Correlation of UV Assisted Fenton Process and Fenton Process for Removal of Reactive Red 2(RR2) Dye Color from Wastewater

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Abstract. Polluted effluents from the textile sector are dumped into the environment in massive quantities. As a result, this study was conducted to assess the efficacy of Fenton and photo-Fenton procedures in removing Reactive red 2 (RR 2) dye and to establish the best conditions for maximum removal. This research was done in laboratory scale. The effect of parameters, including Fe (II) concentration (0.1–0.15 mM), H_2O_2 concentration (0.1–1 mM), and dye concentration (0.06–0.1 mM) of dye removal were studied, and the best settings were found based on the maximum dye removal efficiency. The dye clearance rate rose as the Fe (II) concentration fell, according to the findings. Fe (II) concentration of 0.1 mM, H_2O_2 concentration of 1 mM, and starting dye concentration of 0.08 mM are the best conditions for RR 2 elimination from aqueous solution, at the reaction time of 45 min with 88.10% efficiency. Where, for the Fenton process the maximum decolorization efficiency (82.18%) of RR 2 dye was obtained at optimum concentrations values of 1 mM of H_2O_2, 0.1 mM of initial RR 2 dye and 0.1 mM of Fe^{+2} concentrations. The consequences of this investigation uncovered that the photo Fenton process was better than the removal of color contrasted with Fenton measure.

Keywords: Dye removal · Reactive red 2 · Fenton · Photo–Fenton

1 Introduction

Lately, wastewater treatments have been separate by the utilization of Advanced Oxidation Processes (AOPs), which proposition promising events to corrupt or even excavator alize defilements using smooth temperature and pressing factor conditions. A portion of the Advanced Oxidation Process that are usually applied incorporate ozonation, Fenton process, photocatalysis, wet air oxidation, microwave upgraded AOP, electrochemical oxidation, bright radiation, and hydrogen peroxide oxidation [1].

Among these AOPs, those including hydrogen peroxide, for example, the Fenton oxidation, and the photo-Fenton oxidation can produce profoundly receptive and no particular extremist species, similar to hydroxyl radical (HO•). H_2O_2/UV is the most every now and again used UV-AOP at large scale and has been explored at the lab and the pilot scales [2]. A lot of investigations have revealed the uses of photon assisted

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AOPS to weaken drugs, eliminate taste and smells, dispose of poisons and improve on the nature of cleaned water [2].

The greater part of the AOPs utilize a mix of solid oxidants, for example, ozone or hydrogen peroxide (H_2O_2) with either heterogeneous or homogeneous catalysts (generally transition metals and iron), semiconductor solids, radiation, or ultrasound to upgrade radical generation. On account of Fenton's reagent, it consolidates H_2O_2 and ferrous particles (Fe^{2+}) in an acidic medium, which prompts the arrangement of $^{\bullet}OH$ radicals through the oxidation of Fe^{2+} to Fe^{3+}. At the same time, Fe^{2+} is recovered by the reaction between Fe^{3+} and H_2O_2. The photo-Fenton measure joins Fenton's reagent with light energy, which quickens the debasement pace of organic pollutants.

Reductive metal particles can catalyze the hydrolysis of H_2O_2 to frame hydroxyl radicals. Fenton's reagent, a combination of ferrous particles and hydrogen peroxide, has been known as a ground-breaking oxidant for organic contaminants. Homogeneous Fenton measure process by iron has a characterized ideal pH of 3.0, which is restricted to a limited operational reach up to 4.0 because of the precipitation of iron hydroxides at higher pH esteems [3].

Late investigation centers around the utilization of AOPs for bioenergy creation [1]. The mix of AOPs can assist with further developing the general interaction execution by ensuring that more receptive radicals are delivered at low oxidant measurement.

1.1 Fenton Process

Fenton oxidation is an AOP whose customary application was in the treatment of recalcitrants in wastewater. H.J. Fenton was the first to report the popular Fenton reaction in 1894 and delineated the oxidation process using hydrogen peroxide as oxidant and iron (Fe) as a catalyst within the sight of acidic (H^+) medium.

