(REFEREED RESEARCH)

THE TREATMENT OF WASTE WATER OF DYEING BY FENTON OXIDATION IN PRESENCE AND ABSENCE OF ULTRASOUND

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ABSTRACT

In this study, degradation of Reactive Red 141 (RR141) present in textile dyeing waste water was investigated by catalytic wet hydrogen peroxide oxidation over iron-containing ZSM-5 zeolite catalysts prepared by ion-exchange and hydrothermal synthesis methods. Higher decolorization (18.3%) and degradation (17.6%) degrees were obtained by waste water of dyeing with 0.5 wt% over ion-exchanged FeZSM-5 catalyst than those with waste water of dyeings in high dye concentration. Color removal was increased with H_2O_2 amount (up to 5 mmol) added to the reaction mixture. Decolorization degree increased from 15.7% to 18.6% in the combination of CWPO and ultrasound for waste water of dyeing with 0.5 wt%. However, as the concentration of dye in the waste water increased, the positive effect of ultrasound on decolorization disappeared.

Key Words: Decolorization of waste water, Degradation of waste water, Fenton's reagent, Fenton + Ultrasound, Catalytic wet peroxide oxidation, FeZSM-5 zeolite, Reactive Red 141.

ÖZET

Bu çalışmada, tekstil boyama suyundaki C.I. Reactive Red 141'in (RR141)'in iyon değişimi ve hidrotermal sentez metodu ile hazırlanmış demir içeren ZSM-5 zeolit katalizörleri üzerinde ıslak peroksit oksidasyonunu (CWPO) ile giderilmesi incelenmiştir. İyon değişimli FeZSM-5 katalizörü üzerinde, 0.5 kütle yüzdesindeki boyama atık suyu için, yüksek boya derişimli atık sulara göre daha yüksek renk giderimi, %18.3 , ve daha yüksek aromatik giderim, %17.6, sonuçları elde edilmiştir. Reaksiyon karışımına eklenen H_2O_2 miktarı (5 mmol'e kadar) ile renk giderimi artmıştır. 0.5 kütle yüzdesindeki boyama atık suyu için ultrases katkılı CWPO ile renk giderimi %15.7'den %18.6'ya çıkmıştır. Bununla birlikte, atık sudaki boya derişimi arttıkça ultrasesin renk giderimi üzerindeki olumlu etkisi kaybolmuştur.

Anahtar Kelimeler: Atık suyun renksizleştirilmesi, Atık suyun parçalanması, Fenton reaktifi, Fenton+ ultrases, Katalitik ıslak peroksit oksidasyonu, FeZSM-5 zeoliti, Ultrases, Reactive Red 141.

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1. INTRODUCTION

Waste water of textile-dyeing industry contains a lot of colored organic conpounds with high chemical oxygen demand. Without appropriate treatment, 90% of dyehouse effluent passes to the surface waters and causes a damaging effect on the aquatic life by inhibiting light penetration and minimizing the photosynthesis. Reactive dyes are hard to decompose biologically. Oxidation by using homogeneous Fenton's reagent, a mixture of H_2O_2 and Fe^{2+}/Fe^{3+}, is effective in decolorization and degradation of the waste water containing various types of dyes. However, regeneration of catalyst is impossible, oxidation reaction occurs at a narrow range of pH values and removal of iron compounds is necessary from purified water when homogeneous catalytic wet peroxide oxidation (CWPO), homogeneous Fenton's reagent, is used. Under these circumstances, a heterogeneous catalytic process where the catalyst is in different phase is needed. In this case, the recovery of catalyst from water and regeneration of catalyst are not so difficult (1,2).

In the present work, dyeing waste water containing C.I. Reactive Red 141 (RR141) in different concentrations was chosen for oxidation. RR141, a bright red colour of azo reactive dye, is widely used for dyeing processes in textile industry. In literature, adsorption (3-5), Fenton's and photo-Fenton processes (6,7), heterogeneous photo catalytic treatment process (8) were used for the removal of RR141.

In the oxidation with Fenton's reagent based on ferrous ion and H_2O_2, hydroxyl radicals ($\cdot OH$) are produced by interaction of H_2O_2 with ferrous salts, equation 1:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\cdot}OH + {}^{\bullet}OH \quad (1)$$

Fe(III) can then react with H_2O_2 in the so-called Fenton-like reaction in order to regenerate iron (III) and thus supporting the Fenton process, through the equations 2-4:

$$Fe^{3+} + H_2O_2 \rightleftharpoons FeOOH^{2+} + H^+ \quad (2)$$

$$FeOOH^{2+} \longrightarrow HO_2^{\cdot} + Fe(II) \quad (3)$$

$$Fe(III) + HO_2^{\cdot} \longrightarrow Fe(II) + {}^{\bullet}O_2 + H^+ \quad (4)$$

The $^{\bullet}OH$ species formed attack the organic substrates present in the waste water, detoxifying it via oxidation. Nevertheless, numerous competitive reactions can also occur, namely the following ones, equations 5 and 6, which negatively affect the oxidation process (9-11):

$$H_2O_2 + HO^{\bullet} \longrightarrow HO_2^{\cdot} + H_2O \quad (5)$$

$$Fe^{2+} + HO^{\bullet} \longrightarrow Fe^{3+} + HO^- \quad (6)$$

Iron-containing zeolites show redox properties because they can change their oxidation states. These materials are effective catalysts for oxidative breakdown of phenolic compounds (12-17), a number of carboxylic acids (18) and ethanol (19).

On the other hand, catalytic methods provide complete degradation of dyes. In last decade, catalytic wet peroxide oxidation (CWPO), as an advanced oxidation process, gradually began to gain importance in oxidation of dyes. Degradation of several dyes, Procion Marine H-EXL, Rhodamine 6G, Methyl Orange, Orange II, was studied by CWPO over FeY, FeZSM-5 or an pillared saponite impregnated with iron salt (1, 20, 21). The usage of hydrogen peroxide as an oxidant is helpful, since no additional pressure is required, as in the case of gaseous oxidants, such as O_2 or O_3.

In advanced oxidation processes (AOP), hydroxyl radicals ($OH^{\bullet}$) which is non-selective and a powerful oxidant, is generated. Hydroxyl radicals impart complete color removal in oxidation of dyes.

