

REMOVAL OF REMAZOL ROSSO RB DYE FROM AQUEOUS EFFLUENTS BY HOMOGENOUS FENTON OXIDATION PROCESSES

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Abstract. The paper presents some data from our laboratory-setup experiments of homogenous oxidative processes with hydrogen peroxide (*i.e.* advanced Fenton oxidation processes) applied for Remazol Rosso RB dye-containing aqueous systems, especially textile effluents. Therefore, some different operating parameters (including pH, concentration of dye, H₂O₂ and ferrous ions, oxidation time, temperature, stirring regime, among its) were tested for determination of the best performance in effluent discoloration and dye removal, meaning the optimal values of each studied parameters for highest discoloration or dye removal. For an effluent loaded with 50 mg/L Remazol Rosso RB dye, there were applied these optimal values that correspond to > 97 % discoloration efficiency performed with 88.24 mM H₂O₂, 0.18 mM FeSO₄, at pH (5.16), temperature of 19-20°C, continuous stirring regime (30 rpm) and minimum 25-30 minutes of homogenous advanced oxidation treatment. If there are not used additional chemical reagents for pH adjustment (minimization reason of treatment operating cost), the performance of this oxidative treatment is closed to above mentioned efficiency by after a higher oxidation time (> 90 min). These results are encouraging and sustain this oxidative process application and optimization for reducing the environmental impact of effluent discharging directly in different natural aquatic receptors and compliance with admissible limits imposed by environmental legislation as well.

Keywords: discoloration, Fenton reagent, homogenous advanced oxidation process, optimal operating parameter, Remazol Rosso RB dye, textile effluent treatment.

Introduction

In the whole world even in the most hardly accessible for tourist geographic zones, the water quality is negatively changing, and the pollution level of natural surface water resources is greatly increasing. One of the most important causes is the non-corresponding quality of final colored or not effluent discharged in natural water resources (water courses or accumulation lakes). Therefore, the wastewater or individual/final effluent treatment must continue to be one of priorities in environmental management (in terms of integrated production water management) even if an environmental prevention and control scheme was implemented in the productive/commercial unit for reduction of generated loaded wastewater amounts, among others. The treated effluents are indicated to be inside recycling/reuse for reduction of fresh water amount in each manufacturing process. One of recognized and viable emerging wastewater treatments in the scientific literature [1-4] is the advanced oxidation process (AOP) (or mineralization) of polluting compounds from wastewaters to carbon dioxides and/or other harmless species. A special attention was given for Fenton and/or Fenton-like oxidation processes applied for discoloration or dye removal purposes, together with its advantages (*i.e.* high efficiency, short operating time, simplicity in destroying the contaminants, stability to treat a wide range of polluting or not toxic species, non-necessity of special equipment and relatively small quantities of iron-based precipitates and sludge) and disadvantages (*i.e.* consumption of chemicals, necessity of iron-based precipitates/sludge separation with supplementary costs and treatment requirements) that select sometimes the environmental options of company management staff in terms of effluent quality and hourly load [5-8].

This research study continues the authors' works concerning the application of Fenton oxidation (FO) treatment using homogenous ferrous-based catalysts for discoloration purposes, and is summarized some results performed at laboratory set-up scale for some aqueous Remazol Rosso RB azo dye solutions concerning the influence of different FO operating parameters.

Experimental

Materials and reagents

Remazol Rosso RB is a commercial available textile azo dye used without further purification in preparation of dyeing bath for cotton fabrics manufacturing, having the following principal characteristics: chemical formula – C₂₀H₁₂N₆O₁₆S₅Na₄, molecular weight (MW) of 824 g/mol; maximum absorbance (λ_{max}) at 517 nm, purity of 82.60%. For further practical working, a stock solution of azo dye (600 mg/L) was prepared for obtaining of diluted samples (with distilled water) in dye content range of 50-100 mg/L [5-7].

