

**EGE UNIVERSITY GRADUATE SCHOOL OF
APPLIED AND NATURAL SCIENCES**

(PhD THESIS)

**DEGRADATION OF REACTIVE YELLOW 84 (RY 84) BY THE
ULTRASOUND ASSISTED PHOTO-FENTON LIKE PROCESS WITH
Fe/TiO₂ and Fe/TiO₂-Ce CATALYSTS**

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İmzası

Özge DÖNMEZ

ÖZET

**Fe/TiO₂ ve Fe/TiO₂-Ce KATALİZÖRLER ÜZERİNDE ULTRASES
DESTEKLİ FOTO-FENTON TİPİ REAKSİYON İLE REACTIVE
YELLOW 84 (RY 84)'ÜN PARÇALANMASI**

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Bu çalışmada, heterojen Fenton prosesinin ultrases (US) varlığında fotokatalizle kombinasyonu olan ve sonofotoFenton prosesi olarak adlandırılan bir hibrit proses, suda çözünmüş Reactive Yellow 84 (RY 84)'ün, farklı miktarlarda demir içeren Fe/TiO₂ ve TiO₂-Ce katalizörleri varlığında bozunmasında kullanılmıştır.

Katalizörler sol-jel ve ıslak emdirme yöntemleri ile hazırlanmış ve XRD, SEM, FTIR, Azot adsorpsiyonu, UV-Vis DRS ve ICP-AES ölçümleri ile karakterize edilmiştir. Hazırlanan katalizörler RY 84'ün sonofotoFenton oksidasyonu ile bozunmasında test edilerek renk giderimi ve mineralizasyonu açısından en iyi katalizör belirlenmiştir. Islak emdirme yöntemi ile hazırlanan ve 300°C'de kalsine edilen, kütlece %1 demir içeren demir titandioksit ((1%Fe/TiO₂ (IW) 300°C) katalizörü en iyi katalizör olarak bulunmuştur. Katalizör, UV, US ve H₂O₂ ile ileri oksidasyon tekniklerinin tekli, ikili ve üçlü kombinasyonlarının RY 84 bozunması üzerindeki etkileri çalışılmıştır.

1%Fe/TiO₂ (IW) 300°C katalizör ile parametrik çalışma yapılarak, RY 84'ün bozunmasına, H₂O₂ miktarı, çözelti başlangıç pH'ı, başlangıç boya derişimi, sıcaklık, katalizör yüklemesi ve US gücü gibi parametrelerin etkileri araştırılmıştır. Katalizör kararlılığı ve yeniden kullanımı incelenmiştir.

Optimum bozunma koşulları: 25 mg/L RY 84 çözeltisi, 0.5 g/L katalizör, 5 mM H₂O₂, 25°C sıcaklık, 4W+4W UV-C lambası ve 40 W ultrases gücü olarak

belirlenmiştir. RY 84'ün renk giderimi birinci mertebe kinetiğe uymakta olup aktivasyon enerjisi 20.7 kJ/mol olarak hesaplanmıştır. Belirlenen optimum koşullarda, sonofotoFenton prosesi ile 45 dakikalık oksidasyon sonunda tam bir renk giderimi sağlanmış, %55'lik COD ve %38'lik TOC giderimi elde edilmiştir. Reaksiyona 120 dakika sonuna kadar devam edildiğinde COD giderimi %90'a, TOC giderimi %57'ye ulaşmıştır. Aynı optimum koşullarda RY 84'ün UV+katalizör+H₂O₂ kombinasyonu ile parçalanması çalışıldığında 45 dakikalık oksidasyon sonunda tam bir renk giderimi sağlanmış, %62'lik COD ve %48'lik TOC giderimi elde edilmiştir. Reaksiyona 120 dakika sonuna kadar devam edildiğinde COD giderimi %87'ye ulaşmış ancak TOC giderimi değişmemiştir.

Anahtar kelimeler : Reactive Yellow 84, SonofotoFenton proses, demir içeren TiO₂ ve TiO₂-Ce katalizörü, kimyasal oksijen ihtiyacı, Toplam organik karbon

ABSTRACT**DEGRADATION OF REACTIVE YELLOW 84 (RY 84) BY THE
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In this study, a hybrid process which is a combination of heterogeneous Fenton Process with Photocatalysis in the presence of ultrasound (US), “Heterogeneous SonophotoFenton Process”, was used to degrade Reactive Yellow 84 (RY 84) dissolved in water by using TiO₂ and TiO₂-Ce catalysts containing iron.

The catalysts were prepared by sol-gel and incipient wetness impregnation methods and characterized by XRD, SEM, FTIR, Nitrogen adsorption, UV-Vis DRS and ICP-AES measurements. The catalysts were tested in the sonophotoFenton degradation of RY 84 in order to determine the most effective catalyst for decolorization and mineralization of RY 84. The TiO₂ catalyst containing 1% (in weight) iron, prepared by incipient wetness impregnation technique and calcined at 300°C (1%Fe/TiO₂ (IW) 300°C) was found to be the most effective catalyst. The effect of individually, binary and ternary combinations of advanced oxidation techniques including catalyst, UV, US and H₂O₂ were studied on the degradation of RY 84. Parametric study of sonophotoFenton process was carried out over 1%Fe/TiO₂ (IW) 300°C catalyst and the effects of H₂O₂ concentration, initial pH of solution, initial dye concentration, temperature, catalyst amount and ultrasonic power were studied on the degradation of dye. Stability and recycling of the catalyst were investigated.

Optimum degradation conditions for the sonophotoFenton process were determined as, 25 mg/L of RY 84 solution, 0.5 g/L of catalyst, 5 mM of H₂O₂, a

temperature of 25°C, 4W+ 4W UV-C lamp and 40 W of ultrasonic power. Decolorization of RY 84 obeyed first order kinetics with an activation energy of 20.7 kJ/mol. At the obtained optimum conditions, with the sonophotoFenton oxidation of RY 84 almost complete color removal (99%), 55% COD, and 38% TOC reductions were obtained after 45 min of oxidation. At the end of the 120 min of oxidation, COD and TOC reductions increased to 90% and 57%, respectively. At the same conditions with the UV+catalyst+H₂O₂ oxidation of RY 84, it was possible to achieve almost complete (99%) color removal, 62% COD reduction, and 48% TOC reduction after 45 min of reaction. After 120 min COD reduction increase to 87%, however, TOC reduction remained constant after 45 min with combined system of UV+catalyst+H₂O₂.

Keywords: Reactive Yellow 84, SonophotoFenton process, Fe-containing TiO₂, Fe-containing TiO₂-Ce, Chemical oxygen demand, total organic carbon.

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TABLE OF CONTENTS

	<u>Page</u>
ÖZET.....	vii
ABSTRACT.....	ix
ACKNOWLEDGEMENT.....	xi
LIST OF FIGURES.....	xviii
LIST OF TABLES.....	xxvi
1. INTRODUCTION	1
1.1 The Aim of the Study and Importance of Treatment of Textile Waste Water and the Treatment Techniques.....	1
1.2 Literature Survey on the Degradation of Reactive Yellow 84	4
1.3 Photo-Fenton Oxidation.....	10
1.4 Oxidation in the Presence of TiO ₂ Catalyst and UV light	13
1.5 Literature survey of degradation of organic compounds on iron containing TiO ₂ and Ce doped TiO ₂ photocatalysts.....	15
1.6 Use of Sonication in The Degradation of Organic Compounds in Wastewater.....	20
1.7 Literature Survey on the Usage of Sonication in the Degradation of Organic Compounds in Wastewater.....	25
2. EXPERIMENTAL STUDY	31

TABLE OF CONTENTS (continued)

	<u>Page</u>
2.1 Catalysts Preparation.....	31
2.1.1 Synthesis of catalysts by incipient wetness impregnation method (x%Fe/TiO ₂ (IW))	31
2.1.2 Synthesis of catalysts by sol-gel method (x%Fe/TiO ₂ (SG))	31
2.1.3 Synthesis of iron containing TiO ₂ -Ce catalysts (x%Fe/TiO ₂ -Ce).....	32
2.2 Catalyst Characterization Studies	33
2.3 Degradation Experiments	33
2.3.1 Sonication experiments (Degradation with ultrasound, US, only)	34
2.3.2 SonophotoFenton degradation experiments	36
2.4 Toxicity Measurements	39
3. RESULTS AND DISCUSSION.....	40
3.1 Catalyst Characterization.....	40
3.1.1 X-ray diffraction studies.....	40
3.1.2 Crystallite size and anatase phase percentages of the samples.....	43
3.1.3 SEM studies	46
3.1.4 FT-IR spectroscopy studies	51
3.1.5 Nitrogen adsorption measurements.....	54

TABLE OF CONTENTS (continued)

	<u>Page</u>
3.1.6 UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS)	59
3.1.7 ICP-AES measurements	61
3.2 Degradation Studies of RY 84 by Ultrasound	62
3.2.1 Ultrasonic degradation of RY 84 in ultrasonic bath	62
3.2.2 Sonication of RY 84 in ultrasonic reactor	64
3.3 Catalyst Activity Experiments – Degradation Studies of RY 84 by SonophotoFenton Reaction	71
3.4 Degradation of RY 84 Using Individual and Combined Advanced Oxidation Processes	82
3.4.1 Effect of individual oxidation process	83
3.4.2 Effect of binary oxidation processes	84
3.4.3 Effect of ternary oxidation processes	85
3.5 Parametric Study with the Selected Catalyst	95
3.5.1 Effect of hydrogen peroxide concentration on the sonophotoFenton oxidation of RY 84	95
3.5.2 Effect of initial pH of the RY 84 solution on the sonophotoFenton oxidation of RY 84	99
3.5.3 Effect of initial dye concentration on the sonophotoFenton oxidation of RY 84	103

TABLE OF CONTENTS (continued)

	<u>Page</u>
3.5.4 Effect of temperature on the sonophotoFenton oxidation of RY 84.....	110
3.5.5 Effect of catalyst loading on the sonophotoFenton oxidation of RY 84	113
3.5.6 Effect of ultrasonic power on the sonophotoFenton oxidation of RY 84...	117
3.5.7 Optimum conditions.....	119
3.5.8 Catalyst Stability at the optimum conditions.....	120
3.5.9 Further experiments at the optimum conditions	123
3.6 Economical Evaluation.....	127
3.6.1 Determination of actual US power.....	128
3.6.2 Economical evaluation of different AOPs.....	129
3.7 Further Investigation of UV+catalyst+H ₂ O ₂ Oxidation of RY 84.....	130
3.7.1 Effect of H ₂ O ₂ concentration on the UV+catalyst+H ₂ O ₂ oxidation of RY 84.....	131
3.7.2 Effect of initial pH of dye on the UV+catalyst+H ₂ O ₂ oxidation of RY 84.	134
3.7.3 Effect of catalyst loading on the UV+catalyst+H ₂ O ₂ oxidation of RY 84.	137
3.7.4 Effect of initial dye concentration on the UV+catalyst+H ₂ O ₂ oxidation of RY 84.....	140
3.8 Comparison of sonophotoFenton oxidation with oxidation of RY 84 by UV+catalyst+H ₂ O ₂ combination	143

TABLE OF CONTENTS (continued)

	<u>Page</u>
3.9 Toxicity Measurements	144
4. CONCLUSION	146
REFERENCES	149

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1.1 Energy band diagram of a spherical titania particle	14
1.2 Bubble in a liquid irradiated with ultrasound	22
1.3 Growth and implosion of cavitation bubble in aqueous solution with ultrasonic irradiation.....	22
1.4 Three reaction zones in the cavitation process	23
2.1 Chemical structure of the C.I. RY 84 azo-dye.....	34
2.2 Experimental Set-up of ultrasonic bath.....	34
2.3 Experimental set-up of ultrasonic reactor.....	35
2.4 Experimental set-up for sonophotoFenton degradation of dye.....	37
2.5 Calibration curve of RY 84 in UV spectrophotometer	39
3.1 XRD patterns of catalysts synthesized by incipient wetness impregnation (IW) method of (r, rutile phase; a, anatase phase).	40
3.2 XRD patterns of catalysts synthesized by sol-gel method (a, anatase phase). .	41
3.3 XRD patterns for 1%Fe/TiO ₂ (IW) catalyst with different calcination temperatures.....	42
3.4 XRD patterns of different Fe/TiO ₂ -Ce catalysts (a, anatase phase).....	43
3.5 SEM micrographs of : (a) pureTiO ₂ (SG), (b) 0.5%Fe/TiO ₂ (SG), (c) 1%Fe/TiO ₂ (SG), (d) 2%Fe/TiO ₂ (SG), (e) 5%Fe/TiO ₂ (SG) catalysts at magnification 5000x and 50000x.....	48

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
3.6 SEM micrographs of : (a)TiO ₂ - P25, (b) 1%Fe/TiO ₂ (IW) 300°C, (c) 1%Fe/TiO ₂ (IW) 500°C, (d) 1%Fe/TiO ₂ (IW) 700°C, (e) 5%Fe/TiO ₂ (IW) catalysts at magnification 5000x and 50000x.....	49
3.7 SEM micrographs of : (a) pure TiO ₂ -Ce, (b) 1%Fe/TiO ₂ -Ce, (c) 5%Fe/TiO ₂ -Ce, catalysts at magnification 5000x and 50000x.	50
3.8 FTIR spectra of the catalysts synthesized by incipient wetness impregnation (IW) method.	52
3.9 FTIR spectra of the 1%Fe/TiO ₂ (IW) catalyst with different calcination temperatures.	52
3.10 FTIR spectra of the catalysts synthesized by sol-gel method.....	53
3.11 FTIR spectra of x%Fe/TiO ₂ -Ce catalysts.....	53
3.12 Classification of adsorption isotherms defined by IUPAC.	54
3.13 Nitrogen adsorption isotherms of catalysts synthesized by using the incipient wetness impregnation method.....	57
3.14 Nitrogen adsorption isotherms of catalysts synthesized by using the sol-gel method.....	57
3.15 Nitrogen adsorption isotherms of x%Fe/TiO ₂ -Ce catalysts.	58
3.16 UV-Vis DRS Spectra for the indirect band gap energy value of 5wt.%Fe doped TiO ₂ (IW) catalyst.	59
3.17 Plot of the band-gap energy vs. Fe loading of the catalysts.....	60

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
3.18 Effect of ultrasonic power on decolorization of 25 mg/L, 150 mL of RY 84 solution in ultrasonic bath.....	63
3.19 Effect of ultrasonic power on decolorization of 25 mg/L, 250 mL RY 84 solution in ultrasonic reactor.....	65
3.20 Effect of dye solution volume on decolorization of 25 mg/L of RY 84 solution at 75 W in ultrasonic reactor.	66
3.21 Effect of initial dye concentration on decolorization of 250 mL RY 84 solution at 75 W in ultrasonic reactor.	67
3.22 Effect of H ₂ O ₂ addition on decolorization of 25 mg/L, 250 mL RY 84 solution at 75 W in ultrasonic reactor.	68
3.23 Effect of H ₂ O ₂ addition on decolorization of 10 mg/L, 250 mL RY 84 solution at 75 W in ultrasonic reactor.	69
3.24 Effect of initial pH of the solution on decolorization of 10 mg/L of 250 mL RY 84 solution at 75 W in ultrasonic reactor.	70
3.25 SonophotoFenton degradation of RY 84 with the catalysts prepared by incipient wetness impregnation method (a) Time dependency of decolorization (b) Decolorization,% after 15 min and COD removal% after 120 min	72
3.26 SonophotoFenton degradation of RY 84 with the catalysts prepared by sol-gel method (a) Time dependency of decolorization (b) Decolorization,% after 15 min and COD removal% after 120 min.	74
3.27 SonophotoFenton degradation of RY 84 with the TiO ₂ -Ce supported catalysts (a) Time dependency of decolorization (b) Decolorization,% after 15 min and COD removal% after 120 min.....	76

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
3.28 First-order kinetic plots for the sonophotoFenton degradation of RY 84 at 20°C with (a) catalysts prepared by incipient wetness impregnation method (b) catalysts prepared by sol-gel method (c) Fe/TiO ₂ -Ce catalysts	78
3.29 Decolorization and COD reduction of RY 84 in the presence of individual processes.....	83
3.30 Decolorization and COD reduction of RY 84 in the presence of binary processes.....	85
3.31 Decolorization and COD reduction of RY 84 in the presence of ternary processes.....	86
3.32 Decolorization of RY 84 under different processes.....	87
3.33 Effect of H ₂ O ₂ on the US+UV+H ₂ O ₂ oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization,% in 15 and 120 min and COD removal% in 120 min	91
3.34 Pseudo-first-order kinetics for US+UV+H ₂ O ₂ oxidation of RY 84 at different H ₂ O ₂ concentrations.....	92
3.35 Effect of ultrasonic power on the US+UV+ H ₂ O ₂ oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization,% in 15 and 120 min and COD removal% in 120 min	93
3.36 Pseudo-first-order kinetics for US+UV+ H ₂ O ₂ oxidation of RY 84 at different H ₂ O ₂ concentrations.....	94
3.37 Effect of H ₂ O ₂ concentration on the sonophotoFenton oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization,% in 15 min and COD removal% in 120 min	97

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
3.38 Pseudo-first-order kinetics for the sonophotoFenton degradation of RY 84 at different H ₂ O ₂ concentrations	98
3.39 Effect of initial pH of the solution on the sonophotoFenton oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization,% in 15 min and COD removal% in 120 min.....	101
3.40 Pseudo-first-order kinetics for the sonophotoFenton degradation of RY 84 at different initial pH of the solution.....	102
3.41 Effect of initial pH of the solution on the pseudo-first-order rate constant.	103
3.42 Effect of initial dye concentration on the sonophotoFenton oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization,% in 15 min and COD removal% in 120 min.....	104
3.43 The change in the absorption spectrum of RY 84 (75 mg/L) during sonophotoFenton oxidation of dye in the presence of 1%Fe/TiO ₂ (IW) 300°C catalyst.	106
3.44 Pseudo-first-order kinetics for the sonophotoFenton degradation of RY 84 at different initial dye concentrations.....	107
3.45 Effect of initial RY 84 concentration on the initial rate of degradation. Inset: Langmuir-Hinshelwood kinetic linear representation of the sonophotoFenton oxidation of RY 84.....	109
3.46 Effect of temperature on the sonophotoFenton oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization,% in 15 min and COD removal% in 120 min	110
3.47 Pseudo-first-order kinetics for the sonophotoFenton degradation of RY 84 at different temperatures.....	112

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
3.48 Plot of $\ln k$ versus $1/T$	113
3.49 Effect of catalyst loading on the sonophotoFenton oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization,% in 15 min and COD removal% in 120 min	114
3.50 Pseudo-first-order kinetics for the sonophotoFenton degradation of RY 84 at different catalyst amounts	116
3.51 Effect of ultrasonic power on the sonophotoFenton oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization,% in 15 min and COD removal% in 120 min	117
3.52 Pseudo-first-order kinetics for the sonophotoFenton degradation of RY 84 at different ultrasonic power	119
3.53 Effect of reusability of catalyst at optimum conditions (a) Time dependency of decolorization (b) Decolorization,% in 15 min and COD removal% in 120 min	121
3.54 Pseudo-first-order kinetics for the fresh and reused catalysts at the optimum conditions	122
3.55 FTIR spectra of the fresh and reused catalysts.	123
3.56 Effect of initial dye concentration on the sonophotoFenton oxidation of RY 84 at the optimum conditions (a) Time dependency of decolorization (b) Decolorization,% in 15 min and COD removal% in 120 min.....	124
3.57 Pseudo-first-order kinetics for the sonophotoFenton degradation of RY 84 at different initial dye concentrations at optimum conditions	125

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
3.58 Effect of temperature on the sonophotoFenton oxidation of RY 84 at different initial dye concentration.....	126
3.59 Effect of US power on the sonophotoFenton oxidation of RY 84 at different initial dye concentrations (a) Time dependency of decolorization (b) COD removal% in 120 min	127
3.60 Calorimetric measurement for actual US power.....	129
3.61 Effect of H_2O_2 concentration on the UV+catalyst+ H_2O_2 oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization,% in 15 min and COD removal% in 120 min	132
3.62 Pseudo-first-order kinetics for the UV+catalyst+ H_2O_2 degradation of RY 84 at different H_2O_2 concentration.....	133
3.63 Effect of initial pH of dye on the UV+catalyst+ H_2O_2 oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization,% in 15 min and COD removal% in 120 min	135
3.64 Pseudo-first-order kinetics for the UV+catalyst+ H_2O_2 degradation of RY 84 at different initial pH	136
3.65 Effect of catalyst loading on the UV+catalyst+ H_2O_2 oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization,% in 15 min and COD removal% in 120 min	138
3.66 Pseudo-first-order kinetics for the UV+catalyst+ H_2O_2 degradation of RY 84 at different catalyst loading	139
3.67 Effect of initial dye concentration on the UV+catalyst+ H_2O_2 oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization,% in 15 min and COD removal% in 120 min.....	141

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Page</u>
3.68 Pseudo-first-order kinetics for the UV+catalyst+H ₂ O ₂ degradation of RY 84 at different initial dye concentrations.....	142
3.69 Comparison of UV+catalyst+H ₂ O ₂ with sonophotoFenton of RY 84.....	144
3.70 Toxicity test for RY 84.....	145

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1.1 Summary of Literature Survey about Degradation of Reactive Yellow 84	8
1.2 Summary of literature Survey about degradation of organic Compounds on Fe/TiO ₂ photocatalysts.....	18
1.3 Summary of Literature Survey about Usage of Sonication in the Degradation of Organic Compounds in Wastewater	29
3.1 Phase Composition and Crystalline Size ^a of samples	44
3.2 Nitrogen adsorption data of the prepared catalysts.....	56
3.3 Fe content of the catalysts measured by ICP analysis.....	61
3.4 The apparent first order rate constants and regression coefficients (R ²) for sonophotoFenton degradation of RY 84 at 20°C over prepared catalysts.....	79
3.5 Results summary of the sonophotoFenton degradation of RY 84 with the prepared catalysts	81
3.6 Iron leaching after 120 min sonophotoFenton oxidation of RY 84 with different iron containing catalysts.....	82
3.7 The apparent first order rate constants (k _{app} , min ⁻¹) and decolorization % of the oxidation systems	88
3.8 The apparent first order rate constants (k _{app} , min ⁻¹) and regression coefficient (R ²) for US+UV+H ₂ O ₂ oxidation of of RY 84 at different H ₂ O ₂ concentrations.....	92
3.9 The apparent first order rate constants (k _{app} , min ⁻¹) and regression coefficients (R ²) for US+UV+ H ₂ O ₂ oxidation of RY 84 at different US powers	94

LIST OF TABLES (Continued)

<u>Table</u>	<u>Page</u>
3.10 The apparent first order rate constants (k_{app} , min^{-1}) and regression coefficients (R^2) for sonophotoFenton degradation of RY 84 at different H_2O_2 concentrations	98
3.11 The apparent first order rate constants (k_{app} , min^{-1}) and regression coefficients (R^2) for sonophotoFenton degradation of RY 84 at different initial pH values of the solution	102
3.12 The apparent first order rate constants (k_{app} , min^{-1}) and regression coefficients (R^2) for sonophotoFenton degradation of RY 84 at different initial dye concentrations	107
3.13 The apparent first order rate constants (k_{app} , min^{-1}) and regression coefficients (R^2) for sonophotoFenton degradation of RY 84 at different temperatures	112
3.14 The apparent first order rate constants (k_{app} , min^{-1}) and regression coefficients (R^2) for sonophotoFenton degradation of RY 84 at different catalyst amounts	116
3.15 The apparent first order rate constants (k_{app} , min^{-1}) and regression coefficients (R^2) for sonophotoFenton degradation of RY 84 at different ultrasonic powers	119
3.16 First order rate constants, k_{app} , and the regression coefficients (R^2) for the sonophotoFenton degradation of RY 84 with fresh and reused catalysts at the optimum conditions	122
3.17 The apparent first order rate constants (k_{app} , min^{-1}) and regression coefficients (R^2) for sonophotoFenton degradation of RY 84 at different initial dye concentrations at optimum conditions	125

LIST OF TABLES (Continued)

<u>Table</u>	<u>Page</u>
3.18 Electric energy estimated for the COD reduction of RY 84 by different treatment methods after 2 h	129
3.19 Electric energy estimated for 100% decolorization of RY 84 with different oxidation systems	130
3.20 The apparent first order rate constants (k_{app} , min^{-1}) and regression coefficients (R^2) for UV+catalyst+ H_2O_2 degradation of RY 84 at different H_2O_2 concentration.....	133
3.21 The apparent first order rate constants (k_{app} , min^{-1}) and regression coefficients (R^2) for UV+catalyst+ H_2O_2 degradation of RY 84 different initial pH	136
3.22 The apparent first order rate constants (k_{app} , min^{-1}) and regression coefficients (R^2) for UV+catalyst+ H_2O_2 degradation of RY 84 at different catalyst loading	139
3.23 The apparent first order rate constants (k_{app} , min^{-1}) and regression coefficients (R^2) for UV+catalyst+ H_2O_2 degradation of RY 84 at different initial dye concentrations.....	142
3.24 Evaluation of degradation performance of UV+cat.+ H_2O_2 and sonophotoFenton hybrid system	144

1. INTRODUCTION

1.1 The Aim of the Study and Importance of Treatment of Textile Waste Water and the Treatment Techniques

Excessive water consumption is a big problem for textile industry; for instance, to treat 1 kg of cotton fiber commonly requires up to 80-100 L water. Such large volumes of water are needed mainly for dyeing and subsequently washing. So, due to residual dyes highly colored waste water is produced (Kritikos et al., 2007). Recycling of waste water would be an opportunity to decrease the cost of water management and benefit environmental and natural resources (Neamtu et al., 2004).

The concentration of dyes in waste water is usually lower than any other chemical present, but they often receive the main attention. Because their strong color makes them visible even at very low concentration, this causes serious aesthetic and pollution problems in wastewater disposal (Kritikos et al., 2007). Dyes also strongly absorb sunlight that enters the water, thus reducing the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem (Solmaz et al., 2006).

Due to their chemical structure, dyes obstruct the penetration of oxygen and cause the formation of some toxic products by hydrolysis (Dukkanci et al., 2010b).

Since dye molecules are stable and include large degree of aromatics, color removal is not possible with biological treatment methods. In addition, degradation is not occurred, the majority of dyes is only adsorbed on the sludge. Moreover, dyes are generally toxic for the bacteria and other microorganisms used in the biological treatment. For these reasons investigations about the color removal of dyes has been received attention. (Konstantinou and Albanis, 2004). Furthermore, it is reported that about 40–70% of chemical oxygen demand (COD) and color in textile finishing industry contaminants after conventional biological treatment are needed to be treated by advanced oxidation processes (Neamtu et al., 2004).

Efficiency of the color removal and degradation methods is variable for different textile waste water. The coagulation is effective for the insoluble dyes but does not effectively remove the color of soluble dyes. It is possible to obtain complete decolorization for almost all types of dye by using the ozonation as an oxidation process but it is not an effective method for COD removal. (Neamtu et al., 2000).

These are the reasons why advanced oxidation processes (AOPs) have been widely investigated in recent years since they are able to deal with the problem of degradation of dyes in the water. Waste water with COD contents lower than 5 g/L can be suitable for the application of AOPs, since higher COD contents would require the consumption of too large amounts of expensive reactants (Andreozzi et al., 1999; Pera-Titus et al., 2004).

Although AOPs have different reaction systems, they are all described by the same chemical feature: production of OH radicals (Andreozzi et al., 1999). OH radicals have the ability of reaction with most organic compounds rapidly. This species starts a sequence of oxidative degradation reactions to achieve the complete mineralization of organic contaminants (Neamtu et al., 2000).

Main AOPs proposed in the literature are UV, $\text{H}_2\text{O}_2/\text{UV}$, $\text{H}_2\text{O}_2/\text{TiO}_2/\text{UV}$, O_3/UV , Fenton's reactions and sonolysis. Combined use of heterogeneous photocatalysis with another AOP is considered to be cost-effective as long as this combination produces a synergistic effect (Bouras and Lianos, 2008).

Since the 1990s, Fenton and photo assisted Fenton reactions have been widely studied in the degradation of organic compounds in industrial wastewater. Generated hydroxyl radicals make this method effective. Hydroxyl radicals are highly reactive and are able to degrade many organic compounds. However, the production of Fe ion sludge with a large volume after Fenton and photo assisted Fenton reactions is a big problem because the removal of the Fe ions at the end of treatment by precipitation and redissolution is a costly process (Feng et al., 2003).

Heterogeneous photo-Fenton or photo-Fenton-like process with the use of Fe ions, Fe oxide or Cu loaded porous catalyst eliminates the disadvantage of the homogeneous photo-Fenton process (Banic et al., 2011). Fenton-like reactions take place over a wide range of pH values with the using the heterogeneous catalysts. This is because the Fe(III) species in the catalysts is stayed within the structure and in the pore/ interlayer space of the catalyst. As a result, the catalyst is active to continue the generation of hydroxyl radicals from H_2O_2 , and iron hydroxide precipitation is prevented. In addition to the low leaching level of iron ions, the catalysts can be recovered from the solution easily after the reaction, and can be efficiently used the during repeated operations (Garrido-Ramirez et al., 2010).

In heterogeneous catalytic systems, the use of ultrasound increases the turbulence in the liquid, so mass transfer limitations are decreased and available surface area increases due to catalyst fragmentation and de-agglomeration. However, combined use of sonication with other oxidation systems is not investigated so much. In recent years, the combination of ultrasound with photocatalysis (sonophotocatalysis) has been studied regarding process efficiency to degrade various organic compounds (Berberidou et al., 2007) and it is reported that sonophotocatalytic oxidation processes show interesting advantages at kinetic level since there is a synergistic effect between sonolysis and photocatalysis (Bejarano-Perez and Suarez-Herrera, 2007).

Considering the information above; in this work, we investigated the degradation of Reactive Yellow 84 by ultrasound assisted photo Fenton-like processes with Fe loaded TiO_2 and TiO_2 -Ce photocatalysts.

1.2 Literature Survey on the Degradation of Reactive Yellow 84

Reactive Yellow 84 (RY 84) is a widely used azo dye in textile finishing processes. In the literature, UV/H₂O₂ oxidation (Neamtu et al., 2002; Neamtu et al., 2000), ozonation (Koch et al., 2002), photo-Fenton and Fenton-like processes (Neamtu et al., 2003), catalytic wet peroxide oxidation (CWPO) (Neamtu et al., 2004), ozone assisted electrocoagulation (He et al., 2007a), sonolytic ozonation (He et al., 2007b), have been reported to destroy RY 84. However, degradation of the dye solution produces intermediates that compete with the dye for OH• radicals. Hence, decolorization measurement is not an enough evaluation for an overall degradation process. The overall degradation process involves the mineralization of dye and its intermediates. The most useful method of estimating the overall degradation is to measure the reduction of total organic carbon (TOC) or chemical oxygen demand (COD).

The goal of this study is to examine the effects of important variables such as pH, dosage of H₂O₂, initial dye concentration, energy density of ultrasound, UV light, catalyst amount and temperature, on the COD reduction of RY 84 by using sono-photo-heterogeneous Fenton-like process in the presence of iron containing TiO₂ as catalyst.

As far as we know there is no study in the literature about the degradation of Reactive Yellow 84 by the sono-photo-heterogeneous Fenton-like process over iron containing TiO₂ and Ce doped TiO₂ catalysts.

In the study Subash et al. (2013), degradation of RY 84 with strontium fluoride-loaded titania (SrF₂-TiO₂) catalyst under solar light was investigated. After 30 min of adsorption in dark they found 19% adsorption at the initial dye pH of 5. After 1 h of reaction time they observed 95% of COD reduction and 100% color removal.

Photocatalytic degradation of RY 84 and RB 5 over FeTiO₃/TiO₂ catalyst in the presence of UV-visible radiation and H₂O₂ had been reported in the study of Sivakumar et al. (2013). The photocatalytic activity of FeTiO₃/TiO₂ was found to be higher than pure TiO₂ and also the addition of H₂O₂ increased the rate of degradation. After 2 h of reaction time they observed, 100% color removal. COD reduction was found to be 71.2% and 76.2% for RY 84 and RB 5, respectively.

Decolorization of RY 84 by adsorption onto hydroxyapatite was studied by Barka et al. (2011). They obtained the maximum adsorption at the pH value of 5. Adsorption was found to be a low temperature dependency with an enthalpy of adsorption of 2.17 kJ/mol.

In another study of Barka et al. (2010), photocatalytic degradation of RY 84 using an industrial titania coated non-woven paper was studied. They observed that the photocatalytic degradation rate was favored by a high concentration of solution in respect to the Langmuir-Hinshelwood model. The maximum dye adsorption and photocatalytic degradation was high for pH<3. Photocatalytic degradation was found to be temperature sensitive with activation energy of 32.95 kJ/mol.

In the study of He et al. (2007a), they achieved a synergistic effect with the combination of electrocoagulation (EC) with ozone for the decolorization of RY 84. Over 97% of the color removal was achieved within 10 min of reaction time. When the complete color removal was obtained, TOC removal was more than 85%.

In another study of He et al. (2007b), mineralization of C.I. Reactive Yellow 84 (RY 84) in aqueous solution was investigated using sonolytic ozonation (US/O₃ oxidation). The maximum mineralization was achieved when the initial pH of the solution was 10.0. Decrease in the initial concentration of RY 84 caused an increase in the degradation rate. Increase in the ozone dose had a positive effect on the mineralization of RY 84 whereas; ultrasound density was slightly affected the mineralization. Observed TOC removals were 9%, 42% and 56% with US, O₃ and US/O₃, respectively. It was concluded that enhanced mass

transfer of ozone to accelerate its direct reactions with RY 8 increased the process efficiency.

In the study of Neamtu et al. (2004), catalytic wet hydrogen peroxide oxidation (CWPO) of Reactive Yellow 84 was investigated over Fe-Y_{11.5} and Fe-Y₅ zeolite. Optimum experimental conditions was obtained as pH= 5, Temperature= 50°C, 1 g/L of catalyst amount and 20 mmol/L H₂O₂, by using Fe-Y_{11.5} catalyst 96.90% of color removal, 70.70% of COD removal and 34.52% of TOC removal were obtained after 60 min of oxidation. On the other hand by using Fe-Y₅ catalyst after 60 min, 99.93% of color removal, more than 74.14% of COD and 64.21% of TOC removal were obtained. The catalysts showed almost complete decolorization of the dye and a significant COD and TOC reduction. Fe leaching was found to be very small.

In the study of Neamtu et al. (2003), degradation of C.I. Reactive Yellow 84 (RY 84) and C.I. Reactive Red 120 (RR 120) by photo-Fenton and Fenton-like oxidation were investigated. Effective system conditions were found to be a pH of 3, hydrogen peroxide-to-iron molar ratio of 20:1 and the presence of UV or solar irradiation. At the effective conditions; the color removal of RY 84 after 15 min reaction time follows the decreasing order: solar/Fe²⁺/H₂O₂ > UV/Fe²⁺/H₂O₂ > UV/Cu²⁺/Fe³⁺/H₂O₂ > UV/Fe³⁺oxalate/H₂O₂ > UV/Fe³⁺/H₂O₂ > dark/Fe²⁺/H₂O₂ > solar/Fe³⁺oxalat/H₂O₂ > UV/H₂O₂ > UV/Fe²⁺ = UV. More than 98% decolorization and 81% COD reduction were achieved with photo-Fenton (UV/Fe²⁺/H₂O₂) oxidation of RY 84 after 15 min of reaction time.

In another study of Neamtu et al. (2002), the photodegradation of three reactive azo dyes (Reactive red 120 (RR 120), Reactive black 5 (RB 5), Reactive yellow 84 (RY 84) was investigated with the UV/H₂O₂ technique. With a dose of 24.5 mmol/L H₂O₂ and a 60 min of (UV) irradiation time the decolorization was greater than 99.6% for all the three dyes. The mineralization rates were 58.5% for RY 84; 52.9% for RR 120 and 81.6% for RB 5, respectively. To use a H₂O₂ dosage higher than 24.5 mmol/L H₂O₂ was not cost effective.

In the study of Koch et al. (2002), ozonation of Reactive Yellow 84 (RY 84) was investigated. Complete color removal was achieved with ozone concentration of 18.5 and 9.1 mg/L, after 60 and 90 min, respectively. 30% of TOC/TOC_0 ratio was achieved with ozonation, the COD reduction was 50%. The BOD_5/COD ratio increased from 0.01 to about 0.8.