One of the well known methods of free radical formation in advanced oxidation processes is ultrasonic irradiation (sonication). Sonochemical degradation of dyes was investigated in literature for several dyes such as C.I. Reactive Black 5 (22), methyl violet (23), C.I Reactive Red 141 (RR141), C.I. Basic Brown 4 and C.I. Basic Blue 3 (24), Rhodamine B (25), C.I. Acid Orange 7 (26), C.I. Acid Red B (27), C.I. Acid Orange 5 (28), C.I. Acid Black 1 (29) and Methyl Orange, C.I. Reactive Orange 16, C.I. Direct Orange 31, C.I. Direct Red 81 (30). Eventhough high degradation efficiency and aromatic removal were achieved at high frequencies such as 520 kHz and 850 kHz (24,30) up to now, no study was reported on heterogeneous catalytic Fenton process and the combination of ultrasound (US) and catalytic Fenton process to treat waste water containing RR141.

The aim of this study is to evaluate the degradation and decolorization of RR141 present in textile dyeing waste water, by catalytic wet hydrogen peroxide oxidation, heterogeneous catalytic Fenton process, over iron-containing ZSM-5 zeolites in absence and presence of ultrasound.

2. MATERIALS AND METHODS

2.1. Materials

ZSM-5 (Si/Al=42) used in catalyst preparation by ion exchange was obtained from Süd- Chemie/Germany. The reactive azo dye Reactive Red 141 was supplied from Dystar and used without further purification. Reactive Red 141, composed of two monochlorotriazine reactive groups, is a homo- bireactive azo dye with commercial names of Procion Red H-E7B and C.I. Reactive Red 141.

The absorption spectra of C.I. Reactive Red 141 is characterized by four main bands, one in the visible region (λ_{max} =543nm) which is responsible for the chromophoric components (for the color of dye arising from aromatic ring connected by azo groups) and the others in the UV region (λ_{max} = 216 nm, λ_{max} =254 nm and λ_{max} =288 nm). The first two bands in the UV region represent the absorption of benzene-like and band at 288 nm the absorption of naphthalene-like structures in the molecule.

Empirical formula of RR141 is $C_{52}H_{22}Na_8O_{26}S_8Cl_2N_{14}$, it has a molecular weight of 1774 g/mol and its solubility is 50 g/l. The hydrogen peroxide solution (35 % in weight) of analytical grade was obtained from Merck.

Figure 1 presents the chemical structure of RR141 (a) and UV-vis absorption spectra of aqueous solution of RR141 (b).

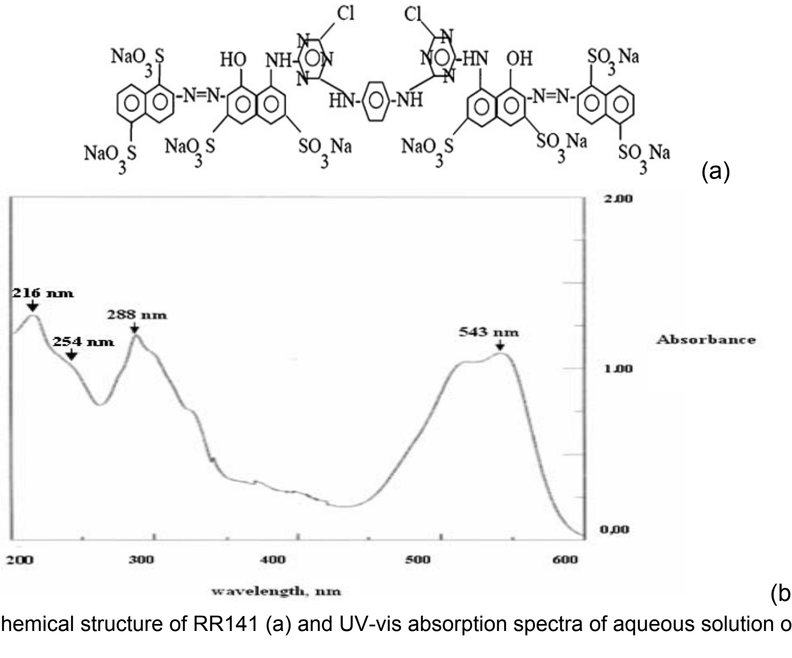


Figure 1. Chemical structure of RR141 (a) and UV-vis absorption spectra of aqueous solution of RR141 (b).

2.2. Catalyst Preparation

Iron-containing ZSM-5 catalysts were prepared by ion-exchange and hydrothermal synthesis methods. The method of Schwidder et al. (2005) (31) was applied with small changes for iron ion-exchange (32) using ZSM-5 zeolite (Si/Al=42). Catalyst obtained was coded as IE-FeZSM-5. The method described in Szostak et al. (1987) (33) was used in the synthesis by hydrothermal conditions and resultant catalyst was called as HT-FeZSM-5.

2.3. Catalyst Characterization Studies

The catalysts were characterized by XRD, SEM, FTIR, nitrogen adsorption and ICP-AES measurements.

XRD patterns of the samples were recorded in the range of 5-70^o by Philips X'Pert Pro with Cu-Kα radiation to determine their crystalline structures. Morphological properties were analysed by Philips SFEG 30S SEM device. Nitrogen adsorption measurements were done at 77 K by Micromeritics ASAP 2010 equipment after degassing the dried samples at 573 K for 24h under 5μm Hg vacuum. FT-Infrared spectra were recorded in 1700-400 cm^{-1} with a Schimudzu FT-IR 8201 spectrometer using KBr pellet containing 1 wt% of sample. Metal content and Si/Al ratio of samples were determined by Varian-96 ICP-AES device with fusion dissolution method.

2.4. Preparation of Dyeing Waste Water

In the oxidation runs textile dyeing solutions in different concentrations were used.

In order to obtain batch dyeing waste water, fabric samples were dyed with C.I. Reactive Red 141. All dyeings were carried out using different dye concentrations (0.5; 1; 2 wt%) with liquor ratio of 20:1 in a laboratory dyeing machine. In a dyebath containing different concentrations of C.I. Reactive Red 141, salt (60 g/l), soda (12 g/l) and scoured, bleached knitted cotton fabric was added at 50^{o}C. The dyeing was maintained at 50^{o}C for 15 min. The temperature was raised to 85^{o}C over 20 min. After that the dyeing was continued at 85^{o}C for 60 min and the temperature was reduced to 70^{o}C. Dyed samples were removed from the dyebath and waste water of the dyeings was used in decolorization processes. Assessment of the decolorization efficiency was monitored spectroscopicly using related calibration curves.

In the study, the effects of catalyst type and concentration of textile dyeing solution on catalytic oxidation were investigated.