- There were also used Fenton reagents ($\text{H}_2\text{O}_2 / \text{Fe}^{2+}$ systems) and pH adjustment solutions, such as [5-6]:
- hydrogen peroxide (H_2O_2 30 %) purchased from S.C. Nordic Invest S.R.L. Company (Cluj Napoca, Romania).
 - ferrous catalyst (Fe^{2+}), prepared from ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) purchased from Fluka Analytical Co. (Germany) or Chemical SRL (Romania), i.e. aqueous stock solution of 20 g/L (2 mL of concentrated H_2SO_4 , purchased from Merck Co., were added in 500 mL solution of prepared ferrous sulphate).
 - pH adjustment solutions such as 0.1N H_2SO_4 and 0.1N NaOH (purchased from Chemical Co., RO).

Equipments and FO Procedure

Some series of homogenous Fenton oxidations of azo dye solutions were carried out in a 300 mL closed glass reactor under magnetic stirrer (AG-2) using the following working methodology [5-8]: in 50 mL-dye solution (known dye concentration) with stabilized temperature (5-45°C, mainly 20°C) and specific pH (2.16-10.50) is introduced with micropipette (EcoLine) a known volume of ferrous catalyst stock solution (0-2.5 mL), under continuous stirring or without stirring, and also a known volume of commercial H_2O_2 30% solution (0-2.5 mL H_2O_2 30%). The start of Fenton oxidation (FO) kinetic study was considering the moment when H_2O_2 was added in the dye solution ('zero' time). During kinetic oxidation experiment, samples (1-3 mL) were collected from FO reactor, and analysed in terms of two quality indicators: colour and dye content (after measurements, samples are quickly reintroduced in reactor for further continuing participation in Fenton oxidation, trying to keep the solution volume as constant as possible). The final inhibition of residual H_2O_2 oxidative activity in each collected sample after FO oxidation (experiment stop) is achieved by increasing of pH to alkaline range (9-12) with help of 5N NaOH solution, and optional by adding of solid MnO_2 (0.2 g MnO_2 for each sample) [6].

The colour and dye concentration were determined by absorbance measurements at different wavelengths [5-8]: (i) 436, 456 (Hazen unit - HU, 50 HU corresponds to an absorbance of 0.069 at 456 nm), 525 and 620 nm for colour, and (ii) 517 nm (λ_{max}) for dye content using a SP 830 Plus spectrophotometer (Metertech Inc.). The experimental data indicate the progress of dye removal or discoloration during homogenous Fenton oxidation process. The initial and final pH measurements were performed at a HACH One-Laboratory pH-meter (Hach Co., USA).

The dye removal and/or discoloration degree or FO efficiency in term of colour was expressed with the general known formula of a treatment degree (Eq.(1)) for colour or Remazol Rosso RB dye concentration (using the established calibration curve for this azo dye concentration at 517 nm) [5,7,8]:

$$\text{Dye removal or discoloration degree (\%)} = \frac{C_i - C_f}{C_i} \cdot 100 \quad (1)$$

where: C_i – the initial colour (HU) or dye concentration (mg/L), and C_f – the color (HU) or dye concentration (mg/L) at t time, mg/L.

Some notifications are necessary to be mentioned for complete understanding of experimental results:

- In further applications/stages from the textile technological manufacturing process (after FO treatment stage), the treated dye-containing solutions will be used in steps where the only imposed restriction is for color and pH, not for salts (fixed residues) and organic loads (toxic, refractory organics expressed by COD, and/or biodegradable organics expressed by BOD) that are important but not restrictively imposed. Therefore, the FO performance is firstly considered only for color (discoloration) or dye decomposition (expressed by dye removal).
- For the final individual or mixed effluent discharged in receptor from outside of plant emplacement is obligatory to have in view the total organic load (toxic and biodegradable ones) together with content of suspended solids, salts and color, and also in some technological manufacturing steps.
- This treated effluent by FO process will be considered only in further controlled activities/technological steps from in-side plant emplacement not individually discharged in nearby sewage system.

