction vessel. The initial pH of the sample was carefully adjusted to 3.5 by pH meter using 0.5 mol L⁻¹ H₂SO₄/1 mol L⁻¹ NaOH. The sample was stirred on magnetic stir bar under radiations at 1500 Lux and the reaction was let running for one hour at 40°C.

The further optimization of parameters (pH, H₂O₂, FeSO₄, temperature and effect of salts) was done by following the same procedure, by varying one factor at a time, keeping others constant.

**Chemical analysis**

Samples of the dye solution were withdrawn during the course of the reaction, at periodic intervals and analyzed by in a UV-Visible scanning spectra from 200 to 800 nm, using a UV/VIS double-beam spectrophotometer (T-60, TG-Instruments, U.K). The efficiency of the process was determined from decolorization of the dye at λ_max 615 nm.

**Decolorization assay via UV-Vis spectroscopy**

The decolorization efficiency of Photo-Fenton’s process was expressed by using the standard method (Van der Zee et al., 2001) using the following equation:

\[
\text{Decolorization} (\%) = (I-F)/I \times 100
\]

Where

\[
I = \text{Absorbance of standard}
\]

\[
F = \text{Absorbance of decolorized medium}
\]

The results were checked statistically by using standard error of means (triplicate values).

**Mineralization Study**

The mineralization study was carried out by measuring the water quality parameters like COD, TOC, TSS and phenolic compounds by following a standard protocols (Greenberg et al., 1985).

**UV-Visible and FTIR Spectral analysis**

Decolorization was monitored by UV-Vis spectrophotometer analysis, whereas degradation analysis was monitored by FTIR. For this purpose, 100 mL of sample (after decolorization) was taken, centrifuged at 10,000 rpm for 20 minute and extraction of metabolites was carried out from supernatant using equal volume of ethyl acetate. The extracts were dried over anhydrous Na₂SO₄ and evaporated to dryness in rotary evaporator. The crystals obtained were dissolved in small volume of analytical grade methanol and used for analysis. During UV-Vis spectral analysis, changes in absorption spectrum in the decolored medium (400-800 nm) were recorded in comparison with the results from the untreated samples (without decolorization). The FTIR analysis (Model no. Tensor 27, Bruker Optics, Germany) was done in the mid IR region of (1000-4000 cm⁻¹) with 16 scan speed and was recorded in comparison with the results from the untreated dye samples.

**RESULTS AND DISCUSSION**

**Chemical decolorization of reactive dye 222**

To evaluate the efficiency of dye decolorization, experiments were carried out under the following conditions:

1. dye + UV/Vis,
2. dye + H₂O₂,
3. dye + UV/Vis + H₂O₂,
4. dye + UV/Vis + Fe²⁺,
5. dye + Fe²⁺ + H₂O₂ (Fenton process),
6. dye + UV/Vis + Fe²⁺ + H₂O₂ (Photo-Fenton process).

It is evident from Figure 1 that dye was almost resistant to the oxidation from H₂O₂ alone. For UV/Vis alone it was observed that the dye decolorized about 43.2% in 50min. For UV/Vis and Fe²⁺ color removal observed was 50.1% in 50min. The combined action of UV/Vis and H₂O₂ caused 58.4% decolorization in 50min. In Fenton’s process, color removal observed was 47.2%, 55.4%, 60.2%, 67.21%, 76.3% and 70.2% decolorization at 10, 20, 30, 40, 50 and 60 min, respectively. In Photo-Fenton’s process, color removal was 57.6%, 67.9%, 75.0%, 84.2%, 95.6% and 90.0% decolorization at 20, 30, 40, 50, 50 and 60 min, respectively. Therefore, Photo-Fenton process alone was found to be more efficient than other experimental conditions.
The effect of pH on color removal of reactive dye 222 was examined by changing the pH between 2.0 to 6.0, while keeping the concentration of FeSO₄ 3.5×10⁻² M, H₂O₂ 1×10⁻² M, temperature 40°C and dye 0.04%, constant. Figure 2 represents the color removal of Reactive dye 222 at different pH. This figure shows that pH significantly influenced the conversion of Reactive dye 222. The rate of photo-bleaching of dye under study increased with increasing pH up to 3.5 and decreased with further increase in pH. At pH 3.5, 95.2% color removal was observed. Kuo (1992) observed 95% decolorization of dye in 50 min. For pH values below 3.5, the reaction of hydrogen peroxide with Fe²⁺ is seriously affected causing the reduction in hydroxyl radical production. Inhibition of radical HO⁺ formation at pH below 3 seems also to be due to the small amount of soluble iron (Fe³⁺), responsible for the continuity of the oxidation process, occurring in the formation of Fe(OH)²⁺ and Fe(OH)²⁺:

\[ \text{HO}⁺ + \text{H}⁺ + e⁻ \rightarrow \text{H}_2\text{O} \]

(Spinks and Woods, 1990; Kuo, 1992; Peres et al., 2004).

Experimental conditions: [Reactive dye 222] = 0.04%; [Fe²⁺] = 3.5×10⁻² M; [H₂O₂] = 1×10⁻² M; temperature 40°C; UV/Visible lamp = 1500 Lux; reaction time = 50 min.

The relative efficiencies of the above processes are in the following order: dye + Fe²⁺ + H₂O₂ + UV/Vis (Photo-Fenton) > dye + Fe²⁺ + H₂O₂ (Fenton) > dye + H₂O₂ + UV/Vis > dye + UV/Vis + Fe²⁺ > dye + UV/Vis > dye + H₂O₂. The high efficiency of Photo-Fenton process is due to the formation of more hydroxyl radical than the other processes. This signifies that UV/Vis lamp has a sensible increase of dye decolorization comparatively to the Fenton’s process. It is also possible to say that the iron catalyzed decomposition of H₂O₂ is more efficient than the UV/Vis catalyzed decomposition of H₂O₂. With the combination of UV/Vis and H₂O₂, the chemical bonds of azo compounds can be directly photolysed by UV/Vis irradiation, but this is a slow process that can be substantially improved in the presence of H₂O₂ (Mehta, Surana, Mehta and so on 2011). Adding Fe²⁺ to UV/Vis radiation improves the action of the UV/Vis wavelength on the dye decolorization. UV/Visible alone can remove dye color but at a lower percentage because UV/Visible light cause breakage of chromophoric group, hence remove dye color. At last, the H₂O₂ alone has less influence on dye decolorization. It is possible to conclude that the oxidizing power of H₂O₂ is not enough to bring about reactive dye 222 decomposition.
Figure 2. Effect of pH on the decolorization of Reactive dye 222 by Photo-Fenton treatment.

UV/Visible lamp = 1500 Lux; reaction time = 50 min.

**Effect of H$_2$O$_2$ dosage**

To optimize the dose of H$_2$O$_2$, different levels of H$_2$O$_2$ (1×10$^{-3}$ to 4×10$^{-2}$ M) were selected, while keeping the concentrations of other parameters (FeSO$_4$ 3.5×10$^{-2}$ M, pH 3.5, temperature 40°C and dye 0.04%) constant. It is evident from the Figure 3 that rate of Photo-bleaching of dye under study increased with increasing H$_2$O$_2$ concentrations up to 1×10$^{-2}$ M. The color removal observed at optimum level of H$_2$O$_2$ (1×10$^{-2}$ M) was 95.2%. It was due to because at higher concentration of H$_2$O$_2$, more hydroxyl radicals are produced which decolorize more dye molecules. Further increase in H$_2$O$_2$ concentration, decolorization efficiency was decreased due to the scavenging nature of H$_2$O$_2$ towards HO$^-$ radicals will occur, which can be expressed by the Eqs. given below:

Eq. 1: \[ \text{HO}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \]

Eq. 2: \[ \text{HO}_2^- + \text{HO}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 \]

(Fernandez et al., 1999; Feng et al., 2003).