In the study of Neamtu et al. (2000) photodegradation of the Reactive Yellow 84 (RY 84) in water by the $\text{UV}/\text{H}_2\text{O}_2$ oxidation was studied. They observed that, with a H_2O_2 dose of 9.8 mmol/L, the $\text{UV}/\text{H}_2\text{O}_2$ process is 85 times faster than the UV process with a color removal of 99% after an irradiation time of 30 minutes. Complete decolorization was achieved after 60 minutes of reaction, with 0.98 mmol/L H_2O_2 , however TOC reduction was 73.42%.

Table 1.1 presents the summary of literature survey about degradation of RY 84.

Table 1.1. Summary of Literature Survey about Degradation of Reactive Yellow 84

Authors	Dye	Conc. of pollutant	Catalyst	Chemical oxidation process	Experimental conditions	Results and remarks
Subash et al., 2013	Reactive Yellow 84	500 mg/L	SrF ₂ -TiO ₂	Photocatalyst/solar light	50 mL of RY 84 pH 5 4g/L cat. Air flow rate 8.1 mL/s	19% adsorption at dark 100% color removal and 95% COD red. After 60 min
Sivakumar et al., 2013	Reactive Yellow 84	100mg/L	FeTiO ₃ /TiO ₂	Photocatalyst/H ₂ O ₂	50 mL 1 g/L cat. 6 mM H ₂ O ₂	100% color removal and 71.2% COD red. After 120 min
Barka et al., 2011	Reactive Yellow 84	10-40 mg/L	hydroxyapatite	adsorption	500 mL 0.4-1.6 g/L 20-50°C pH 2.1-10	Enthalpy of adsorption was 2.17 kJ/mol Adsorption was max at pH 5
Barka et al., 2010	Reactive Yellow 84	12 mg/L	TiO ₂ coated media	Photocatalytic degradation	500 mL 25°C pH 2-10	activation energy 32.95 kJ/mol adsorption was high in acidic medium (pH<3)
He et al., 2007a	Reactive Yellow 84	100 mg/L	-----	Electrocoagulation combined with ozonation	K ₂ SO ₄ 2000 mg/L, pH 6.5, ozone flow rate 20 mL min ⁻¹ , temperature 30 °C, current density 15 mA/ cm ² and interelectrode distance 3 cm.	color removal >97% after 10 min. TOC red.>85%
He et al., 2007b	Reactive Yellow 84	500 mg/L	-----	sonolytic ozonation (US/O ₃ oxidation)	US frequency 20 kHz PH 10 O ₃ dosage 4.5 g/h	increasing ozone dose increase the mineralization. TOC red. were 9%, with US 42% with O ₃ 56% with US/O ₃

Table 1.1 (Continued)

Authors	Dye	Conc. of pollutant	Catalyst	Chemical oxidation process	Experimental conditions	Results and remarks
Neamtu et al., 2004a	Reactive Yellow 84	100 mg/L	Fe-Y _{11.5} Fe-Y ₅	catalytic wet hydrogen peroxide oxidation (CWPO)	pH 5, Temperature 50°C, catalyst 1 g/L 20 mmol/L H ₂ O ₂ ,	After 60 min of oxidation Fe-Y _{11.5} catalyst color removal 96.90%, COD red.70.70% TOC red. 34.52% Fe-Y ₅ catalyst color removal 99.93%, COD red.> 74.14% TOC red.> 64.21%
Neamtu et al., 2003	Reactive Yellow 84	100 mg/L	-----	photo-Fenton and Fenton-like oxidation	pH 3, hydrogen peroxide-to-iron molar ratio of 20:1 15 W UV lamp or solar irradiation	color removal after 15 min solar/Fe ²⁺ /H ₂ O ₂ > UV/Fe ²⁺ /H ₂ O ₂ > UV/Cu ²⁺ /Fe ³⁺ /H ₂ O ₂ > UV/Fe ³⁺ oxalate/H ₂ O ₂ > > UV/Fe ³⁺ /H ₂ O ₂ > dark/Fe ²⁺ /H ₂ O ₂ > solar/Fe ³⁺ oxalat/H ₂ O ₂ > > UV/H ₂ O ₂ > UV/Fe ²⁺ = UV . With photo-Fenton (UV/Fe(II)/H ₂ O ₂) oxidation color removal> 98% COD red. 81% , after 15 min
Neamtu et al., 2002	Reactive Yellow 84 Reactive red 120, Reactive black 5	100 mg/L	-----	UV/H ₂ O ₂	15 W UV lamp 24.5mM H ₂ O ₂	TOC red. after 60min 58.5% for RY 84; 52.9% for RR 120 and 81.6% for RB 5, decolorization > 99.6% hydrogen peroxide dosage higher than 24.5 mmol/L was not cost effective.

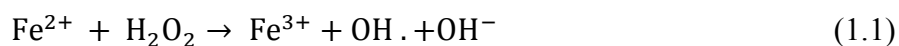
Table 1.1 (Continued)

Authors	Dye	Conc. of pollutant	Catalyst	Chemical oxidation process	Experimental conditions	Results and remarks
Koch et al. (2002)	Reactive Yellow 84	200 mg/L	-----	ozonation	PH 3.3 ozone/air stream 20 l/h initial conditions: COD 160 mg/L BOD5/COD 0.01 pH 6.3 TOC 45 mg/L	Decolorization was almost complete after 60 min with 18.5 mg/L ozone after 90 min with 9.1 mg/L, ozone. 30% of TOC/TOC ₀ ratio was achieved with ozonation, the COD reduction was 50%. The BOD ₅ /COD ratio increased from 0.01 to about 0.8.
Neamtu et al., 2000	Reactive Yellow 84	100 mg/L	-----	UV/H ₂ O ₂	25°C 15 W UV lamp 0.98 mmol/L H ₂ O ₂	Complete color removal and 73.42% TOC red. were achieved

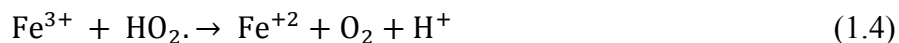
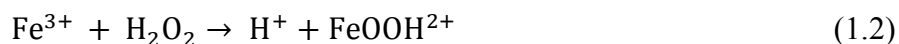
1.3 Photo-Fenton Oxidation

In the last century, it was reported by Fenton that, ferrous ions strongly promote the oxidation of malic acid by hydrogen peroxide (Fenton, 1894). After then, it has been demonstrated that combination of H₂O₂ and ferrous salt which is called “Fenton’s reagent” is able to destroy toxic organic compounds in waste water.

With the addition of H₂O₂ to Fe²⁺ salts hydroxyl radicals are produced. Hydroxyl radicals are powerful oxidizing reagents with an oxidation potential of 2.33 V and exhibit faster rates of oxidation reactions as compared to that using conventional oxidants like hydrogen peroxide or KMnO₄. Hydroxyl radicals react with most organic and many inorganic solutes with high rate constants (Gogate and Pandit, 2004). In the Fenton’s reaction, hydroxyl radicals are generated by the catalytic decomposition of H₂O₂ in acidic medium (pHs 2–5) (Oliveros et al., 1997).



Fe^{3+} can then react with hydrogen peroxide in the so called Fenton-like reaction and reduced to Fe^{2+} (Eqns 1.2–1.4),



The advantages of this system are; it is a very easy way of producing OH radicals, OH radicals have a high oxidation potential and can oxidize several compounds (Gogate and Pandit, 2004), Fe is very abundant and non-toxic element and H_2O_2 is easy to find and environmentally safe (Andreozzi et al., 1999).

Also the following reactions take place which negatively affect the oxidation process:



Photo-Fenton oxidation is the photocatalytically enhanced version of the Fenton process. OH radicals are produced using $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ system in the Photo-Fenton process. UV light irradiation causes an increase in the $\text{HO} \cdot$ formation rate and efficiency via photo reduction of Fe^{3+} to Fe^{2+} , thus further reacts with more hydrogen peroxide molecules as long as H_2O_2 is available (Arslan-Alaton et al., 2010; Pignatello, 1992; Torrades et al., 2004).

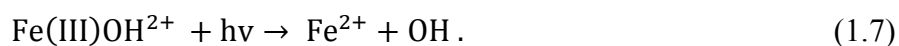
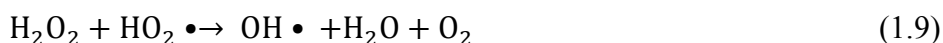


Photo-Fenton-like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$) oxidation has been studied with fewer researchers when compared to Photo-Fenton process, although reaction efficiency is thought to be practically same with that of the Photo-Fenton process due to the fact that the rate-limiting step of Fe-based advanced oxidation processes is the

relatively slow catalytic reaction between ferric ion and hydrogen peroxide (Arslan-Alaton et al., 2010).

On the other hand when Fenton reaction is in combination with UV light, the O-O bond in a hydrogen peroxide is cleaved by light to produce two hydroxyl radicals, and following reactions can take place:



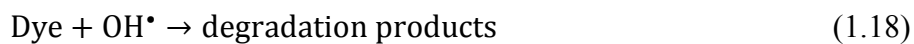
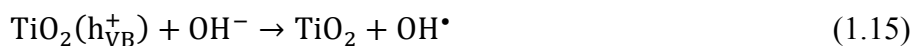
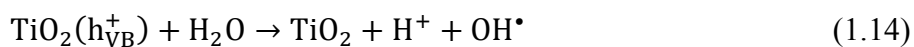
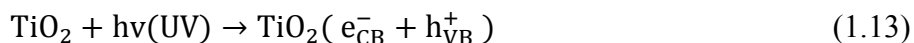
Reaction in the Eq. 1.8 is the rate-limiting reaction, because this reaction rate is much slower than others. Theoretically in UV/H₂O₂ process, as the amount of initial H₂O₂ concentration increases concentration of generated hydroxyl radical increases and thus the amount of decomposition of target organic compound also increases. However, excess hydrogen peroxide would react with hydroxyl radicals and formed less reactive perhydroxyl radicals (Eq. 1.5) (Dutta et al., 2001; Torrades et al., 2004).

It should be kept in mind that the homogeneous Fenton process has a significant disadvantage. For homogeneous catalytic reactions up to 50–80 mg/L of Fe ions are needed in the solution, this is above the European Union directives which allows only 2 mg/L of Fe ions in treated water to give directly into the environment (Sabhi and Kiwi, 2001). Moreover, at the end of the treatment a sludge-containing Fe ions is produced and it is expensive and needs large amount of chemicals and manpower to remove this sludge (Ramirez et al., 2007a). To overcome the disadvantages of the homogeneous Fenton process, heterogeneous catalysts, prepared by adding Fe ions or Fe oxides into porous supports had been started to investigate.

1.4 Oxidation in the Presence of TiO₂ Catalyst and UV light

When TiO₂ is irradiated with light energy greater than its band gap energy (E_g , 3.2 eV), conduction band electrons (e^-) and valence band holes (h^+) are generated. (Figure 1.1)

Dye could be reduced by photogenerated electrons or photogenerated electrons react with electron acceptors such as O₂ adsorbed on the Ti(III)-surface, and this reaction produces the superoxide radical anion O₂^{•-}. The photogenerated holes can oxidize the organic molecule to form R⁺, or react with OH⁻ or H₂O oxidizing them into OH[•] radicals. OH[•] radicals and peroxide radicals are reported to be responsible for the heterogeneous TiO₂ photodecomposition of organic substrates as dyes. The degradation reactions at the TiO₂ surface can be expressed as follows:



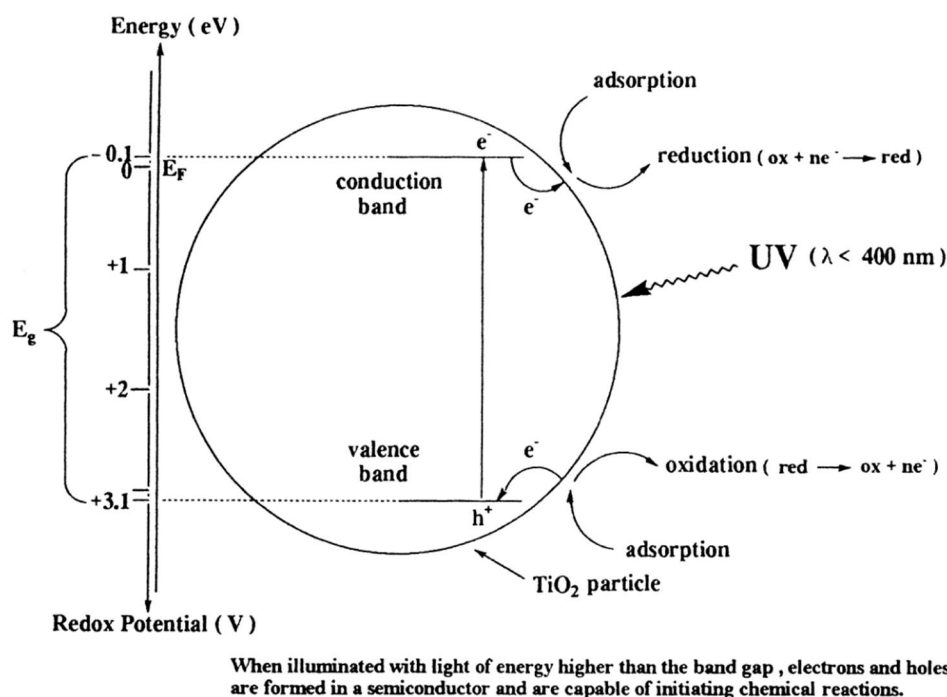


Figure 1.1. Energy band diagram of a spherical titania particle (Herrmann, 1999)

The key advantage is its inherent destructive nature: it does not include mass transfer; it can be used at ambient conditions and complete mineralization can be achieved. In addition, TiO_2 photocatalyst is easy to find, inexpensive, non-toxic and shows relatively high chemical stability. (Konstantinou and Albanis, 2004). However, rate limiting factor controlling the photocatalytic efficiency is the high degree of recombination of electrons and holes (Yu et al., 2009). Doping of metal ions such as Fe, Pt, Mo, V, and Ag (transition metals and noble metals) into TiO_2 reduces the recombination rate so that this application improves the degradation efficiency and degradation rate of organic contaminants in aqueous solutions (Parshetti and Doong, 2011). Added metal ions may act as electron or hole traps and, as a result, change the electron-hole pair recombination rates (Piera et al., 2003).

When Fe or other metals are added to the TiO_2 the surfacial complexing properties may change. The formation of surfacial complexes in photochemical reactions may exhibit charge-transfer absorption bands in ranges similar to those corresponding to homogeneous complexes, and similar photolytic behaviors. The use of these semiconductors is very interesting because they both exhibit

homogeneous and heterogeneous catalytic properties (Arana et al., 2002). The association of the catalyst ability to give highly active radicals with the complexing capacity of the dopant has been observed by Fe-doped catalysts (Arana et al., 2001).

1.5 Literature survey of degradation of organic compounds on iron containing TiO₂ and Ce doped TiO₂ photocatalysts

Souza et al., (2011) investigated the photocatalytic discoloration of Reactive Blue 5G. They observed the discoloration was completed 100% with the use of 8.8% Ag/CeO₂-TiO₂-Al₂O₃, 8.6% Fe/CeO₂-TiO₂-Al₂O₃ and pure TiO₂. Ordering of 100% discoloration was Fe/CeO₂-TiO₂-Al₂O₃ < Ag/CeO₂-TiO₂-Al₂O₃ < TiO₂.

Methylene blue (MB) was chosen by Buddee et al., (2011) for the photocatalytic activity test of Cr-TiO₂, Fe-TiO₂ and commercial TiO₂ samples. Under UV irradiation after 5h, decolorization efficiency of 0.1 mol% doped TiO₂ was the same with commercial TiO₂ samples (P25 and anatase). Under visible light the use of doped sample was more effective than both P25 and anatase.

It is shown by Shi et al. (2011) that, Ce doping (optimum doping value is 0.15 mol%) increases the photocatalytic activity of TiO₂/Fe₃O₄ for phenol degradation. Degradation of phenol reaches about 93% after 4 hour of irradiation time with the 0.15 mol% Ce-TiO₂/Fe₃O₄. Degradation of phenol was ≈85% and ≈78% with TiO₂ and TiO₂/Fe₃O₄, respectively. They also tested the cycling usage of the 0.15 mol% Ce-TiO₂/Fe₃O₄ and found that degradation percentage of phenol was still higher than 85% after used for four times.

In the study of Zhao et al. (2011), catalytic wet hydrogen peroxide oxidation of H-acids with the TiO₂-CeO₂ and Fe/TiO₂-CeO₂ catalysts was investigated. Most effective catalysts were found to be TiO₂-CeO₂ with the Ti/Ce ratio of 9/1 and Fe/TiO₂-CeO₂ with Ti/Ce 9/1, 2% Fe. Using the TiO₂-CeO₂ (Ti/Ce 9/1) catalyst color removal was 89.1% whereas COD and TOC reductions were 69.6% and 35.8%, respectively. Using the Fe/TiO₂-CeO₂ (Ti/Ce 9/1, 2%) under the same

reaction conditions they achieved 98.1%, 89.6% and 65.4%, color removal, COD and TOC reductions, respectively.

In the study of Liu et al. (2006), catalytic wet hydrogen peroxide oxidation of methyl orange with the Fe_2O_3 - CeO_2 - TiO_2 / γ - Al_2O_3 catalysts was investigated for the optimization of the preparation conditions of the catalysts and found 1.0wt% as an optimum Ti doping amount, calcination temperature and time were 450°C for 2 h, respectively. For the catalytic activity measurements; catalytic wet air oxidation (CWAO) process was chosen for treating actual dye wastewater with main dye of Reactive Black 5. They obtained 50.12% color, 62.23% COD, and 41.26% TOC removal in 3 h. Also, BOD_5/COD was increased from 0.19 to 0.30. They also observed that Fe was located on the catalyst surface as Fe_2O_3 , and Ce and Ti existed as compounds in oxides form, CeO_2 and TiO_2 .

In the study of Feng et al. (2004), the photocatalytic activities of Fe^{3+} doped TiO_2 nanocatalysts for the color removal and mineralization of Orange II in the presence of UVC light and O_2 were investigated. It was observed that the 0.05 at.% Fe^{3+} -doped TiO_2 nanocatalyst was the most effective catalyst for both TOC reduction and decolorization, more than 75% TOC removal was achieved after 150 min. When compared to the undoped TiO_2 , it was shown that Fe loading increased the photocatalytic activity to an optimum loading. 100% color removal was achieved with the 0.05 at.% Fe^{3+} - doped TiO_2 after 150 min. Higher Fe^{3+} dopant concentration decreased the activity.

In the study of Arana et al. (2003), formic acid degradation was studied. They found the catalyst with lower Fe content (0.5 wt.%) and prepared from $\text{Fe}(\text{NO}_3)_3$ by the incipient wetness impregnation method to be more active than the undoped TiO_2 and the Fe-doped catalysts prepared by other methods. They also observed that, the photoactivity of the formed complexes was affected with the catalyst preparation method. Formed complexes with the interaction of Fe^{3+} with formic and maleic acids could generate the degradation of corresponding acid much more quickly than the undoped TiO_2 . After the degradation Fe^{2+} ions that remain in solution turn back to the catalyst surface due to their reaction with the photogenerated holes in the TiO_2 . As a result the catalyst is reactivated

In another study of Arana et al. (2002) it was shown that the interaction of maleic acid with Fe^{3+} ions gives photoactive complexes. The formation of these complexes results in the extraction of iron from the catalyst surface which is found as Fe_2O_3 . Degradation of these complexes produces CO_2 , H_2O and also Fe^{2+} ions. They proposed that Fe^{2+} ions turned back to the catalyst surface by means of their interaction with generated holes, and the catalyst could be used again. They showed that at the lower Fe content (0.15Fe-TiO₂ and 0.5Fe-TiO₂) degradation was faster than undoped TiO₂.

In the study of Ranjit and Viswanathan (1997), photocatalytic reduction of nitrite and nitrate ions on Fe doped TiO₂ was investigated. They prepared the catalysts by using two different methods, coprecipitation and sol-gel. Sol-gel-derived Fe-doped catalysts showed the presence of rutile and pseudobrookite phases, whereas coprecipitated catalysts showed only the anatase phase of TiO₂. For the sol-gel derived catalysts, there is an optimum iron content in the photocatalytic activity. 1.48 wt.% of Fe doped catalyst showed the maximum activity. Catalytic activity was very low to be negligible with high Fe doped sample (1.76 wt% Fe). They concluded that an increase in iron content favored electron-hole separation and therefore enhanced the photoactivity. However, after a certain level, all of the electromagnetic radiation was absorbed by iron oxide surface and the core phase cannot be activated directly, the space charge layer becomes thicker, and the probability of carrier recombination is increased.

Table 1.2 presents the summary of literature survey about degradation of organic compounds on Fe/TiO₂ photocatalysts.

Table 1.2. Summary of literature Survey about degradation of organic Compounds on Fe/TiO₂ photocatalysts

Authors	Contaminants degraded	Conc. of pollutant	Catalyst	Chemical oxidation process	Experimental conditions	Results and remarks
Souza et al., 2011	Reactive blue 5G	70 mg/L	Fe/CeO ₂ -TiO ₂ -Al ₂ O ₃ Ag/CeO ₂ -TiO ₂ -Al ₂ O ₃ -TiO ₂ .	Photocatalytic oxidation	125 W medium pressure UV lamp. Wetness impregnation	100% discoloration order is Fe/CeO ₂ -TiO ₂ -Al ₂ O ₃ < Ag/CeO ₂ -TiO ₂ -Al ₂ O ₃ < TiO ₂ .
Buddee et al., 2011	Methylene blue (MB)	2.5x10 ⁻⁵ M	Cr-TiO ₂ , Fe-TiO ₂ , TiO ₂	Photocatalytic oxidation	Modified impregnation	After 5 h decrease in dye concentration for *commercial TiO ₂ P25 is ≈96% * 0.1Cr-TiO ₂ , 0.1Fe-TiO ₂ and Anatase TiO ₂ is ≈92%
Shi et al., 2011	Phenol	50 mg/L	Fe-TiO ₂ , TiO ₂ /Fe ₃ O ₄ , Ce-TiO ₂ /Fe ₃ O ₄	Photocatalytic oxidation	20 W UV lamp	Degradation of phenol concentration ≈85% with TiO ₂ ≈78% with TiO ₂ /Fe ₃ O ₄ , 93% with 0.15 mol% Ce-TiO ₂ /Fe ₃ O ₄ after 4 h.
Zhao et al., 2011	H-acids	10 g/L	TiO ₂ -CeO ₂ , Fe/TiO ₂ -CeO ₂	CWPO	reaction temperature 100 °C, atmospheric pressure, catalyst 1.0 g, H ₂ O ₂ amount 17.6 mL and reaction time 90 min,	TiO ₂ -CeO ₂ (Ti/Ce 9/1) catalyst 89.1% color removal, 69.6% COD and 35.8% TOC reductions Fe/TiO ₂ -CeO ₂ (Ti/Ce 9/1, 2%) 98.1% color removal, 89.6% COD and 65.4% TOC reductions
	methyl orange	500 mg/L		CWPO	Reaction Temperature 25°C, atmospheric pressure, catalyst 3.0 g, H ₂ O ₂ amount 33mg/100mL water	optimum Ti doping 1.0wt% optimum calcination temperature and time 450°C for 2 h.
Liu et al., 2006	Actual dye waste water (the main dye of Reactive Black 5)	COD 915.2 mg/L BOD 171.6 mg/L	Fe ₂ O ₃ -CeO ₂ -TiO ₂ /γ-Al ₂ O ₃	CWAO	PH 7-8 bubbled air at 50°C normal pressure catalysts 3 g 100 mL of dye wastewater air flow rate 400 mL/min	50.12% color, 62.23% COD, and 41.26% TOC removal in 3 h. BOD ₅ /COD was increased from 0.19 to 0.30

Table 1.2 (Continued)

Authors	Contaminants degraded	Conc. of pollutant	Catalyst	Chemical oxidation process	Experimental conditions	Results and remarks
Feng et al., 2004	Orange II	0.2 mM	Fe ³⁺ -doped TiO ₂	UV assisted CWAO	8 W UVC at the center of the reactor normal pressure catalysts 3 g 0.4 L of dye wastewater air flow rate 10 L/min	0.05 at.% Fe ³⁺ - doped TiO ₂ color removal 100% TOC removal >75% after 150 min which is similar with the photocatalytic activity of Degusa P25. Degusa 25 > 0.05 at.% Fe ³⁺ TiO ₂ > 0.1 at.% Fe ³⁺ TiO ₂ > 0.5 at.% Fe ³⁺ TiO ₂ > undoped TiO ₂ > 1.0 at.% Fe ³⁺ TiO ₂ > only UVC
Arana et al., 2003	formic acid	50 mg/L	Fe-TiO ₂	Photocatalytic oxidation	800 W Xe UV lamp Incipient wetness impregnation Sol-gel	0.5Fe- TiO ₂ prepared from Fe(NO ₃) ₃ by the incipient wetness impregnation method is the most photoactive catalyst TOC reduction time of the catalysts: 0.5Fe- TiO ₂ 0.45 h bare TiO ₂ 1 h 5Fe- TiO ₂ 1.5 h
Arana et al., 2002	Maleic Acid	50 mg/L	Fe-TiO ₂	Photocatalytic oxidation	800 W Xe UV lamp Incipient wetness impregnation	100% TOC reduction 0.15Fe- TiO ₂ at 2h 0.5Fe- TiO ₂ at 2.5 h TiO ₂ at 5 h 2Fe- TiO ₂ at 5.5 h 5Fe- TiO ₂ TOC degradation is ≈65% after 5.5 h
Ranjit and Viswanathan, 1997	nitrite and nitrate ions	-----	Fe-TiO ₂	Photocatalytic oxidation	450 W Xe Lamp coprecipitation and sol-gel.	Sol-gel- Fe-doped catalysts showed rutile and pseudobrookite phases, coprecipitated catalysts showed only the anatase Anatase to rutile phase transformation is dependent on the nature of precursor. For the sol-gel derived catalysts, there is an optimum iron content in the photocatalytic activity

1.6 Use of Sonication in the Degradation of Organic Compounds in Wastewater

The main aim is to generate more free radicals with the AOPs therefore, various combinations of AOPs have been investigated and reported in literature. Combination of Ultraviolet (UV) irradiation and ultrasound (US) irradiation together with heterogeneous catalysts and oxidizing agents (i.e. Fenton reagent, hydrogen peroxide (H_2O_2) and ozone) is the most popular combination to increase the efficiency and decrease the operating cost (Pera-Titus et al., 2004). The combined use of ultrasound with other AOPs or conventional biological processes has been found to be effective in toxicity reduction. Different combinations like H_2O_2 , ozone, UV, photocatalysis and solution chemistry modification enhance the efficiency of free radical generation through cavitation (Adewuyi, 2001).

Sonochemistry enhances or promotes chemical reactions and mass transfer. Reaction cycles gets shorter, cheaper reagents and less extreme physical conditions are required as a result less expensive and perhaps smaller plants are required (Adewuyi, 2001).

Since 1990, use of ultrasound to degrade the organic contaminants in wastewater has been investigated increasingly. Use of ultrasound in the wastewater treatment has the advantages of safety, cleanness, high penetrability in water medium, high degradation efficiency and energy conservation without generation of any other pollutants (Pang et al., 2011).

However, to obtain total mineralization is difficult with the use of ultrasound alone. Moreover, where the final products are determined to be carbon dioxide, short-chain organic acids, and/or inorganic ions to obtain the complete mineralization, the reaction time and the required power are not economically or practically acceptable. Therefore, combined use of ultrasound with other AOPs or conventional biological processes is found to be effective. Sonication improves mass transfer and chemical reaction and is expected to reduce or eliminate chemical usage, resulting in minimal sludge and disposal problems (Adewuyi, 2001).

Ultrasound occurs at a frequency above 16 kHz, which is higher than the ability of hearing of the human ear, and is typically associated with the frequency range of 20 kHz to 500 MHz (Thompson and Doraiswamy, 1999).

When ultrasonic (or sonic) energy applied to a liquid, a “cold boiling” termed cavitation takes place. Cavitation is the formation, growth, and sudden collapse of bubbles in liquids. Ultrasonic vibration reduces the thickness of liquid films, enhances gas transfer, and reduces bubble coalescence, which increases the interfacial area for gas transfer. For example, the diffusion of liquids through porous media is enhanced by ultrasound (Adewuyi, 2001).

In the sonochemical oxidation techniques sonic or ultrasonic waves are used to produce an oxidative environment with cavitation that generate localized microbubbles and supercritical regions in the aqueous phase. The collapse of these bubbles leads to high local temperatures and pressures. Locally, the high temperature and pressure may reach up to and above 5000 K and 1000 atm, respectively. These conditions continued very shortly but this short time is enough to generate highly reactive species including hydroxyl ($\text{OH}\bullet$), hydrogen ($\text{H}\bullet$) and hydroperoxyl ($\text{HO}_2\bullet$) radicals, and H_2O_2 . With these radicals it is available to initiate or promote many fast reduction-oxidation (REDOX) reactions. These reactions with inorganic and organic substrates are fast and often near the diffusion-controlled rate.

In Figure 1.2, cavitation bubble in a liquid irradiated with ultrasound is shown. Cavitation bubbles will grow over a few cycles by entrapping most of the vapor from the medium to reach a critical size before the implosion of the bubbles occurs (shown in Figure 1.3). The radius of the bubble before collapsing when irradiated at 20 kHz is estimated to be in the order of several hundred micrometers. The collapse of bubbles is occurred within the time than 100 ns. The critical size of cavitation bubbles formed in water is inversely proportional to the frequency of the ultrasound (Pang et al., 2011).

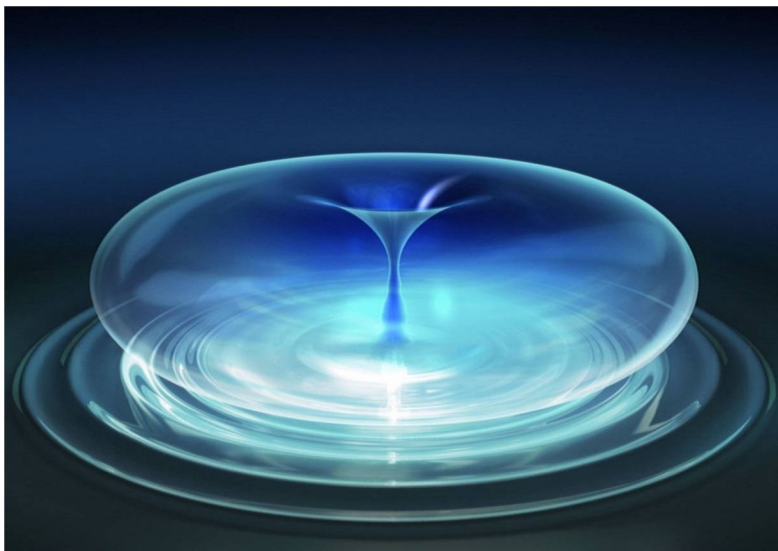


Figure 1.2. Bubble in a liquid irradiated with ultrasound (Brown and Wren, 2015)

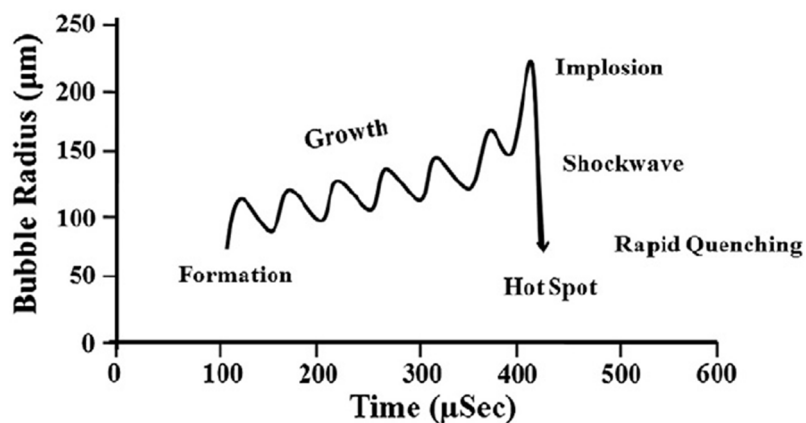


Figure 1.3. Growth and implosion of cavitation bubble in aqueous solution with ultrasonic irradiation (Pang et al., 2011).

In the “structured hot spot” model shown in Figure 1.4 (Adewuyi, 2001), three regions for the occurrence of chemical reactions have been defined:

The first is a gas phase cavity in this part extremely high temperature and pressure are occurred on the order of 5000 K and on the order of 1000 atm, respectively. In this high temperature and pressure condition, water molecules dissociate into $\text{OH}\cdot$ and $\text{H}\cdot$. The radicals can be recombined or reacted with other

gaseous substrates within the cavity. When the volatile substrate is taken into the cavity, its main decomposition reaction pathway may be pyrolysis within the cavitation bubble.

The second region is the interfacial zone between the gas phase and the bulk solution. In this region also large temperature ($\approx 2000\text{K}$) and pressure gradients exist. In the second region substrate can be degraded by two reaction pathways, either by oxidation with $\text{OH}\cdot$ or by thermal reaction.

The third possible reaction region is the bulk solution media. Pollutants are degraded with ultrasonically produced bubbles of $\text{OH}\cdot$ diffusing into the bulk solution. So, the reaction zone where the substrate is degraded depends on its chemical nature, like, its volatility, solubility, and chemical structure (Nam et al., 2003).

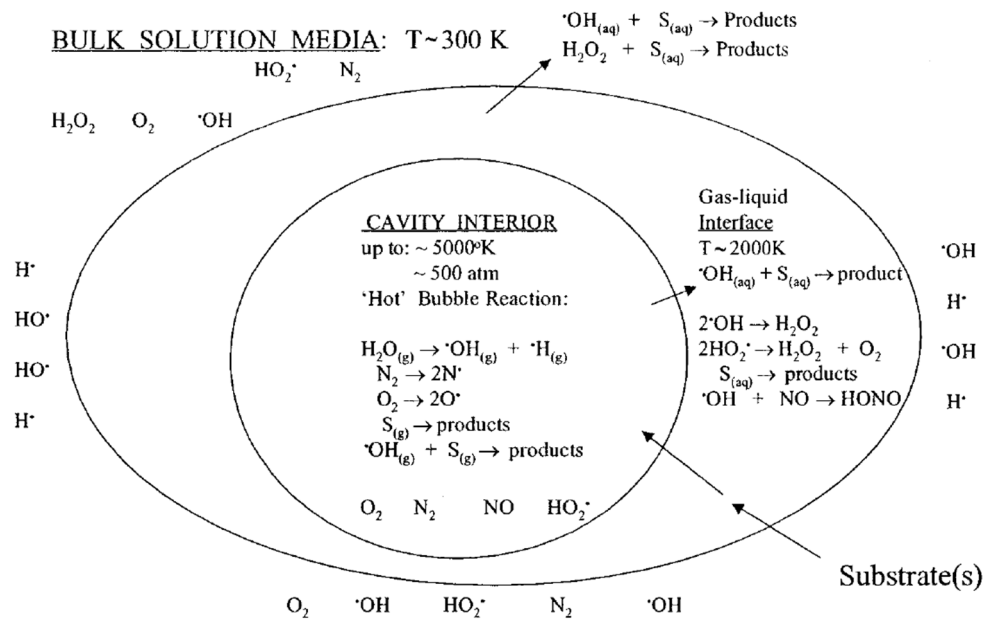


Figure 1.4. Reaction regions in the cavitation process (Adewuyi, 2001).

Reactions occurring during the sonication of water are listed above (where))) represents ultrasound):



The sonochemical degradation of azo dyes has been studied by many researchers worldwide. However, to obtain the complete mineralization is not so possible in short reaction times. Some possible reasons of this long reaction time are, formation of hydrophilic intermediate products, volatility of the pollutants, and reaction volume. Therefore, the combination of sonolysis with other advanced oxidation processes could be suitable to overcome the limitations. The combined use of ultrasound with photocatalysis (sonophotocatalysis) is a suitable application because sonolysis is able to degrade the hydrophobic products and photocatalysis can degrade the hydrophilic products (Madhavan et al., 2010b).