Results and discussion

The known mechanism of an advanced Fenton-like oxidative process is based on reaction of formed or existing hydroxyl radicals ($\text{HO}\cdot$) with ferrous ions (Fe^{2+}) or organics (ionic or molecular organic species - R) to form ferric ions (Fe^{3+}) and different final or intermediary oxidation products (P) (low molecular weight oxygenated compounds or, in some instances, CO_2 and H_2O). Hydroxyl radical generation is enhanced at low pH (2.5-5.0), and some sludge amounts can be formed (iron hydroxide precipitates).

Some previous authors' reports of homogenous Fenton-like oxidation processes [5-8] indicated that the principal factors influencing the FO-like processes in terms of discoloration or dye removal applied for different industrial wastewaters, especially textile effluents, depended on operating parameters such as initial pH, concentration of H_2O_2 , ferrous ions, temperature, (FO) oxidation time, stirring regime, etc.

pH Influence in FO Process

It is known that the pH affects greatly the FO process performance of azo dye-containing solutions, especially the HO \cdot generation/formation and availability of catalyst species (at pH > 5.3 can precipitate ferric and ferrous hydroxides or other iron hydroxo complexes) [5-8].

In the case of commercial Remazol Rosso RB azo dye, the pH influence vs. discoloration degree and dye removal is illustrated in Figure 1 (a, b) as results of different kinetic experiments of homogenous FO process applied for 50 mg/L-dye containing solutions, 120 min-working with 176.47 mM H₂O₂, 0.36 mM FeSO₄, at room temperature (20°C), under continuous stirring (30 rpm).

It is observed that the highest FO discoloration performance (*i.e.* 96.43% after 10 min of FO process, with decreasing behavior further at 83.48% after 60 min, or 84.375% after 120 min) and dye removal (*i.e.* 96.33% after 5 min of FO process, with decreasing at 82.45% after 60 min, or 83.27% after 120 min) were performed at pH 5.16 (no precipitates formed, no registered turbidity variation). The dye oxidation rate decreased for other pH values (*e.g.*, only 33.69–54.98% after 60 min at pH (8.93-10.50) or 9.52–63.74% at pH 2.45), excepting the pH value of 7.745 (*i.e.* 93.33% after 30 min, with in time-decreasing discoloration behavior until 83.59% after 60 min, or 69.79% after 120 min), because mainly of new types of ionic or molecular species formation/production (or lower catalytic activity of different iron ionic species in solution).