2.5. Catalytic Activity Tests

2.5.1. Catalytic Wet Peroxide Oxidation Studies in the Absence of Ultrasound

The oxidative degradation of textile dyeing waste water containing RR141 was performed under isothermal conditions, 333 K (for runs with sonication at 298 K) in a shaded temperature-controlled glass batch reactor equipped with a mechanic stirrer (280 rpm) and a pH electrode. In a typical run, 0.15 dm^3 of aqueous dye solution was placed into the reactor and the temperature was adjusted to 333 K. When the temperature reached to 333 K, pH of the solution was measured and 0.15 g of catalyst was introduced into the solution under continuous stirring. Analysis of the solution, after 10 minutes, showed no remarkable adsorption of dye on the catalyst. Then 5 mmol H_2O_2 was added to the solution and this time was recorded as the starting time of the reaction. The samples, taken periodically at every 15 min were diluted and after centrifugation for 30 min to remove the catalyst, were analyzed by UV spectrophotometer (Jasco 7800 UV/Vis) to determine the decolorization degree at 543 nm and the degradation degree at 254 nm (8,24). The decay in absorption band at 543 nm was followed as a function of time for the determination of decolorization (color disappearance) degree. Because the band located at 543 nm in the visible region is due to the chromophore containing azo linkage. The decay in the absorbance peak at 543 nm by oxidation reflects the destruction of chromophoric group. On the other hand, the bands observed in the UV region at 216 nm, 254 nm are due to the benzene ring and at 288 nm due to the naphthalene ring of RR141. The decrease in the intensities of those bands is attributed to the formation of intermediates, resulting from the degradation of the azo dye which still contain benzoic- and naphthalene- type rings (21). In this study, in the light of the study done by Guyer and Ince (24), the decrease of the intensity of band at 254 nm was taken as a measure of degradation degree.

Activity of parent ZSM-5 was also determined in CWPO of dye solution.

2.5.2. Catalytic Wet Peroxide Oxidation Studies in the Presence of Ultrasound

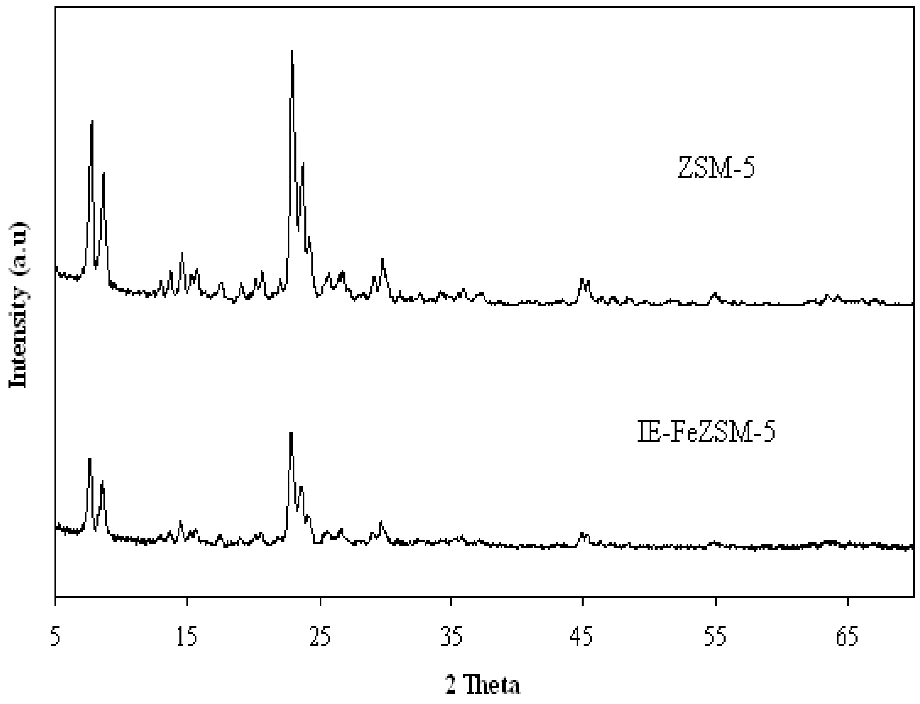
Catalytic oxidation runs were also performed in the presence of ultrasound using an ultrasonic reactor (Meinhardt, Model 5/1575) with a frequency of 850 kHz in order to observe the potential benefit of combined use of ultrasound irradiation and CWPO. Continuous sinusoidal ultrasonic waves were used. These experiments were carried out at a temperature of 298±3 K which was kept constant by circulating water in the jacket around the reactor.

In a typical sonication run with catalyst, 0.3 dm^3 of aqueous dye solution with a known concentration was charged to the reactor. Power was adjusted to 25 W. When the temperature reached to 298 K, 0.3 g of catalyst and 10 mmol of H_2O_2, which was determined by sonication of solution in the presence of H_2O_2 without catalyst, were introduced into the solution under continuous stirring. The samples taken periodically from reaction mixture were analyzed as explained in part 2.3.1. Oxidation of dye solution by sonication alone and contribution of H_2O_2 to oxidation by sonication at 298±3 K were also studied for comparison.

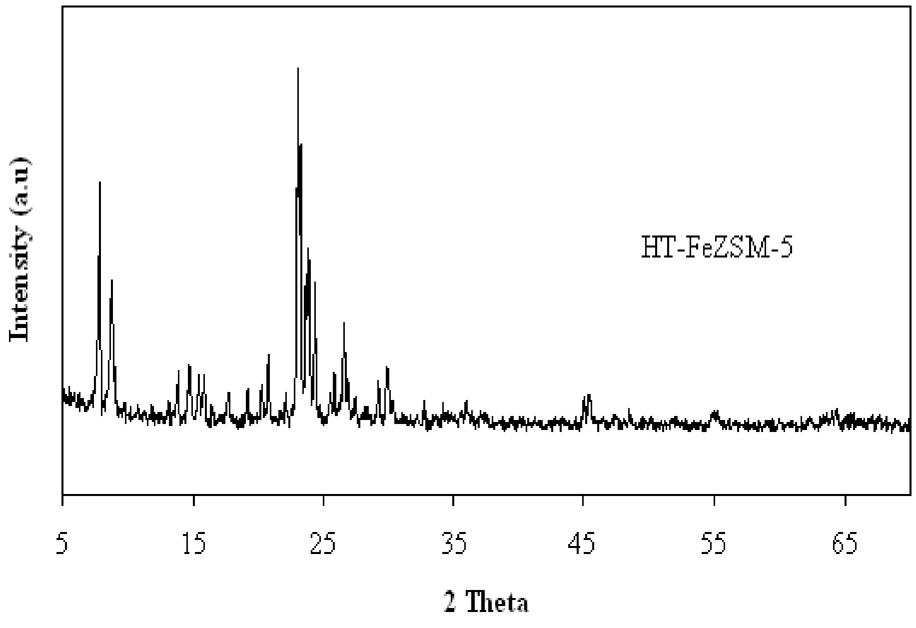
3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization Studies

XRD patterns of FeZSM-5 samples prepared by the methods of ion-exchange and hydrothermal synthesis exhibited the typical diffractograms of the ZSM-5 zeolite, MFI framework, at 2θ = 7-9^o and 23-25^o given in literature (1, 13, 19, 34-39). It emphasized that high dispersion of Fe ions in compensating positions inside zeolites did not damage the crystallinity of zeolite. However, decreases in peak insensities observed in IE-FeZSM-5 sample were attributed to the enhanced absorption of X-ray due to iron cations and also to the reduction in crystal size of zeolite as a result of acid treatment (40), Figure 2.