1.7 Literature Survey on the Usage of Sonication in the Degradation of Organic Compounds in Wastewater

In the study of Jamalluddin and Abdullah (2011), sonocatalytic degradation of Reactive Blue 4 (RB4) dye with the Fe(III)/TiO₂ catalyst, it was observed that 0.4 mol% Fe(III)/TiO₂ catalyst with a calcination temperature of 500°C showed the highest sonocatalytic activity. Used catalyst amount was also investigated and obtained removal efficiencies of RB4 within 60 min were 50%, 82%, 90% with the catalyst amount of 0.5 g/L, 1.0 g/L, and 1.5 g/L, respectively. Further increase in the catalyst content up to 2.0 g/L slightly decreased the removal of RB4. They showed also, the removal of RB4 decreased with the increase in initial dye concentration. Finally increase in sonocatalytic degradation was obtained with the continuously introducing air into the RB4 solution. Removal percentages of RB4 at catalyst dosage of 1.5 g/L, initial dye concentration of 70 mg/L and pH 4 are 96% with the US+airation+0.4 mol% Fe(III)/TiO₂ catalyst system; ≈88% with US+catalyst; ≈18% with US+aeration and ≈10% with US only.

In the study of Madhavan et al. (2010a), the sonolytic, photocatalytic and sonophotocatalytic degradation of acid red 88 (AR88) in the presence of homogeneous (Fe³⁺) and heterogeneous (TiO₂) photocatalysis was studied. Sonophotocatalytic degradation efficiency was found to be greater than that observed with sonolysis or photocatalysis alone. The synergy index calculated for TiO₂ sonophotocatalysis was 1.3, it can be said that the combined use of sonolysis with TiO₂ resulted in a small synergetic effect. Photocatalytic TOC removal using

TiO₂ was achieved 93% in 4 h. Sonophotocatalysis achieved higher TOC removal than the individual processes. No significant TOC removal was also observed during the sonolysis and photolysis process in the presence of Fe³⁺. However, 7% TOC removal was measured for the sonophotocatalysis until 2 h of irradiation and at the end of 4 h 37% mineralization was obtained by using Fe³⁺. The sonophotocatalysis in the presence of Fe³⁺ was synergistic with a synergy index of 2.3.

In the study of Yuan et al. (2009), sonophotocatalytic degradation of methylene blue (MB) was investigated. As the catalyst TiO₂ nanotube array was used, it was observed that degradation was highly affected by ultrasonic frequency. When the frequency increased from 18 kHz to 27 kHz, the reaction rate constant increased from 0.9×10^{-4} to $7.2 \times 10^{-4} \text{ min}^{-1}$ however when the frequency increased from 27 kHz to 30 kHz, the reaction rate constant sharply decreased from 7.2×10^{-4} to $1.4 \times 10^{-4} \text{ min}^{-1}$. The reaction rate constants of degradation in the presence or absence of TiO₂ and UV light are significantly higher at 27 kHz than at other frequencies. At the frequency of 27 kHz, after 3 h degradation of MB is about 53%, 34%, 12% and 3% with US+UV+TiO₂, US+TiO₂, US only, and UV+TiO₂, respectively. With the use of formulation in the study, synergistic effect between ultrasound and UV at 24 and 27 kHz were calculated to be 12.4% and 22.1%, respectively.

In the study of Maezawa et al. (2007), sonolytic and photocatalytic degradation of Acid Orange 52 was studied. They achieved the complete color removal within the 480 min with sonolysis whereas it was 35% in 480 min with photocatalytic degradation. On the other hand, TOC removal was only 13% in 480 min with sonolytic degradation. When the ultrasound combined with photocatalysis complete color removal was achieved within 240 min and TOC removal was 87% in 480 min. These results indicated that the ultrasonic irradiation enhanced the photocatalytic degradation. Photocatalytic efficiency decreased with the addition of chloride ion (50 mg/L) into Acid Orange 52 solution. In the sonolysis and sonophotocatalysis oxidation, chloride ion did not change the decomposition efficiency significantly.

In the study of Kritikos et al. (2007) photocatalytic degradation of reactive Black 5 (RB5) was investigated in the presence or absence of ultrasound irradiation and H_2O_2 addition. It was observed that photocatalytic degradation increased with increasing TiO_2 loading (in the range 0.05–1 g/L) and decreasing dye concentration (in the range 120–20 mg/L) and solution pH (in the range 9–2.6). With the addition of H_2O_2 decolorization decreased when compared to photocatalytic run without H_2O_2 . In the presence of 0.25 g/L TiO_2 , decolorization after 90 min was 53% with 0.005M H_2O_2 , and 26% with 0.01M H_2O_2 the respective value for the run without H_2O_2 was almost 100%. At the conditions of 60 mg/L dye, 0.25 mg/L catalyst, initial pH of 5.8, complete decolorization was achieved after 60 min of reaction. With the combined photocatalytic and sonolytic degradation (sonophotocatalytic) complete decolorization could be achieved after 25 and 40 min at the initial concentrations of RB5 40 and 60 mg/L, respectively.

In the study of An et al. (2003), decolorization and COD removal from waste water containing Reactive Brilliant Orange K-R (RBOKR) dye using sonophotocatalytic system was investigated. Both decolorization and COD removal obeyed to the pseudo first-order kinetics. The rate constants of sonophotocatalysis were greater than those of both the photocatalytic and sonochemical processes either in the use of individual or as a sum of the processes.

Stock et al. (2000) studied degradation of Naphthol Blue Black (NBB) with photocatalysis, sonolysis and the combination of photocatalysis and sonolysis. TOC removal of NBB solution was 35% when the sonolysis was used only and it was 68% when photocatalysis was used only, in 12 h. Combining the two methods enhanced the mineralization. Nearly 50% TOC removal was achieved in first 4 h and 80% in 12 h with the simultaneous photocatalysis and sonocatalysis. Although the rate constant for the disappearance of NBB remains almost the same at TiO_2 concentrations greater than 0.1 g/L, with the increase in TiO_2 concentration mineralization rate increases, at 2.0 g/L concentration of TiO_2 ; $\approx 90\%$ NBB was mineralized after 6 h of simultaneous sonolysis and photocatalysis. These results showed that TiO_2 as the photocatalyst enhanced

oxidation of reaction intermediates. They conclude that the irradiation of ultrasound promotes the rupture of azo bond and the oxidation of reaction intermediate is promoted by photocatalysis.

Table 1.3 presents the summary of literature survey about usage of sonication in the degradation of organic compounds in waste water.

Table 1.3.Summary of Literature Survey about Usage of Sonication in the Degradation of Organic Compounds in Wastewater

Authors	Comp.	Conc. of pollutant	Catalyst	Chemical oxidation process	Experimental conditions	Results and remarks
Jamalluddin and Abdullah 2011	Reactive Blue 4 (RB4)	70 mg/L	0.4 mol% Fe(III)/TiO ₂	Sonocatalytic Oxidation	Ultrasonic bath, 50W, 35 kHz air catalyst 1.5 g/L PH 4	Removal percentages of RB4 96% with the US+airation+catalyst ≈88% with US+catalyst; ≈18% with US+aeration and ≈10% with US only
Madhavan et al., 2010a	acid red 88 (AR88)	0.09 mM	TiO ₂ (Degusa P25) Fe ³⁺	photocatalytic Sonocatalytic Sonophotocatalytic oxidation	213 kHz, 55mW/mL 450 W Xenon arc lamp (>320 nm) TiO ₂ 1 g/L [Fe ³⁺] = 0.05 mM with PH 2.7 soln.	The synergy index for sonophotocatalysis With TiO ₂ 1.3 With Fe ³⁺ 2.3 In the sonophotofenton process TOC red With TiO ₂ 93% in 4 h. With Fe ³⁺ 7% after 2 h 37% after 4 h
Yuan et al., 2009	methylene blue (MB)	6.0 g/L	TiO ₂ nanotube array film	Sono-photo-catalytic	18, 20, 24, 27, 30 kHz ultrasound source with a power of 24W 16 W UV lamp	Optimum frequency is 27 KHz At 27 kHz after 3 h degradation of MB is about with US+UV+TiO ₂ 54% with US+TiO ₂ , 34 % with US only 12%, with UV+TiO ₂ , 3% With the use of formulation in the study, synergistic effect between ultrasound and UV at 24 and 27 kHz calculated 12.4% and 22.1%, respectively. Rate constants at 27 kHz with US+UV+TiO ₂ 35.6×10 ⁻⁴ min ⁻¹ with US+TiO ₂ 23.3×10 ⁻⁴ min ⁻¹ with US only 7.2×10 ⁻⁴ min ⁻¹

Table 1.3 (Continued)

Authors	Comp.	Conc. of pollutant	Catalyst	Chemical oxidation process	Experimental conditions	Results and remarks
Maezawa et al., 2007	Acid Orange 52	25 mg/L	Sol-gel made TiO ₂	photocatalytic Sonocatalytic Sonophotocatalytic Oxidation with aeration gas air	Transducer 200 kHz, 600 W 20 W low pressure mercury lamp Air 50 mL/min Catalyst 0.6 g/L	UV+TiO ₂ 35% color removal in 480 min, US 100% color removal in 300 min, TOC red. 13% in 480 min. UV+TiO ₂ +US, 100% color removal in 240 min TOC red. 87% in 480 min.
Kritikos et al., 2007	reactive black 5 (RB5)	60 mg/L 40 mg/L	TiO ₂ – mediated UVA photocatalyt	photocatalytic Sonocatalytic oxidation	9 W UVA irradiation lamp Horn type generator 80 KHz, 135 W Catalyst 0.25 g/L	with photocatalytic process degradation of 60 mg/L of RB5 with no H ₂ O ₂ 100 % after 60 min with 0.005M H ₂ O ₂ 53% after 90 min, with 0.01M H ₂ O ₂ 26% after 90 min With sonophotocatalytic process 100 % color removal 25min for 40 mg/L RB5 40min for 60 mg/L RB5
An et al., 2003	Reactive Brilliant Orange K-R (RBOKR)	0.5 mmol/L	TiO ₂ (Degusa P25)	photocatalytic Sonocatalytic oxidation	Ultrasonic cleaner 47 kHz, 30 W 500 W mercury lamp 0.1 m ³ /h air flow 0.75 g/L catalyst	The rate constants of sonophotocatalysis were greater than those of both the photocatalytic and sonochemical processes either in the use of individual or as a sum of the processes.
Stock et al., 2000	naphthol blue black (NBB)	50 ± 5 µM	TiO ₂ (Degusa P25)	photocatalytic Sonocatalytic oxidation	Transducer 240W UV lamp	TOC removal: sonolysis only 35% in 12 h photocatalysis only 68% in 12 h. simultaneous photocatalysis and sonocatalysis 50% in first 4 h and 80% in 12 h.

2. EXPERIMENTAL STUDY

2.1 Catalysts Preparation

In this study, iron containing TiO_2 catalysts were prepared by two different methods: sol-gel and incipient wetness impregnation methods at different Fe contents. TiO_2 -Ce supported catalyst was prepared by modified sol-gel method and iron was added to the TiO_2 -Ce by incipient wetness impregnation method.

2.1.1 Synthesis of catalysts by incipient wetness impregnation method ($x\%\text{Fe}/\text{TiO}_2$ (IW))

Catalysts were prepared by incipient wetness impregnation method given by Arana et al. (2003). The commercial TiO_2 (Sigma-Aldrich P-25) (80% anatase) was added, under stirring, to an aqueous solution of $\text{Fe}(\text{NO}_3)_3$ (Sigma-Aldrich) containing the required amount of iron (1% and 5% wt.) in the minimum amount of distilled water. After stirring at room temperature for 48 h, the catalysts were dried at 120°C for 24 h. For calcination, the dried samples were heated to 500°C at a heating rate of $50^\circ\text{C}/\text{min}$ and kept there for 3 h. The catalysts have been denoted as TiO_2 (P-25), for bare TiO_2 and $x\%\text{Fe}/\text{TiO}_2$ (IW) for the Fe doped catalysts, where x is the iron weight percentage in the catalyst. Catalyst containing 1 wt% iron was calcined at 300°C , 500°C and 700°C in order to investigate the effect of calcination temperature on the catalytic activity in the degradation of RY 84. The dried powder was heated to 300°C at a heating rate of $72^\circ\text{C}/\text{min}$ and 700°C at a heating rate of $24^\circ\text{C}/\text{min}$ and kept there for 3 h.

2.1.2 Synthesis of catalysts by sol-gel method ($x\%\text{Fe}/\text{TiO}_2$ (SG))

Pure TiO_2 and Fe-doped TiO_2 type catalysts were prepared by the sol-gel method according to the process given by Sun et al. (2012).

In order to prepare Fe-doped TiO_2 catalysts tetra-n-butyl titanium ($\text{Ti}(\text{OC}_4\text{H}_9)_4$) (Aldrich) was used as a precursor. The synthesis was as follows: 20 mL $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was added to 80 mL absolute ethanol (Merck) then, as the Fe loading, certain amount of $\text{Fe}(\text{NO}_3)_3$ (Sigma-Aldrich) according to the desired

weight percentages of Fe (0.5% to 5%) in 3 mL distilled water was added to the $\text{Ti}(\text{OC}_4\text{H}_9)_4$ – ethanol mixture under continuous stirring. Afterwards, obtained solution was added drop-wise to the mixture solution containing 80 mL ethanol, 3 mL distilled water and 8 mL acetic acid (Merck) under vigorous stirring. The resulting colloidal suspension was stirred for 2-9 h and aged till the formation of gel. The gel was dried at 80°C for 48 h. For calcination, the dried samples were heated to 500°C at a heating rate of 50°C /min and kept there for 3 h. Pure TiO_2 was prepared by using the above procedure in the absence of Fe loading. The catalysts have been denoted as TiO_2 (SG) for pure TiO_2 and x%Fe/ TiO_2 (SG) for the Fe doped catalysts, where x is the iron weight percentage in the catalyst.

2.1.3 Synthesis of iron containing TiO_2 -Ce catalysts (x%Fe/ TiO_2 -Ce)

Fe/ TiO_2 -Ce catalyst is prepared by impregnating $\text{Fe}(\text{NO}_3)_3$ (Sigma-Aldrich) into the sol-gel synthesized TiO_2 -Ce catalyst. First step is the preparation of TiO_2 -Ce sample by the sol-gel method.

Synthesis of 1 wt.% cerium added TiO_2 catalyst was done by modifying the route described by Sun et al. (2012) to the as follows: Solution-A was prepared by drop-wise addition of 20 mL $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (Aldrich) into the dissolved $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Merck) in 80 mL absolute ethanol under continuous stirring. Solution-B was the mixture of 80 mL ethanol, 6 mL distilled water and 8 mL acetic acid. Under vigorous stirring solution-A was added drop-wise to the solution-B. After 8h stirring the suspension was aged till the formation of gel. Aging of the solution was completed up to form gel. Gel was dried at 80°C for 48 h. Ce added TiO_2 was used as support for the preparation of iron containing Ce-doped TiO_2 catalysts (1wt%Fe/ TiO_2 -Ce).

For the Fe loading $\text{Fe}(\text{NO}_3)_3$ solution was impregnated into the sol-gel synthesized TiO_2 -Ce catalyst. Certain amount of $\text{Fe}(\text{NO}_3)_3$ according to the desired weight percentage of Fe (1 and 5 wt.%) in distilled water was added drop-wise under stirring to the TiO_2 -Ce catalyst. After stirring at room temperature for 48 h the catalyst was then dried at 120°C for 24 h. For calcination, the dried samples were heated to 500°C at a heating rate of 50°C /min and kept there for 3

h. Finally catalyst was calcined at 500°C for 3 h. The catalysts have been denoted as TiO₂-Ce for TiO₂-Ce and x%Fe/TiO₂-Ce for the Fe doped catalysts, where x is the iron weight percentage in the catalyst.

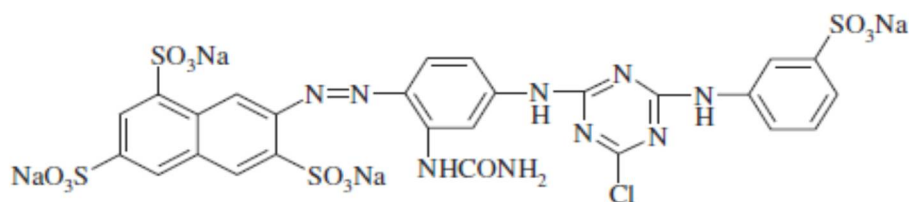
2.2 Catalyst Characterization Studies

The prepared catalysts were characterized by XRD, SEM, FTIR, Nitrogen adsorption, UV-Vis DRS and ICP-AES measurements. Powder X-ray diffraction (XRD) patterns of the catalysts were recorded in the range of 5–80° by Philips X'Pert Pro with Cu-K α radiation to determine the crystalline structure of the samples. Morphological properties were analyzed by scanning electron microscopy (SEM) (FEI Quanta250 FEG). FT-IR spectra were recorded in the 650–3650 cm⁻¹ with a Perkin Elmer Spectrum 100 spectrometer. Nitrogen adsorption isotherms at 77 K were measured using Micromeritics ASAP 2010 equipment. UV-visible diffuse reflectance spectra (UV-Vis DRS) were recorded on UV-Vis DRS Shimadzu 2600 spectrometer. The contents of iron of the samples were determined by a Varian-96 inductively coupled plasma atomic emission spectrometer (ICP-AES) with fusion dissolution method as follows: 0.2 g of each sample was mixed with 1 g of lithium tetraborate and 1 g of lithium metaborate in a platinum crucible, then mixture was fused in furnace at 1000°C for 1 h and without cooling sample in the platinum crucible was wetted with distilled water and allowed molten to crack. Catalyst crystal was dissolved in beaker containing 125 mL 5%v/v HNO₃ solution stirring by a magnetic stirrer after all the crystals were dissolved, platinum crucible was got out of the beaker and the solution was completed to 250 mL by ensuring 2.5% v/v HNO₃ solution and stored in the refrigerator until analysis.

2.3 Degradation Experiments

The Reactive Yellow 84 azo-dye was obtained from DYSTAR under the trade name "ProcionYellow H-E4R" and used without further purification. The absorption spectrum of RY 84 is characterized by a main band at 408 nm. The chemical structure of RY 84 is presented in Figure 2.1. The hydrogen peroxide solution (35%) of analytical grade was obtained from Merck. The aqueous

solution containing RY 84 was prepared with deionized water from a Millipore Direct Q purification unit.



Chemical formula: $C_{26}H_{16}ClN_9O_{13}S_4Na_4$
Molecular mass: 918 g/mol

Figure 2.1. Chemical structure of the C.I. RY 84 azo-dye (Barka et al., 2011).

2.3.1 Sonication experiments (Degradation with ultrasound, US, only)

Experiments of dye degradation by ultrasound (sonication) were performed by using ultrasonic bath and ultrasonic reactor to investigate the effect of ultrasound (US) at different powers and frequencies on degradation of dye and to compare the effect of direct and indirect sonication on decolorization of RY-84.

2.3.1.1 Sonication in ultrasonic bath

Effects of ultrasonic power and volume of dye solution on sonolytic degradation of RY 84 were investigated by using C.E.I.A., CP102 model ultrasonic bath (Figure 2.2). The ultrasonic bath operates at 40 kHz and at an ultrasound power in the range 70–140 W. Operating temperature of the bath can be regulated between 20 and 80 °C. Sonication time can be adjusted to a desired value in the range of 1–60 min.



Figure 2.2. Experimental Set-up of ultrasonic bath

For a typical run, ultrasonic bath was filled with deionized water. 150 mL or 350 mL of dye solution with 25 mg/L or 75 mg/L was filled into a spherical pyrex-glass flask with three necks and then it was placed into the ultrasonic bath with the same distance from the bottom of the bath at all experiments for indirect sonication of dye. Temperature, time and power were adjusted to the desired values. The samples of 5 mL were taken and the temperature of dye solution was recorded in every 15 min. Also, the pH of dye solution was measured at the beginning and at the end of each experiment. All the experiments were repeated at least 2 times, mostly 5 times.

2.3.1.2 Sonication in ultrasonic reactor

The experimental set-up of ultrasonic reactor was shown in Figure 2.3. Ultrasonic reactor consists of ultrasonic signal generator (Meinhardt, Model K80), ultrasonic transducer (Meinhardt, Model E/805/T) and an ultrasonic reactor with a jacket (Meinhardt, Model 5/1575). Temperature is kept constant by circulating water in jacket. The frequency of ultrasound is 850 kHz. The maximum power is 100 W and can be adjusted in four steps to maximum. The high frequency generator was used in the continuous (sinusoidal) mode.

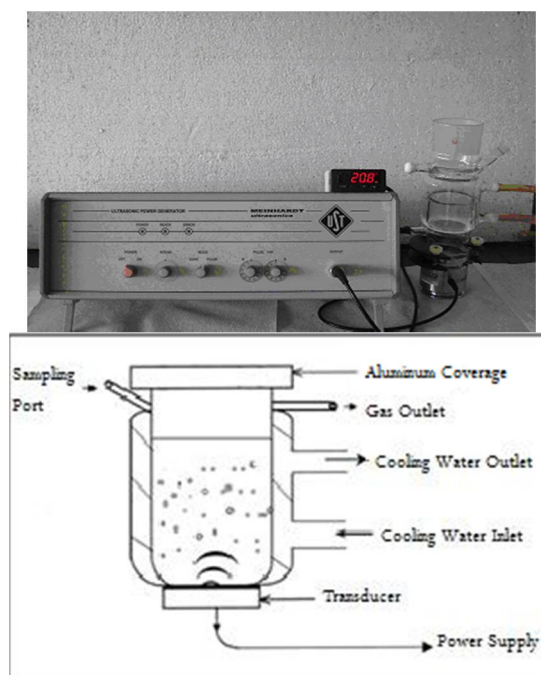


Figure 2.3. Experimental set-up of ultrasonic reactor

In a typical experiment, 250 or 350 mL of dye solution with specified concentration (10, 25 or 75 mg/L) was put into the ultrasonic reactor. Then, the power of ultrasound (25, 50 or 75 W) was adjusted. Dye solution was sonicated directly in the ultrasonic reactor. For the investigation of the effect of the dye solution pH on decolorization degree, experiments were started at acidic pH (≈ 3.7) and at the dye pH of 6. pH was adjusted by using 0.1 M H_2SO_4 aqueous solution to 3.7 for acidic pH studies. No attempt was made to change the solution pH during the runs. Temperature was kept constant at 25 °C by circulating water in jacket during the experiment. The samples were taken and the temperature of dye solution was controlled in every 15 min. Also, the pH of dye solution was measured at the beginning and at the end of each experiment. In order to see the effect of H_2O_2 amount on the degradation of RY 84, H_2O_2 in different amounts (0.5, 2, 5 and 35 mM) was introduced to the system. All the experiments were repeated at least 3 times, mostly 5 times to obtain more accurate results.

In ultrasonic reactor system, the effects of ultrasonic power, solution volume, addition of hydrogen peroxide, initial dye concentration and initial pH on decolorization of RY 84 were examined and optimum conditions were determined.

2.3.2 SonophotoFenton degradation experiments

In order to find the most effective catalyst and then the optimum conditions for degradation of RY 84 by sonophotoFenton process, a sonophotoFenton experimental set-up shown in Figure 2.4 was installed. UVC irradiation was provided by two 4 W lamps (Philips, 4 W, 254 nm). The reaction mixture was placed in the reaction vessel and the inner quartz glass was fixed to two sides of the inside the reaction vessel. The lamp was placed inside the inner quartz tube. System was effectively cooled by cooling water jacket. Ultrasound irradiation was provided by an Ultrasound generator (BANDALIN HD 3200) operating at 20 kHz frequency with a maximum 200W of electric power output.

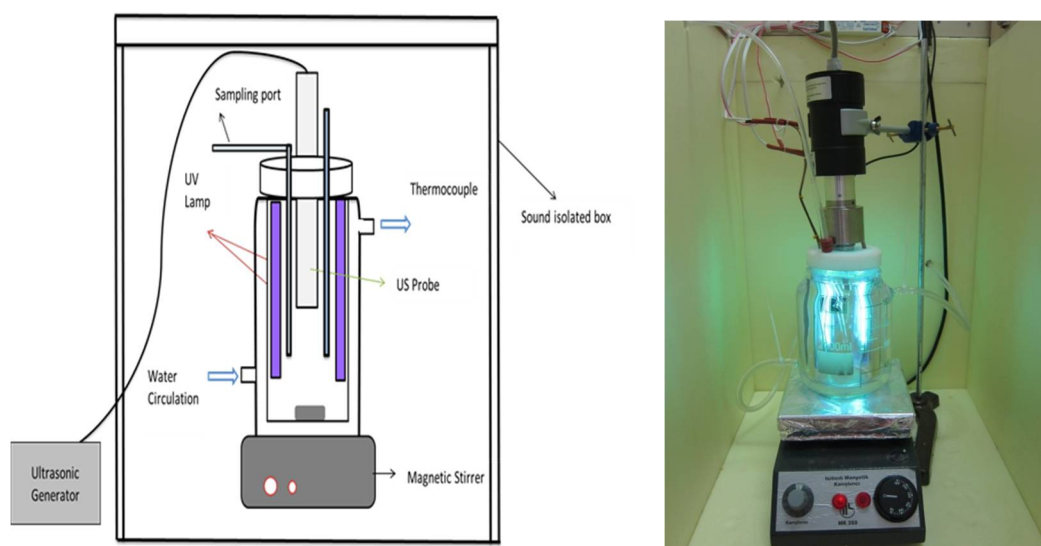


Figure 2.4. Experimental set-up for sonophotoFenton degradation of dye.

Photocatalytic experiments were performed as follows: 650 mL of RY 84 solution was introduced in the reaction vessel and a known amount of catalyst was added to the reaction mixture. The resulting catalyst suspension was magnetically stirred for 30 min in the dark to ensure complete equilibration of adsorption/desorption of RY 84 on the catalyst surface. The amount of the dye adsorbed by the catalyst was determined by measuring the dye concentration after 30 min in the absence of UV illumination and ultrasound. After that period of time, the appropriate amount of 35% w/w solution of H_2O_2 was added to achieve the degradation by Fenton reaction. This time was taken as “time zero” for the total degradation reaction, then the UV lamp and ultrasonic power were turned on, while the reaction mixture was continuously stirred. Experiments were performed at dye solution pH and didn’t adjust during the oxidation. Samples periodically drawn from the reaction vessel were centrifuged for 45 min to remove catalyst particles and then subjected to analysis for determination of decolorization degree and COD removal of dye. The degree of decolorization was determined by using UV spectrophotometer (Shimadzu UV-1800) with the calibration curve method. The wavelength of the maximum of absorption (λ_{max}) was 408 nm. After the determination of the concentration of RY 84 by using the calibration line (Figure 2.5) which was drawn by known concentrations of dye solution and measured corresponding absorbances, decolorization degree of the dye was calculated by the Eqn. 2.1.

$$\text{Decolorization, \%} = \frac{C_0 - C}{C_0} * 100 \quad (2.1)$$

Where; C_0 was the initial concentration and C was the calculated concentration of the RY 84 at the corresponding time.

Chemical Oxygen Demand (COD) reduction measurements were done according to the Eqn.2.2 by using Lovibond COD test kits.

$$\text{COD reduction, \%} = \frac{\text{COD}_0 - \text{COD}}{\text{COD}_0} * 100 \quad (2.2)$$

where; COD_0 was the COD value at $t=0$ and COD was the COD value of the RY 84 at the corresponding time.

The standard deviation of the average of independent decolorization experiments was in the range of ± 0.01 to ± 4.67 . The standard deviation of COD measurement was in the range of ± 0.3 to ± 2.6 .

In addition to these measurements, total organic carbon (TOC) removal was determined using a Teledyne Tekmar Lotix TOC Analyzer for the sonophotoFenton and UV+Catalyst+ H_2O_2 oxidations of dye at the optimum conditions. TOC was calculated as the difference between the total carbon (TC) and inorganic carbon (IC) in the liquid sample.

Total Organic Carbon (TOC) reduction calculations were done according to the Eqn. 2.3.

$$\text{TOC reduction, \%} = \frac{\text{TOC}_0 - \text{TOC}}{\text{TOC}_0} * 100 \quad (2.3)$$

where; TOC_0 was the initial TOC value of the RY 84 and TOC was the TOC value of the RY 84 at the corresponding time.

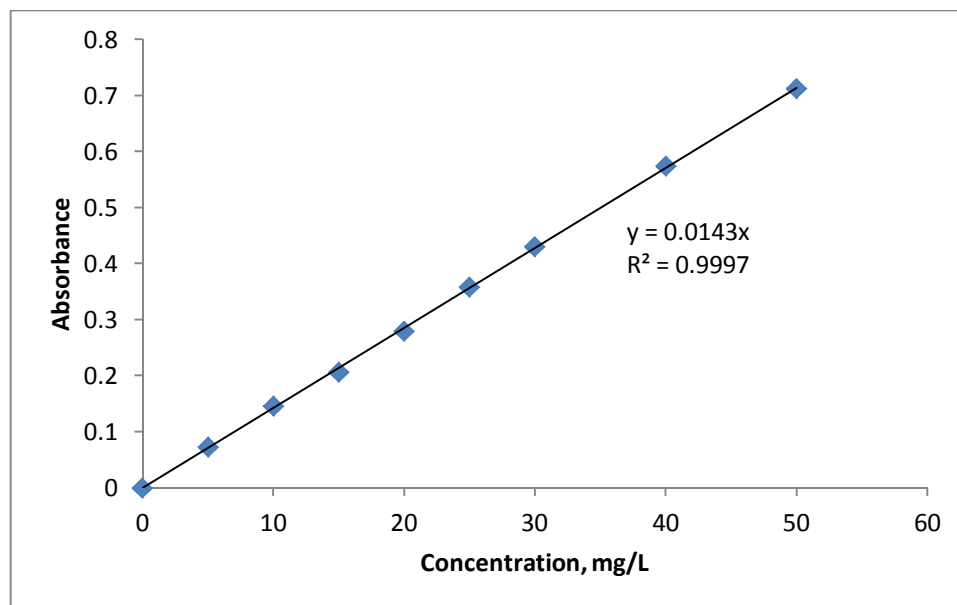


Figure 2.5. Calibration curve of RY 84 in UV spectrophotometer

2.4 Toxicity Measurements

In this study, *Lepidium Sativum* L. (Garden cress) seeds were used to determine the reduction of the toxicity of Rh6G prior to and the treatment after 120 min. For this purpose, 5 mL of untreated and treated RY 84 solution were pipetted onto a filter paper fitted into a 9 cm glass petri dish. Then 25 seeds of cress were distributed evenly on them. These petri dishes were placed in the dark for 120 hours at room temperature, after that, root lengths of seeds were measured for treated and untreated wastewaters, and the root length growth% was calculated for treated waste water with respect to the untreated waste water.

3. RESULTS AND DISCUSSION

3.1 Catalyst Characterization

3.1.1 X-ray diffraction studies

Figures 3.1 and 3.2 show X-ray patterns of catalysts synthesized by incipient wetness impregnation (IW) and sol-gel methods, respectively. The XRD results obtained are similar with the ones in literature (Arana et al., 2001; Castro et al., 2011; Sun et al., 2012). In all cases, anatase phase with peaks at 2θ angles of 25.4° , 37.9° , 48.1° , 55.1° , 62.8° are present.

Anatase (a) in a larger extent, and rutile (r) phases have been identified in IW synthesized catalysts. Rutile phase peaks at 2θ angles of 36.0° and 41.2° were getting disappeared with the Fe-loading. Also after loading iron, the intensity of the peaks was slightly weakened and broaden indicating the weaker crystallinity of the anatase phase (Jamalluddin and Abdullah, 2011).

With increasing Fe-doping, peak intensities of anatase phase slightly decreased and the width of (1 0 1) plane diffraction peak of anatase ($2\theta=25.4^\circ$) became broader. Thus, it could be deduced that, with increasing the Fe-doping level, crystallization of TiO_2 powder got poorer and the crystallite size of the TiO_2 got smaller (as shown in Table.3.1), which was in accordance with the results reported by Zhou et al. (2006), and Jamalluddin and Abdullah (2011). Incorporation of iron into the TiO_2 structure, particularly in Fe/ TiO_2 catalysts with iron content greater than 0.5wt.%, caused a decrease in peak intensity. This might be attributed to the enhanced absorption of X-ray due to iron cations. (Arana et al., 2001).

In accordance with the study of Arana et al. (2003), and Zhou et al. (2006), as shown in Figure 3.2, for the catalysts prepared by sol-gel method only the diffraction peaks of anatase phase were observed, also iron oxides or Fe_xTiO_y phases iron peak or TiO_2 peak for rutile phase was not detected. According to the Zhou et al. (2006), there are two probable reasons of these observations; one is the Fe-doping is not enough to be detected by XRD. Other is the similarities of the

radii of the Ti^{4+} (0.68 Å) ion with Fe^{3+} (0.64 Å) ion, because of this similarity it is possible that iron is dispersed as fine crystallites in the catalysts.

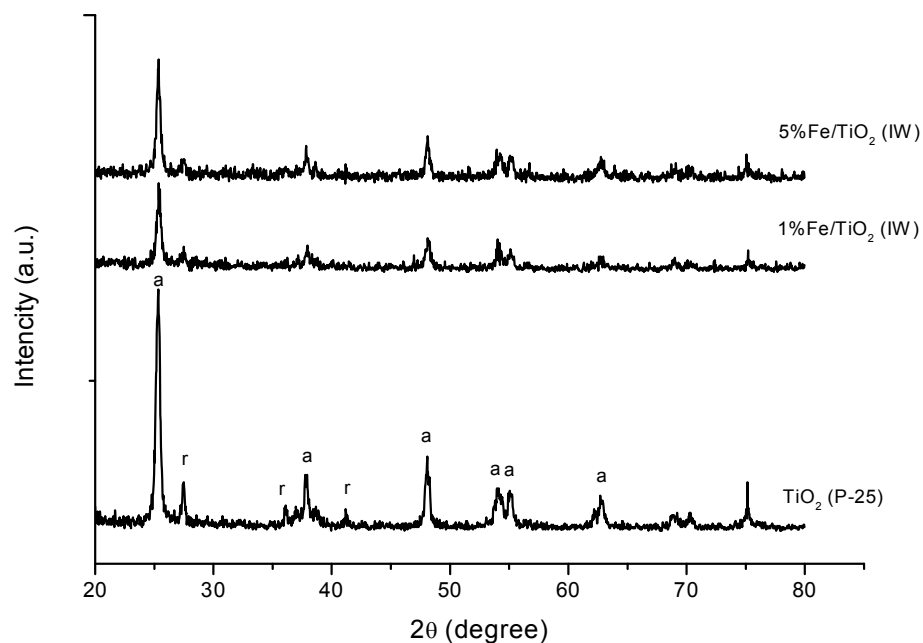


Figure 3.1. XRD patterns of catalysts synthesized by incipient wetness impregnation (IW) method of (r, rutile phase; a, anatase phase).

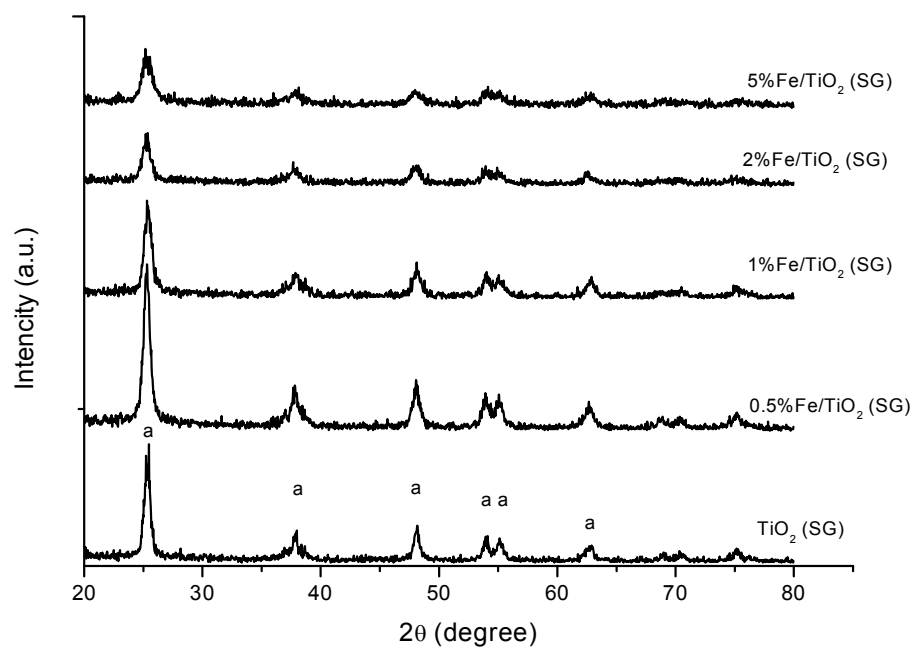


Figure 3.2. XRD patterns of catalysts synthesized by sol-gel method (a, anatase phase).