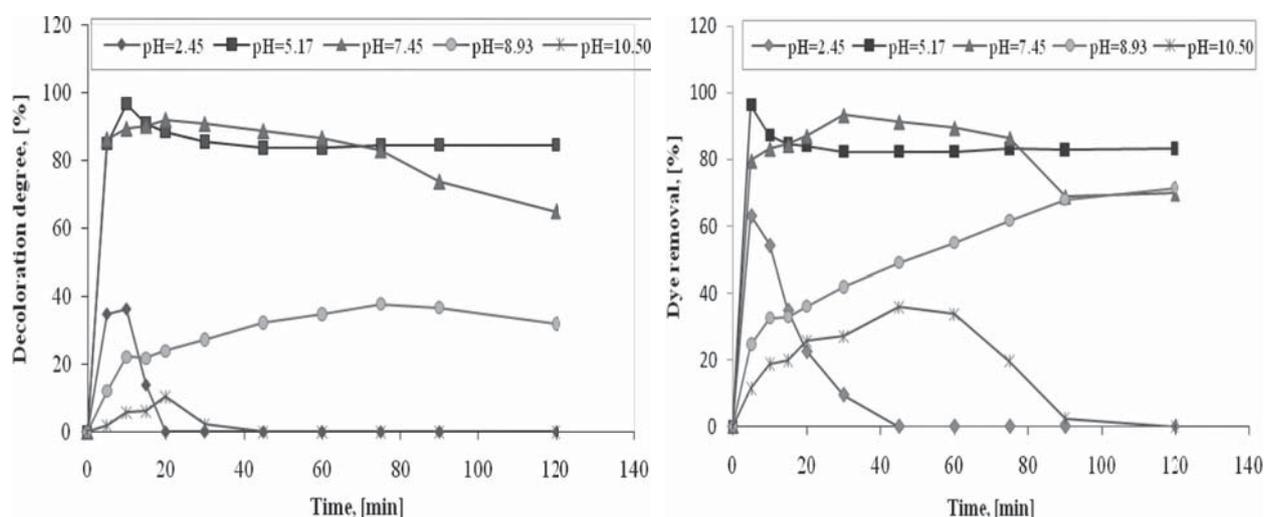


Figure 1. pH influence vs. homogenous FO process kinetic and performance of Remazol Rosso RB dye solution: (a) discoloration degree and (b) dye removal.

The most adequate pH for Remazol Rosso RB removal by FO process with ferrous sulphate as catalyst is 5.13-5.16, being obviously necessary a neutralization step before direct discharge of treated dye solution in different receptors or inside reuse, but good results can be performed at neutral pH of 7.47-7.745 (no neutralization step necessary, and no addition of chemical reagents for Fenton-like oxidation process).

H₂O₂ Concentration Influence in FO Process

Some kinetic experiments of Fenton oxidation process were performed with 50 mg/L-dye containing solutions, 120 min-working with 0.18 mM FeSO₄ and different H₂O₂ doses, at pH (7.47-7.745), temperature of 20°C, under continuous stirring (30 rpm).

All results were presented in Figure 2 (a, b) with clearly visual zones where competitive reactions take place in excess of hydrogen peroxide (HO \cdot) with acting of some inhibitory effects referring to dye removal or dye solution discoloration (*e.g.*, some inhibitory effect can appear at H₂O₂ doses in range of 44.12-264.71 mM H₂O₂ and type of oxidative process is changing, homogenous processes being competitive with Fenton-like processes).

Continuous increasing discoloration or dye removal is registered for H₂O₂ dose of 17.64 mM at pH 7.745 and room temperature (57.10% after 120 min), and also at the extreme testing H₂O₂ range working with 264.71 mM and 352.92 mM H₂O₂ (*i.e.* 45% and 69.47% after 120 min for discoloration degree, and 77.99% and 94.64% after 120 min for dye removal, respectively).

In Figure 3 (a, b) it is shown that relative high discoloration (37.91-100%) and also dye removal (6.89-100%) is registered in the first 10 min of FO process at pH 5.16 working in the H₂O₂ dose range of 17.67-264.71 mM with 0.18 mM FeSO₄. Complete discoloration at pH 5.16 (no precipitates formed, homogenous Fenton processes acting) was performed working with 88.24 mM and 176.47 mM H₂O₂.