(a)



(b)

Figure 2. X-ray diffraction patterns of prepared FeZSM-5 samples and parent ZSM-5 zeolite.

SEM images of IE-FeZSM-5 and parent ZSM-5 zeolite (Si/Al=42) depicted that the crystallites were as spherical shape with a length of 500 nm, Figure 3. It couldn’t be clearly observed the incorporation of iron cations into the zeolite structure. The grains of HT-FeZSM-5 samples were relatively identical with the size of 1 μm with no evidence for the presence of iron ions. This manifested the high dispersion of iron ions in zeolite structure as evoked by XRD data.

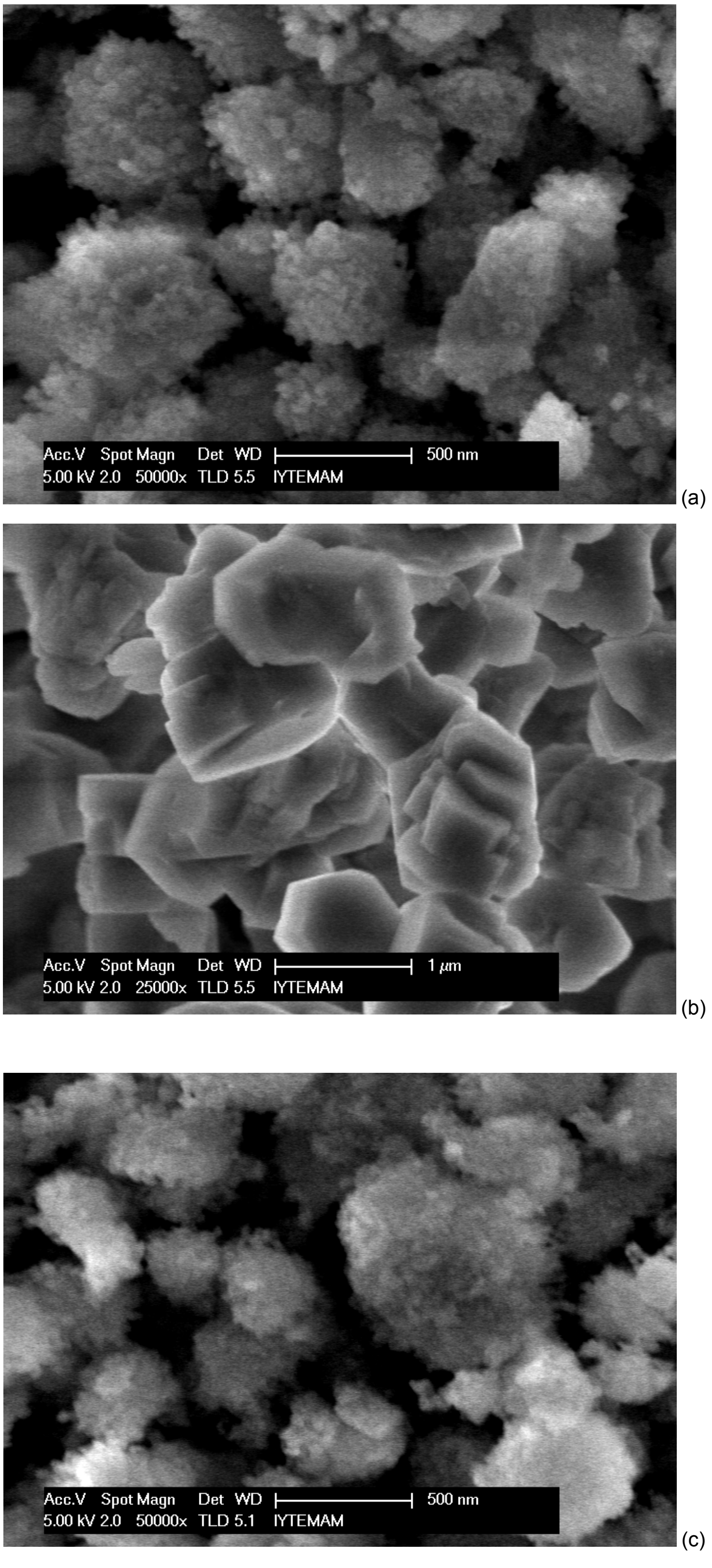


Figure 3. SEM images of catalysts prepared by ion exchange and hydrothermal methods (a) IE-FeZSM-5 (b) HT-FeZSM-5 (c) ZSM-5.

All FTIR spectra, Figure 4, showed that bands at 445, 550, 800, 1100, 1225 and 1650 cm^{-1} which were assigned to different vibrations of tetrahedral and framework structure of ZSM-5 zeolite associated with minor changes as a result of Fe incorporation (13, 35, and 36).

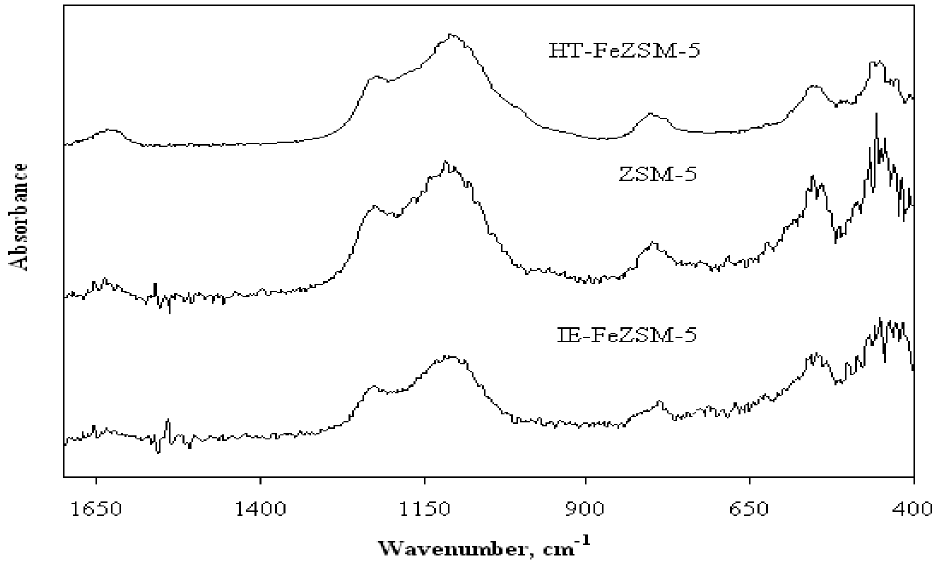


Figure 4. FTIR spectra of parent ZSM-5 zeolite and prepared FeZSM-5 catalysts.