Figure 3.3 shows the XRD patterns for 1%Fe/TiO₂ catalyst with different calcination temperatures. In accordance with the study of Jamalluddin and Abdullah (2011), rutile phase peak intensity increases with increase in the calcination temperature from 300°C to 700°C showing the occurrence of the transformation of anatase to rutile phase.

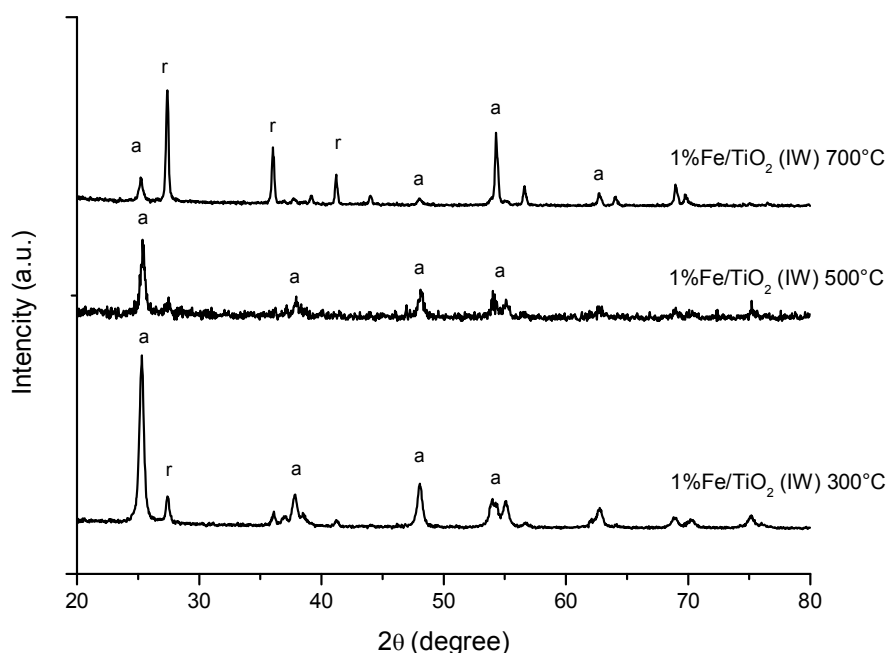


Figure 3.3. XRD patterns for 1%Fe/TiO₂(IW) catalyst with different calcination temperatures.

Figure 3.4 presents the XRD patterns of TiO₂-Ce and Fe-doped TiO₂-Ce samples. In accordance with the study of Zhao et al. (2011), the XRD patterns of Fe doped TiO₂-Ce catalysts almost coincide with the TiO₂-Ce showing no crystalline phase attributed to iron oxide. Only the diffraction peaks of anatase phase were observed, iron peak or TiO₂ peak for rutile phase was not detected. Anatase type structure is kept almost same in Fe-doped TiO₂-Ce catalysts. Only the peaks of anatase titania became much stronger than pure TiO₂-Ce alone. So it can be said that doping level of Fe as well as the calcination temperature of 500°C did not cause the anatase-rutile phase transition. The absence of any peak for iron indicates that iron is dispersed as fine crystallites in the catalysts (Arana et al.,

2003). No peak for Ce could be detected due to the low Ce content in the catalyst.

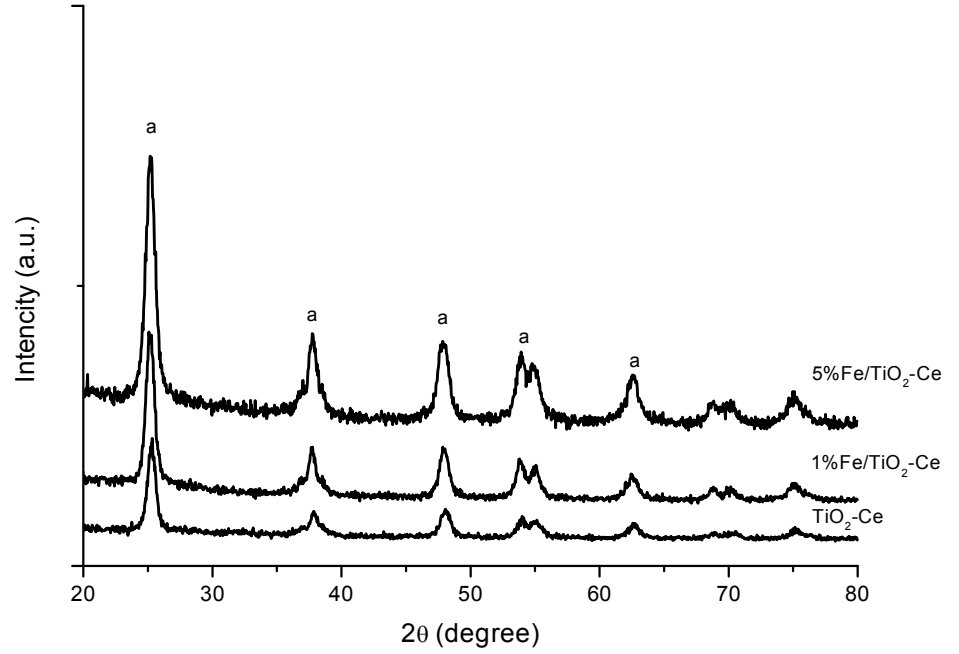


Figure 3.4. XRD patterns of different Fe/TiO₂-Ce catalysts (a, anatase phase)

3.1.2 Crystallite size and anatase phase percentages of the samples

Crystallite sizes and percentages of anatase of the samples are shown in Table 3.1. Crystallite sizes of the samples were calculated from the half-height width of different peaks of anatase and rutile using the Scherrer Equation (Eq. 3.1), (Tayade et al., 2007). Characteristic peaks of $2\theta = 25.4$ for anatase and $2\theta = 27.5$ for rutile with a shape factor K of 0.9 was used in the Scherrer formula.

$$C_s = \frac{K\lambda}{B \cdot \cos(\theta)} \quad (3.1)$$

where B = line width at half maximum height

λ = wave length of X-ray radiation (CuK α =0.15405 nm)

θ = diffraction angle

The percentages of anatase, A (%) was determined as follows (Tayade et al., 2007):

$$A (\%) = \frac{100}{1+1.265 (I_R/I_A)} \quad (3.2)$$

where I_R = intensity of rutile peak

I_A = intensity of anatase peak

Table 3.1. Phase Composition and Crystalline Size^a of samples

Catalyst	Crystalline Size (diameter in nm)		
	Anatase	Rutile	% Anatase
TiO ₂ (P 25) - 500 ^b	20.7	36.9	79.8
1%Fe/TiO ₂ (IW) - 300 ^b	20.9	27.3	81.0
1%Fe/TiO ₂ (IW) - 500 ^b	24.0	65.4	73.3
1%Fe/TiO ₂ (IW) - 700 ^b	40.7	31.4	15.9
5%Fe/TiO ₂ (IW) - 500 ^b	22.6	121.1	80.3
TiO ₂ (SG) - 500 ^b	17.7	-	100
0.5%Fe/TiO ₂ (SG) - 500 ^b	15.7	-	100
1%Fe/TiO ₂ (SG) - 500 ^b	12.9	-	100
2%Fe/TiO ₂ (SG) - 500 ^b	12.9	-	100
5%Fe/TiO ₂ (SG) - 500 ^b	10.9	-	100
TiO ₂ -Ce - 500 ^b	11.2	-	100
1%Fe/TiO ₂ -Ce - 500 ^b	10.9	-	100
5%Fe/TiO ₂ -Ce - 500 ^b	9.5	-	100

^aCrystalline size was calculated with Scherrer Equation by using the 2θ angle 25.4° and 27.5° peaks of anatase and rutile phases, respectively.

^b Calcination temperature

Increase in calcination temperature decreases the anatase phase ratio and increases the rutile phase ratio of the 1% Fe loaded TiO_2 (P-25). Also crystal size of the 1% Fe loaded TiO_2 (P-25) increases with increasing calcination temperature from 300°C to 500 and 700°C. at the calcination temperature of 700°, the anatase phase decreases to 15.9% and the rutile phase increases to 84%. These calculations are in good accordance with the FT-IR and XRD results.

The crystal size of anatase phase for the catalyst prepared by sol-gel method was decreased from 17.7 nm to 15.7 nm with the addition of 0.5 wt% iron into TiO_2 . The crystal size was reduced to 10.9 nm with increasing iron content. The crystallite size of the catalysts prepared by incipient wetness impregnation method and calcined at 500°C were 24.0 nm and 22.6 nm for 1 wt% and 5 wt% iron containing samples, respectively, while it was 20.7 nm for TiO_2 (P-25).

Crystal size of the anatase phase of the catalysts prepared by sol-gel method decreased with the Fe loading. Crystal size of sol-gel prepared TiO_2 was given as 17.02 nm in the study of Sun et al. (2012), the crystal size of 0.7%(mole) Fe containing Fe- TiO_2 sample was calculated to be 12.08 nm in their study and they showed that the crystal size of the Fe loaded TiO_2 decreased with increasing the Fe loading which is similar with our results.

Jamalluddin and Abdullah (2011) reported that the crystal size of Fe- TiO_2 (anatase) samples prepared by sol-gel method decreased from 48 nm to 9.2 nm with the increase in iron content from 0.4 to 1% mole in the catalyst.

Tayade et al. (2007) calculated the crystal sizes for the anatase and rutile TiO_2 samples prepared by sol-gel method to be 14 and 32 nm, respectively. The crystal size for rutile is very close to that calculated in our study (36.9 nm) for TiO_2 (P-25).

In another study, the crystal sizes for anatase phase TiO_2 were calculated to be 10.8, 30.2, 37.1 and 24.1 nm for water to titanium tetraisopropoxide (TPT) mole ratios of 1, 2, 3 and 4, respectively (Hafizah and Sopyan, 2009).

Mi et al. (2013) prepared anatase TiO_2 in high purity and iron doped TiO_2 nanocrystals with a continuous flow synthesis method and they reported that crystal size of Fe- TiO_2 catalysts changed from 8.4 nm to 8.7, 8.7, 8.5 and to 8.3 nm with the increase in iron content of catalysts from zero to 0.5, 1, 2 and 5 mole%.

Tong et al. (2007) prepared Ce- TiO_2 catalysts by controlled hydrolysis of titanium alkoxide based on esterification reaction and found the crystal size of 1 % Ce- TiO_2 to be 14.3 nm. Pavar et al. (2012) prepared 0.5 mol% Ce(III)-doped TiO_2 particles by sol-gel auto combustion method and calcined it at 600°C. The average crystallite size of this catalyst was reported as 13.5 nm.

Zhao et al. (2011) prepared $\text{TiO}_2 - \text{CeO}_2$ and Fe/ $\text{TiO}_2 - \text{CeO}_2$ catalysts by the methods of co-precipitation and impregnation, respectively. They reported that crystal size changed from 11.7 nm to 12.7, 12.2, 13.1 and 12.4 nm with the iron loading of 0.5, 1, 2 and 3 wt.%, respectively.

3.1.3 SEM studies

Figures 3.5 to 3.7 present SEM images of prepared catalysts. SEM images of catalysts prepared by sol-gel method of TiO_2 , 0.5%Fe/ TiO_2 , 1%Fe/ TiO_2 , 2%Fe/ TiO_2 and 5%Fe/ TiO_2 are shown in Figure 3.5. It was seen that the shape of the catalyst particles were in irregular shape and non-homogeneous. They seem to be in the layered forms. In accordance with the study of Castro et al. (2011), large particles with straight edges and sharp corners were observed.

Figure 3.6 shows the SEM images of the TiO_2 (P25), 1%Fe/ TiO_2 catalyst calcined at three different temperature (300°C, 500°C and 700°C) and 5% wt. Fe loaded catalyst calcined at 500°C which are prepared by using incipient wetness impregnation method. Catalysts have spongy morphology and particles are not uniform. Similar with the study of Qourzol et al. (2009), TiO_2 (P25) consists of agglomerates of particles in nanometer size. Increase in the calcination temperature from 300°C to 700°C increases the agglomerates' crystal sizes.

Figure 3.7 presents the three representative SEM images of the following samples: $\text{TiO}_2\text{-Ce}$, $1\%\text{Fe/TiO}_2\text{-Ce}$ and $5\%\text{Fe/TiO}_2\text{-Ce}$. It was seen that the shape of the catalyst particles were in irregular shape and non-homogeneous.

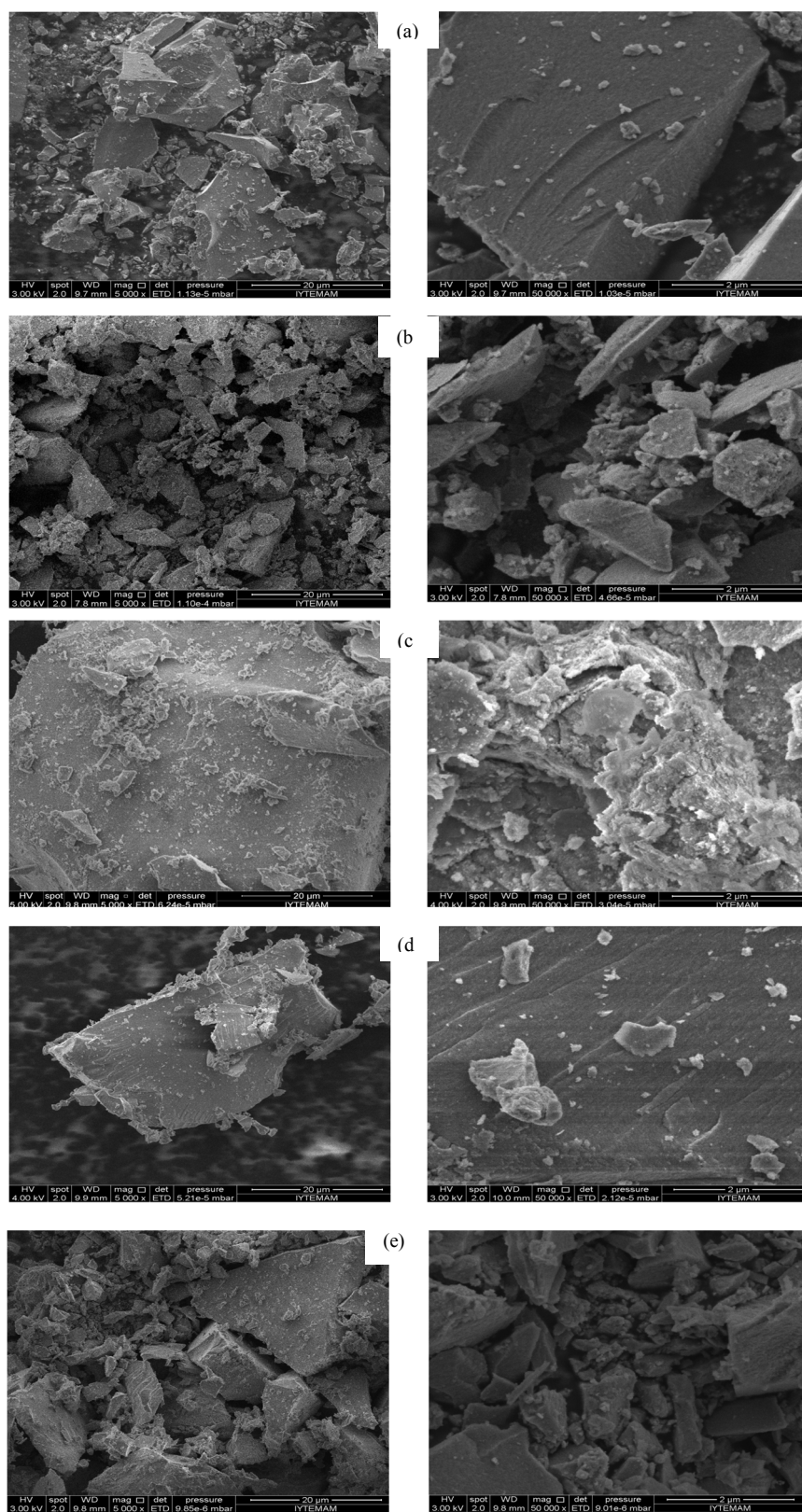


Figure 3.5. SEM micrographs of : (a) TiO_2 (SG), (b) 0.5%Fe/ TiO_2 (SG), (c) 1%Fe/ TiO_2 (SG), (d) 2%Fe/ TiO_2 (SG), (e) 5%Fe/ TiO_2 (SG) catalysts at magnification 5000x and 50000x.

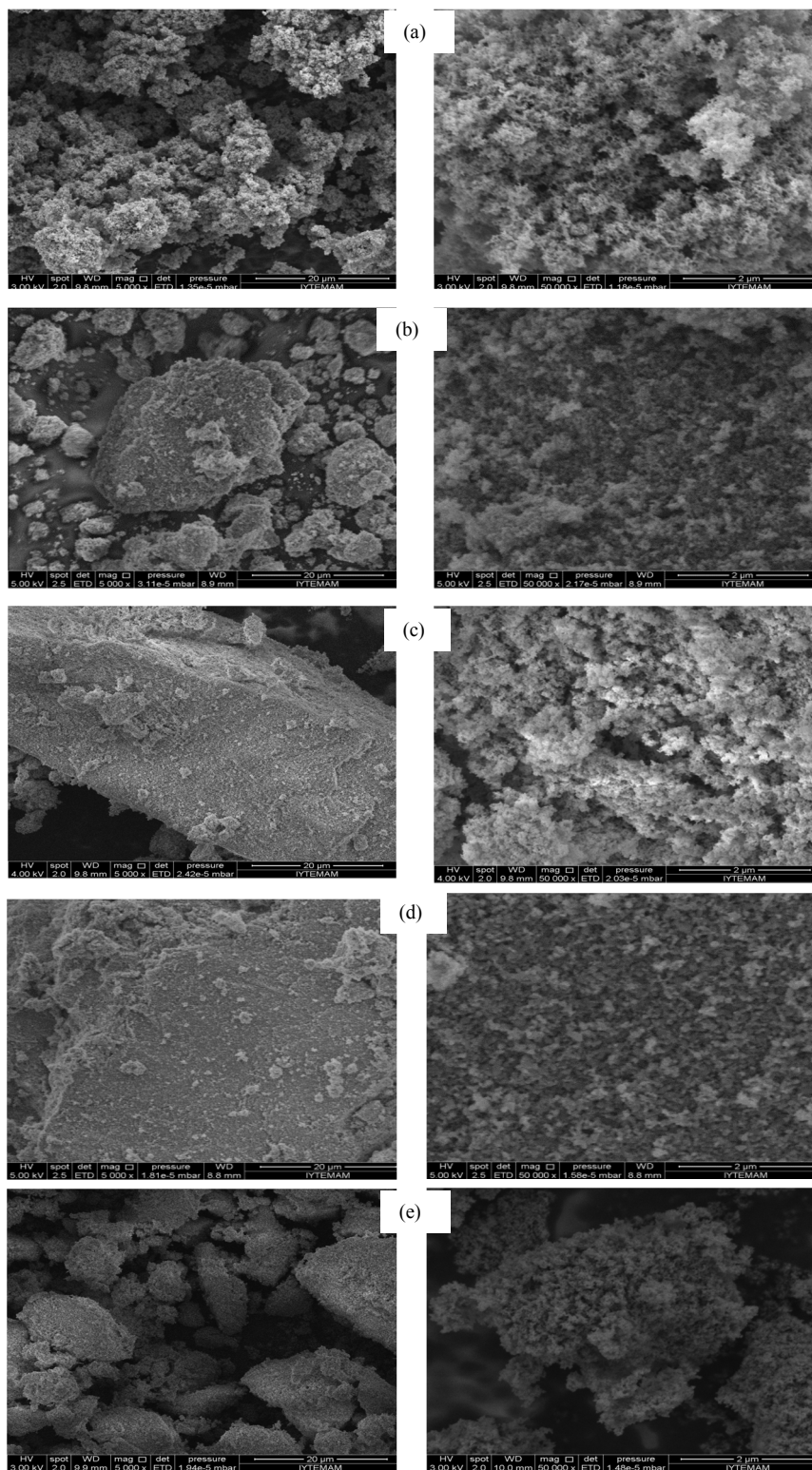


Figure 3.6. SEM micrographs of : (a)TiO₂- P25, (b) 1%Fe/TiO₂ (IW) 300°C, (c) 1%Fe/TiO₂ (IW) 500°C, (d) 1%Fe/TiO₂ (IW) 700°C, (e) 5%Fe/TiO₂ (IW)catalysts at magnification 5000x and 50000x.

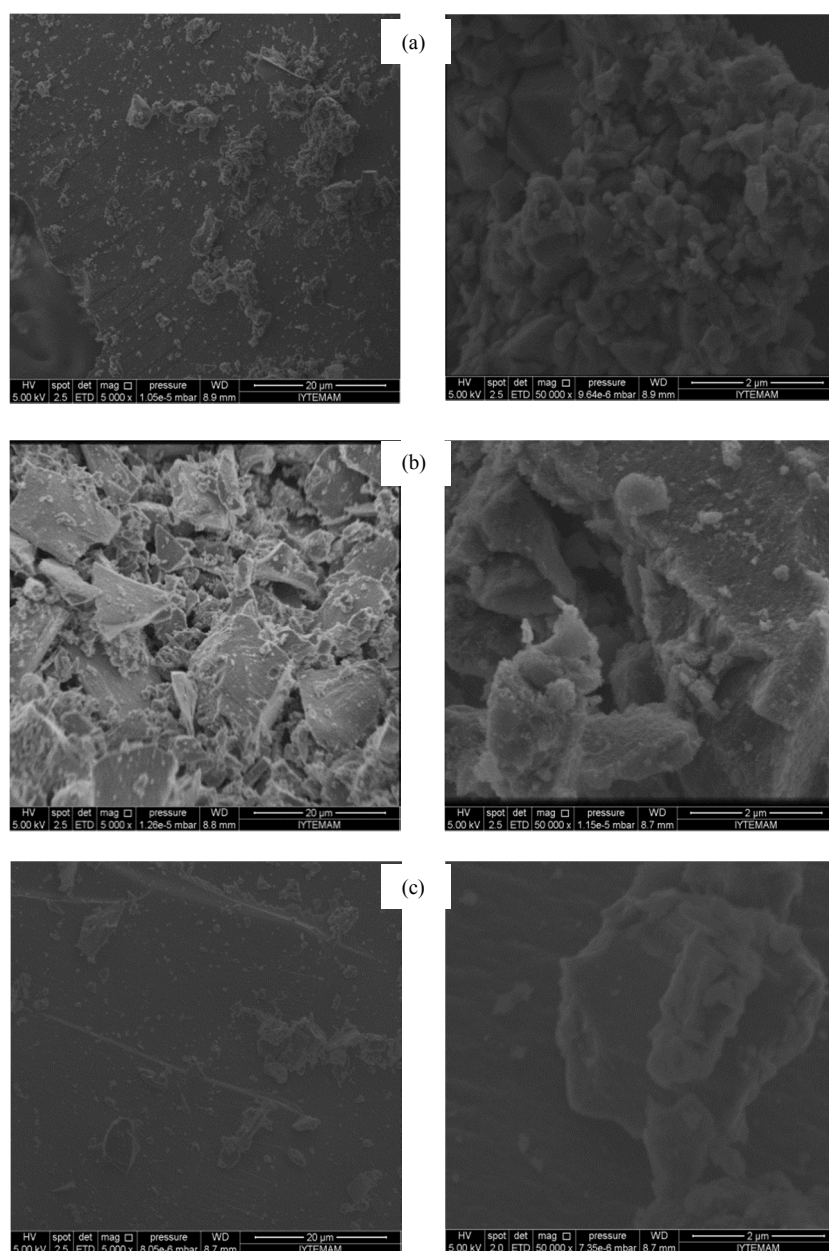


Figure 3.7. SEM micrographs of : (a) $\text{TiO}_2\text{-Ce}$, (b) $1\%\text{Fe}/\text{TiO}_2\text{-Ce}$, (c) $5\%\text{Fe}/\text{TiO}_2\text{-Ce}$, catalysts at magnification 5000x and 50000x.

3.1.4 FT-IR spectroscopy studies

The FTIR spectra of samples prepared by incipient wetness impregnation (IW) method are shown in Figure 3.8. Spectra show a broad band in the region 3600–2800 cm^{-1} with a shoulder attributed to the stretching vibrations of O–H. The band centered at 1630 cm^{-1} belongs to O–H bending vibration of surface adsorbed water indicating that samples have hydroxylase surfaces (Castro et al., 2011; Tasbihi et al., 2012).

As shown in Figure 3.9 the increase in calcination temperature from 300 to 500°C does not affect the FTIR spectrum. On the other hand, calcination at a higher temperature of 700 °C, all these bands disappeared as a result of thermal treatment. This shows the calcination temperature of 700°C causes the anatase-rutile phase transition (Arana et al., 2001; Khalid et al., 2011)

Figure 3.10 shows the FTIR spectra of the catalysts prepared by sol-gel method. In accordance with the literature the spectra exhibit absorption band at 1640 cm^{-1} which is attributed to hydroxyl group (Khalid et al., 2011). Intensity of band at 1640 cm^{-1} slightly decreases with the increase in iron content of the catalyst.

Figure 3.11 shows the FTIR spectra of the x%Fe/TiO₂-Ce catalysts. With the addition of iron a broad band at the range of 3150-3650 cm^{-1} was observed which is assigned to the Ti-OH stretching band. The band at 1640 cm^{-1} indicates the deformation vibration which is evidence for the large amount of water molecules (Tayade et al., 2007).

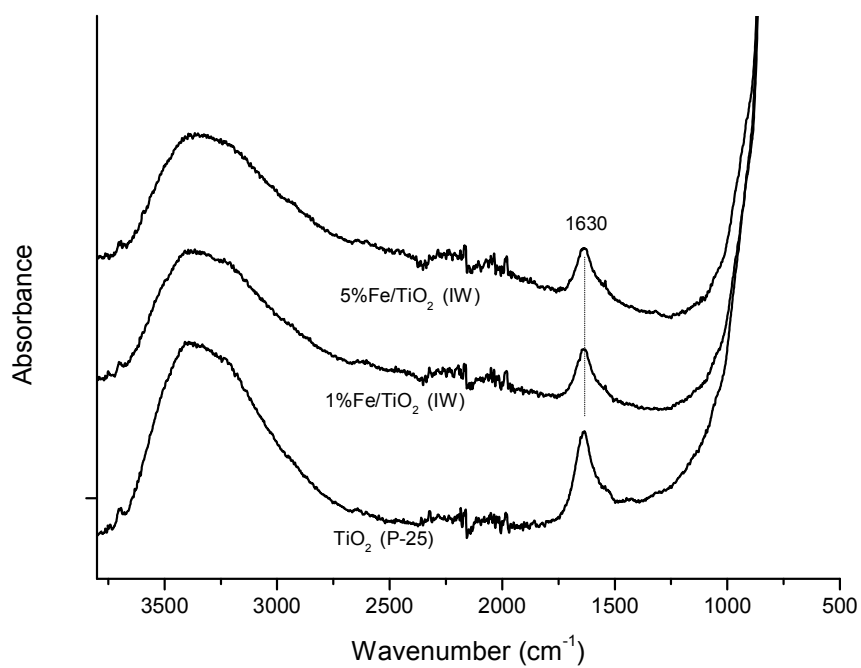


Figure 3.8. FTIR spectra of the catalysts synthesized by incipient wetness impregnation (IW) method.

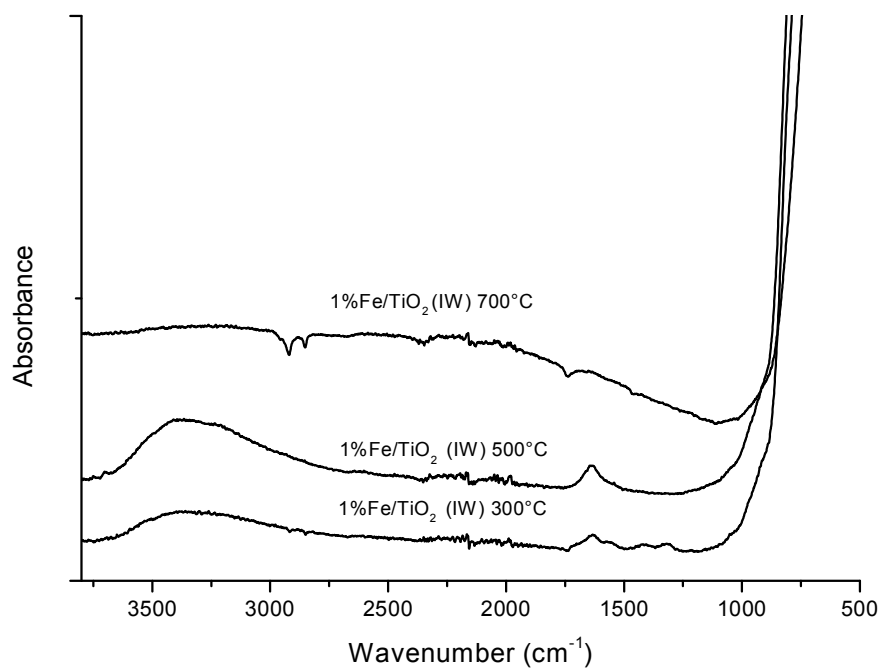


Figure 3.9. FTIR spectra of the 1%Fe/TiO₂ (IW) catalyst with different calcination temperatures.

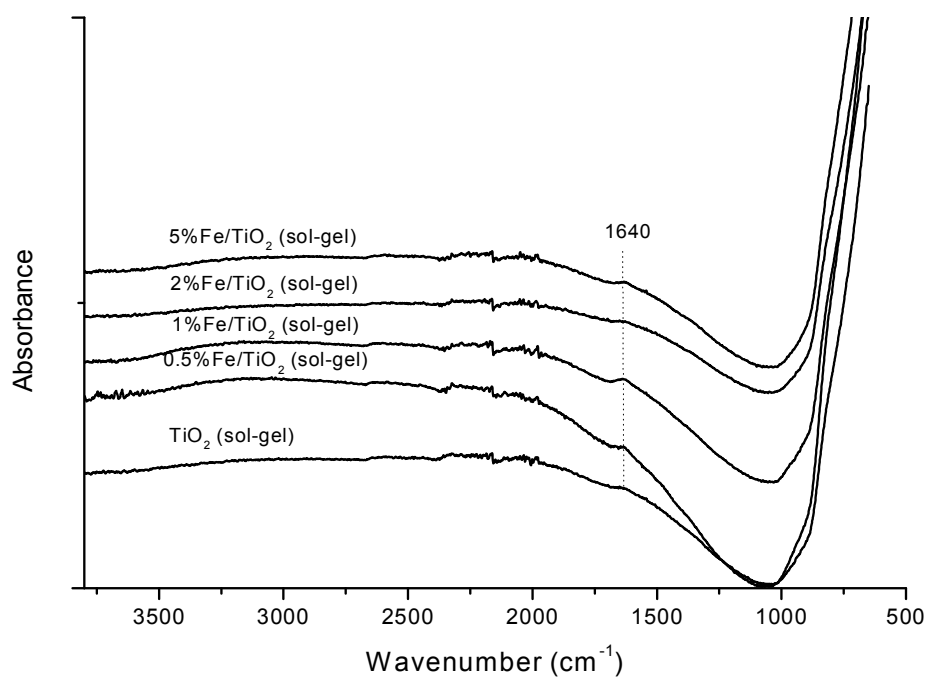


Figure 3.10. FTIR spectra of the catalysts synthesized by sol-gel method.

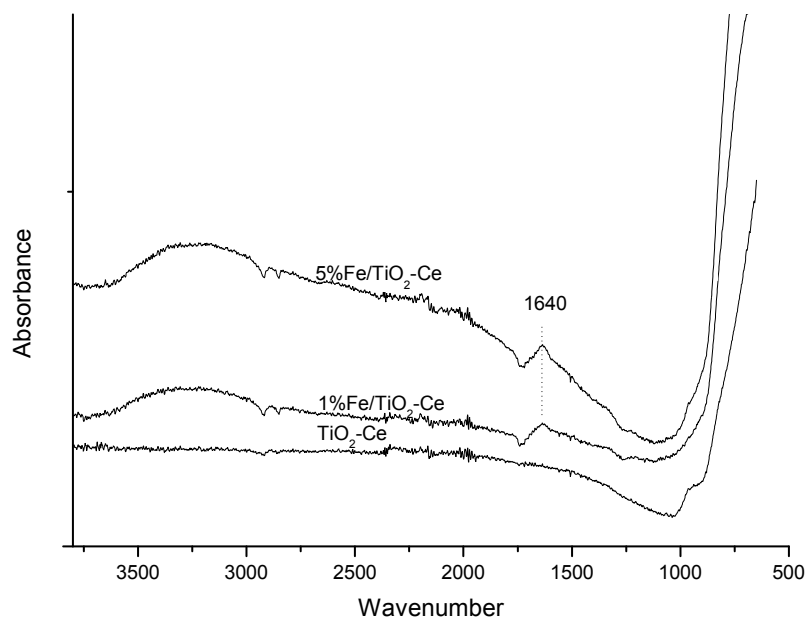


Figure 3.11. FTIR spectra of $x\%\text{Fe}/\text{TiO}_2\text{-Ce}$ catalysts.

3.1.5 Nitrogen adsorption measurements

Figure 3.12 presents the adsorption isotherms according to IUPAC classifications. Type I corresponds to a complete monolayer formation and is typical for microporous materials. Types II and III describe adsorption on macroporous and non-porous adsorbents with strong and weak adsorbate–adsorbent interactions, respectively. Types IV and V occur for strong and weak fluid-wall forces, respectively, when the material is mesoporous and capillary condensation occurs; these types exhibit hysteresis loops. Type VI occurs for some materials with relatively strong fluid-wall forces, usually when the temperature is near the melting point for the adsorbed gas (Balbuena and Gubbins, 1993; Sangwichien et al., 2002).

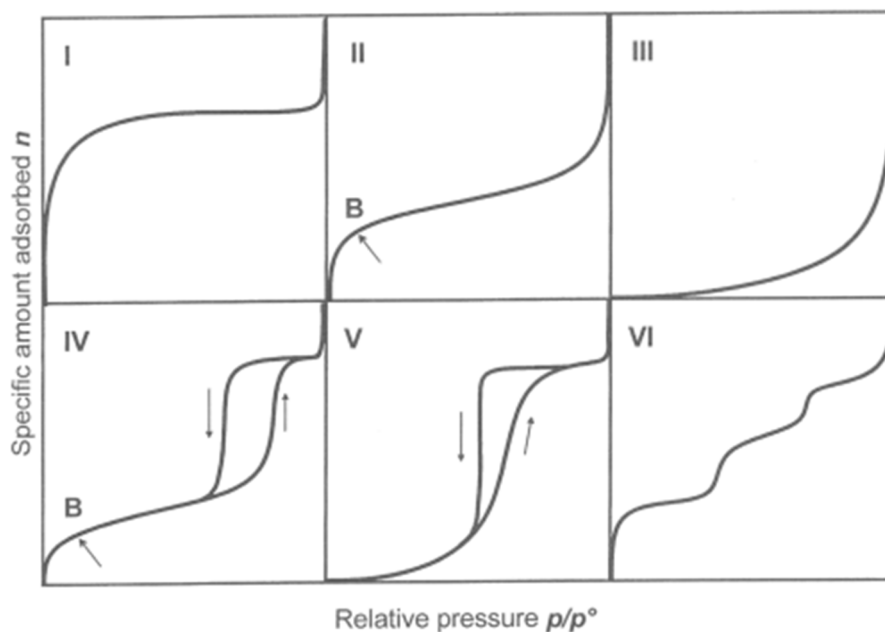


Figure 3.12. Classification of adsorption isotherms defined by IUPAC. (BEL Japan Inc., 2015).

Table 3.2, gives the nitrogen adsorption results of prepared catalysts and commercial (P-25) catalyst used in the study. Figures 3.13-3.15 show nitrogen adsorption isotherms of the catalysts.