The Fenton process can be arranged into two general classes—homogeneous and heterogeneous processes. In homogeneous cycles, iron species are in a similar stage as the reactants and there is no impediment for mass exchange. In heterogeneous catalysis, iron is supported inside the catalytic structure and can effectively invigorate the degradation of refractory materials without the development of ferric hydroxide sludge [4].

Generally accepted Fenton reaction mechanism utilizes hydrogen per oxides (H_2O_2) and ferrous iron to produce OH radicals (Eq. (1)) [5]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^* \tag{1}$$

The breaking down of H_2O_2 to create OH revolutionaries is begun and catalyzed by ferrous particles. The OH radical framed assaults and oxidizes/mineralizes the waste. It in like manner oxidizes the organics by pondering of protons subsequently making natural revolutionaries (Eq. (2)). The revolutionary conveyed may respond with other natural substrates thus extending the chain.

$$RH + {}^*OH \rightarrow R^* + H_2O \tag{2}$$

In case of abundance impetus, the OH radicals are rummaged (Eq. (3)) subsequently diminishing the oxidation potential.

$$Fe^{2+} + OH^{*} \rightarrow Fe^{3+} + OH^{-} \tag{3}$$

The exemplary Fenton was the primary sort of Fenton oxidation where the oxidants are responded at pH 3 [6]. The cycle was confined by the huge costs of reagents and pH changes. The waste treatment by Fenton extends the biodegradability. It tends to be used for shading expulsion from the profluent before discharge. A part of the new progressions in the process fuses the usage of photograph Fenton where the energy from the sun or UV light is used to support the plan of revolutionaries from the reagents. This declines the use of engineered compounds and grows the viability of oxidation. Another headway is heterogeneous Fenton where the impetus or the corrosive gathering is embedded on a strong impetus. The interaction ensures that the catalysts are recovered for reuse and enable the action at higher pH regards [1]. [7] examined a combination of the Fenton process with CaO as a coagulant for the treatment of corrosive colors and found that the color of the dye solution was totally eliminated and up to 90% COD was taken out.

The Fenton process is utilized often for the degradation of a wide scope of synthetic substances, for example, anthraquinone, azo colors, phenol subordinates, feed addatives, pharmaceutical drugs, sweet-smelling hydrocarbons, pesticides, and herbicides, just as in the treatment of landfill leachates and other modern effluents. The utilization of Fenton reagent for textile wastewater brought about a viable technique for decolorization, moderate COD, yet the moderate TOC evacuation and detoxification of textile wastewater and synthesized dye solutions. The inadequate mineralization of the organic matter has been accounted for with the Fenton framework [5].

1.2 Photo-Fenton and Related Processes

The improved type of the ordinary Fenton oxidation reaction within the sight of UV–visible light beneath 600 nm frequency is known as the photo-Fenton reaction [4]. In acid solution and in obscurity, the disintegration of H_2O_2 catalyzed by Fe^{2+} in leads prompts the creation of hydroxyl radicals, as indicated by the notable warm Fenton response [4]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{-} + HO^{\bullet} \quad k = 76\ M^{-1}s^{-1} \tag{4}$$

The overall pace of the photo Fenton oxidation measure is compelled by the speed of the photolytic step that changes over Fe^{3+} back to Fe^{2+}, and the constant Fe(II)/Fe (III) reuse makes the association autocatalytic. The most standard use of the photo Fenton measure has been the treatment of industrial waters and lixivi-ates. Photograph Fenton cycles can utilize daylight rather than UV light with a minor de-wrinkle in the pace of debasement. This is a vital factor for the scale-up and business utilization of a PAOP, since the expenses of medicines will be considerably brought down in case daylight is utilized. The photo-Fenton process can benefit from the presence of constituents of real effluents such as iron or copper salts, avoiding the need for additional