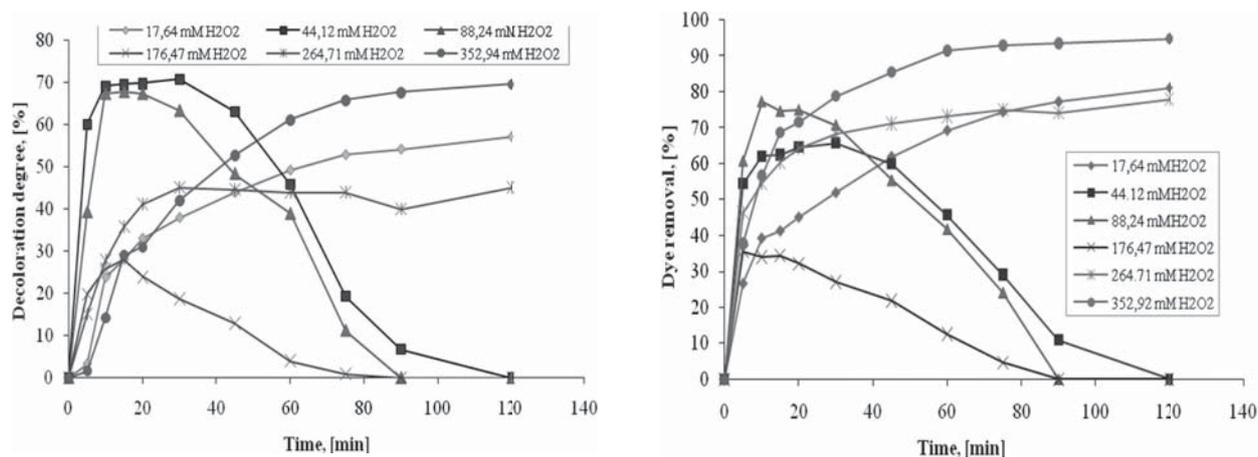


Figure 2. H₂O₂ dose influence vs. homogenous FO process kinetic and performance of Remazol Rosso RB dye solution (pH 7.745): (a) discoloration degree and (b) dye removal.

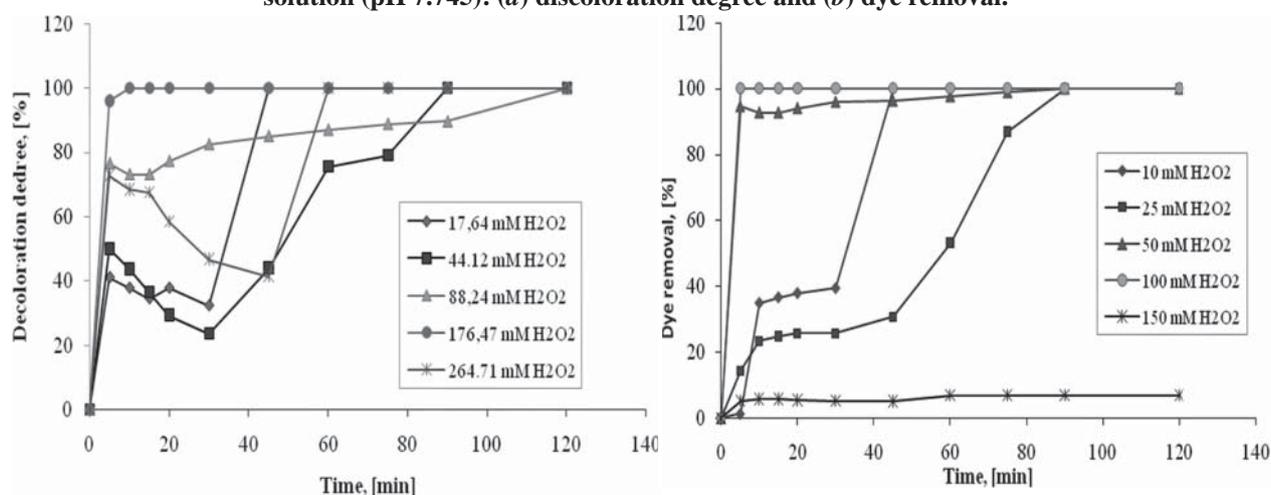


Figure 3. H₂O₂ dose influence vs. homogenous FO process kinetic and performance of Remazol Rosso RB dye solution (pH 5.16): (a) discoloration degree and (b) dye removal.

Ferrous Ions-Based Catalyst Influence in FO Process

Some kinetic experiments of homogenous Fenton oxidation process were performed with 50 mg/L-dye containing solutions, 120 min-working with 176.47 mM H₂O₂ and different FeSO₄ doses, at pH (5.13-5.16), room temperature (20°C), under continuous stirring (30 rpm), and the results are presented in Figure 4 (a, b).