Effect of calcination temperature on surface characteristics was investigated with the 1%Fe/TiO₂ (IW) catalyst. As seen from the Table 5, increase in the calcination temperature decreases the average pore diameter and total pore

volume. In accordance with the study of Jamalluddin and Abdullah (2011), when the calcination temperature increases to 700 °C, surface area of the catalyst decreases sharply as observed in this study. This effect can also be seen from the adsorption isotherms.

Similar with the study of Arana et al. (2002; 2003) and Akpan and Hameed (2009), the catalysts prepared with incipient wetness impregnation method at the calcination temperature of 500 °C, increasing Fe loading from 1wt.% to 5wt.% slightly decreases the surface area. As seen from the Figure 3.13, the adsorption isotherms of catalysts prepared by the incipient wetness impregnation method are of type II according to the IUPAC classification. It is well known that the isotherm of type II corresponds to multilayer formation and is commonly obtained in the case of physical adsorption. These results are in accordance with the study of Wang et al. (2004).

In the catalysts prepared by sol-gel method, Fe loading increases the surface area. This effect is seen both in the Fe loaded TiO₂ (SG) catalysts and Fe loaded TiO₂-Ce catalyst. 1%Fe/TiO₂-Ce has the highest BET surface area. Also for these catalysts microporous structure did not occur and the pores are in the form of macro+mesopores. According to the IUPAC classification nitrogen adsorption isotherms of both Fe/TiO₂ (SG) catalysts and Fe/TiO₂-Ce catalysts display type IV, Figures 3.14 and 3.15. These results are in accordance with the literature (Lopez et al., 2004; Wang et al., 2004).

Table 3.2. Nitrogen adsorption data of the prepared catalysts

Catalyst	BET surface Area, m ² /g	Langmuir Surface area, m ² /g	Micropore Area, m ² /g	External Surface Area, m ² /g	Total pore volume, cm ³ /g	Micropore volume, cm ³ /g	Macro+Mesopore volume, cm ³ /g	Max. volume adsorbed, cm ³ /g	Average pore diameter (4V/A by BJH), nm
TiO ₂ (P-25)	54.09	74.70	8.20	45.89	0.014	0.003372	0.010628	51.70	5.91
1%Fe/TiO ₂ 300 °C calcination(IW)	52.23	79.45	5.96	46.27	0.016	0.002661	0.013339	89.36	10.02
1%Fe/TiO ₂ 500 °C calcination(IW)	55.52	76.26	1.80	53.73	0.015	0.000425	0.014575	85.15	8.64
1%Fe/TiO ₂ 700 °C calcination(IW)	18.55	28.39	2.12	16.43	0.0058	0.000903	0.004897	20.98	6.89
5%Fe/TiO ₂ (IW)	50.49	68.74	3.18	47.32	0.013877	0.001165	0.012712	78.65	8.85
TiO ₂ (SG)	39.51	54.05	-	39.51	0.010464	-	0.010464	30.21	4.305
0.5%Fe/TiO ₂ (SG)	44.45	66.71	-	44.45	0.011167	-	0.011167	31.67	3.86
1%Fe/TiO ₂ (SG)	58.86	83.79	-	58.86	0.014556	-	0.014556	44.34	4.18
2%Fe/TiO ₂ (SG)	55.49	75.76	-	55.49	0.014015	-	0.014015	37.76	3.88
5%Fe/TiO ₂ (SG)	75.48	102.60	-	75.48	0.021958	-	0.021958	46.49	3.54
TiO ₂ -Ce	55.99	76.08	-	55.99	0.012067	-	0.012067	44.10	4.15
1%Fe/TiO ₂ -Ce	123.04	190.31	-	123.04	0.037688	-	0.037688	183.63	7.29
5%Fe/TiO ₂ -Ce	110.96	150.34	1.11	109.86	0.016935	-	0.016935	99.67	4.70

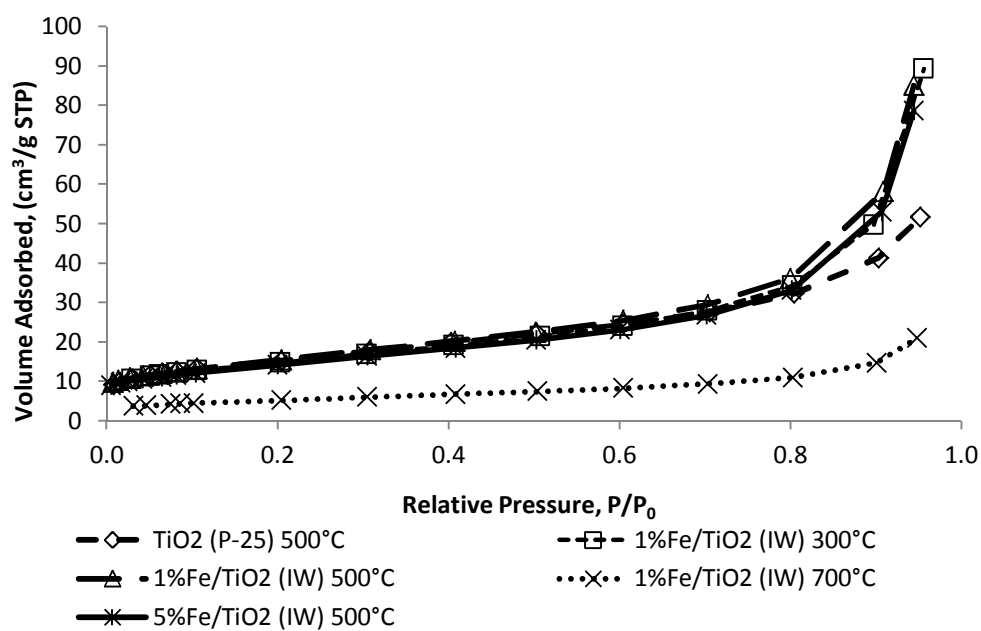


Figure 3.13. Nitrogen adsorption isotherms of catalysts synthesized by using the incipient wetness impregnation method.

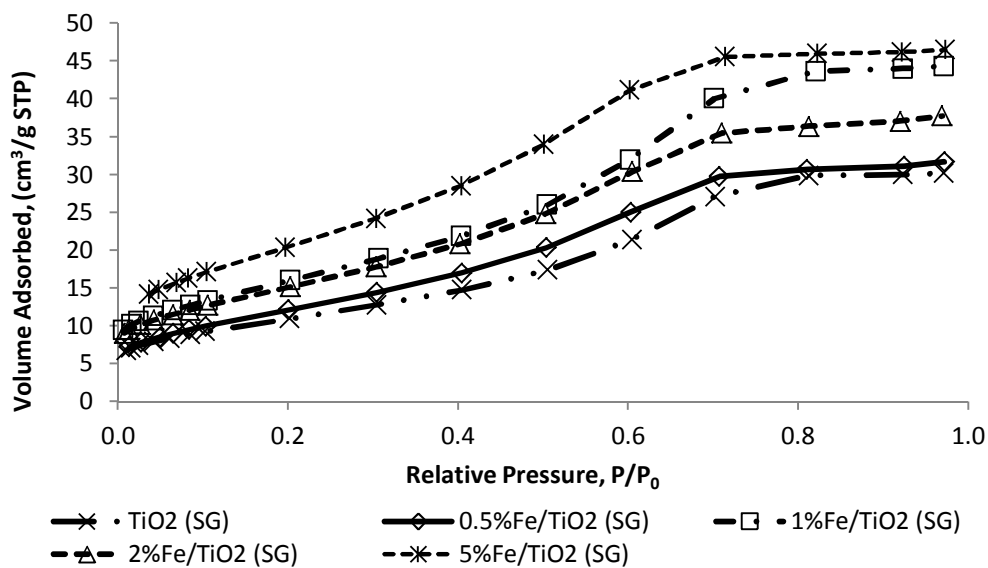


Figure 3.14. Nitrogen adsorption isotherms of catalysts synthesized by using the sol-gel method.

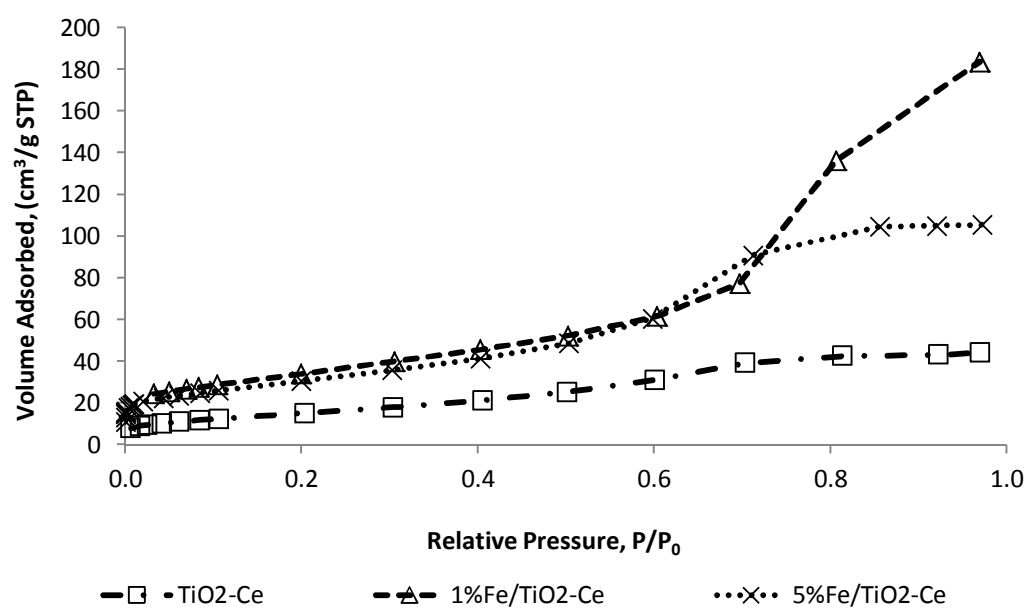


Figure 3.15. Nitrogen adsorption isotherms of $x\%\text{Fe}/\text{TiO}_2\text{-Ce}$ catalysts.

3.1.6 UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS)

A modified Kubelka-Munk function in the literature was used for determining the band gap energy (E_g) of the catalyst from the diffuse reflectance spectra (Mi et al., 2013):

$$(F(R) * hv)^{1/n} = B(hv - E_g) \quad (3.3)$$

where h is the Planck's constant, v is the light frequency, B is a constant,

$$F(R) = \frac{(1-R)^2}{2R}, \quad R \text{ is the reflectance.}$$

n can take different values depending on the type of electronic transition, where $n=2$ for an indirect allowed transition. TiO_2 is considered as an indirect semiconductor so we use $n=2$ for indirect transition in this study.

Figure 3.16 shows the $(F(R) * hv)^{1/2}$ versus energy (hv) curve as an example to show how we calculate the band gap energy. The value of the band gap energy (eV) can be obtained by extrapolating the linear part of the curve to the horizontal axis (hv axis) for intersection.

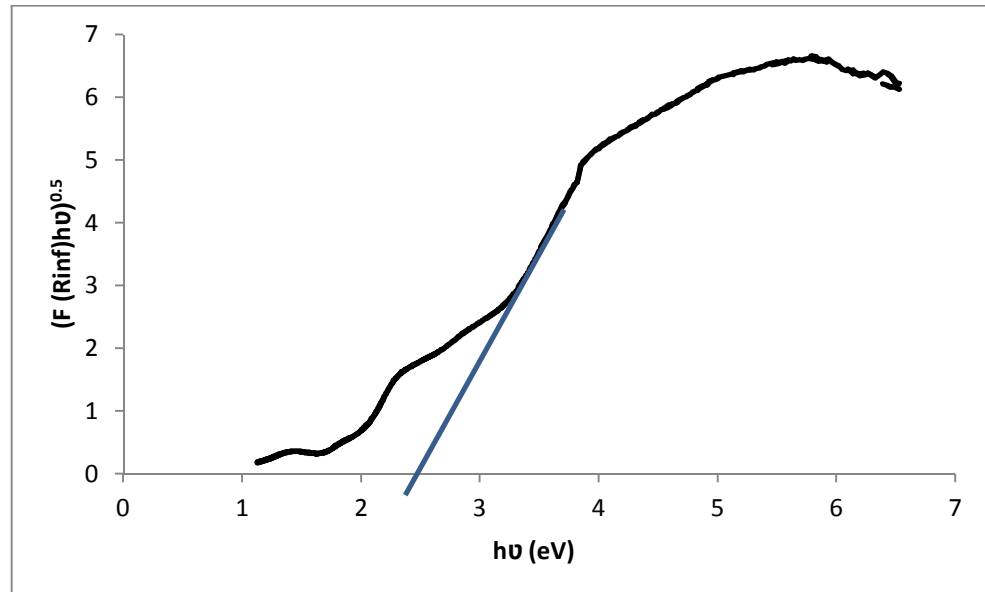


Figure 3.16. UV-Vis DRS Spectra for the indirect band gap energy value of 5wt.%Fe doped TiO_2 (IW) catalyst.

For the catalysts prepared by IW method the indirect band gap energy values are obtained to be 3.05, 2.89, 2.9, 2.78 and 2.5 eV for samples TiO_2 (P-25) 500, 1%Fe/ TiO_2 (IW) 300, 1%Fe/ TiO_2 (IW) 500, 1%Fe/ TiO_2 (IW) 700 and 5%Fe/ TiO_2 (IW), respectively.

For the catalysts prepared by sol-gel method the indirect band gap energy values are found to be 3.0, 2.44, 2.32, 2.03 and 1.68 eV for the samples of TiO_2 (SG), 0.5%Fe/ TiO_2 (SG), 1%Fe/ TiO_2 (SG), 2%Fe/ TiO_2 (SG), and 5%Fe/ TiO_2 (SG), respectively.

The relationship between the band gap energy and Fe loading is shown in Figure 3.17. As seen clearly from the figure band gap energy gradually decreases by increasing the Fe content. These results are in a good accordance with the literature (Yalcin et al., 2010). It can be attributed to the increasing charge transfer between the d electrons of Fe and the TiO_2 conduction or valence band, with the increase of Fe doping concentration, since the Fe dopant could introduce impurity levels within the band gap of TiO_2 .

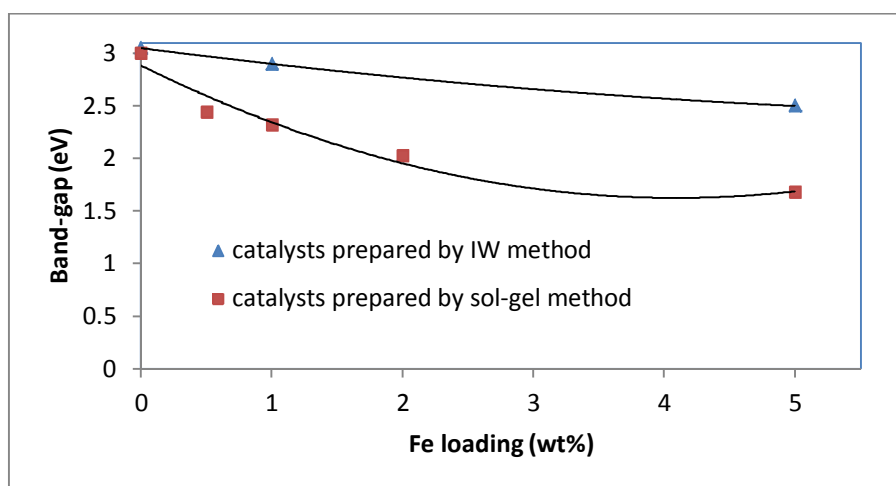


Figure 3.17. Plot of the band-gap energy vs. Fe loading of the catalysts

For the x% TiO_2 -Ce catalysts the indirect band gap energy values are 2.44, 2.65 and 1.47 eV for samples TiO_2 -Ce, 1%Fe/ TiO_2 -Ce and 5%Fe/ TiO_2 -Ce, respectively. Dopping of Ce into the TiO_2 significantly decreased the

corresponding band gap energy, that is much lower than that of the commercial TiO₂ (P25, 3.05 eV) and TiO₂ prepared by sol-gel method (3.0 eV). Similar result was observed in the study of Xiao et al. (2013), they observed a decrease in band gap energy from 2.756 to 1.678 eV with the addition of Ce into the TiO₂.

3.1.7 ICP-AES measurements

Iron contents of the catalysts were determined by ICP-AES technique. Table 3.3 presents iron contents of the catalysts.

Table 3.3. Fe content of the catalysts measured by ICP analysis

Catalyst	Fe (wt. %)	
	Intended Loading	Actual Loading (ICP)
1%Fe/TiO ₂ (IW) 300°C	1	0.93
1%Fe/TiO ₂ (IW) 500°C	1	0.93
1%Fe/TiO ₂ (IW) 700°C	1	0.93
5%Fe/TiO ₂ (IW) 500°C	5	4.46
0.5%Fe/TiO ₂ (SG)	0.5	0.42
1%Fe/TiO ₂ (SG)	1	0.87
2%Fe/TiO ₂ (SG)	2	1.78
5%Fe/TiO ₂ (SG)	5	3.64
1%Fe/TiO ₂ -Ce	1	0.83
5%Fe/TiO ₂ -Ce	5	4.15

As shown in Table 3.3, iron contents of the 1 wt% iron containing TiO₂ catalysts prepared by incipient wetness impregnation and sol-gel methods were measured as 0.93% and 0.87%, respectively. Iron content of 1 wt% iron containing TiO₂-Ce catalyst was measured as 0.83. These results are very close to the theoretical amount. The amount of iron in the 5 wt% iron containing TiO₂ catalyst

prepared by the sol-gel method was measured as 3.64% which is lower than the theoretical amount. When iron was loaded with the use of incipient wetness impregnation method, Fe content was very close to the theoretical value particularly for 5%Fe/TiO₂ (IW) catalyst (4.46%). Iron content was determined to be 4.15 for 5%Fe/TiO₂-Ce catalyst. The Fe contents were very close to the theoretical values for the 2 wt% and 0.5 wt% iron containing catalysts prepared by sol-gel method as 1.78% and 0.42%, respectively.

3.2 Degradation Studies of RY 84 by Ultrasound

3.2.1 Ultrasonic degradation of RY 84 in ultrasonic bath

The effects of ultrasonic power, volume of dye solution and initial dye concentration on decolorization of RY 84 were investigated in ultrasonic bath as indirect ultrasonic degradation application by using 25 mg/L RY 84 solution at 25 °C. Sonication time was taken as 1 h.

Effect of ultrasonic power

The effect of ultrasonic power in ultrasonic bath was examined for powers of 70, 84 and 98 W for 25 mg/L, 150 mL RY 84 solution and the obtained results were given in Figure 3.18. Color removal degree was achieved as 2.8 %, 2.6 % and 3.3 % for powers of 70, 84 and 98 W, respectively. The highest decolorization degree was observed at the highest power of 98 W. The standard deviation of the average of independent experiments changed in the range of ± 0.07 to 1.33.

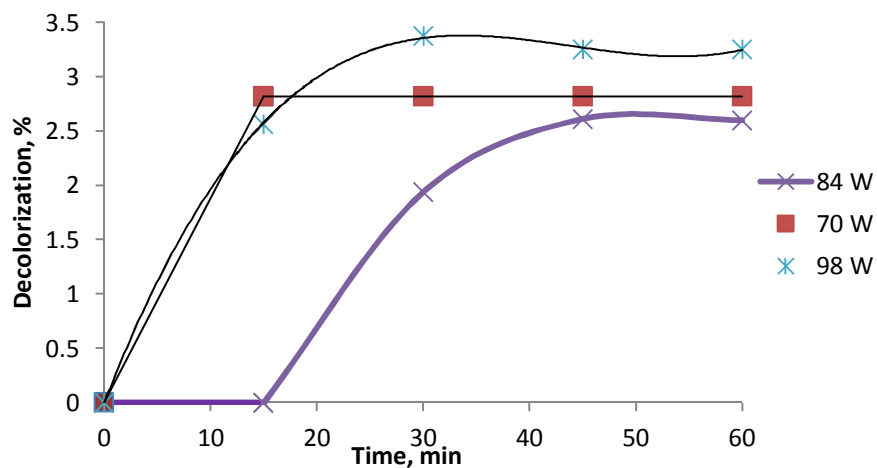


Figure 3.18 .Effect of ultrasonic power on decolorization of 25 mg/L, 150 mL of RY 84 solution in ultrasonic bath.

Ultrasound intensity is defined as the ratio of the power input to the system to the vibration area (power/vibration area). When power is increased at the same reactor area, ultrasound intensity increases. An increase in ultrasound intensity means an increase in the acoustic amplitude. The collapse time, the temperature and the pressure on collapse are all dependent on the acoustic amplitude; the cavitation bubble collapse will be more violent at higher acoustic amplitudes. An increase in intensity will thus result in greater sonochemical effects in the collapsing bubble (Dukkanci and Gunduz, 2006). Therefore, because of the increasing acoustic amplitudes, decolorization of RY 84 increases.

Effect of volume of dye solution

The experiments were also performed by 350 mL of dye solution at the same conditions (25 mg/L, 98 W) but no color removal could be obtained. This is because the power intensity (power/volume) is too low and enough OH radicals cannot be produced to degrade the dye.

Effect of initial dye concentration

To observe the effect of initial dye concentration on degradation in ultrasonic bath, the experiments were done with 75 mg/L, 150 mL of dye solution at 98 W, as well. However, no color removal could be obtained with this initial dye concentration.

These results indicate that low dye concentration and long sonication time may be more efficient in degradation of dye.

3.2.2 Sonication of RY 84 in ultrasonic reactor

The effects of ultrasonic power, volume of dye solution, initial dye concentration, addition of H_2O_2 and initial pH of dye solution on decolorization of RY 84 were studied in ultrasonic reactor as direct ultrasonic degradation application by using 250 mL of RY 84 solution at 25 °C.

Effect of ultrasonic power

Figure 3.19 shows the effect of ultrasonic power on sonication of 25 mg/L of 250 mL RY 84 solution. It was observed that color removal increased by increasing ultrasonic power. The highest decolorization degree of 28.8 % was observed at the highest power (75 W). Figure 3.19 also shows the results with a standard deviation range of ± 0.09 to ± 1.4 .

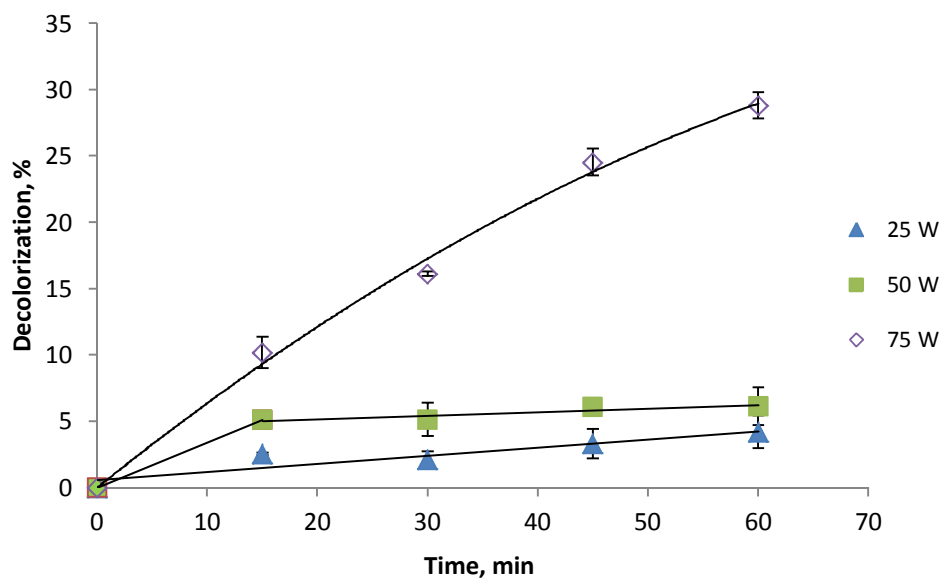


Figure 3.19. Effect of ultrasonic power on decolorization of 25 mg/L, 250 mL RY 84 solution in ultrasonic reactor

As mentioned before, more $\text{OH}^\bullet$ radicals, which are produced with the increasing ultrasonic power, caused to increase the power intensity and more color removal could be achieved.

Effect of volume of dye solution

The effect of volume of dye solution on decolorization was determined with 250 and 350 mL of 25 mg/L RY 84 aqueous solutions at a power of 75 W in ultrasonic reactor. As it is seen in Figure 3.20, decolorization degree of the dye solution increased from 23.3 % to 28.8 % with decreasing the volume of the RY 84 solution from 350 mL to 250 mL and the standard deviation of the average of independent runs varied in the range of ± 0.45 to ± 2.55 .

As explained in power effect, ultrasonic intensity is defined as the ratio of the power input to the volume. Therefore, the increase in volume of sonication decreases the power intensity (power/volume) causing a decrease in dye decolorization degree.

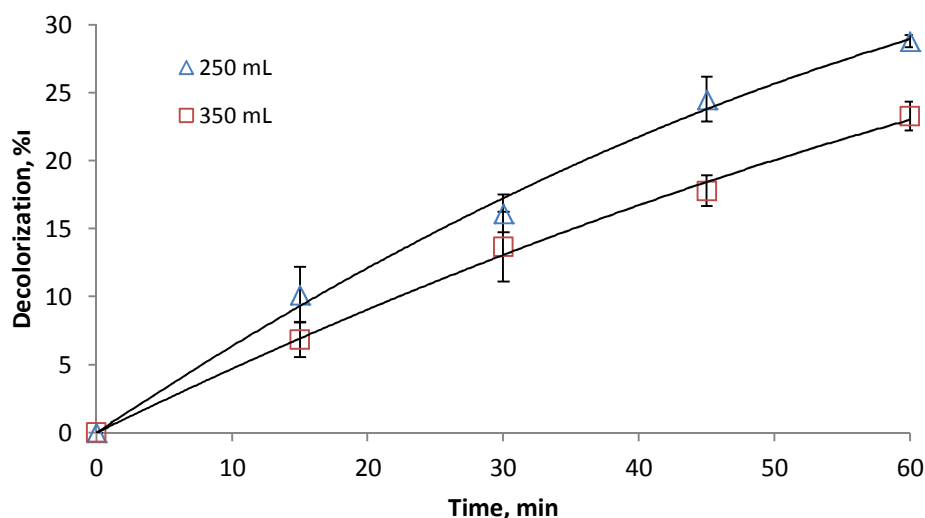


Figure 3.20. Effect of dye solution volume on decolorization of 25 mg/L of RY 84 solution at 75 W in ultrasonic reactor.

Effect of initial RY 84 concentration

Effect of initial RY 84 concentration results with a standard deviation range of ± 0.09 to ± 4.1 are shown in Figure 3.21. Experiments were performed by 250 mL of 10, 25 and 75 mg/L RY 84 aqueous solutions in ultrasonic reactor at a power of 75 W. As the initial concentration increased from 10 mg/L to 25 mg/L and then to 75 mg/L, decolorization degree decreased from 36.9 % to 28.8 % and to 17.9 %, respectively. The highest decolorization degree, 36.9 %, was observed with the lowest initial concentration of RY 84, namely 10 mg/L. This observation agrees with the results of other studies (Findik and Gunduz, 2007; Gultekin and Ince, 2006; He et al., 2007b; Kritikos et al., 2007)

According to Kim et al. (2001) most reaction takes place at the bubble-liquid interface and decomposition of volatile compound may be limited by available interfacial area. The higher initial concentration of volatile compound and corresponding higher amounts of the intermediates at the interface may inhibit the overall pollutant decomposition (Jiang et al., 2002).

On the other hand, as known the ratio of constant pressure and constant volume heat capacities of gas mixtures decreases with increasing concentration of volatile compound. The decrease in specific heat ratio lowers the temperature and

pressure within the cavitation bubbles causing a decrease in sonochemical degradation of volatile compound (Findik and Gunduz, 2007). Decolorization degree of RY 84 is inversely proportional to the initial concentration of dye solution sonicated.

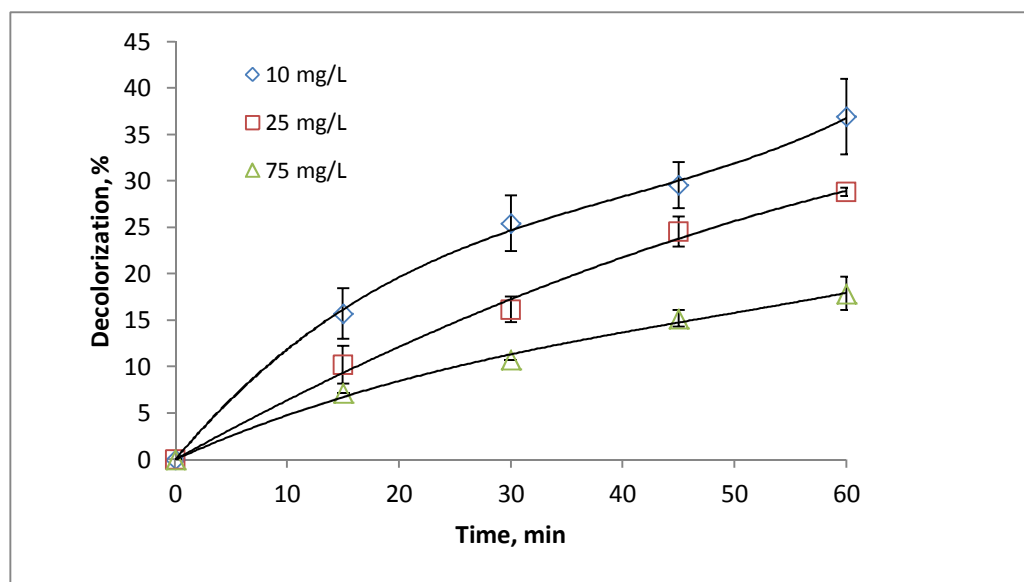


Figure 3.21. Effect of initial dye concentration on decolorization of 250 mL RY 84 solution at 75 W in ultrasonic reactor.

Effect of H_2O_2 addition

In further experiments, the effect of H_2O_2 addition to the 250 mL of solution containing 25 mg/L RY 84 at a power of 75 W was studied. Results are shown in Figure 3.22 with a standard deviation range of ± 0.16 to ± 2.28 .

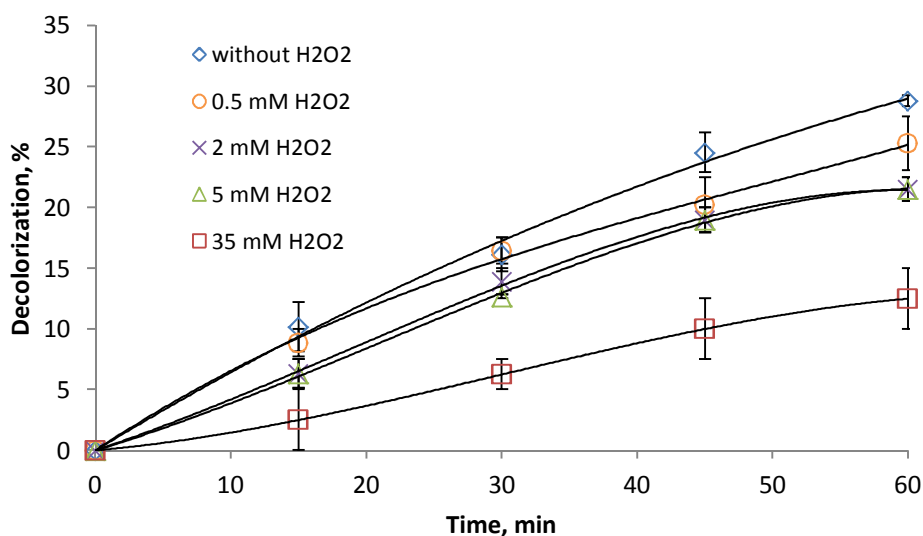


Figure 3.22. Effect of H₂O₂ addition on decolorization of 25 mg/L, 250 mL RY 84 solution at 75 W in ultrasonic reactor.

The highest decolorization degree of 28.8% was observed without H₂O₂ addition. Decolorization degree decreases with the addition of H₂O₂. The lower decolorization degree in the presence of H₂O₂ may be attributed to the increased level of OH• scavenging by H₂O₂ itself. As concentration of H₂O₂ increased, its OH• scavenging effect may increase causing a decrease in degradation.

Also, the effect of H₂O₂ addition was studied with 250 mL of 10 mg/L RY 84 aqueous solutions with the addition of 0.5 and 2 mM H₂O₂. As it is seen in Figure 3.23, the highest decolorization degree of 36.9 % was observed without H₂O₂ addition. In Figure 3.23 results are given with a standard deviation range of ±0.14 to ±4.09.

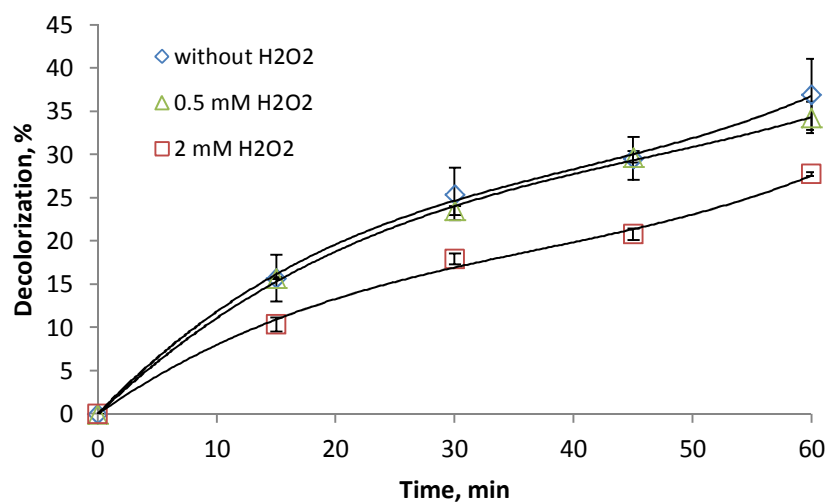


Figure 3.23. Effect of H₂O₂ addition on decolorization of 10 mg/L, 250 mL RY 84 solution at 75 W in ultrasonic reactor.

Effect of initial pH solution

Figure 3.24 shows RY 84 decolorization as a function of irradiation time during ultrasonic degradation under acidic and alkaline conditions. In Figure 3.24 results are given with a standard deviation range of ± 1.13 to ± 4.09 . As can be seen, slightly higher decolorization degree of RY 84 was observed at pH of 3.7 (38.1 %) than that at dye pH of 6 (36.9 %). Acidic pH had a positive influence on the reactivity of the system and generation of free radicals was enhanced when the pH decreased. The reaction of OH• radicals with RY 84 can be more efficient at low pH (He et al., 2007b).

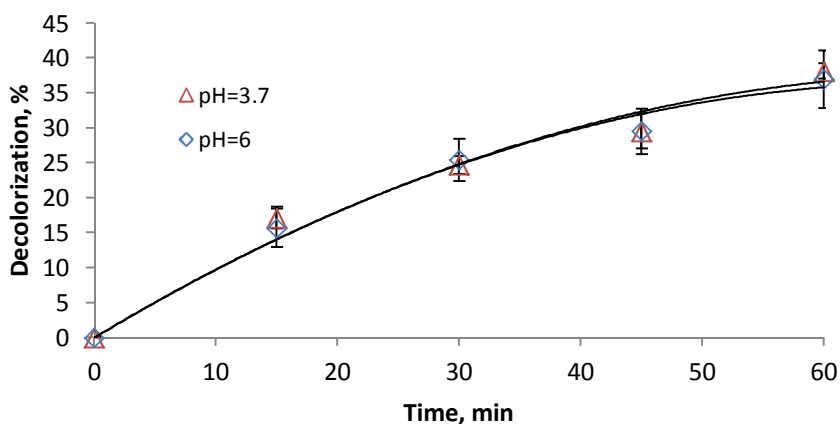


Figure 3.24. Effect of initial pH of the solution on decolorization of 10 mg/L of 250 mL RY 84 solution at 75 W in ultrasonic reactor.

Effect of ultrasonic frequency

The effect of ultrasonic frequency was examined by comparing the experiments in ultrasonic bath (40 kHz) and ultrasonic reactor (850 kHz). According to all experiments, it was observed that 3.3 % decolorization degree was obtained in ultrasonic bath whereas the optimum decolorization degree occurred as 38.1 % in ultrasonic reactor. As frequency increases, the pulsation and collapse of the bubble occur more rapidly, number of cavitation bubbles increases and realizing a higher concentration of OH^* radicals into the aqueous dye solution. These hydroxyl radicals react with the dye in the solution (Dukkanci and Gunduz, 2006; Dukkanci et al., 2012). Due to this radical reaction, the color removal rate of RY 84 in the ultrasonic reactor was increased 10 times of that in ultrasonic bath.