dosage, and oligocarboxylic acids such as oxalate or ethylenediaminetetraacetic acid (EDTA), which form photo-chemically active iron (III) complexes and improve the process. The iron salts should be chosen carefully, and the oxalate particulate should be used. The job of iron on the debasement of various natural mixtures, varying in their construction (aliphatic versus fragrant) and iron complex development limit, by traditional and photo Fenton process. These substance features have been shown to have an impact on the level of treatment in terms of COD (chemical oxygen demand) and TOC (total organic carbon) expulsions. While aromatic combinations showed a rapid and articulated drop in COD using the Fenton method, aliphatic mixtures required UV light to improve treatment results [8].

S.K. Petal [5] concluded that Photo Fenton combined with titanium dioxide (PF-TiO_2) for removal of TOC was more efficient than Photo-Fenton or combination with AC. Also, The Photo-Fenton process was reported as a comparatively efficient method for the degradation of various synthetic dyes [4].

Therefore, the objectives of this research were: 1) to determine low Fenton reagent concentrations suitable for the degradation of reactive red dye; 2) to compare the degradation of reactive red dye using the Fenton (H_2O_2/Fe^{2+}) process, and photo-Fenton ($UV/H_2O_2/Fe^{2+}$) processes.

2 Methodology

2.1 Chemicals and Equipment's

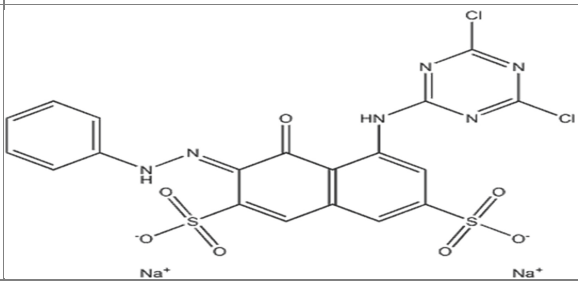
Equipment like jar test, beaker, test tubes, measuring cylinders, pipette, pH meter, electronic balance and UV/Vis spectrometer (PerkinElmer lambda 35) were frequently used to perform the experiment. Laboratory reagent like distilled water, powder of reactive red dye 2, powder of ferric sulphate hydrate ($Fe_2 (SO_4)_3 \times H_2O$), H_2O_2 (30% w/w) and sulfuric acid were also used in the experimentation process.

2.2 Preparation of Stock Solution

Reactive red 2 dye (RR 2 dye) was collected from Research Grade Laboratory, Bahir Dar Institute of Technology, Bahir Dar, Ethiopia. The physical state of RR2 dye is powder solid with a molecular formula of $C_{19}H_{10}C_{l2}N_6Na_2O_7S_2$ and molecular weights of 615.34 g/mol. The stock solution (10 mM) of RR2 dye was prepared by dissolving 3.06 g of in 250 mL of distilled water. The maximum wavelength, λ_{max}, and absorbance of RR2 dye solution was scanned from 200 to 700 nm using UV/VIS spectrometer (PerkinElmer Lambda 35) and obtained at 539 nm. Dye absorbance values were determined at a maximum wavelength of 539 nm.

An amount of azo dye containing 0.06 mM is ready by dissolving the required amount in distilled water and leaving it in the dark. All volumetric flags are covered with aluminum foil to block light. All H_2O_2 working solutions were prepared from a commercial solution (H_2O_2, 30%) by dilution in distilled water to the required concentration. The estimation of the pH was carried out using a HACH pH meter

Table 1. Nomenclature and structure of reactive red dye 2

Parameter	Characteristic
Chemical name	Reactive red 2 dye
Molecular formula	C19H10Cl2N6Na2O7S2
Molecular weight	615.33 g/mol
UV absorption (maximum wavelength)	539 nm
Molecular structure	

calibrated with standard vials pH 4.01 and 7.00 at (25 °C), then the pH was adjusted to the ideal value by expanding a few drops of H_2SO_4 (0.1 M).