Table 1. Surface characteristics and composition of the catalyst used in the study.

Catalysts	$S_{BET,}$ (m^2/g)	$S_{Lang,}$ (m^2/g)	$d_{ave,}^{*}$ (nm)	$S_{\mu,}$ (m^2/g)	Si/Al	Si/Fe	Fe, %
ZSM-5-42	478.4	701.0	0.72	199.3	42.3	1663.2	0.06
IE-FeZSM-5 (42-1)	468.7	681.0	0.73	235.8	42.8	17.8	4.98
HT-FeZSM-5-1	344.4	507.5	1.10	235.5	-	35.9	2.44

* Horvath-Kawazoe method

The surface characteristics of parent ZSM-5 and prepared FeZSM-5 catalysts determined by nitrogen adsorption measurements were given in Table 1. Incorporation of iron cations into the zeolite structure by ion-exchange decreased BET and Langmuir surface areas, S_{BET} and S_{Lang}, respectively. This can be due to the occurence of some iron species inside zeolite pores and thus blocking them. Acid used during the synthesis affects the average pore size (d_{ave}) and surface area of samples. Incorporation of iron into ZSM-5 structure enhanced the micropore area. Table 1 also presents the composition of prepared FeZSM-5 samples and parent zeolite determined by ICP-AES method. Parent ZSM-5 includes iron as impurity. More iron was loaded to zeolite by ion-exchange.

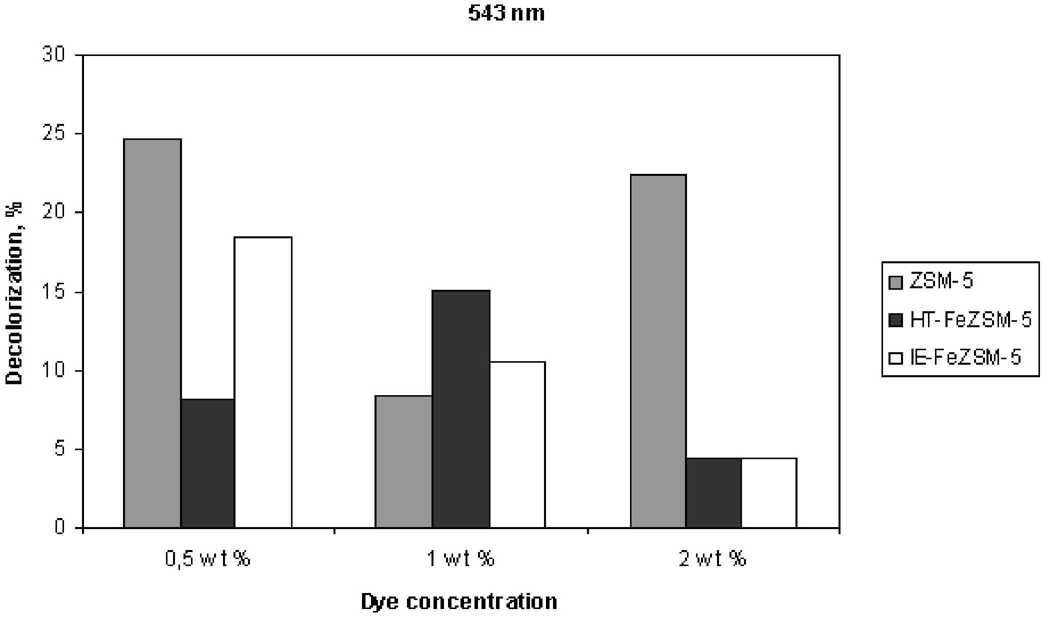
3.2. Catalytic Activity Tests

3.2.1. CWPO Studies in the Absence of Ultrasound

The CWPO experiments of textile dyeing waste water were carried out over prepared catalyst and parent ZSM-5 zeolite at 333 K by using 0.15 dm^3 of waste water of dyeing at a known concentration, 0.15 g of catalyst, 5 mmol H_2O_2. Figure 5 presents decolorization (Figure 5a), and degradation (Figure 5b) results after a reaction duration of 2h. Higher decolorization (18.3%) and degradation (17.6%) degrees were obtained by waste water of dyeing with 0.5 wt% of dye than those with waste water of dyeings in higher dye concentrations over IE-FeZSM-5 catalyst. Incorporation of iron into ZSM-5 structure by ion-exchange enhances degradation degree from 8.5% to 17.6%, while a decrease in decolorization degree is observed from 24.6% to 18.3% with 0.5 wt % of dye. Eventhough the greatest decolorization (15%) was achieved over HT-FeZSM-5 zeolite, parent ZSM-5 zeolite was the best for degradation (7.9%) of waste water of dyeing with 1 wt% of dye. High decolorization (22.4%) and degradation degrees (17.6%) could be achieved only on parent ZSM-5 zeolite for oxidation of waste water of dyeing with 2 wt%.

The highest color removal degree was obtained to be 24.6% (for 0.5 wt% of dye) over ZSM-5 zeolite. This decolorization was lower than those reported in literature. Complete color removal was achieved by Stolyarova et al.(1) in the CWPO of Rhodamine 6G over FeZSM-5 zeolites, by Neamtu et al.(20) in the oxidation of Procion Marine H-EXL over Fe- exchanged Y zeolite and by Ramirez et al.(21) in the Fenton- like oxidation of Orange II over iron loaded saponite clay catalyst.

It is known that direct and reactive dyes are decolorized by using Fenton’s reagent, but most disperse dyes are not (41). However, in Fenton-like oxidation of dyes over FeZSM-5 zeolites, oxidation state of iron (Fe^{2+} or Fe^{3+}) and the ratio of Fe^{2+} amount to Fe^{3+} (Fe^{2+}/ Fe^{3+}) in the catalyst affect its activity in catalytic oxidation. Catalyst type, reaction conditions and H_2O_2 amount used have great influence on decolorization and degradation of dye. It was reported that degradation and decolorization degrees of dye molecules decreased with increasing molecular weight of dye. A degradation of 11.2 % could be achieved in the oxidation of RR141 which had a molecular weight of 1774 g/mol. However, degradation degrees of 93 % could be achieved by using basic dyes such as Basic Blue 3 (24). On the other hand, the electrolytes such as salt (NaCl), soda (Na_2CO_3) added to dye during the dyeing process in this study, may cause extra load in decolorization. The studies indicate that products such as naphthalene diazonium, p-dinitrobenzene and 2-nitroso naphthol are formed through monoazo and triazine diol intermediates during the degradation of RR141 (42). Product concentration which is dependent on the initial dye concentration may affect the next routes in the degradation pathway resulting in different decolorization and degradation degrees of dye over different ZSM-5 catalysts. Hence, a linear change in degradation of RR141 with the catalyst used can not be observed.