According to the investigation of the effects on sonication of RY 84, the optimum color removal efficiency (38.1 %) was obtained by 250 mL of 10 mg/L RY 84 aqueous solution in ultrasonic reactor at a power of 75 W, in the absence of H_2O_2 , under acidic pH of 3.7. However, there was no COD removal at these optimum conditions.

3.3 Catalyst Activity Experiments – Degradation Studies of RY 84 by SonophotoFenton Reaction

Synthesized catalysts were tested, in order to determine the most active catalyst, in the sonophotoFenton degradation of RY 84 with the experimental set-up given in Figure 2.4. The runs were carried out under the same reaction conditions of 25 mg/L initial dye concentration, 0.5g/L catalyst loading, 35 mM H_2O_2 addition, constant temperature at 20°C, 40W ultrasonic power and 20 kHz frequency and two UV lamps with 4 W. The experiments were done at the dye pH of 6.

In order to determine the most effective catalyst, color removal efficiency and COD removal % after 120 min were taken into account. COD analysis is a widely used technique to determine the mineralization degree of organic pollutants in water. The analysis measures the chemical oxygen demand of compounds in water.

Degradation runs of RY 84 were done by sonophotoFenton oxidation process firstly on the catalyst prepared by incipient wetness impregnation method.

Before starting the sonophotoFenton process; after addition of the catalyst into the dye solution, the suspension was left 30 minutes in dark to establish the adsorption-desorption equilibrium of dye on surface. Adsorption of RY 84 for 30 min in the dark onto the incipient wetness impregnated catalysts surfaces were found to be 14.6%, 14.4%, 13.4%, 9.7% and 12.4% for TiO_2 (P 25), 1%Fe/ TiO_2 300°C, 1%Fe/ TiO_2 500°C, 1%Fe/ TiO_2 700°C and 5%Fe/ TiO_2 500°C, respectively.

Results of the sonophotoFenton degradation of RY 84 with the presence of catalysts prepared by incipient wetness impregnation method are shown in Figure 3.25.

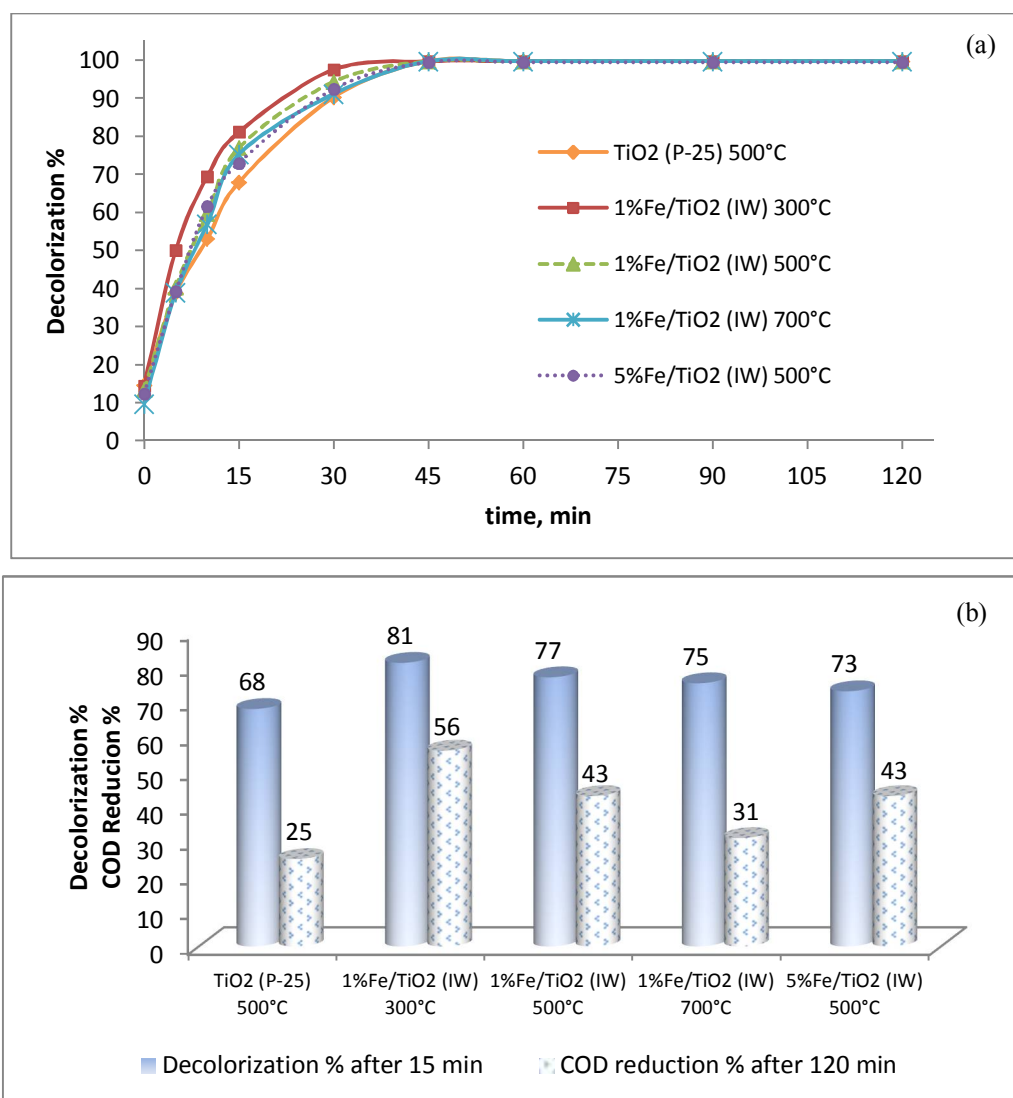


Figure 3.25. SonophotoFenton degradation of RY 84 with the catalysts prepared by incipient wetness impregnation method (a) Time dependency of decolorization (b) Decolorization,% after 15 min and COD removal% after 120 min

(20°C, initial RY 84 concentration of 25 mg/L, 35 mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

As shown in Figure 3.25 all catalysts achieved over 90% color removal within 30 min. Color removal achieved by Fe-containing catalysts are significantly faster than those obtained with the non-doped TiO₂ (P 25). Addition of 1 wt.% iron into the TiO₂ (P-25) calcined at 500°C increases the initial color removal from 68% to 77% and COD reduction from 25% to 43% after 15 min of degradation time. As the calcination temperature of the catalyst was increased from 300°C to 700°C, RY 84 removal after 15 min. and COD reduction after 120 min reduced from 81% to 75 % and 56% to 31%, respectively. This result might be contributed by the presence of anatase phase in the 1 wt.% iron containing

TiO₂ (P 25) calcined at 300°C. As seen from the Table 3.1, anatase phase percentage decreases from 81% through 73.3% to 15.9% with increasing the calcination temperature from 300°C to 500°C and to 700°C, respectively. Also as seen from the surface analysis of the catalysts (Table 3.2), a sharp decrease in BET surface area (from 52.23 m²/g to 18.55 m²/g) and total pore volume (0.016 cm³/g to 0.0058 cm³/g) occurred when the calcination temperature was increased from 300°C to 700°C. High percentage of the anatase phase was the main influence factor of the catalytic activity of the catalysts prepared by incipient wetness impregnation method. Similar results were observed in the sonocatalytic process (Jamalluddin and Abdullah, 2011) where high fraction of anatase phase enhanced the catalytic activity and higher calcination temperature caused anatase to rutile phase transformation with decrease in the BET surface area and total pore volume. So a decrease was observed in the efficiency of the catalyst. COD reduction was always less than the decolorization degree. It may be due to the presence of some more stable uncolored intermediates (Sivakumar et al., 2013).

It is well known that, the photocatalytic efficiency of a photocatalyst depends on the adsorption ability, quantum efficiency of the photo-generation of the electron-hole pair and the diffusion speed (separation) of the electron-hole pair. The incorporation of Fe³⁺ into the TiO₂ promotes the formation of electron-hole pairs, lowers the recombination rate of electron-hole pairs and increases the separation efficiency because the Fe³⁺ can act as an electron-trapped agent. It is seen that the highest electron-hole separation efficiency may be obtained with 1wt.%Fe/ TiO₂ (IW) catalyst calcined at 300°C which has the photocatalytic activity.

Results of the sonophotoFenton degradation of RY 84 with the presence of catalysts prepared by sol-gel method are shown in Figure 3.26.

As seen from the Figure 3.26, iron loading to the catalysts prepared by sol-gel method didn't affect the COD reduction and color removal. Within the 15 min of degradation, color removal was higher than that with the catalysts prepared by incipient wetness impregnation method. Adsorption of RY 84 for 30 min in the

dark onto the catalysts surfaces prepared by sol-gel was found to be practically negligible (less than 4%).

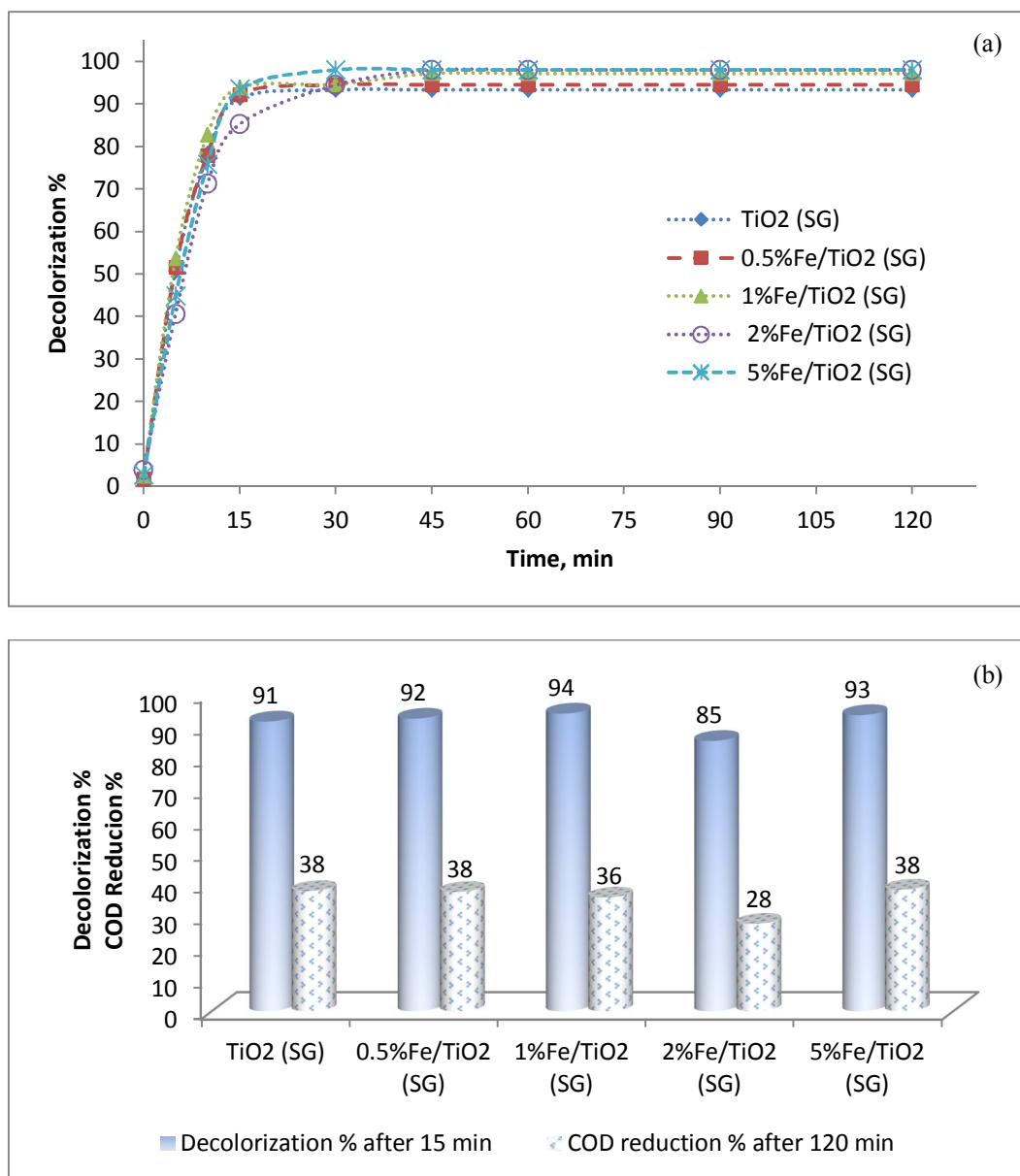


Figure 3.26. SonophotoFenton degradation of RY 84 with the catalysts prepared by sol-gel method (a) Time dependency of decolorization (b) Decolorization,% after 15 min and COD removal% after 120 min

(20°C, initial RY 84 concentration of 25 mg/L, 35 mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

Results of the sonophotoFenton degradation of RY 84 with the presence of TiO₂-Ce support catalysts are shown in Figure 3.27.

As shown in the Figure 3.27, addition of iron into the $\text{TiO}_2\text{-Ce}$ support slightly decreases the decolorization efficiency of the catalyst. It may be due to the enhancement in the visible-light photocatalytic activity rather than in the UV light photocatalytic activity. On the other hand, COD reduction increases with the 5wt.%Fe/ $\text{TiO}_2\text{-Ce}$ catalyst.

It was desired to test also the catalytic performances of the catalysts prepared by sol-gel method and supported on $\text{TiO}_2\text{-Ce}$ and calcined at 300°C . Unfortunately, 300°C is not an appropriate temperature for calcination of these catalysts. Because, the temperature of 300°C was not an enough temperature for the complete combustion of carbon in tetra n-butyl titania which was used as titania source during the preparation of these catalysts. So the mentioned catalysts could not be calcined at 300°C and their catalytic performances could not be tested in sonophotoFenton oxidation of RY 84.

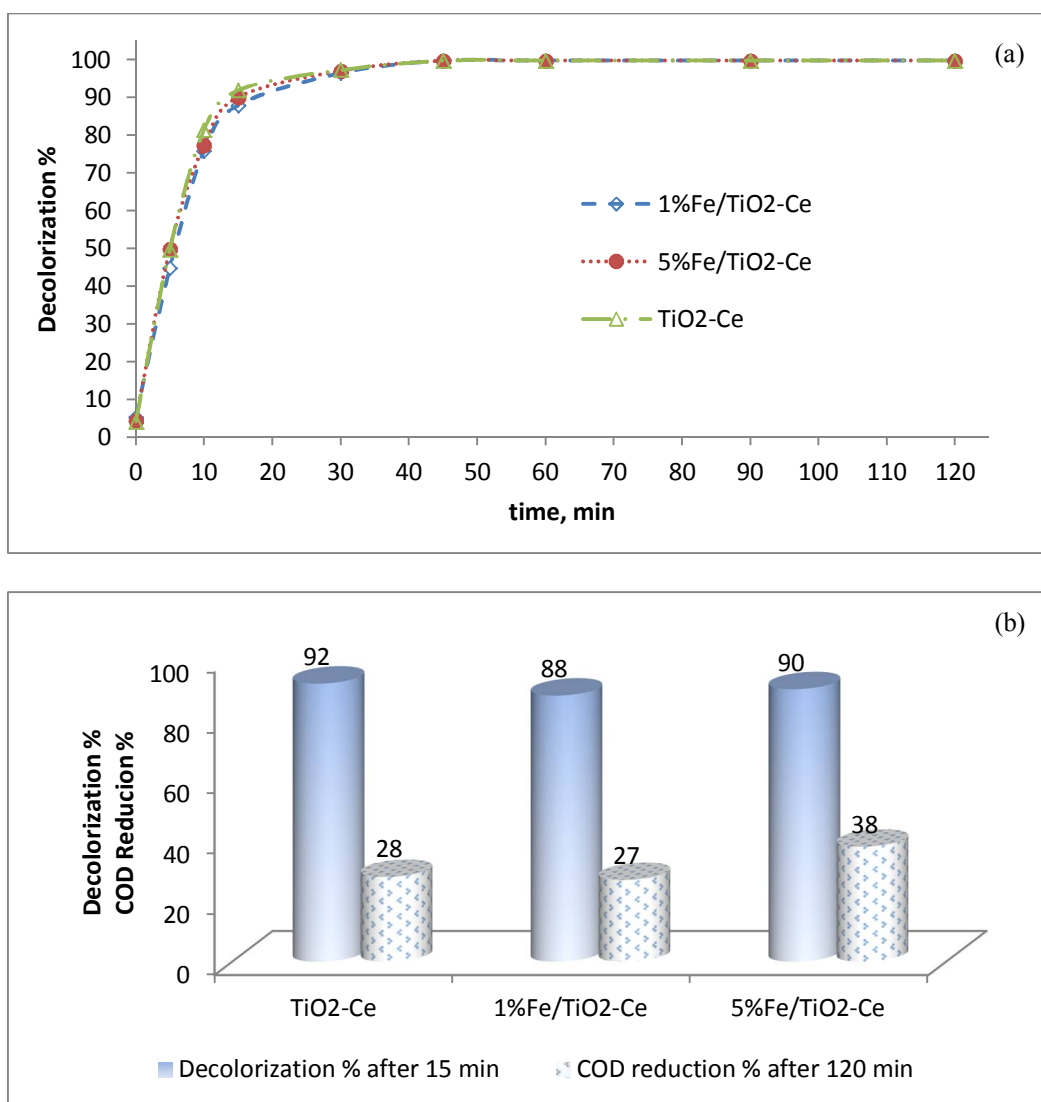


Figure 3.27. SonophotoFenton degradation of RY 84 with the TiO₂-Ce supported catalysts (a) Time dependency of decolorization (b) Decolorization,% after 15 min and COD removal% after 120 min

(20°C, initial RY 84 concentration of 25 mg/L, 35 mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

In order to compare the catalytic activity of the catalysts in terms of reaction rate constants, kinetic study was done for the sonophotoFenton degradation of RY 84 with the prepared catalysts. During the runs the reaction mixture was stirred vigorously at around 350 rpm. This vigorous stirring and turbulence created by ultrasound waves eliminate the external diffusion resistance between the bulk solution and the catalyst surface. Internal diffusion resistance was also negligible due to the catalyst particles in nano size. It was found that pseudo-first order kinetics was obeyed for the sonophotoFenton degradation of

RY 84. The apparent first order rate constant was calculated by using Eq 3.4 which fit the experimental data:

$$-\ln\left(\frac{C}{C_0}\right) = k_{app} t \quad (3.4)$$

where k_{app} is the apparent rate constant, C is the concentration of RY 84 remaining in the solution at time of t , and C_0 is the concentration at $t=0$.

In these calculations initial rate data were used.

The plot of $-\ln (C/C_0)$ versus time data is shown in Figure 3.28 for different prepared catalysts. The figure shows that the sonophotoFenton degradation of RY 84 follows the pseudo-first order kinetics. The calculated rate constants, k_{app} , were listed in Table 3.4 with regression coefficients (R^2).

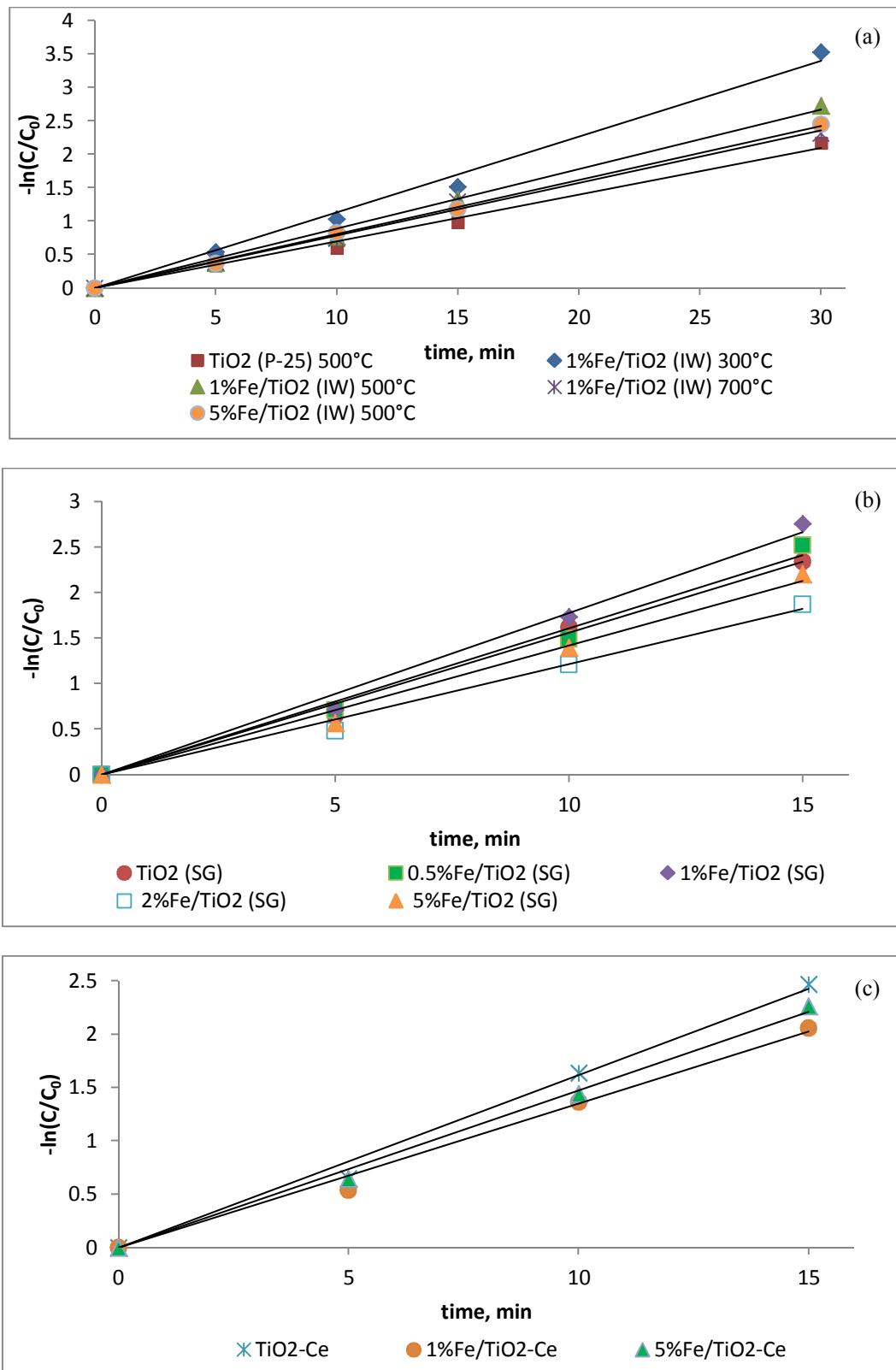


Figure 3.28. First-order kinetic plots for the sonophotoFenton degradation of RY 84 at 20°C with (a) catalysts prepared by incipient wetness impregnation method (b) catalysts prepared by sol-gel method (c) Fe/TiO₂-Ce catalysts

(20°C, initial RY 84 concentration of 25 mg/L, 35 mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

Table 3.4. The apparent first order rate constants (k_{app} , min^{-1}) and regression coefficients (R^2) for sonophotoFenton degradation of RY 84 at 20°C over prepared catalysts.

Catalyst	k_{ap} (min^{-1})	R^2
TiO ₂ P-25 500°C	0.069	0.9925
1%Fe/TiO ₂ (IW) 300°C	0.113	0.9912
1%Fe/TiO ₂ (IW) 500°C	0.089	0.9947
1%Fe/TiO ₂ (IW) 700°C	0.079	0.9947
5%Fe/TiO ₂ (IW) 500°C	0.081	0.9989
TiO ₂ (SG)	0.156	0.9937
0.5%Fe/TiO ₂ (SG)	0.161	0.9904
1%Fe/TiO ₂ (SG)	0.178	0.9905
2%Fe/TiO ₂ (SG)	0.122	0.9909
5%Fe/TiO ₂ (SG)	0.142	0.9902
TiO ₂ -Ce	0.162	0.9917
1%Fe/TiO ₂ -Ce	0.135	0.9921
5%Fe/TiO ₂ -Ce	0.147	0.9959

It is clearly seen that, the rate constants obtained for the catalysts prepared by sol-gel method and the catalysts with TiO₂-Ce support are much higher than those for the catalysts prepared by incipient wetness impregnation method. Nevertheless, it should kept in mind that not only the rate constants but also COD removal is significant for the decision of the performance of a catalyst.

The results on the decolorization degrees after 15 min and 120 min and COD removal after 120 min of the sonophotoFenton degradation of RY 84 with all the prepared catalysts were summarized in the Table 3.5.

As seen in Table 3.4 and as summarized in Table 3.5, iron addition to the commercial TiO₂ (P-25) enhanced the removal efficiency. 1%Fe/TiO₂ which was

calcined at 300°C has the highest COD removal% and apparent rate constant among the catalysts prepared by incipient wetness impregnation method. Rate constants in sonophotoFenton degradation of catalysts prepared by sol-gel and TiO₂-Ce support catalysts were higher than that of 1%Fe/TiO₂ catalyst which was calcined at 300°C. However, after 120 min of sonophotoFenton degradation color removal was the same with all the catalysts but maximum COD reduction was obtained with the 1%Fe/TiO₂ which was prepared by incipient wetness impregnation method and calcined at 300°C (56%). The reduction in the COD indicates that not only a color removal is obtained but also a mineralization takes place. Dye solution mineralized into smaller molecules like CO₂, H₂O, NO₂ and so on. In accordance with the literature COD reduction% was less than the color removal%. This result, as mentioned earlier, may due to the presence of some more stable uncolored intermediates (Sivakumar et al., 2013). According to the results given in the literature during the oxidation of dye, when the solution is still colored there is only small decrease in COD. This is because dye molecules are decomposed to compounds that have lower molecular weight and the resulting intermediates still induce to the COD of the solution. After the complete color removal of the solution, COD decreases and reaches a stable level. Decrease in COD corresponds to the oxidation of most stable compounds. This indicates that almost complete mineralization of intermediates has occurred (Konstantinou and Albanis, 2004).

As a consequence, 1%Fe/TiO₂ which was prepared by incipient wetness impregnation method and calcined at 300°C was decided to select as the most effective catalysts for the sonophotoFenton degradation of RY 84 at the operating conditions of 20°C, initial RY 84 concentration of 25 mg/L, 35 mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps.

Table 3.5. Results summary of the sonophotoFenton degradation of RY 84 with the prepared catalysts

(20°C, initial RY 84 concentration of 25 mg/L, 35 mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

Catalyst	Decolorization, %		COD reduction, %
	t=15 min	t=120 min	COD _{t=120}
TiO ₂ (P-25) 500°C	68	99	25
1%Fe/TiO₂ (IW) 300°C	81	100	56
1%Fe/TiO ₂ (IW) 500°C	77	100	43
1%Fe/TiO ₂ (IW) 700°C	75	100	31
5%Fe/TiO ₂ (IW) 500°C	73	100	43
TiO ₂ (SG)	90	95	38
0.5%Fe/TiO ₂ (SG)	92	96	38
1%Fe/TiO ₂ (SG)	94	98	36
2%Fe/TiO ₂ (SG)	85	99	28
5%Fe/TiO ₂ (SG)	93	98	38
TiO ₂ -Ce	92	99	28
1%Fe/TiO ₂ -Ce	88	100	27
5%Fe/TiO ₂ -Ce	90	100	38

The amount of iron dissolved in the solution was determined after 120 min of sonophotoFenton oxidation. Table 3.6 summarizes the leaching level of iron species (mg/L) in the reaction medium and iron loss% of the catalyst at the end of each catalytic test. As seen from the Table 3.6 Fe leaching remained very low during the processes. Although a small amount of iron was observed in the aqueous solution, it can be said clearly that the sonophotoFenton oxidation is

mainly due to the heterogeneous active sites from the catalysts, instead of homogeneous Fe dissolved species.(Zhong et al., 2011)

Table 3.6. Iron leaching after 120 min sonophotoFenton oxidation of RY 84 with different iron containing catalysts

(20°C, initial RY 84 concentration of 25 mg/L, 35 mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

Catalyst	Iron leaching, mg/L	Iron loss % of the catalyst*
1%Fe/TiO ₂ (IW) 300°C	0.11	2.4
1%Fe/TiO ₂ (IW) 500°C	0.17	3.7
1%Fe/TiO ₂ (IW) 700°C	0.29	4.1
5%Fe/TiO ₂ (IW) 500°C	0.32	0.9
0.5%Fe/TiO ₂ (SG)	0.16	7.6
1%Fe/TiO ₂ (SG)	0.15	3.4
2%Fe/TiO ₂ (SG)	0.46	5.2
5%Fe/TiO ₂ (SG)	0.33	1.5
1%Fe/TiO ₂ -Ce	0.07	1.7
5%Fe/TiO ₂ -Ce	0.05	0.2

*Based on the actual iron loading of the catalysts

3.4 Degradation of RY 84 Using Individual and Combined Advanced Oxidation Processes

Before starting the parametric study, the studies on individually, binary and ternary combinations of advanced oxidation processes (catalyst, UV, US and H₂O₂) were studied in the experimental set-up shown in Figure 2.4.

3.4.1 Effect of individual oxidation process

Decolorization and COD reduction of 650 mL of 25 mg/L RY 84 was investigated at 20°C when only H_2O_2 (35 mM) or only catalyst (0.5 g/L of %1 Fe/TiO₂ (IW) calcined at 300°C) or only UV (4 W+4 W UV-C lamp) or only US (40W) was used for the degradation of dye. The results for decolorization% after 15 and 120 min reaction time and COD reduction% after 120 min results are given in Figure 3.29.

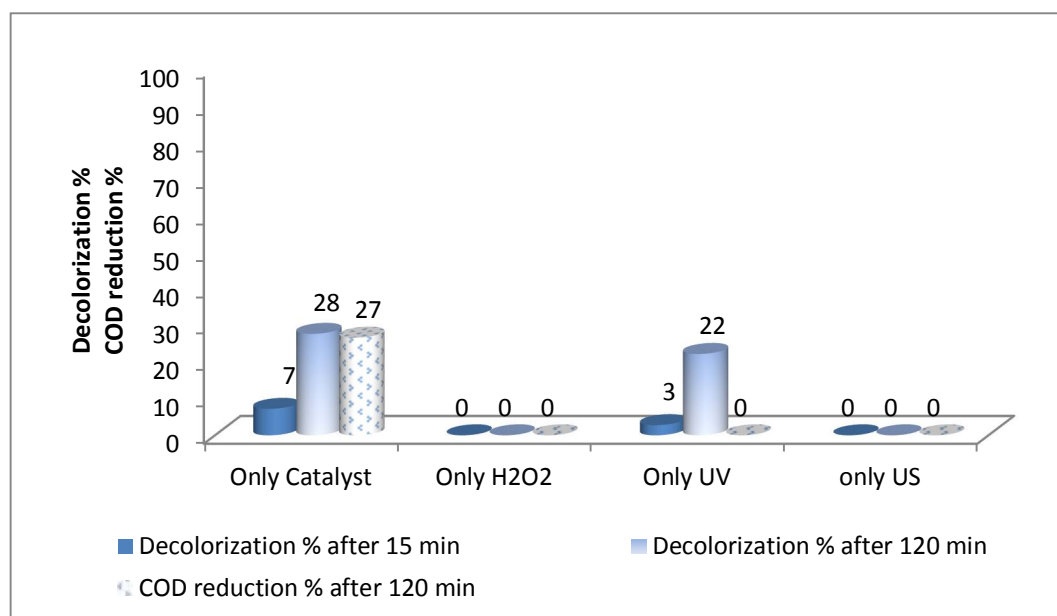


Figure 3.29. Decolorization and COD reduction of RY 84 in the presence of individual processes

(20°C, initial RY 84 concentration of 25 mg/L, according to the oxidation technique; 35 mM H_2O_2 , 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

No color removal and no COD reduction could be achieved when only US or only H_2O_2 was used for degradation of dye. UV light or catalyst alone provides a little color removal after 15 minute, 3% and 7% respectively. Color removal reaches to 22% with UV only and 28% with catalyst only. On the other hand, COD reduction could be achieved in the run with the catalyst only. This COD reduction and color removal may be due to the adsorption of the dye molecules on the catalyst surface. In the runs when only H_2O_2 or only US is applied, $\text{OH}^\bullet$ radicals formed are not high enough to react with the dye molecules.

3.4.2 Effect of binary oxidation processes

Decolorization and COD reduction of 650 mL of 25 mg/L RY 84 was investigated at 20°C with the combination of two individual processes. In these combinations, depending on the type of combination 35 mM H₂O₂, 0.5 g/L catalyst (%1 Fe/TiO₂ (IW) calcined at 300°C), UV lamp (4 W+4 W UV-C lamp) and 40 W US power were used. The results for decolorization% after 15 and 120 min reaction time and COD reduction% after 120 min results are given in Figure 3.30.

The highest color removal is obtained in the UV+H₂O₂ combination system being 71% and 92% after 15 and 120 minute of oxidation time, respectively. The decolorization efficiencies after 120 minute of these processes are in the following order:

$$\text{catalyst+UV} > \text{UV+H}_2\text{O}_2 > \text{UV+US} > \text{catalyst+US} > \text{catalyst+ H}_2\text{O}_2 > \text{US+H}_2\text{O}_2$$

Combination of UV with catalyst or H₂O₂ increases the color removal of 120 minute oxidation time from 22% to 97% and from 22% to 92%, respectively. This may be explained with the increasing amount of OH $\cdot$ radicals in the UV+ catalyst and UV+H₂O₂ combined processes.

Also the lower decolorization after 15 minute of reaction time in the UV+catalyst system shows that the 15 minute is not enough to form the sufficient amount of OH $\cdot$ radicals.

COD reduction measurements showed that the highest COD reductions are in the UV+ catalyst and UV+H₂O₂ combined systems being 50% and 37%, respectively.

Presence of catalyst in the US process, increases the efficiency. Catalyst could increase the rate of formation of cavitation bubbles and enhance the formation of H₂O₂ molecules. So, more hydroxyl radicals will form for degradation of dye molecules (Jamalluddin and Abdullah, 2011).

Experiments showed that catalyst has a positive effect on the oxidation with UV or US.

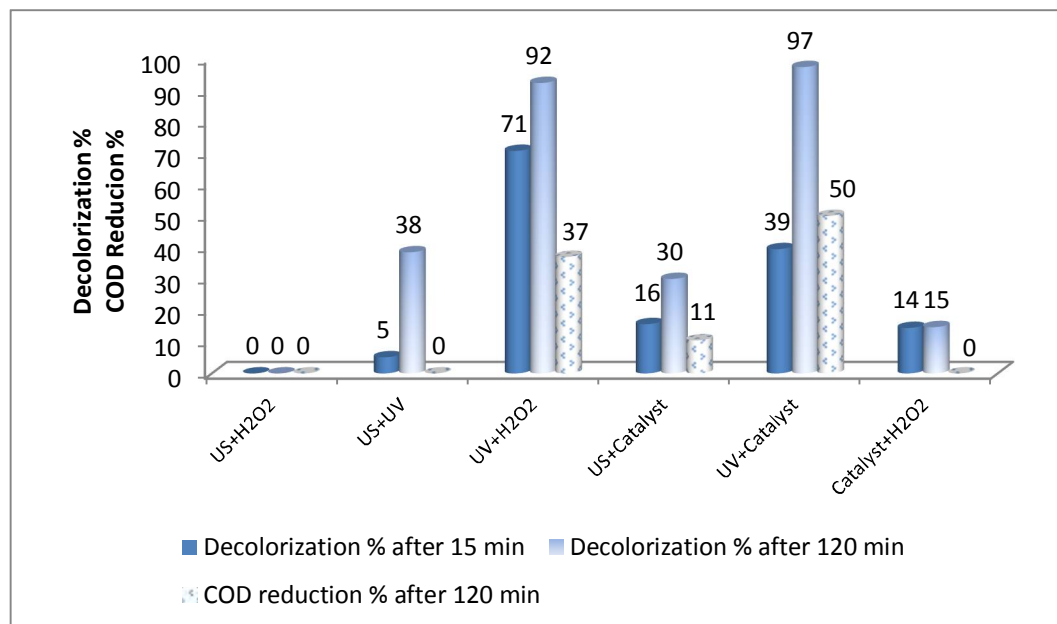


Figure 3.30. Decolorization and COD reduction of RY 84 in the presence of binary processes

(20°C, initial RY 84 concentration of 25 mg/L, according to the combination; 35 mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

3.4.3 Effect of ternary oxidation processes

Decolorization and COD reduction of 650 mL of 25 mg/L RY 84 was investigated at 20°C with the combination of three individual processes. In these combinations, depending on the type of combination 35 mM H₂O₂, 0.5 g/L catalyst (%1 Fe/TiO₂ (IW) calcined at 300°C), UV lamp (4 W+4 W UV-C lamp) and 40 W US were used. The results on decolorization% after 15 and 120 min reaction time and COD reduction% after 120 min results are given in Figure 3.31.