Adjust the pH value of the dye synthesis solution, the iron solution, and the H_2O_2 solution to the desired value. In the Fenton photographic test, Fe^{2+} particles are first added to the color array and homogenized for 15 min. Then add the H_2O_2 device at this time and the reaction will last 30 min. It is possible to notice that the Fe^{2+} particles are given by the arrangement of Fe_2 $(SO_4)_3$ × H_2O (1 mM).

When applying Fenton photo measurement, the pH value of all reagents is adjusted to 3. First add driving force to the color arrangement, homogenize the combination for 15 min, and then add H_2O_2 immediately. Turn on the light and the bleaching takes 30 min.

For all AOPs, logical examples of 5 ml were removed at known stretches and analyzed utilizing the UV–vis spectrophotometer. Color removal of Azo dye was monitored by estimating absorbance at a most extreme assimilation frequency of 539 nm. The decolorization productivity was controlled by Eq. 5:

$$\%\, Decolorization = \left(\frac{A_o - A_t}{A_o}\right) * 100 \tag{5}$$

where A_0 is the underlying assimilation of azo color, and A_t is the retention of azo color at response time [2].

A Shellett UV lamp ZW30S19W (Y)-Z894 disinfection lamp 30W sterilizing lamp tube was placed horizontally in the reactor for the performance of the UV/Fenton process.

2.3 Experimental Design and Description

The experimental design was designed by response surface method as shown in (Table 1) below. The three factors i.e., initial RR 2 dye concentration, concentration of ferric sulphate and concentration of hydrogen peroxide were adjusted to determine the decolorization efficiency of RR 2 dye from aqueous solution. All experiments were conducted according to experimental design of initial concentration (0.06, 0.08 and 0.1 mg/mM), concentration of ferric sulphate (0.1, 0.125 and 0.15 mg/mM) and concentration of hydrogen peroxide (0.1, 0.55 and 1 mg/mM) at constant pH of 3, reaction time of 45 min and at room temperature. At the end of each experiment, small amount of the solutions was taken to determine the absorbance value for all experiments using UV/Vis spectrometer (PerkinElmer lambda 35) and the finial RR 2 dye concentration was calculated as per the calibration curve in Fig. 1 (Table 2).

Table 2. Variables and levels of factors used for optimization

Variable	Level		
	Low (−)	Middle (0)	High (+)
Dye conc. (mM)	0.06	0.08	0.1
$FeSO_4 \times H_2O$ conc. (mM)	0.1	0.125	0.15
H_2O_2 conc. (mM)	0.1	0.55	1

mM = millimolar

2.4 Preparation of Standard Solution

To calculate the final dye concentration from each run, a calibration curve first prepared by using the standard dye solution with known concentrations. Different concentrations were prepared and absorbance values were recorded at λ_{max} of the dye using UV/VIS spectrometer. Linear calibration curve of this data was served as the basis for determining the final dye concentration. Absorbance values have been presented in Table 3.

Table 3. Standard concentration and their absorbance values

Maximum wavelength (nm)	539				
Dye concentration (mM)	0.000	0.060	0.073	0.080	0.100
Absorbance value	0.000	0.697	0.874	0.911	1.911