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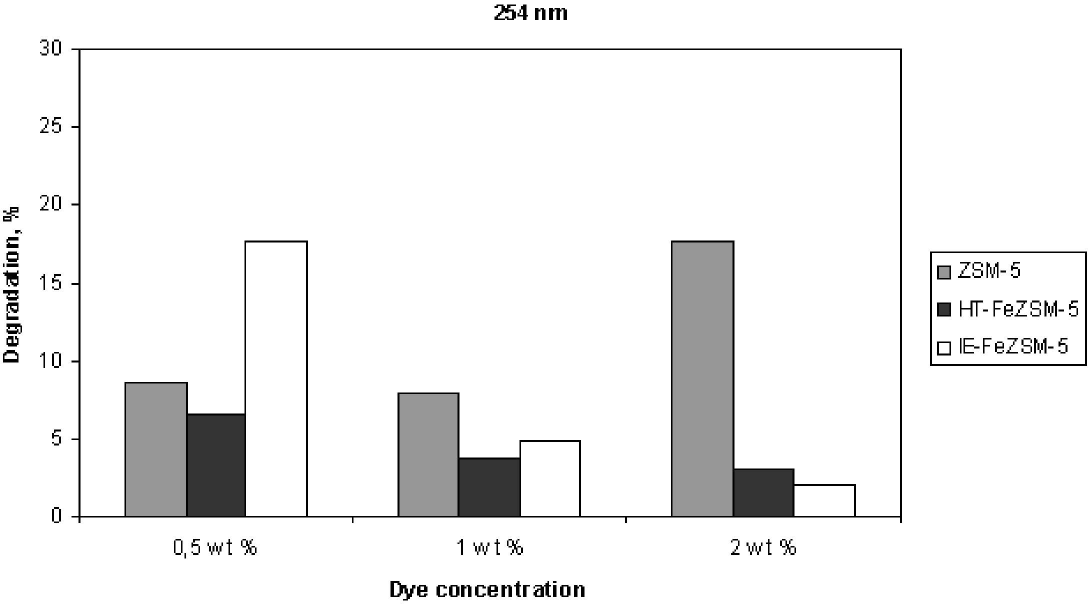
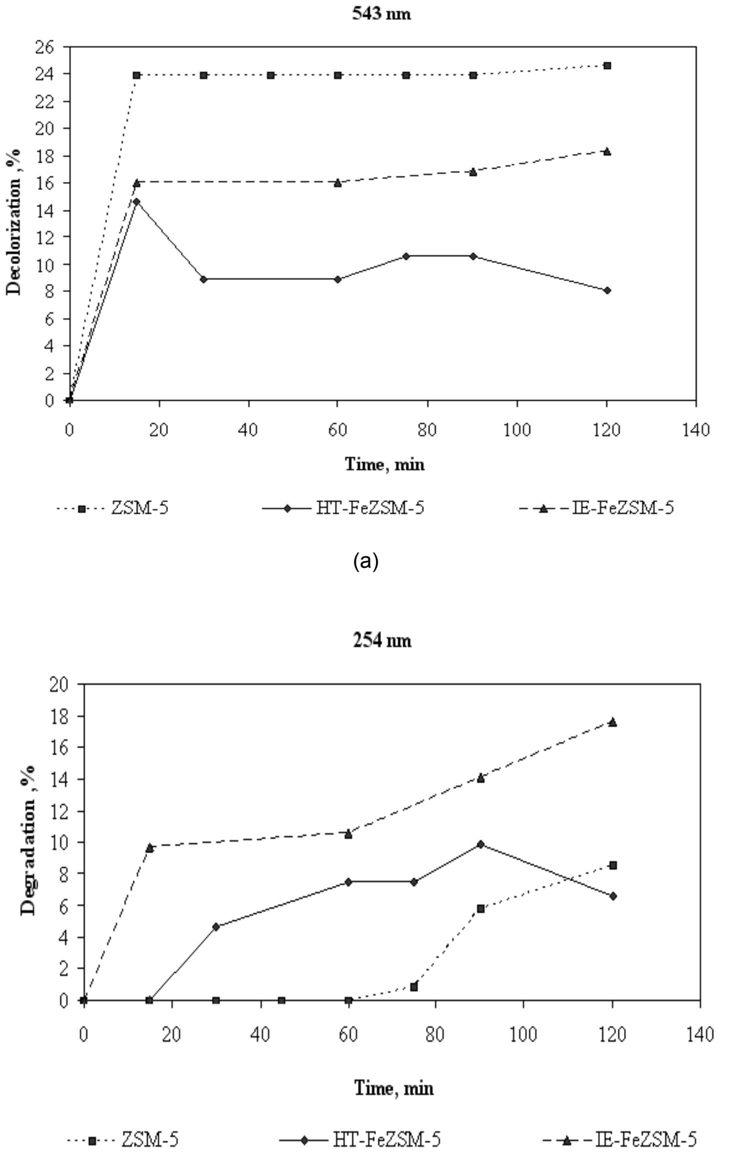


(b)

Figure 5. Effect of dye concentration in dyeing solution on CWPO over different types of catalysts a) Decolorization, b) Degradation.Reaction conditions: Volume of waste water of dyeing= 0.15 dm^3,catalyst amount= 0.15 g, H_2O_2 amount= 5 mmol, temperature= 333K.



(a)

(b)

Figure 6. The effect of catalyst type on color removal and aromatic content removal as a function of time on CWPO of dyeing waste water with 0.5 wt % of dye a) Decolorization, b) Degradation. Reaction conditions: same as in Figure 5.