Addition of H₂O₂ to the US+UV combination increases the decolorization after 120 minute from 38% to 89% and a COD reduction of 48% was obtained.

When the catalyst is added to the US+UV combination, decolorization after 120 minute of reaction increases from 38% to 100% and COD reduction of 17% was measured.

Catalyst addition to the US+ H₂O₂ combination slightly affects the efficiency. Decolorization after 120 minute of reaction increases from 0% to 16% and no COD reduction is achieved.

Addition of US to the combination of catalyst+UV increases the decolorization from 39% to 46% after oxidation of 15 minute but decreases the COD reduction from 50% to 17%. Decrease in COD reduction may be due to the negative effect of the observed turbidity on the penetration of UV light to the dye solution. Turbidity increases in the presence of US because of the decrease in catalyst particle size with ultrasound.

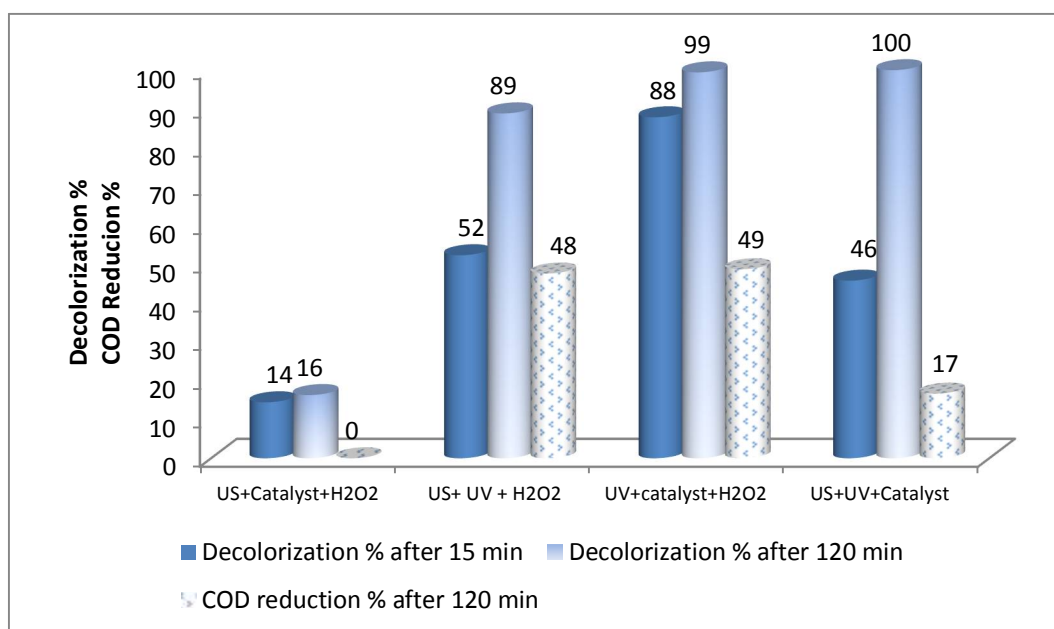


Figure 3.31 Decolorization and COD reduction of RY 84 in the presence of ternary processes

(20°C, initial RY 84 concentration of 25 mg/L, according to the combination; 35 mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

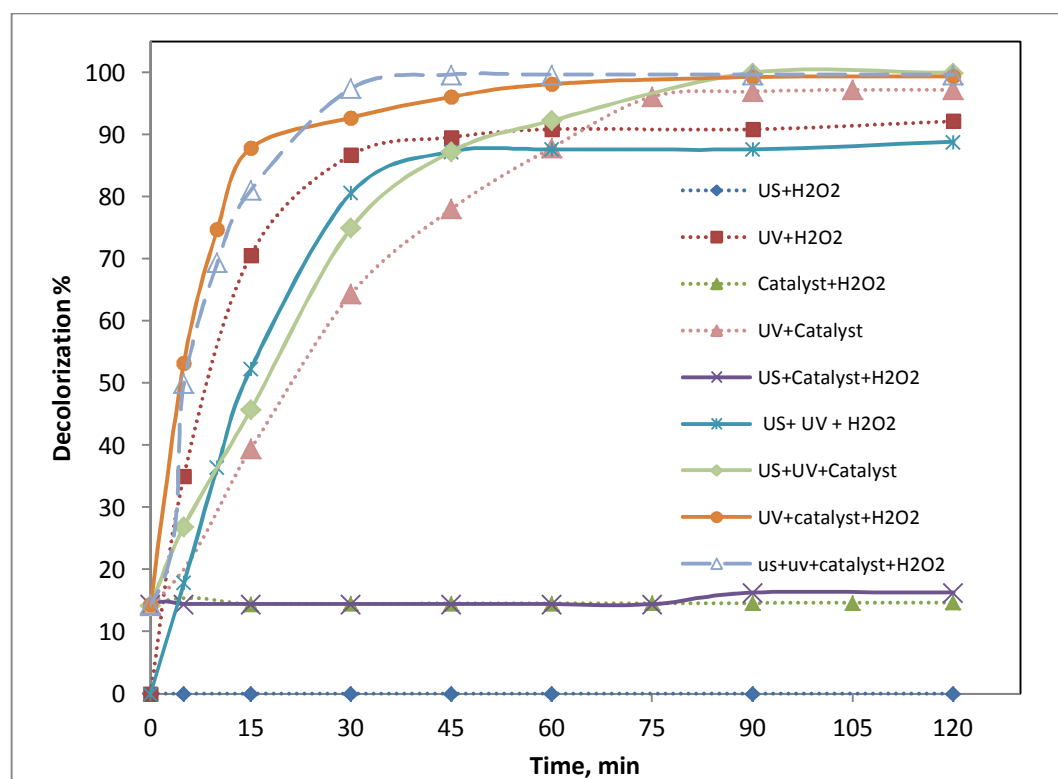


Figure 3.32. Decolorization of RY 84 under different processes

(20°C, initial RY 84 concentration of 25 mg/L, according to the combination; 35 mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

Figure 3.32 shows the evaluation of the decolorization of RY 84 using the different oxidation systems. It is clearly seen that, heterogeneous sonophotoFenton process demonstrates a higher efficiency. It can be said that ultrasound has a slightly positive effect on the heterogeneous photoFenton oxidation. Increase in efficiency can be related to the continuous cleaning of the catalyst surface using ultrasound leading to an increase in activity of the heterogeneous catalyst (Zhong et al., 2011). The turbulence created by ultrasound reduces also the mass transfer limitations. Ultrasound is also known for its ability to disperse agglomerated particles and generate hydroxyl radicals during sonication of the aqueous phase. These effects can also be considered as reasons of the high efficiency of the process. Catalyst deagglomeration can increase the overall accessible surface of the solid particles, and hence will provide more active sites to generate reactive oxygen species necessary for the RY 84 conversion (Madhavan et al., 2010b).

First order reaction rate constants (k_{app}) and decolorization, % after 120 min are presented in the Table 3.7 for the individual and combined advanced oxidation systems.

Table 3.7 The apparent first order rate constants (k_{app} , min^{-1}) and decolorization, % of the oxidation systems

(20°C, initial RY 84 concentration of 25 mg/L, according to the combination; 35 mM H_2O_2 , 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

Oxidation system	k_{app} , min^{-1}	Decolorization, % (after 2h)
Only catalyst	0.0026	28
Only H_2O_2	0.0000	--
Only UV	0.0018	19
Only US	0.0000	--
US+ H_2O_2	0.0000	--
Catalyst + H_2O_2	0.0003	15
US+ Catalyst	0.0020	30
US+UV	0.0040	38
UV+ H_2O_2	0.0838	92
UV+ Catalyst	0.0322	97
US+catalyst+ H_2O_2	0.0002	16
US+UV+ H_2O_2	0.0527	89
UV+catalyst+ H_2O_2	0.1190	99
US+UV+catalyst	0.0412	100
US+UV+catalyst + H_2O_2	0.1130	100

For any hybrid technology of AOPs, it is expected that the efficiency of the hybrid system should be higher than the sum of the efficiencies of the two

individual processes. As can be seen from the Table 3.7 UV addition to the systems enhances the decolorization efficiency. However, UV alone is only achieved 19% color removal of RY 84. On the other hand, almost 100% color removal was achieved when UV was combined with Fenton like (catalyst+H₂O₂), sonocatalysis (catalyst+US) and sonoFenton like (US+catalyst+ H₂O₂) systems. For these combination systems synergetic index can be described as follows (Eqs.3.5 -3.7) (Dukkancı et al., 2014; Madhavan et al., 2010c):

$$\text{Synergy index} = \frac{k_{UV+US+cat}}{k_{UV}+k_{US+cat}} \quad (\text{For sonophotocatalysis oxidation}) \quad (3.5)$$

$$\text{Synergy index} = \frac{k_{UV+cat+H_2O_2}}{k_{UV}+k_{cat+H_2O_2}} \quad (\text{For photoFenton like oxidation}) \quad (3.6)$$

$$\text{Synergy index} = \frac{k_{sonophotoFenton}}{k_{UV}+k_{sonoFenton}} \quad (\text{For sonophotoFenton like oxidation}) \quad (3.7)$$

Rate constants of UV and sonocatalysis; UV and Fenton like; UV and sonoFenton like processes gave synergetic index of 10.8, 65, and 56.5, respectively. The observed synergy in these combined systems was mainly due to the enhancement of H₂O₂ decomposition to yield more OH• radicals formation. (Dukkancı et al., 2014)

Effect of H₂O₂ and US power on the US+UV+ H₂O₂ combination in the oxidation of RY 84

Among the triple combined use of oxidation techniques, although one of the highest COD reduction efficiency (48%) was obtained with US+UV+H₂O₂ combination, 100% color removal could not be obtained after 120 min of reaction. Therefore, the effects of H₂O₂ and US power were investigated on the US+UV+H₂O₂ system to see if nearly 100% of color removal would be obtained.

Figure 3.33 shows the US+UV+H₂O₂ oxidation of RY 84 at different H₂O₂ concentrations. From the results shown in Figure 3.33, it can be seen that the decrease in H₂O₂ concentration, increases the color removal and COD reduction efficiency. Initial color removal in 15 min of reaction increases from 52% to 95% when the H₂O₂ concentration decreases from 35mM to 2.5mM, respectively. Similarly, the decrease in the H₂O₂ concentration from 35mM to 2.5mM enhances the COD reduction from 48% to 93%. It would be expected that the increase of H₂O₂ concentration would enhance the decolorization efficiency. However at high concentration, the excess of hydrogen peroxide reacts with OH• radicals according to the eq. 3.8 to produce HO₂• radicals which are less reactive than OH• radicals (Kritikos et al., 2007; Muruganandham and Swaminathan, 2004; Zhong et al., 2011). This opposite effect of increasing concentration of H₂O₂ on degradation of RY 84 with US+UV+H₂O₂ oxidation, is supported by the decolorization rate constants calculated for each H₂O₂ concentration, as well.



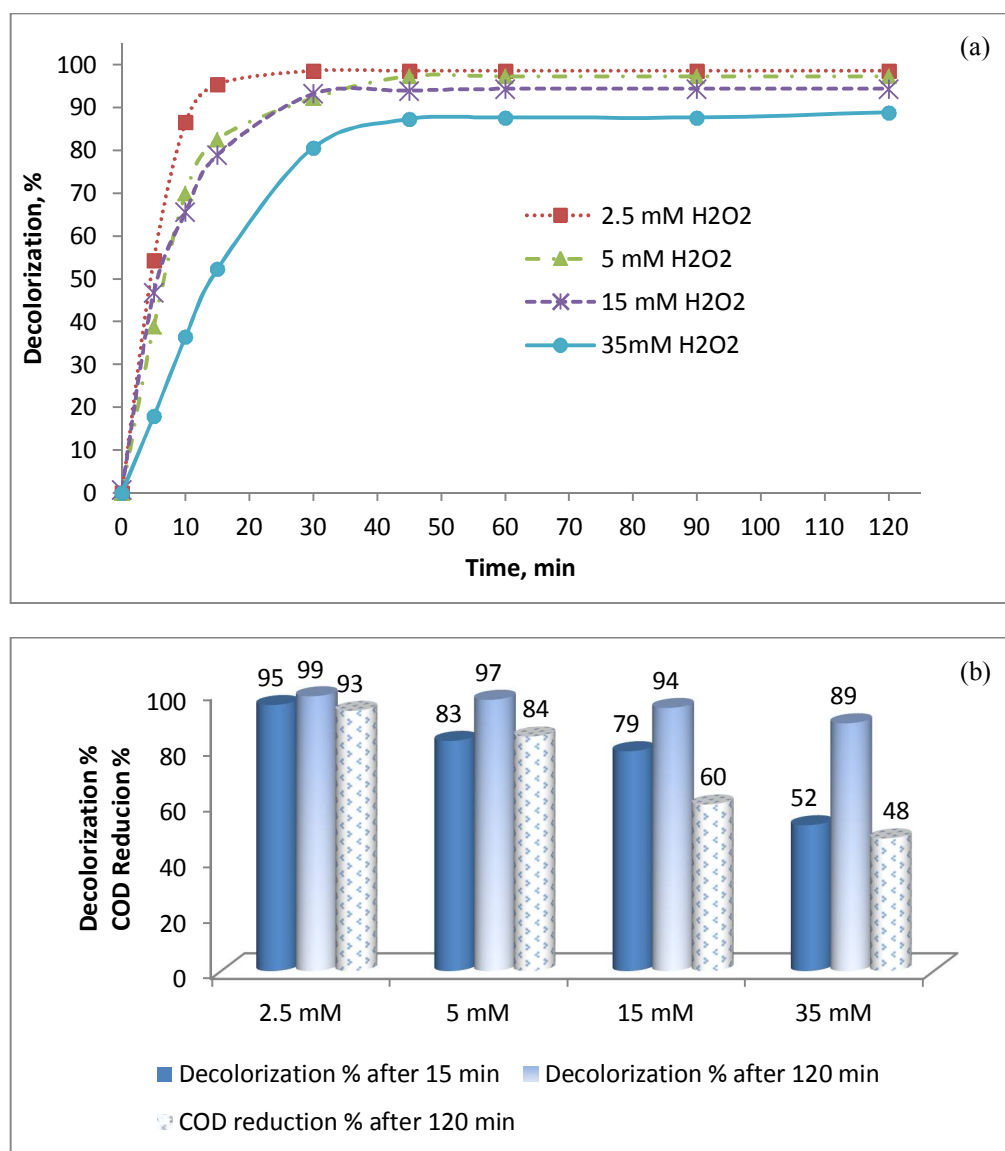


Figure 3.33. Effect of H₂O₂ on the US+UV+H₂O₂ oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization,% in 15 and 120 min and COD removal% in 120 min

(20°C, initial RY 84 concentration of 25 mg/L, 40W US power, 4+4 W UV-C lamps, initial dye pH of 6).

For this purpose, the plot of $-\ln (C/C_0)$ versus time data is presented in Figure 3.34 for different H₂O₂ concentrations. The figure shows that the sonophotoFenton degradation follows the pseudo-first order reaction. The calculated rate constants, k_{app} , were listed in Table 3.8. As seen, the first order rate constant decreases with increasing concentration of H₂O₂. The highest k_{app} value is obtained at the lowest H₂O₂ concentration studied.

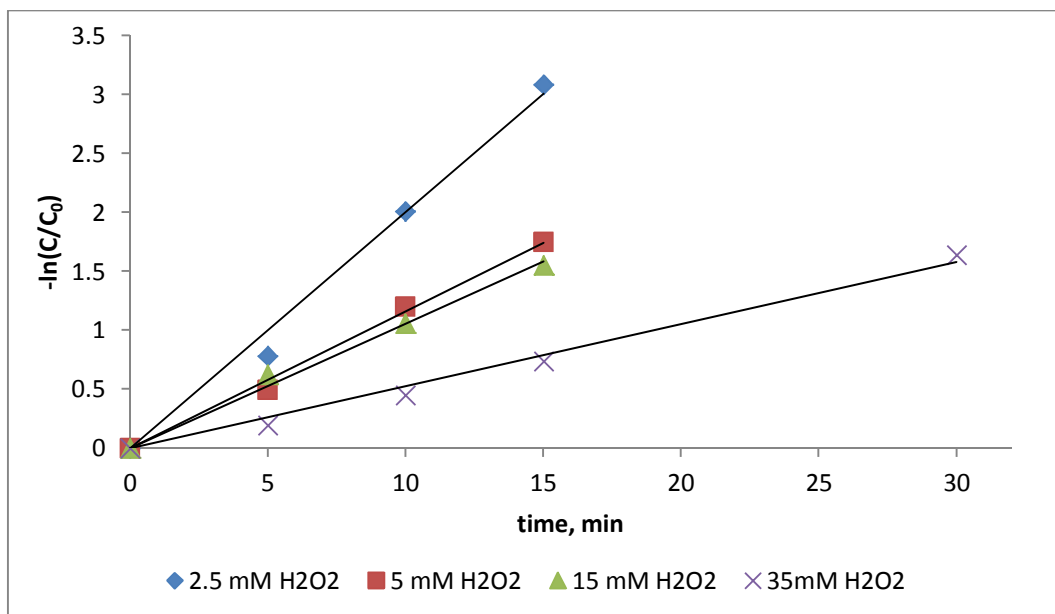


Figure 3.34. Pseudo-first-order kinetics for US+UV+H₂O₂ oxidation of RY 84 at different H₂O₂ concentrations

(20°C, initial RY 84 concentration of 25 mg/L, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6)

Table 3.8. The apparent first order rate constants (k_{app} , min⁻¹) and regression coefficient (R^2) for US+UV+H₂O₂ oxidation of of RY 84 at different H₂O₂ concentrations

(20°C, initial RY 84 concentration of 25 mg/L, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye PH of 6)

H ₂ O ₂ concentration	k_{app} , min ⁻¹	R^2
2.5 mM	0.201	0.9902
5 mM	0.116	0.9946
15 mM	0.105	0.9921
35 mM	0.053	0.9902

Figure 3.35 shows the US+UV+H₂O₂ oxidation of RY 84 at different US powers. As seen from the results in Figure 3.35, the increase in the ultrasonic power from 40W to 80W increases the initial decolorization rate significantly. Decolorization% after 15 min rises from 52% to 88%. After 120 min a slight increase in color removal, from 89% to 94%, is achieved. However, a slight decrease in COD removal after 120 min is observed (from 48% to 44%).

Nevertheless, further increase in US power to 100 W decreases the efficiency of the system.

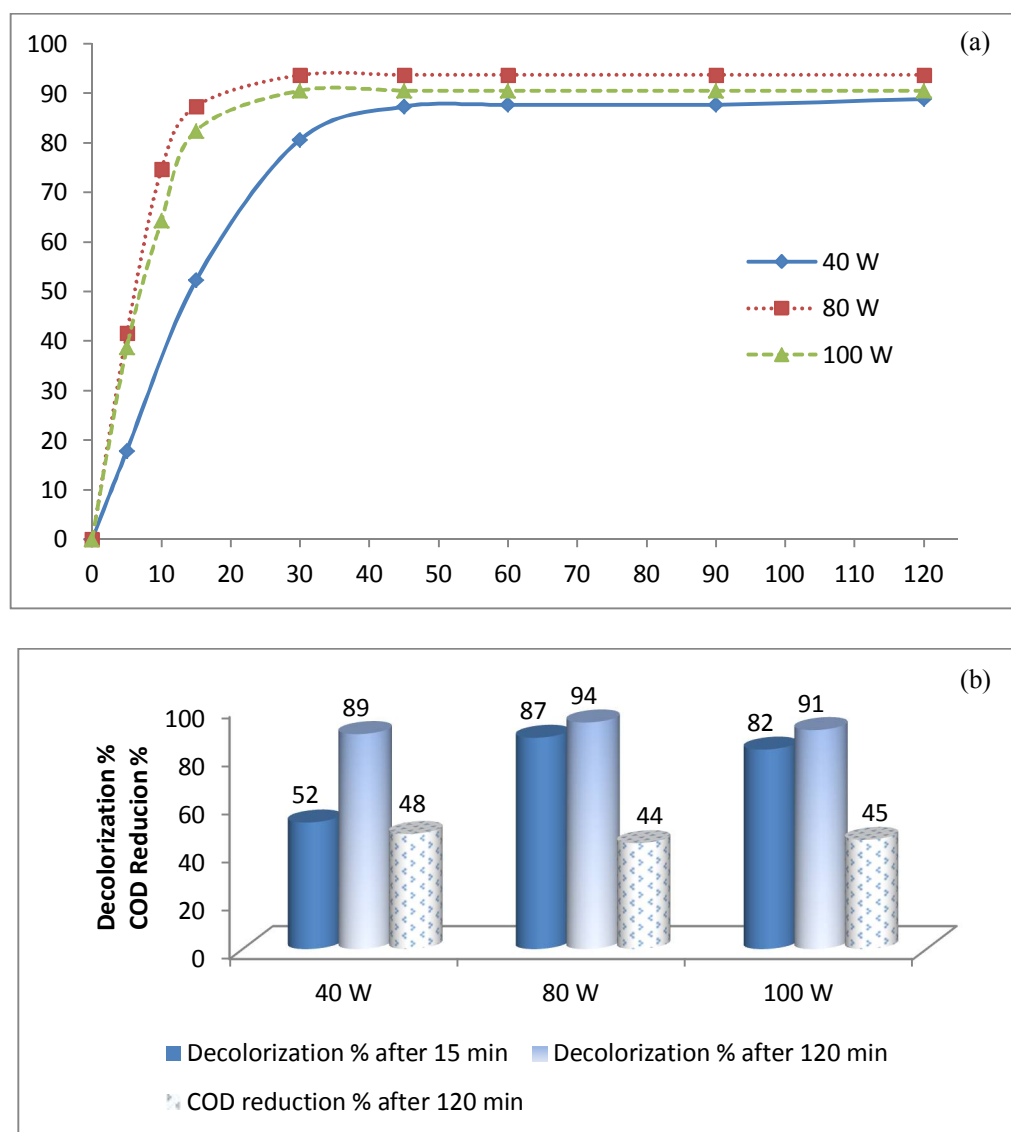


Figure 3.35. Effect of ultrasonic power on the US+UV+ H_2O_2 oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization, % in 15 and 120 min and COD removal % in 120 min

(20°C, initial RY 84 concentration of 25 mg/L, 35 mM H_2O_2 , 4+4 W UV-C lamps, initial dye pH of 6).

The effect of US power on degradation of RY 84 can be given in terms of the rate constants, as well. The plot of $-\ln (C/C_0)$ versus time is shown in Figure 3.36 for different US powers applied. The figure shows that the sonophotoFenton degradation follows the pseudo-first order reaction. The calculated rate constants,

k_{app} , were listed in Table 3.9 decolorization rate constant is the highest for the US power of 80W applied to the system.

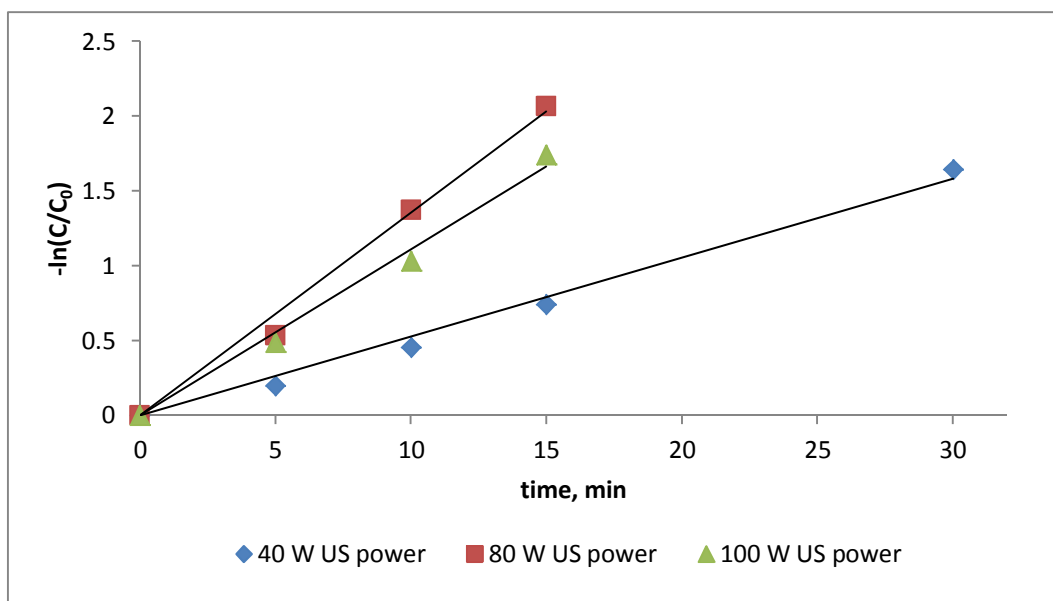


Figure 3.36. Pseudo-first-order kinetics for US+UV+ H_2O_2 oxidation of RY 84 at different H_2O_2 concentrations

(20°C, initial RY 84 concentration of 25 mg/L, 35 mM H_2O_2 , 4+4 W UV-C lamps, initial dye pH of 6).

Table 3.9. The apparent first order rate constants (k_{app} , min^{-1}) and regression coefficients (R^2) for US+UV+ H_2O_2 oxidation of RY 84 at different US powers

(20°C, initial RY 84 concentration of 25 mg/L, 35 mM H_2O_2 , 4+4 W UV-C lamps, initial dye pH of 6).

Ultrasonic power	k_{app} , min^{-1}	R^2
40 W	0.053	0.9902
80 W	0.136	0.9915
100 W	0.111	0.9904

3.5 Parametric Study with the Selected Catalyst

In this part of the study, parametric studies were performed to determine optimum operating conditions in degradation of RY 84 by sonophotoFenton process with 1%Fe/TiO₂ catalyst, prepared by incipient wetness impregnation method and calcined at 300°C, which was selected as the most effective catalyst. The effects of H₂O₂ concentration, initial pH of solution, initial dye concentration, temperature, catalyst amount and ultrasonic power were studied on the degradation of sonophotoFenton oxidation of RY 84.

3.5.1 Effect of hydrogen peroxide concentration on the sonophotoFenton oxidation of RY 84

Effect of hydrogen peroxide concentration on the sonophotoFenton oxidation of RY 84 was studied with the H₂O₂ concentrations of 2.5 mM, 5 mM, 15 mM, 35 mM and 40 mM while maintaining all other parameters constant. (20°C, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6). Results are presented in Figure 3.37.

Initial color removal within the 15 min increases from 77% to 88% when the H₂O₂ concentration increases from 2.5 mM to 5 mM. COD reduction after 120 min of oxidation enhances from 61% to 83% with increasing the H₂O₂ concentration from 2.5 mM to 5mM, respectively. Low efficiency at 2.5 mM H₂O₂ concentration arises from the fact that low concentration of H₂O₂ is not sufficient to generate high enough hydroxyl radicals. On the other hand, the increase in the efficiency is due to the increase in OH• radical formation with the increase in H₂O₂ concentration to an optimum level. In opposition addition of larger quantity of H₂O₂ causes a slight decrease in color removal efficiency. The decrease in color removal efficiency is followed by a sharp decrease in COD reduction from 83% to 35%, with the increasing H₂O₂ concentration from 5mM to 40mM. At high concentrations of H₂O₂, the excess of hydrogen peroxide would compete with the reaction for the OH• radicals. Instead of being consumed by dye molecules, the produced OH• radicals will react with the excess of hydrogen

peroxide as given by the equations below: (Kritikos et al., 2007; Muruganandham and Swaminathan, 2004; Zhong et al., 2011).



Similar results were obtained in the literature, in the study of Kritikos et al. (2007). In their study, photocatalytic decolorization of reactive black 5, after 90 min of reaction time decreased from 53% to 26% when the H_2O_2 was doubled.

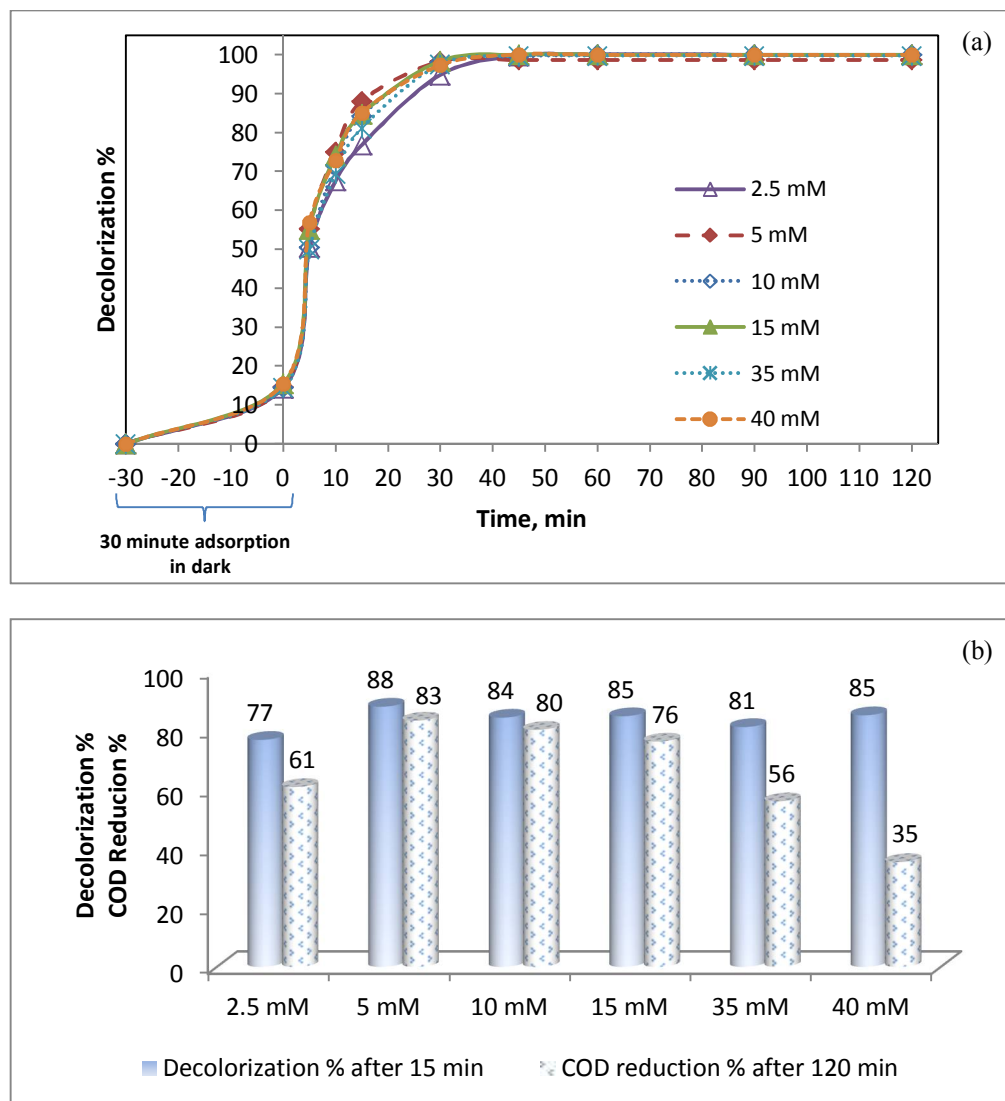


Figure 3.37. Effect of H_2O_2 concentration on the sonophotoFenton oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization, % in 15 min and COD removal % in 120 min

(20°C, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6).

The apparent first order rate constants, k_{app} , of the degradation after 30 min of reaction time were calculated from the linear regression $-\ln(C/C_0)$ versus time plots presented in Figure 3.38. The apparent first order rate constants (k_{app}) and regression coefficients at different H_2O_2 concentrations are listed in Table 3.10.

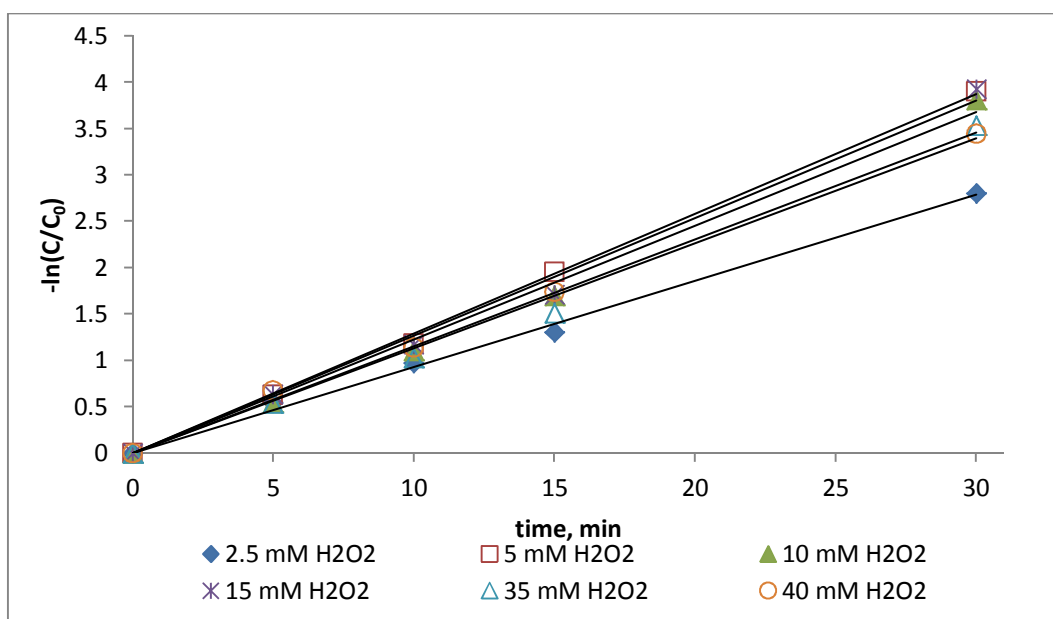


Figure 3.38. Pseudo-first-order kinetics for the sonophotoFenton degradation of RY 84 at different H_2O_2 concentrations

(20°C, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6).

Table 3.10. The apparent first order rate constants (k_{app} , min^{-1}) and regression coefficients (R^2) for sonophotoFenton degradation of RY 84 at different H_2O_2 concentrations

(20°C, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6)

H_2O_2 concentration (mM)	k_{app} , min^{-1}	R^2
2.5	0.093	0.9963
5	0.129	0.9984
10	0.123	0.9933
15	0.127	0.9934
35	0.113	0.9912
40	0.115	0.9984

As seen from the Table 3.5, higher initial reaction rate constant was obtained with the 5mM H_2O_2 . The decolorization degree was not affected by the H_2O_2 concentration after 40 min for all the H_2O_2 concentration studied. The

higher mineralization to CO_2 was obtained with the H_2O_2 concentration of 5mM. It can be concluded that H_2O_2 dosage higher than 5mM leads to an unprofitable consumption of H_2O_2 , such as $\text{OH}^\bullet$ radical scavenging reaction. So the optimum H_2O_2 concentration 5mM was selected due to the highest COD reduction after 120 min of sonophotoFenton oxidation and higher initial degradation rate.

Neamtu et al. (2002) investigated the decolorization of RY 84 by UV/ H_2O_2 treatment and found the optimum dose of H_2O_2 as 417.02 mol H_2O_2 /mol dye. Our finding leads to a ratio of 185.2 mol H_2O_2 /mol dye.

3.5.2 Effect of initial pH of the RY 84 solution on the sonophotoFenton oxidation of RY 84

The effect of pH on the degradation of RY 84 in the sonophotoFenton reaction was studied with the different initial pHs of 3.5, ≈ 6 (which is the dye pH), and 10 to find out the optimum pH for maximum efficiency while maintaining all other parameters constant. (20°C, initial RY 84 concentration of 25 mg/L, 5mM H_2O_2 , 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps). Results are presented in Figure 3.39.

The pH of the solution was adjusted before the reaction and it was not controlled during the reaction.