Experimental conditions: [Reactive dye 222] = 0.04%; pH = 3.5; [Fe$^{2+}$] =3.5×10$^{-2}$M; temperature= 40°C; UV/Visible lamp = 1500 Lux; reaction time = 50 min.

**Effect of ferrous dosage**

The effect of the addition of Fe$^{2+}$ ion on the decolorization of reactive dye 222 has been studied. The results are shown in Figure 4. The amount of ferrous ion is one of the main parameters influencing the Photo-Fenton's process. The results indicate that the extent of decolorization increased with the increase in initial Fe$^{2+}$ concentration. The effect of Fe$^{2+}$ concentration on color removal of Reactive dye 222 was examined by changing the Fe$^{2+}$ concentration between 0.5 × 10$^{-5}$ to 4.5 × 10$^{-5}$M, while keeping the concentration of H$_2$O$_2$ 1×10$^{-2}$ M, pH 3.5, temperature 40°C and dye 0.04 constant. By increasing the concentration of Fe$^{2+}$ from 0.5 × 10$^{-5}$ to 3.5 × 10$^{-5}$M, the dye decolorization efficiency was increased from 14.4% to 95.28%.

The concentrations higher than 3.5 × 10$^{-5}$M resulted in decrease in decolorization (%) of dye under study. It may be explained by the redox reactions since HO$^+$ radicals may be scavenged by the reaction with the hydrogen peroxide or with another Fe$^{2+}$ molecule. The lower decolorization capacity of Fe$^{2+}$ at small concentration might be attributed due to the less hydroxyl radical production (Lucas and Peres, 2006). According to the literature, increasing ferrous salt concentration, degradation rate of organic compound also increases, to certain level where further addition of iron becomes inefficient (Rathi et al., 2003; Kusic et al., 2006).

Experimental conditions: [Reactive dye 222] = 0.04%; pH = 3.5; [H$_2$O$_2$] = 1×10$^{-2}$M; temperature= 40°C; UV/Visible lamp = 1500 Lux; reaction time = 50 min.

**Effect of temperature**

To study the effect of reaction temperature on the decolorization of Reactive dye 222, a series of experiments were conducted at different temperatures ranging from 30 to 60°C, by keeping other factors (pH
Figures 3. Effect of $\text{H}_2\text{O}_2$ on the decolorization of Reactive dye 222 by Photo-Fenton treatment.

Figure 4. Effect of $\text{FeSO}_4$ on the decolorization of Reactive dye 222 by Photo-Fenton treatment.

3.5; $\text{H}_2\text{O}_2$, $1 \times 10^{-2} \text{ M}$; $\text{FeSO}_4$, $3.5 \times 10^{-5} \text{ M}$) constant. When the reaction temperature was increased from 30 to 50°C, the color removal efficiency was increased from 80.12% to 95.72%. The decolorization efficiency was decreased to 60.2%, as temperature was raised to 60°C (Figure 5). It can be explained that Photo-Fenton’s process could be accelerated by raising temperature which improves the generation of $\text{HO}^-$ radical and therefore enhance the decolorization of reactive dye 222 up to optimum level. The temperature higher than optimum value resulted in decrease in decolorization efficiency due to scavenging effect of $\text{HO}^-$ Radical (Sun et al., 2008; Panizza and Cerisela, 2009).

Experimental conditions: [Reactive dye 222] = 0.04%; pH = 3.5; [Fe$^{2+}$] = $3.5 \times 10^{-2} \text{ M}$; [H$_2$O$_2$] = $1 \times 10^{-5} \text{ M}$; UV/Visible lamp = 1500 Lux; reaction time = 50 min.