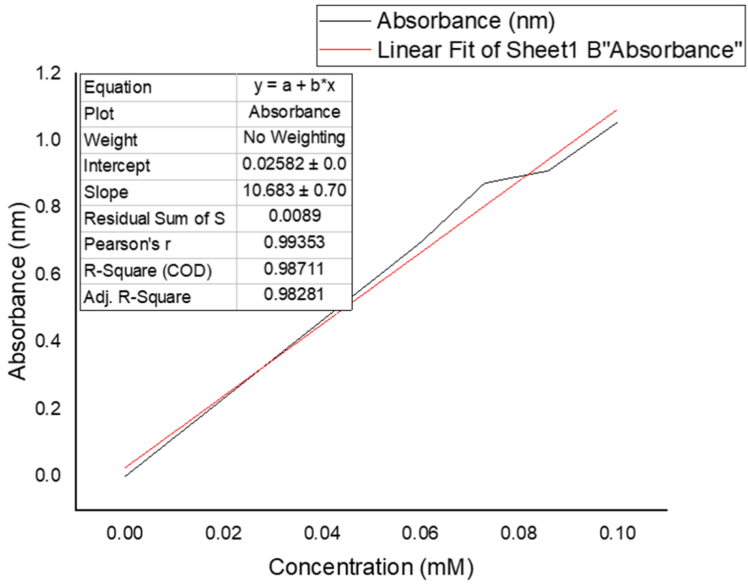


Fig. 1. Calibration curve of standard solution

3 Results and Discussions

3.1 Effect of H_2O_2 Concentration

The effect of H_2O_2 concentration on the decolorization of the aqueous solution containing RR 2 dye was investigated by ranging the values of H_2O_2 concentration from 0.1 to 1 mM. The experiments were done at pH 3 and at room temperature. As shown in Fig. 2 for Fenton process, the decolorization efficiency was increased from 59.08 to 72.12%, 61.9 to 79.01% and 64.72 to 82.18% for 0.06, 0.08 and 0.1 mM of initial dye concentration, respectively as concentration of H_2O_2 increased from 0.1 to 1 mM after 45 min and at optimum 0.1 of Fe^{+2} ion. For photo-Fenton process, the decolorization efficiency was increased from 76.5 to 79.05%, 60.9 to 88.1% and 67.6 to 85.8% for 0.06, 0.08 and 0.1 mM of initial dye concentration, respectively as concentration of H_2O_2 increased from 0.1 to 1 mM after 45 min and at optimum 0.125 of Fe^{+2} ion. In the Fenton process cases of initial dye concentrations i.e. 0.06, 0.08 and 0.1 mM the decolorization efficiency of dye increases as the concentration of H_2O_2 increases. However, for the photo-Fenton the maximum efficiency was seen at 0.08 mM dye concentration. The decrease of removal effeminacy at low concentrations of H_2O_2, it could not generate enough OH radicals, and the oxidation rate decreases.

Therefore, the addition of a higher H_2O_2 concentration does not improve the degradation with the simple Fenton process. The present circumstance was likewise revealed and clarified in [9]. The explanation of this may be the age of hydroperoxyl revolutionaries (HO_2) within the sight of an overabundance of H_2O_2. Although HO_2 advances revolutionary chain responses and is a successful oxidant itself, its oxidation potential is a lot of lower than that of hydroxyl extremist (■OH).