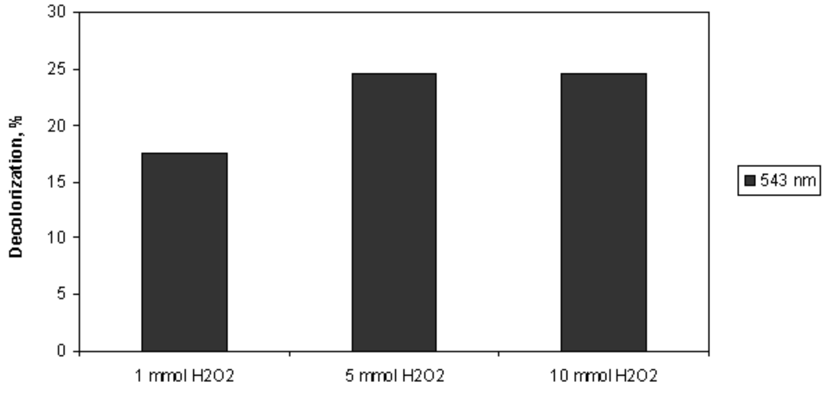


Figure 7. The effect of H_2O_2 amount on color removal for parent ZSM-5 zeolite and waste water of dyeing with 0.5 wt% of dye on CWPO. Reaction conditions: Volume of waste water of dyeing= 0.15 dm^3, catalyst amount= 0.15 g, temperature= 333K.

Figure 6 displays the change of decolorization (Figure 6a) and degradation (Figure 6b) degrees as a function of time for dyeing water concentration of 0.5 wt%.

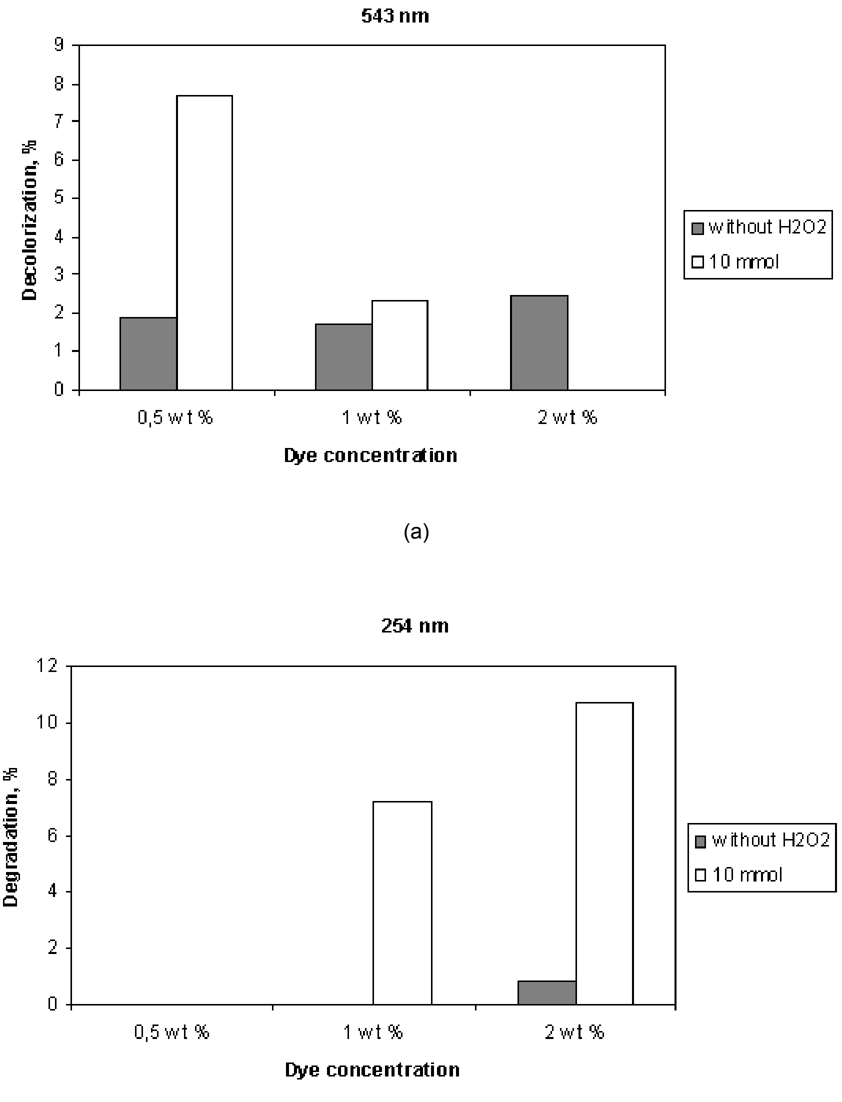
The effect of H_2O_2 amount on CWPO of dye was investigated for dyeing waste water concentration with 0.5 wt% over parent ZSM-5 zeolite where the highest decolorization degree was achieved.

Figure 7 presents this effect. As seen, the increase in H_2O_2 concentration from 1 mmol to 5 mmol caused an enhancement in color removal from 17.6% to 24.6%. This is expected because of the increase of $OH^{\cdot}$ Radicals produced with increasing amount of H_2O_2. When H_2O_2 amount is enhanced from 5 mmol to 10 mmol, decolorization degree remains unchanged.Because, at high H_2O_2 concentrations, eventhough more hydroxyl radicals are generated, a competition of $OH^{\cdot}$ radicals clutching between the substrate and H_2O_2 begins and H_2O_2 reacts with $OH^{\cdot}$ radicals, equation 5, to constitute less reactive perhydroxyl radicals, $OH_2^{\cdot}$. Dominant response from these two opposite effects directs the reaction. Similar results have been reported in literature (20, 21).

3.2.2. CWPO Studies In The Presence Of Ultrasound

3.2.2.1. Sonication of Textile Dyeing Waste Water

In the first group of runs, 0.3 dm^3 of waste water of dyeing at a known concentration was sonicated at 298±3 K in an ultrasonic reactor at a power of 25 W using continuous sinusoidal waves. In the second group of experiments, the effect of 10 mmol H_2O_2 addition on sonication was determined. For this purpose, waste water of dyeing was sonicated in the presence of 10 mmol H_2O_2 under the same conditions as sonication alone. As sonication runs were carried out with 0.3 dm^3 of waste water, 10 mmol H_2O_2 was added to the solution in sonication runs.It should be kept in mind that 5 mmol H_2O_2 was used in CWPO of 0.15 dm^3 waste water. Figure 8 presents the results. Ultrasound alone was not very effective in decolorization of dyeing waste water. 1.9% of decolorization could be provided in the presence of ultrasound alone for oxidation of waste water of dyeing with 0.5 wt% of dye. For decolorization of waste water of dyeings with 1 and 2 wt% of dye, 1.7% and 2.5% were measured respectively.



(a)

(b)

Figure 8. Effect of dye concentration in dyeing solution on sonication in the presence of H_2O_2 with different amounts a) Decolorization, b) Degradation. Reaction conditions: Volume of waste water of dyeing= 0.3 dm^3, H_2O_2 amount= 10 mmol, temperature= 298±3 K, ultrasonic power= 25 W.