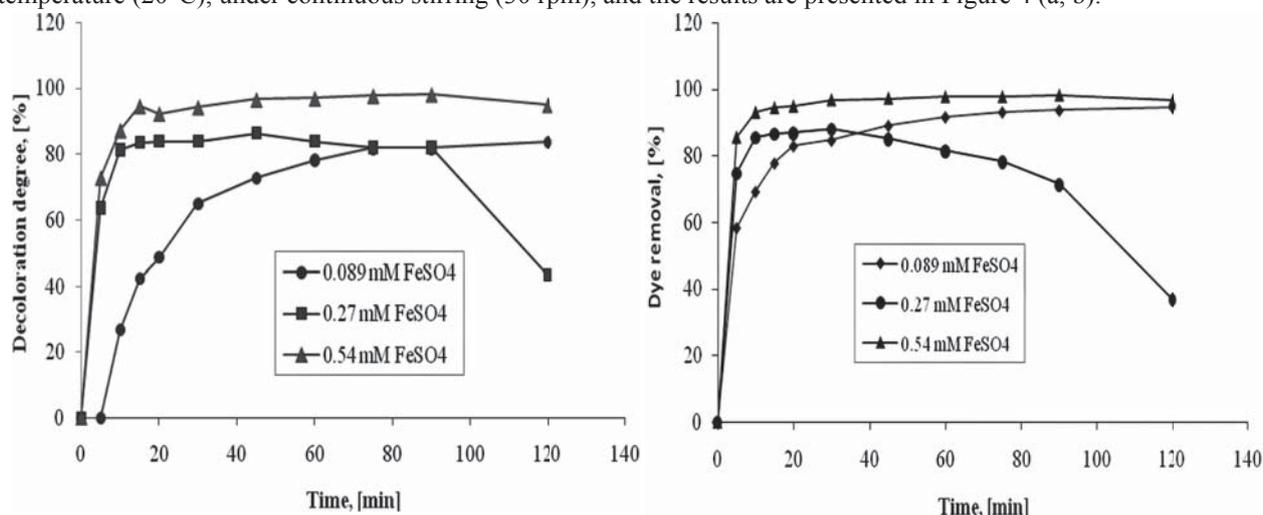


Figure 4. Ferrous catalyst dose influence vs. homogenous FO process kinetic and performance of Remazol Rosso RB dye solution (pH 5.16): (a) discoloration degree and (b) dye removal.

It seems that some increasing rates of FO process appear with ferrous catalyst concentration increases (adequate concentration range of 0.18-0.54 mM FeSO_4 at pH of 5.16). Higher ferrous catalyst concentration faster dye FO rate (more radical species formed), especially in the first FO period of (5-20 min) (*i.e.* discoloration of 81.25%-87.17% after 10 min of dye FO with 0.27 mM and 0.54 mM FeSO_4 , respectively). The treated aqueous solution can be discharged in natural receptor or urban sewerage system having admissible values of total iron concentration < 0.5 -1 mg/L, or mainly inside reuse.

The dye removal is rapid in the first 10-20 min and after a slow increasing progress until the maximal value of 86.33-98.05% in the range of 0.089-0.54 mM FeSO_4 . A little different behavior is remarked for a dose of 0.27 mM FeSO_4 , meaning a sharply increasing in the first 10 min followed by decreasing until 43.36% for discoloration degree, and 36.75% for dye removal after 120 min, respectively.

Temperature and Oxidation Time Influence in FO Process

The influence of temperature in dye FO oxidation is investigated at neutral (7.47-7.745) and low acid pH (5.13-5.16) in terms of discoloration degree or dye removal by performing some kinetic experiments with 50 mg/L dye, working with 88.24 mM H_2O_2 , 0.18 mM FeSO_4 , the results being illustrated in Figure 5 (a, b).

Higher part of discoloration or dye removal was rapidly performed in the first 5-30 min, but the maximal or complete discoloration after more than 60 min.