Effect of salts

Huge amounts of salts are used in coloring up variety of dyes on textiles and hence, they are co-existed with dyes in effluent, which could effect the treatment of wastewater.
Effect of NaCl

In the present study, the effect of NaCl (0.3, 6.9 & 12g/L) on the decolorization of Reactive dye 222 was investigated, by keeping all other factors (pH 3.5; H$_2$O$_2$, 1 × 10$^{-2}$ M; FeSO$_4$, 3.5 × 10$^{-5}$ M; temperature, 50°C) constant. It is evident from the Figure. 6 that the addition of NaCl to the dye solution caused a decrease in decolorization percentage. The decolorization efficiency within 60min reaction decreased from 95.12% to 44.67%, as a consequence of increasing the concentration of NaCl (Figure. 6). Literature survey showed the inhibitive effect of chloride ion (generated from NaCl) on the decolorization of reactive azo dyes happened due to the scavenging effect of chloride ion to HO$^-$ radical, and the following chemical reactions might happened (Ashraf et al., 2006).

\[
\text{HO}^- + \text{Cl} \rightarrow \text{ClOH}^- + \text{OH}^-
\]

\[
\text{ClOH}^- + \text{Fe}^{2+} \rightarrow \text{Cl}^- + \text{OH}^-
\]

The chloride anion can quench the hydroxyl radicals which further affect the decolorization as well as degradation rate (Pappolymerou et al., 2007). The presence of inorganic anions reduces the electrostatic repulsion between dye molecules which leads to aggregation making it less susceptible to hydroxyl radical attack (Dong et al., 2007).

Experimental conditions: [Reactive dye 222] = 0.04%; pH = 3.5; [Fe$^{2+}$] = 3.5 × 10$^{-5}$M; [H$_2$O$_2$] = 1 × 10$^{-2}$M; temperature= 50°C; UV/Visible lamp = 1500 Lux; reaction time = 50 min.

Effect of Na$_2$SO$_4$

Different concentrations of Na$_2$SO$_4$ (0.3, 6.9 & 12g/L) were used to study their impact on decolorization efficiency of reactive dye 222, by keeping all other factors (pH 3.5; H$_2$O$_2$, 1 × 10$^{-2}$ M; FeSO$_4$, 3.5 × 10$^{-5}$ M; Temperature, 50°C) constant. It is evident from the Figure 7 that sulphate ion had a negative impact on the decolorization of reactive dye 222 by Photo-Fenton oxidation. The decolorization efficiency within 60min reaction decreased from 95.34% to 44.12%, as a consequence of increasing the concentration of Na$_2$SO$_4$ (Figure 7).

The sulphate anion can form strong complex with Fe$^{2+}$/Fe$^{3+}$ ions thereby reducing concentration of free iron ions in the solution which are necessary for the Photo-Fenton mechanism (Orozco et al., 1981). The sulphate anion can quench the hydroxyl radicals which further affect the decolorization as well as degradation rate (Muruganandham and Swaminathan, 2004; Pappolymerou et al., 2007). The presence of inorganic anions reduces the electrostatic repulsion between dye molecules which leads to aggregation making it less susceptible to hydroxyl radical attack (Dong et al., 2007).

Experimental conditions: [Reactive dye 222] = 0.04%; pH = 3.5; [Fe$^{2+}$] = 3.5 × 10$^{-5}$M; [H$_2$O$_2$] = 1 × 10$^{-2}$M; temperature= 50°C; UV/Visible lamp = 1500 Lux; reaction time = 50 min.

Mineralization study

Analysis of water quality parameters like COD, TOC, TSS and Phenolics were carried out during Photo-Fenton treatment of azo dye to show the mineralization efficiency of the Photo-Fenton process. Photo-Fenton oxidation of initial azo dye solutions led to a gradual increase in removal (%) of all water quality parameters with the increase in reaction time which indicated the mineralization progress. There was 94% reduction in COD, 92.1% TOC, 91.2% TSS and 85% Phenolics color removal after 50 minutes of reaction time (Figure. 8). Kuo (1992) reported approximately 90% chemical oxygen demand (COD) removal in 30 min.