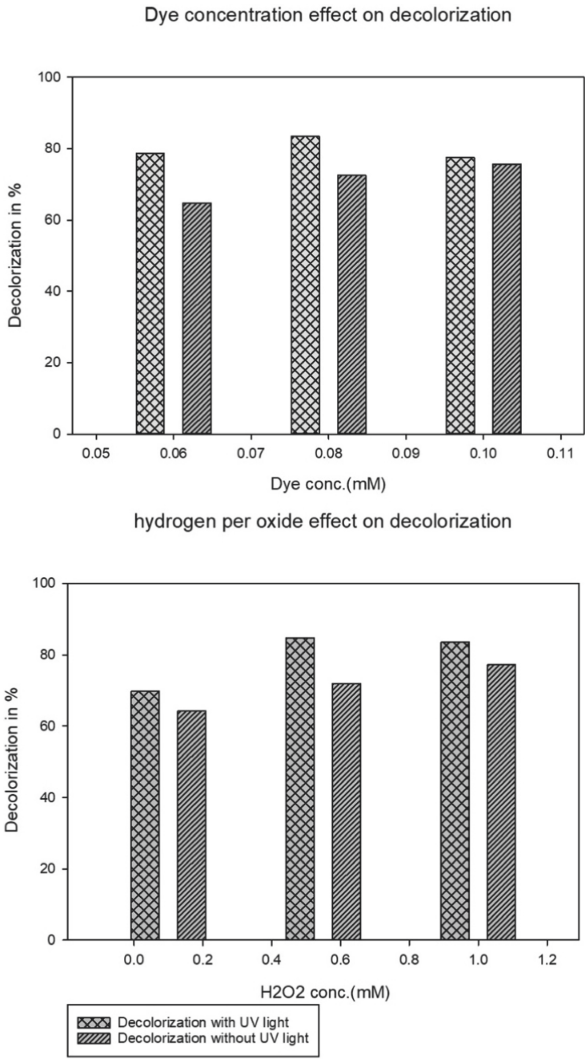


Fig. 2. Effect of H_2O_2 on decolorization of RR 2 dye from aqueous solution

3.2 Effect of Ferrous Ion (Fe^{+2}) Concentration

The effect of ferrous ion concentration on the decolorization of the aqueous solution containing RR 2 dye was investigated by ranging the values of ferrous ion concentration from 0.1 to 0.15 mM. As shown in Fig. 3, the decolorization efficiency was decreased from 66.27 to 54.12%, 75.98 to 70.98% and 82.18 to 78.22% for 0.06, 0.08 and 0.1 mM of initial dye concentration, respectively as concentration of ferrous ion increased from 0.1 to o.15 mM after 45 min and at optimum 1 mM of H_2O_2 concentration.

For UV/Fenton Process the decolorization efficiency was decreased from 80.35 to 75.20%, 87.40 to 78.60% and 78.25 to 75.15% for 0.06, 0.08 and 0.1 mM of initial dye concentration, respectively as concentration of ferrous ion increased from 0.1 to o.15 mM after 45 min and at optimum 1 mM of H_2O_2 concentration. Therefore, in both Fenton and photo-Fenton process, the dye reduction rate increased with Fe (II) concentration up to a specific level (0.1−0.125 mM) and then began to decrease (0.125−0.15 mM).

In light of this examination, the utilization of a lot higher Fe^{2+} impetus focus could prompt oneself rummaging of ▪OH revolutionaries by Fe^{2+}. In addition, it likewise initiated a decrease in the degradation rate [9].

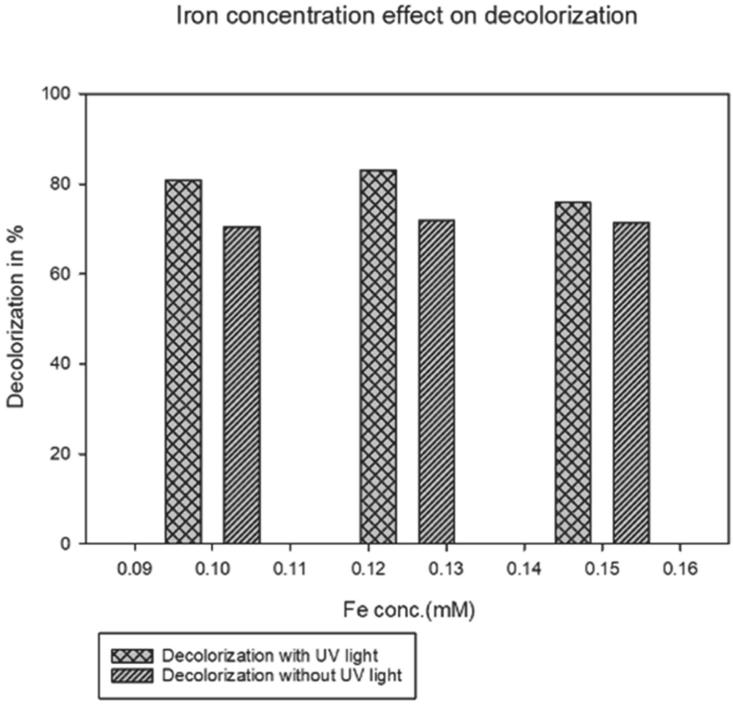


Fig. 3. Effect of ferrous ion (Fe (II)) on the removal of RR-2 by Fenton and photo–Fenton processes (pH = 3, initial dye concentration = 0.06 mM, reaction time = 45 min.)