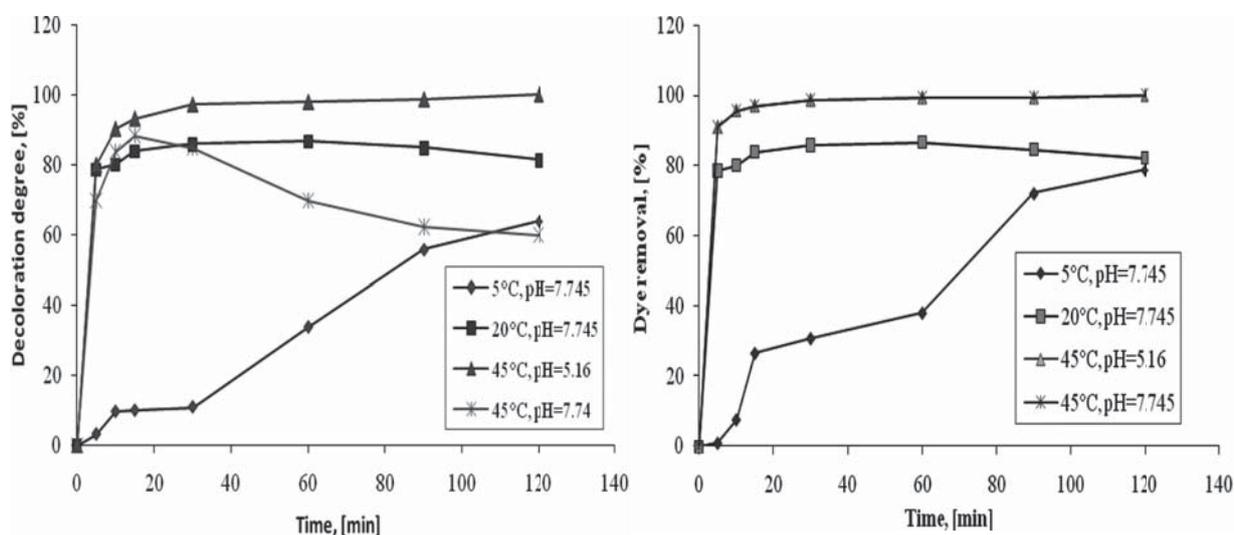


Figure 5. Temperature influence vs. homogenous FO process kinetic and performance of Remazol Rosso RB dye solution: (a) discoloration and (b) dye removal.

The dye FO kinetic results applied in the mentioned operating conditions (88.24 mM H_2O_2 , 0.18 mM FeSO_4 , pH 7.745 or 5.16, different temperatures, continuous stirring) were shown that the best performances were achieved at pH 5.16 and high temperature (45°C) for both discoloration degree and dye removal (100% after 15 min). Moreover, after only 15 min of FO process, there were performed discolorations and dye removals higher than 80% at pH 5.16 and 7.745 at 20° and 45°C, respectively.

These results indicated that even in cool season condition (5°C), the ferrous-based Fenton oxidation process can be achieved for aqueous solutions containing 50 mg/L Remazol Rosso RB azo dye.

Stirring Regime Influence in FO Process

Some kinetic experiments of homogenous Fenton oxidation process were performed with 50 mg/L-dye solutions, 120 min-working with 88.46 mM H_2O_2 and 0.18 mM FeSO_4 , at pH (5.16 and 7.745), room temperature (20°C), under continuous stirring (30 rpm) or without stirring.

The results are shown in Figure 6 (a, b), indicating that FO rate is increasing in time but a sharp increasing is registered only in the first 10-15 min, and after low increasing occurred.

In general, it seems that the continuous stirring with low rate (30 rpm) is beneficial for increasing of discoloration degree and dye removal, *i.e.* 26.566% at 5°C, 83.903% at 20°C, or 97.00% at 45°C after only 15 min of advanced FO oxidation, with maximal performance of 78.746% at 5°C, 82.11% at 20°C, and 100% at 45°C after 120 min. The treated dye solution can be safely discharge in any kind of aquatic receptor or urban sewerage system but mainly inside reuse, if necessary (the final pH value is not in the admissible range of 6.50-8.50), a neutralization stage is needed.