An increase in decolorization degree from 1.9% to 7.7% was achieved with 10 mmol H_2O_2 introduction to waste water of dyeing with 0.5 wt% of dye and from 1.7% to 2.3 % for waste water of dyeing with 1 wt % of dye, while decolorization was completely inhibited when waste water of dyeing with 2 wt% of dye was sonicated in the presence of 10 mmol H_2O_2. The effect of sonication on oxidation decreases with increasing concentration of organic compound dissolved in water (43, 44). As the initial concentration of organic compound increases, more $OH^{\cdot}$ radicals are required. However, in the presence of H_2O_2, scavenging effect of $H_2O_2\cdot$ (equation 5) with the formation of less reactive $HO_2^{\cdot}$ radicals may become significant and this undesired reaction causes a decrease in $OH\cdot$ radicals in the medium which are necessary for oxidation.

It couldn't be possible to degrade textile dye in waste water with 0.5 wt % of dye when ultrasound used alone or in the presence of 10 mmol H_2O_2.However, a degradation of 0.8 % could be obtained by sonication without H_2O_2 for waste water of dyeing with 2 wt% of dye. Nevertheless, high degradation degrees, 7.1% and 10.7% were achieved in sonication of waste water of dyeings with 1 and 2 wt% of dye in the presence of 10 mmol $H_2O_2\cdot$ The destruction of aromatic carbons in azo dyes is slower than that of color because of the priority of hydroxyl radical attack on N=N bands and increases with the increasing amount of H_2O_2 (24).

Figure 9 shows the contribution of sonication to catalytic wet peroxide oxidation of waste water of dyeings with 0.5,1 and 2 wt% of dye. Because sonication runs were carried out in ultrasonic reactor at 298 K with and without H_2O_2, in order to observe the effect of sonication on CWPO, the runs of CWPO alone and CWPO in the presence of ultrasound were done at the same temperature over the active catalyst. Catalyst amount was doubled as 0.3 dm^3 of waste water of dyeing was used instead of 0.15 dm^3. Parent ZSM-5 zeolite was used in CWPO in the presence of ultrasound for oxidation of waste water of dyeings with 0.5 and 2 wt% of dye and HT-FeZSM-5 for waste water of dyeing with 1 wt% of dye, because the highest decolorization degrees were obtained over those catalysts for corresponding dyeing waste water concentrations, Figure 4.

Decolorization degrees achieved by CWPO alone at 298 K for waste water of dyeing concentrations of 0.5 wt %, 1 wt % and 2 wt % were found to be 15.7%, 6.4 % and 14.8 %, respectively. As remembered, decolorization degrees of 24.6 %, 15 % and 22.4 % were obtained in CWPO runs at 333K for corresponding waste water of dyeing concentrations.This result shows that decolorization increases with increasing temperature.

The runs at 298 K clearly indicate that decolorization degree increases from 15.7% to 18.6% in the combination of CWPO and ultrasound for waste water of dyeing with 0.5 wt%. However, as the waste water of dyeing concentration increases the positive effect of ultrasound on decolorization disappear, being as 4.8% and 9.5% for waste water of dyeings with 1 and 2 wt% of dye, respectively. This result can be attributed to the scavenging effect of H_2O_2 on $OH^{\cdot}$ radicals which becomes dominant at high concentrations of dyeing waste water.

No degradation was achieved in CWPO of all waste water of dyeings used in the study in the absence or presence of ultrasound. Degradation could be measured only when ultrasound was used alone for waste water of dyeings with 1 and 2 wt% of dye being as 7.1 and 10.7%, respectively, Figure 8b.

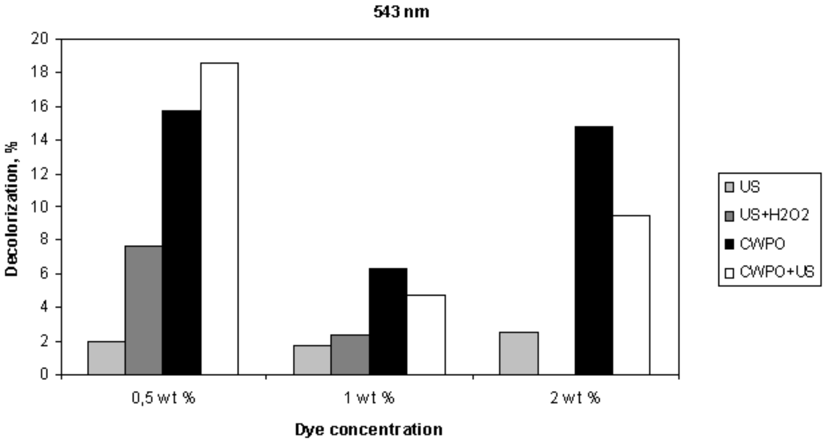


Figure 9. Effect of dye concentration in dyeing solution on decolorization degree in CWPO with sonication. Reaction conditions: Volume of waste water of dyeing= 0.3 dm^3, H_2O_2 amount= 10 mmol (in runs of US+ H_2O_2 and CWPO+US), temperature= 298±3 K, catalyst amount= 0.3 g, ultrasonic power= 25 W.

4. CONCLUSIONS

In this study, degradation of Reactive Red 141 (RR141) present in textile dyeing waste water was investigated by catalytic wet peroxide oxidation (CWPO) over iron-containing ZSM-5 zeolite catalysts. The catalysts were prepared by ion-exchange and hydrothermal synthesis methods and characterized by XRD, SEM, FTIR, nitrogen adsorption and ICP-AES measurements. The following observations summarize the results:

- Incorporation of iron into ZSM-5 structure by ion-exchange increased degradation degree from 8.5% to 17.6% for waste water of dyeing with 0.5 wt% of RR141.
- Higher decolorization (18.3%) and degradation (17.6%) degrees were obtained over IE-FeZSM-5 catalyst for waste water of dyeing with dye concentration of 0.5 wt% than those with waste water of dyeings in high dye concentrations.
- The increase of H_2O_2 amount from 1 mmol to 5 mmol caused an enhancement in color removal from 17.6% to 24.6% for waste water of dyeing with dye concentration of 0.5 wt%.
- At high H_2O_2 concentrations formation of perhydroxyl radicals affects oxidation of dye in waste water negatively.
- Ultrasound alone was not very effective in decolorization of waste water of dyeing. However, the decolorization degree increased from 15.7% to 18.6% in the combined use of CWPO and ultrasound for waste water of dyeing with 0.5 wt% of RR141. It is important to highlight that CWPO+US simultaneous combination implies synergetic effects rather than the addition of these effects.

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