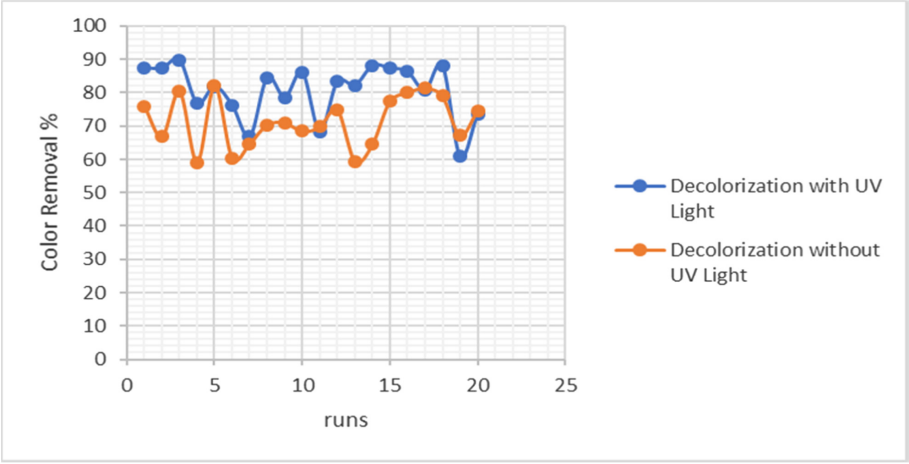


Fig. 4. Performance of photo-Fenton process over Fenton process for the run

3.3 Effect of RR2 Initial Concentration

The initial concentrations of RR–2 at three levels (0.06, 0.08 and 0.1 mM) had a considerable effect on the reduction rate of the dye in the aqueous phase. The effect of initial dye concentration on its removal efficiency is shown in Fig. 2. As the initial dye concentration increased from 0.06 to 0.08 mM, the removal efficiency was increased and shows decrease beyond that in the photo–Fenton process. Therefore, the maximum removal rate in the photo–Fenton process (88.10%) was observed at the concentration of 0.08 mM. However, in the Fenton process, an increase in the concentration of the dye from 0.06 to 0.1 mg/L had a significant increase in its removal rate. In the Fenton process, the maximum removal rate (82.18%) was observed at the RR–2 concentration of 0.1 mM.

Overall, as it can be seen on Fig. 4 above the photo Fenton process shows greater decolorization as compared to traditional Fenton process.

4 Conclusions and Recommendations

4.1 Conclusions

Fenton's and photo - Fenton process is a type of advanced oxidation processes which is an effective method for degradation of organic matter from wastewater. It is also the most effective to decolorize the dyes from aqueous solution. In this research work RR 2 dye has been taken as a modal pollutant in aqueous solution. Fenton's and photo - Fenton process has been applied to decolorize this dye from aqueous solution in comparison. Different types of operation factors such as H_2O_2, initial RR 2 dye and Fe^{2+} catalyst concentrations were investigated on decolorization efficiency of RR 2 dye at constant pH 3, reaction time of 45 min and at room temperature. The maximum degradation efficiency (82.18%) was obtained at 1 mM of H_2O_2, 0.1 mM of initial RR

2 dye and 0.1 mM of Fe^{2+} catalyst concentrations Fenton process. Whereas for photo Fenton, the maximum degradation efficiency (88.10%) was obtained at 1 mM of H_2O_2, 0.08 mM of initial RR 2 dye and 0.125 mM of Fe^{2+} catalyst concentrations. It was found out that the photo-Fenton process can be successfully applied for the decolorization of RR 2 in aqueous solution.

4.2 Recommendation

In this research work degradation and mineralization are not determined due to the limitations of some equipment and chemical reagents. Therefore, degradation and mineralization should be performed.

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