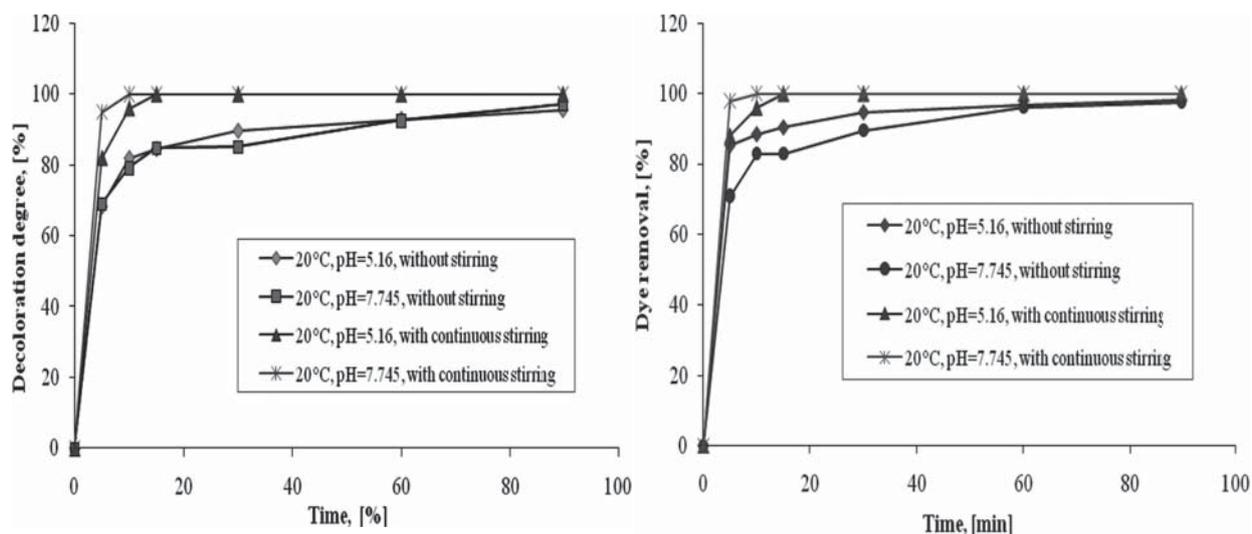


Figure 6. Stirring regime influence vs. homogenous FO process kinetic and performance of Remazol Rosso RB dye solution (pH 7.745, and 5.16): (a) discoloration degree and (b) dye removal.

Conclusions

The Remazol Rosso RB azo dye can be eliminated from aqueous systems by advanced ferrous-based Fenton oxidation processes (*i.e.* dye removal > 90%, even complete discoloration in specific operating conditions).

The influence of some FO operating parameters was investigated, *i.e.* pH, H_2O_2 and ferrous-based catalyst dose, temperature, operating oxidation time and stirring regime, for discoloration of 50 mg/L dye-containing solution. The recommended values for H_2O_2 and ferrous-based catalyst doses are 88.24–176.47 mM H_2O_2 and 0.36–0.54 mM $FeSO_4$ at a pH of 5.16, or 7.745, and temperature of 20°C.

The dye Fenton oxidation is indicated to be performed in low acidic conditions (*i.e.* 5.10–5.16) at room temperature, but good results (>70%) can be obtained also at pH 7.47–7.745 with no necessity of additional neutralization step (in rest, the dye oxidation rate diminished; changing of homogeneous Fenton oxidation type with competitive Fenton-like oxidative processes).

The advanced ferrous-based catalytic oxidation with hydrogen peroxide can be considered suitable treatment for discoloration purposes of industrial effluents, if the optimal operating conditions were established.

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