Malik and Saha (2003) observed that at the optimal ratio of [Fe$^{2+}$]: [H$_2$O$_2$]: [dye] (initial concentration ratio) and at 30°C with pH 3, 70% COD removal can be achieved in 60 min. Shu et al. (2004) studied the degradation of acridine orange using the Photo-Fenton reaction. They obtained 75% of mineralization. Research done on textile wastewaters by Photo-Fenton treatment resulted in 70% reduction in TSS in comparison with untreated wastewater (Azizullah et al., 2011). Comparison of researches has shown that up to 75% reduction in phenolic contents by using Photo-Fenton treatment (Hosseini et al., 2007).

Analysis of the decolorized products

To disclose the decolorization and degradation of the reactive dye 222, the analysis of the transformation of reactive dye 222 by FTIR spectral studies was done. FTIR analysis was done to characterize the metabolites formed by Photo-Fenton treatment of dye under study. FTIR spectrum of control dye with metabolites extracted after complete decolorization indicated the degradation of the parent dye compound by Photo-Fenton treatment. FTIR spectrum of untreated dye displayed peaks at 3344.59, 2352.21, 1646.3, 619.15 and 613.956 cm$^{-1}$ for O=C stretch, 1451.205 cm$^{-1}$ for C-H bending, 2936.64 cm$^{-1}$ and 2830.22 cm$^{-1}$ for C-H stretching of alkyl benzene, 2351 cm$^{-1}$ for =C=H stretch, 1748.29 cm$^{-1}$ for O=C stretch, 1451.205 cm$^{-1}$ for -C-H bending, 610-680 cm$^{-1}$ along with overtone at 1233.93 cm$^{-1}$ for -C-H deformation and 1034.39 cm$^{-1}$ along C-O...
Figure 5. Effect of temperature on the decolorization of Reactive dye 222 by Photo-Fenton treatment.

Figure 6. Effect of NaCl on the decolorization of Reactive dye 222 by Photo-Fenton treatment.

Figure 7. Effect of concentrations of Na\(_2\)SO\(_4\) on the decolorization of Reactive dye 222 by Photo-Fenton treatment.
Figure 8. Effect of Photo-Fenton-liquid contact time water quality parameters.

Figure 9(a). FTIR spectrum of reactive dye 222 before Photo-Fenton treatment.

Figure 9(b). FTIR spectrum of reactive dye 222 after Photo-Fenton treatment.
stretches (Figure 9b). Absence of peaks between 3400 to 3380 cm⁻¹ for –NH stretches indicated that no aliphatic and aromatic amines were formed by photo-Fenton. FTIR spectral analysis indicated that decolorization of dye under study was due to degradation of dye in to intermediate products. The peak characteristic of azo bond at 1646.3 cm⁻¹ of dye was absent in the decolorized medium, indicating degradation of dye due to aromatic amines as intermediate products which are subjected to oxidation giving rise to simpler compounds. This ensures that decolorization of Reactive dye 222 was complete. Thus, Photo-Fenton processes can be efficiently & cost effectively is used for the treatment of textile effluents.

Conclusion

Photo- Fenton process was found to be more efficient for the photo catalytic degradation of Reactive dye 222. Based on the results, it can be concluded that the decolorization of dye is strongly dependent on various reaction parameters e.g. pH, concentration of H₂O₂, concentration of FeSO₄ and reaction temperature. Water quality parameters (COD, TOC, TSS and Phenolics) analyzed after the Photo-Fenton treatment of textile effluent which showed a major reduction in pollution load. FTIR spectral analysis of decolorized products confirmed the degradation of dye under study into simpler compounds indicating the efficiency of Photo-Fenton process for effective treatment of hazardous chemicals like textile wastewater having azo dyes.

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