Figure 3.39 indicates that in acidic medium (pH=3.5) the amount of dye adsorbed is higher (34.5% dye removal by adsorption) and adsorption decreases with increasing initial pH. Removal of dye by adsorption was measured to be 14.4% at dye pH (pH ≈ 6) and 4.7% at pH=10. Similar results were obtained in the literature. Photocatalytic degradation of RY 84 using industrial titanium dioxide coated non-woven paper was studied by Barka et al. (2010), and they showed that amount of RY 84 adsorbed on the photocatalyst decreased with the pH value higher than 3. According to the studies of Konstantinou and Albanis (2004) and Barka et al. (2010), this result may be due to the influence of the solution pH on both the surface state of TiO_2 and the ionization state of ionisable organic molecule of the dye. Electrostatic attraction of the positively charged TiO_2 with dye leads to a strong adsorption of dye on TiO_2 particles at pH<6. On the

contrary, at high pH values scavenging of hydroxyl radicals occur. The decrease in color removal and in degradation at high pH was attributed to the accelerated formation of less reactive hydroperoxyl radicals, $\text{HO}_2\cdot$ rather than $\text{OH}\cdot$ radicals. As a result of scavenging, hydroxyl radicals do not have opportunity to react with dye (Dukkanci et al., 2010a).

However, change in the initial pH of the solution did not affect the overall color removal. The higher the pH value, the longer the time was required for complete decolorization. While 100% color removal was obtained within the 30 min of reaction with the initial pH values of 3.5 and 6, corresponding time was 45 min for higher pH value (pH 10). The highest COD reduction was obtained with acidic pH of 3.5 (86%). The COD removal obtained at dye pH (≈ 6) was rather close (83%) to the one at pH of 3.5.

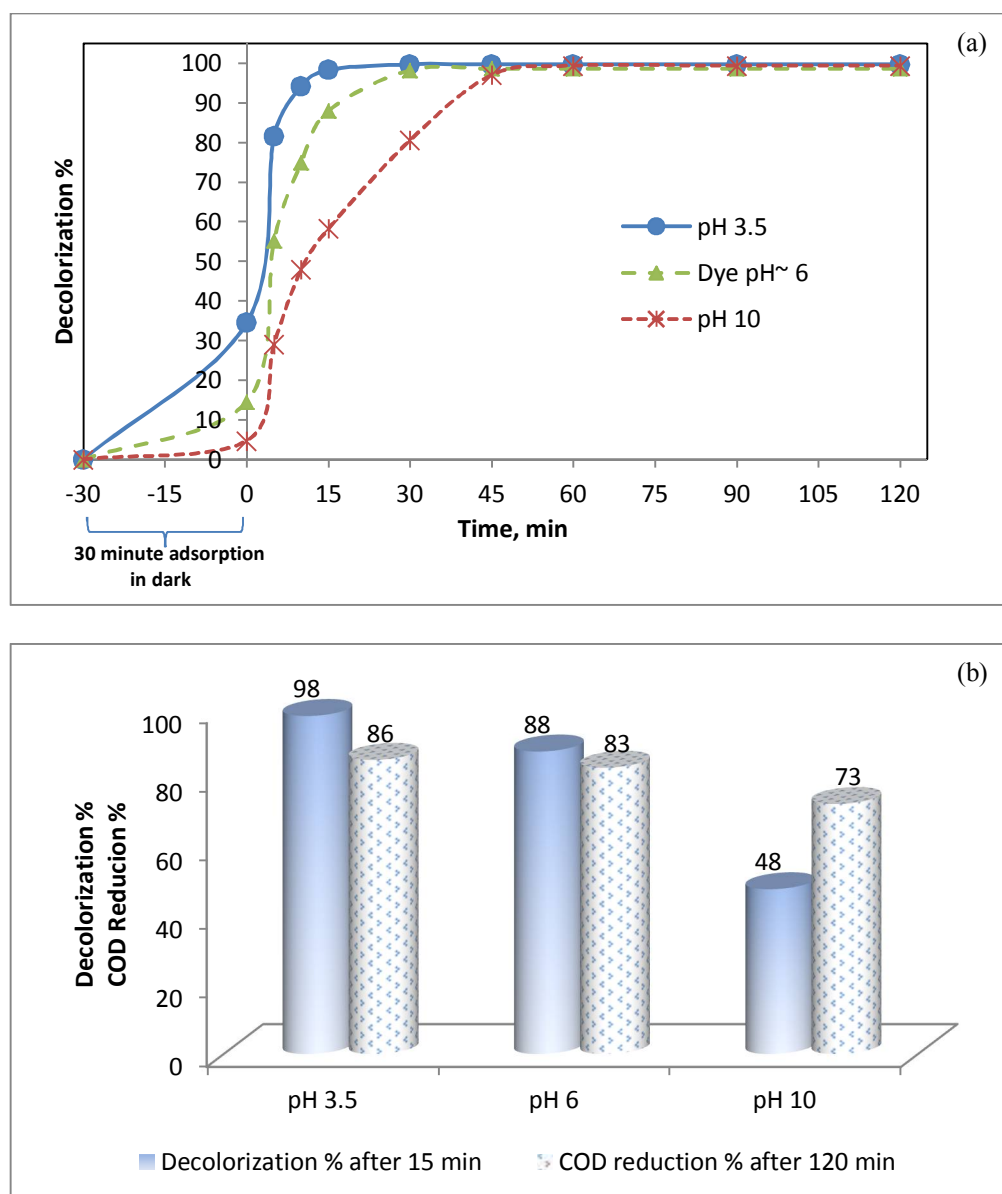


Figure 3.39. Effect of initial pH of the solution on the sonophotoFenton oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization,% in 15 min and COD removal% in 120 min

(20°C, initial RY 84 concentration of 25 mg/L, 5mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps).

The apparent first order rate constants, k_{app} , of the degradation were calculated for different initial pH values of the oxidation system from the linear regression $-\ln(C/C_0)$ versus time plots and the results were shown in Figure 3.40. The apparent first order rate constants (k_{app}) and regression coefficients at different pH values were listed in Table 3.11. Figure 3.40 shows that sonophotoFenton degradation obeys the pseudo-first-order kinetics with respect to initial pH of the solution.

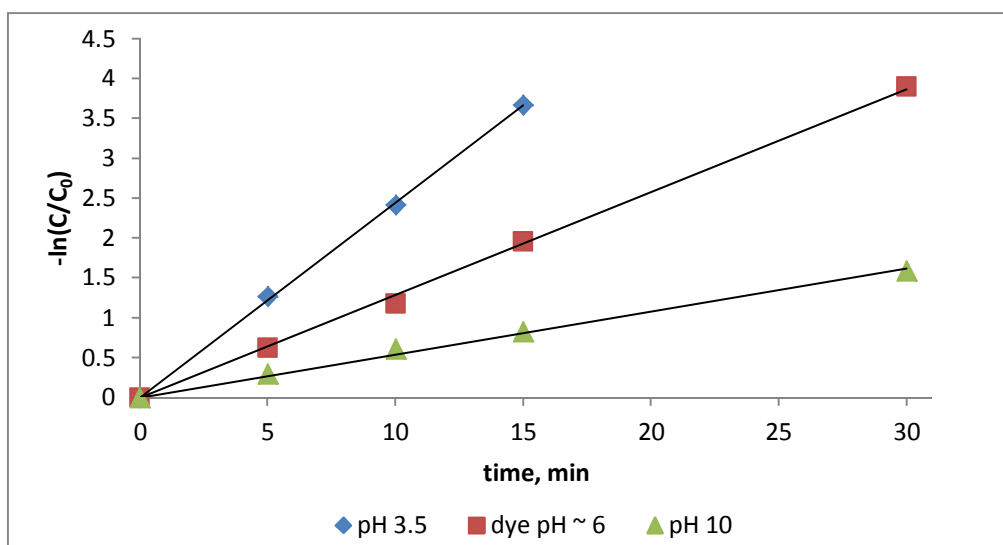


Figure 3.40. Pseudo-first-order kinetics for the sonophotoFenton degradation of RY 84 at different initial pH of the solution

(20°C, initial RY 84 concentration of 25 mg/L, 5mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

Table 3.11. The apparent first order rate constants (k_{app} , min⁻¹) and regression coefficients (R^2) for sonophotoFenton degradation of RY 84 at different initial pH values of the solution

(20°C, initial RY 84 concentration of 25 mg/L, 5mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

pH	k_{app} , min ⁻¹	R^2
3.5	0.244	0.9996
6	0.129	0.9984
10	0.054	0.9960

Figure 3.41 shows graphically the change in rate constants of the sonophotoFenton degradation with varying the initial pH of the RY 84 solution. The high adsorption of the dye on the catalyst leads to a fast reduction in the dye concentration at acidic condition. It can be said from the results that, the effect of initial pH on decolorization kinetics is due to the dye adsorption on the catalyst.

Although initial color removal rate was high with the acidic pH, the dye pH (≈ 6) was selected as the optimum initial pH of the solution. Because the fast decrease of the dye color is due to the adsorption in acidic medium. But we want to remove the RY 84 with sonophotoFenton process. Since change in the initial pH of the solution did not affect the overall color removal (after 30 min almost 100% color removal was obtained with the initial pH values of 3.5 and 6) and the COD reduction percentages are very similar for these two initial pH values, it was decided to select the dye pH (≈ 6) as the optimum initial pH of the solution.

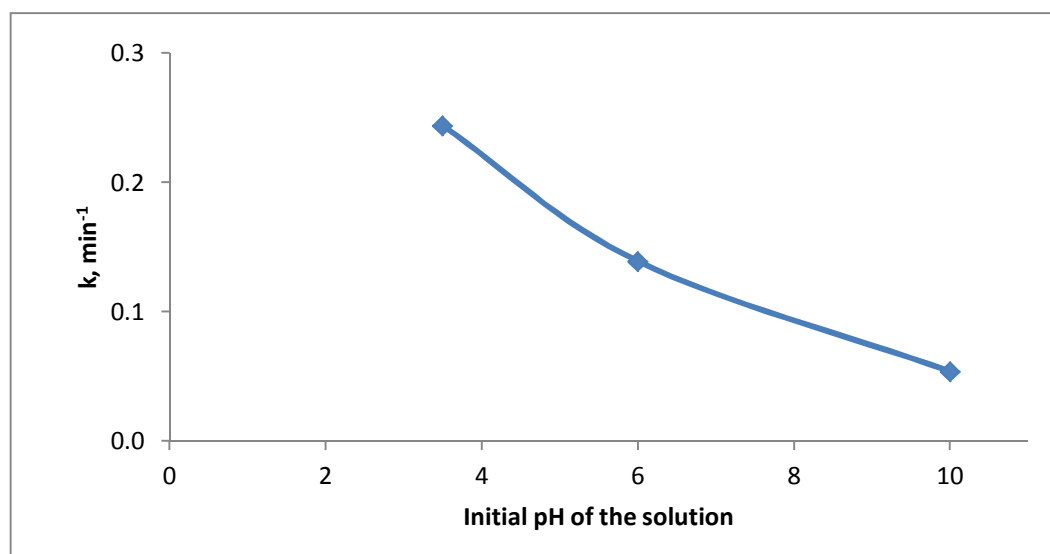


Figure 3.41. Effect of initial pH of the solution on the pseudo-first-order rate constant

(20°C, initial RY 84 concentration of 25 mg/L, 5mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

3.5.3 Effect of initial dye concentration on the sonophotoFenton oxidation of RY 84

The effect of initial dye concentration on the degradation of RY 84 in the sonophotoFenton reaction was studied with the different initial dye concentrations of 5, 15, 25, 50 and 75 mg/L to find out the optimum dye concentration for maximum efficiency while maintaining all other parameters constant. (20°C, 5mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6). Results are presented in Figure 3.42.

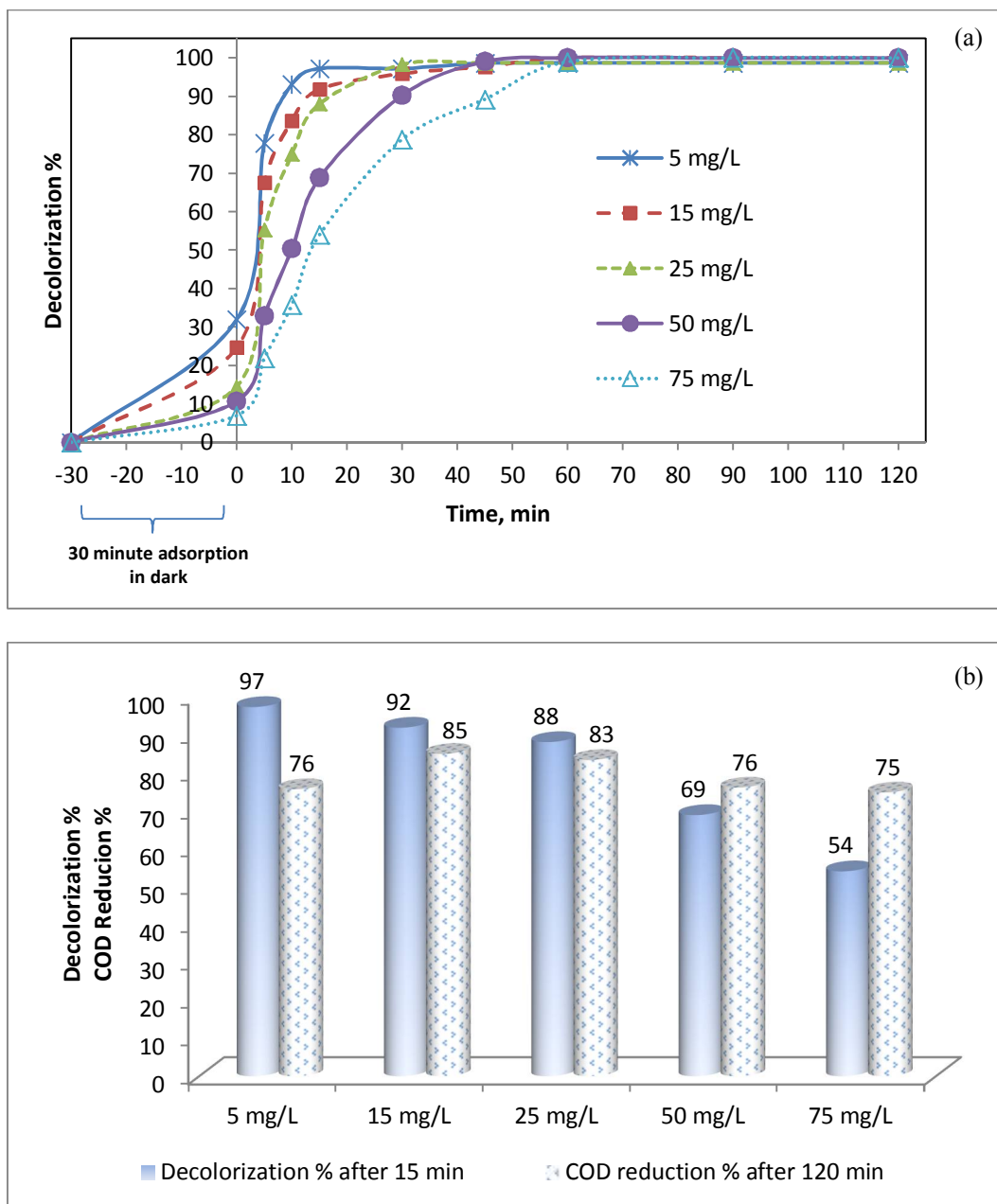


Figure 3.42. Effect of initial dye concentration on the sonophotoFenton oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization, % in 15 min and COD removal % in 120 min

(20°C, 5mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6).

As seen from Figure 3.42, the initial decolorization efficiency in 15 min of reaction decreased from 97% to 92%, 88%, 69% and to 54% with the increase in the initial dye concentration from 5 to 15, 25, 50 and 75 mg/L, respectively. Because the formed OH• radicals are not enough for oxidation of increased amount of dye. Another presumed reason is that, at high concentrations of dye the

active sites of the catalyst are covered by dye molecules so the generation of $\text{OH}\cdot$ radicals are reduced on the surface of the catalyst.

Also at high dye concentrations, a significant amount of UV may be absorbed by dye itself rather than the catalyst and that reduces the catalytic activity and so the formation of $\text{OH}\cdot$ and $\text{O}_2\cdot$ radicals (Zhong et al., 2011) (Konstantinou and Albanis, 2004). At high concentration of dye the UV light penetration is also retarded. It is concluded that the catalyst surface needed for the degradation also increases at high concentrations of dye.

COD reduction efficiency decreased from 85% to 83%, 76% and to 75% with the increase in the initial dye concentration from 15 to 25, 50 and 75 mg/L, respectively. The decrease in COD reduction may due to the formation of stable intermediates in higher concentrations. If it is assumed that most of the reactions take place at the bubble–liquid interface, due to the increase in the initial concentration of dye and correspondingly intermediates, dye degradation would be limited by the available interfacial area and OH radicals (Aguilar et al., 2014).

The change in the absorption spectrum at 408 nm for 75 mg/L of RY 84 with time is given in Figure 3.43. The decrease in the intensity of the absorption spectrum with increasing time is clearly seen. It vanishes almost within 45 min. The rapid disappearance of the absorption at 408 nm suggests that the chromophoric group responsible for the characteristic color of the dye is degrading down.

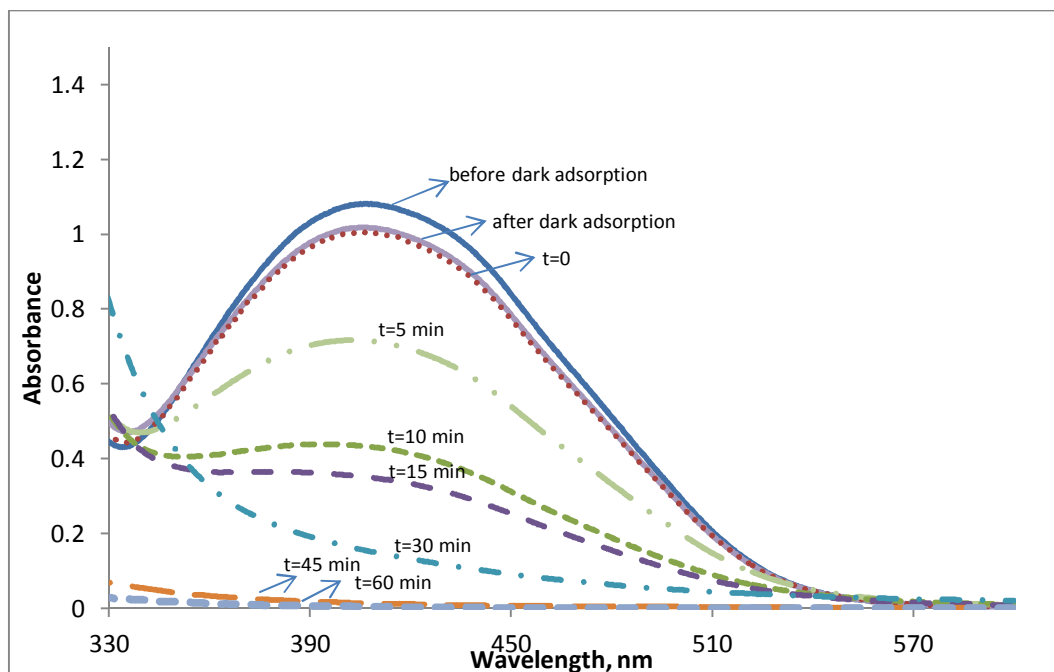


Figure 3.43. The change in the absorption spectrum of RY 84 (75 mg/L) during sonophotoFenton oxidation of dye in the presence of 1%Fe/TiO₂ (IW) 300°C catalyst.

The apparent first order rate constants, k_{app} , of the degradation were calculated from the linear regression $-\ln(C/C_0)$ versus time plots and the results were shown in Figure 3.44. The apparent first order rate constants (k_{app}) and regression coefficients at different initial dye concentrations are listed in Table 3.12. Figure 3.44 shows that sonophotoFenton degradation obeys the pseudo-first-order kinetics with respect to initial dye concentration.

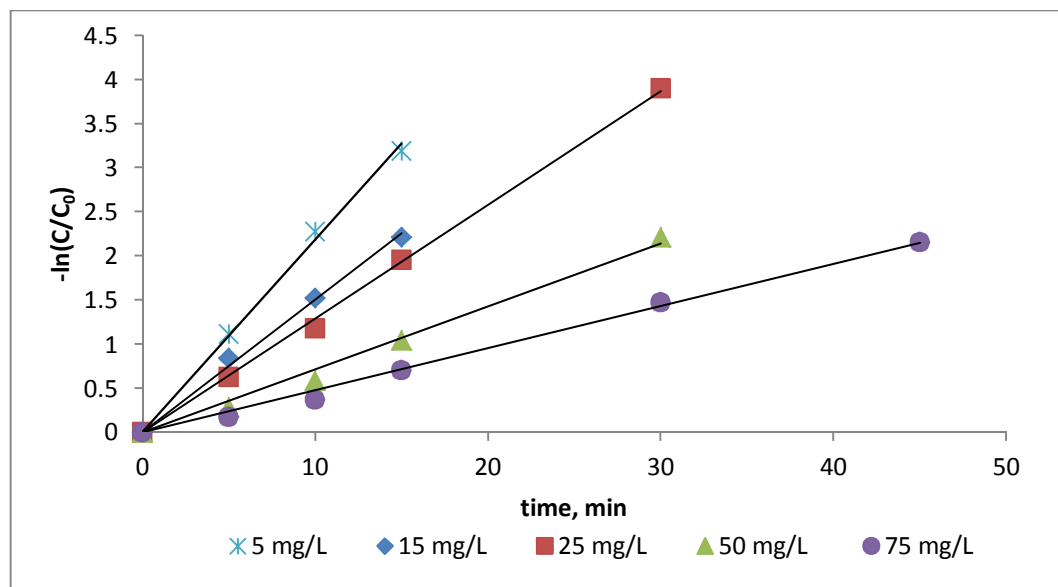


Figure 3.44. Pseudo-first-order kinetics for the sonophotoFenton degradation of RY 84 at different initial dye concentrations

(20°C, 5mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6)

Table 3.12. The apparent first order rate constants (k_{app} , min⁻¹) and regression coefficients (R^2) for sonophotoFenton degradation of RY 84 at different initial dye concentrations

(20°C, 5mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6)

initial dye concentration (mg/L)	k_{app} , min ⁻¹	R^2
5	0.218	0.9972
15	0.151	0.9962
25	0.129	0.9984
50	0.072	0.9911
75	0.048	0.9950

During the experiments with initial dye concentrations of 5 mg/L and 15 mg/L there was a turbidity problem. Especially with the 5 mg/L of initial dye concentration, after 30 min, turbidity was so much that a long time of centrifugation was required (45 minute) to measure the UV absorbance for concentration determination. Fe leached to the solution was 0.6 mg/L after 120

min of oxidation. The pH of the solution was measured as 5.4 after 120 min. In these conditions, leached iron ions may be formed into iron oxyhydroxide ions (FeOOH_2^+) by hydrolysis and precipitate. This may cause the turbidity and leads to loss of active iron ions, so reduce the formation of hydroxyl radicals (Gogate and Pandit, 2004) . Low COD reduction (76%) of 5 mg/L initial concentration may be due to the turbidity problem.

With the initial dye concentration of 25 mg/L, turbidity was seen only after 90 min and after 120 min of oxidation, the pH of the solution and iron leached from catalyst to solution were measured as 4.5 and 0.8 mg/L, respectively. The turbidity was not observed when testing the higher dye concentrations of 50 mg/L and 75 mg/L. However COD reduction obtained with 25 mg/L is higher than that of 50 mg/L and 75 mg/L. For this reason, 25 mg/L was selected as the optimum initial dye concentration.

The effect of initial RY 84 concentration on the initial rate of degradation is shown in Figure 3.45. The figure indicates that the rate of decolorization increases with increasing initial concentration of RY 84 which corresponds to the Langmuir–Hinshelwood model according to the following equation:

$$r_0 = k_{\text{app}} C_0 = \frac{k_c K C_0}{1 + K C_0} \quad (3.12)$$

where,

r_0 is the initial rate of the sonophotoFenton oxidation ($\text{mg L}^{-1} \text{ min}^{-1}$),

k_{app} is apparent rate constant (min^{-1}) and

k_c is a constant depending on the other factors influencing the process.

K is the Langmuir equilibrium constant (L mg^{-1})

A linear expression can be conventionally obtained by plotting the inverse of initial rate (r_0) versus initial concentration (C_0):

$$\frac{1}{r_0} = \frac{1}{k_c K} \frac{1}{C_0} + \frac{1}{k_c} \quad (3.13)$$

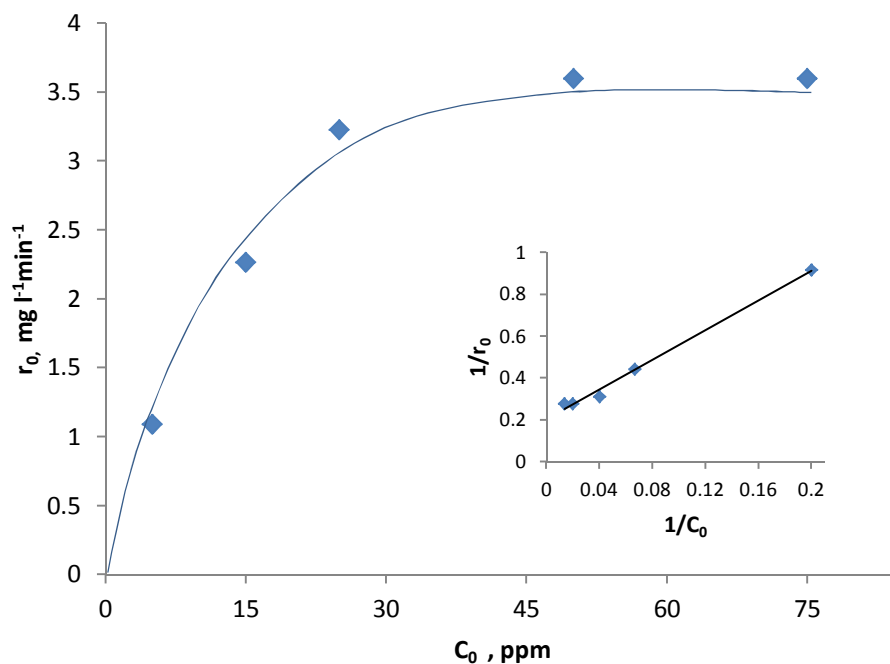


Figure 3.45. Effect of initial RY 84 concentration on the initial rate of degradation. Inset: Langmuir-Hinshelwood kinetic linear representation of the sonophotoFenton oxidation of RY 84.

(20°C, 5mM H_2O_2 , 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6)

As indicated in the inset figure in Figure 3.45, the $1/r_0$ versus $1/C_0$ plot yields a straight line. From the linear fit the Langmuir-Hinshelwood kinetic constants for the sonophotoFenton oxidation of RY 84 are found to be $k_c = 4.9 \text{ mgL}^{-1} \text{ min}^{-1}$ and $K = 0.06 \text{ L mg}^{-1}$.

This result shows that the sonophotocatalytic degradation rate of RY 84 can be explained in terms of Langmuir-Hinshelwood kinetic model. Such a study was carried out with Barka et al. (2010) for photocatalytic degradation of RY 84 in water using an industrial TiO_2 coated media.

3.5.4 Effect of temperature on the sonophotoFenton oxidation of RY 84

The effect of temperature on the degradation of RY 84 in the sonophotoFenton reaction was studied with the different temperatures of 20°C, 25°C, 30°C, and 35°C to find out the optimum temperature for maximum efficiency while maintaining all other parameters constant. (5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6). Results are presented in Figure 3.46.

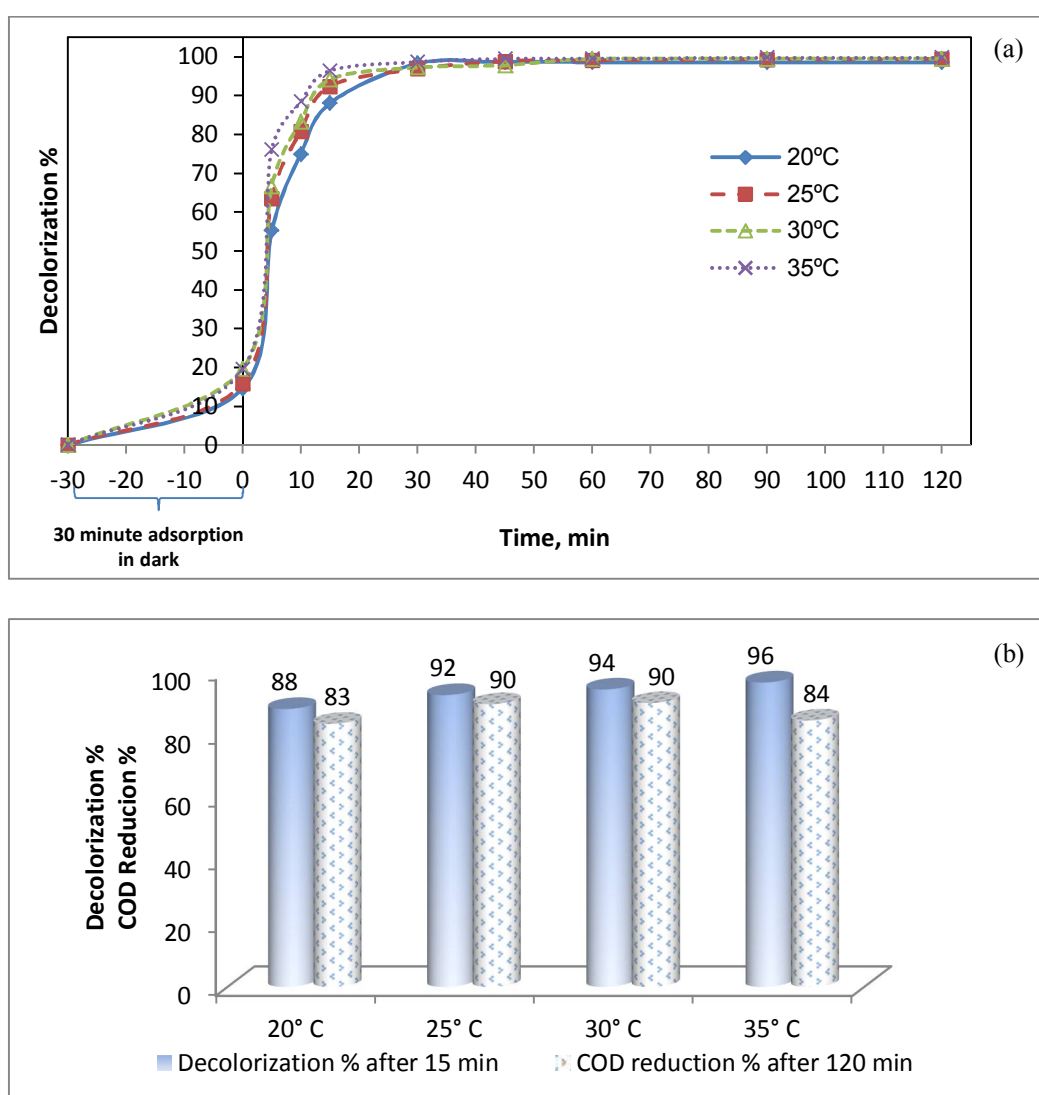


Figure 3.46. Effect of temperature on the sonophotoFenton oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization, % in 15 min and COD removal % in 120 min

(5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6).

As shown in Figure 3.46 color removal in 15 min increased from 88% to 92%, 94% and to 96% with the increase in temperature from 20°C to 25°C, 30°C and to 35°C, respectively. Since the photocatalytic oxidation is not a temperature dependent process, increase of sonophotoFenton oxidation efficiency with the increasing temperature can be explained by the increase in the rate constant of heterogeneous Fenton-like reaction exponentially with increasing temperature according to the Arrhenius expression.

In the study of Wang et al. (2003), they showed that the ultrasonic degradation rate was not affected with the temperatures in the range of 20-40°C, however when the temperature increases to 80°C ultrasonic degradation rate was decreased remarkably. At higher temperatures of the solution, the number of the cavitation bubbles is reduced and the bubbles collapse less violently resulting in the decrease in degradation of dye.

After 45 min of reaction, almost complete decolorization was obtained at all the temperatures tested. COD removal also increased from 83% to 90% with the increase in temperature from 20°C to 25°C while no change was observed in COD removal at 30°C. However, the COD reduction obtained at 35°C was lower (84%) than those at 25°C and 30°C (90%). Similar result was found during the heterogeneous Fenton-like degradation of Rhodamine 6G over CuFeZSM-5 zeolite catalysts (Dukkanci et al., 2010a). The lower COD removal at higher temperature (35°C) may be explained by the production of side products which are not completely mineralized under the oxidation conditions used. On the other hand, the decomposition of H_2O_2 into oxygen and water may be accelerated at high temperature, resulting in a decrease in COD removal. So the optimum temperature was selected as 25°C.

The apparent first order rate constants, k_{app} , of the degradation were calculated from the linear regression of $-\ln(C/C_0)$ versus time plots and the results were shown in Figure 3.47. The apparent first order rate constants (k_{app}) and regression coefficients at different temperatures are listed in Table 3.13. Figure 3.47 shows that sonophotoFenton degradation obeys the pseudo-first-order kinetics with respect to temperature.

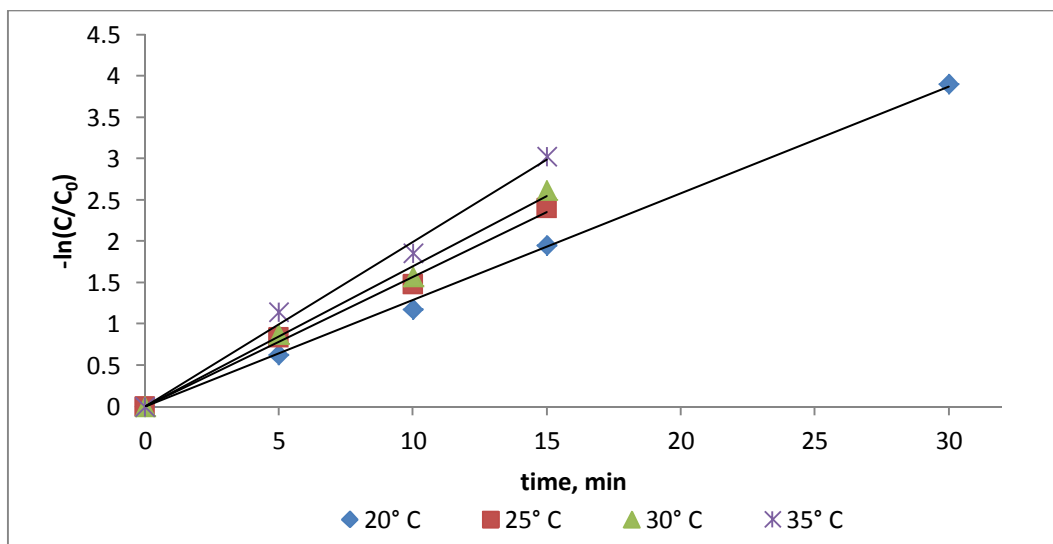


Figure 3.47. Pseudo-first-order kinetics for the sonophotoFenton degradation of RY 84 at different temperatures

(5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6).

Table 3.13. The apparent first order rate constants (k_{app} , min⁻¹) and regression coefficients (R^2) for sonophotoFenton degradation of RY 84 at different temperatures

(5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6).

Temperature	k_{app} , min ⁻¹	R^2
20 °C (293 K)	0.129	0.9984
25 °C (298 K)	0.157	0.9960
30 °C (303 K)	0.170	0.9939
35 °C (308K)	0.199	0.9915

Activation energy of decolorization reaction was calculated using k_{app} vs temperature data. The reaction rate constants are plotted against the inverse of temperature (1/T) according to Eqn. 3.14

$$k_{app} = Ae^{\frac{-E_a}{RT}} \quad (3.14)$$

$$\ln k_{app} = \ln A - \frac{E_a}{R} \frac{1}{T} \quad (3.15)$$

From the slope of Arrhenius plot (Figure 3.48.), $-E_a/R$, where R was universal gas constant (8.314×10^{-3} kJ/mol K), activation energy (E_a) was calculated. The rate of sonophotoFenton oxidation for decolorization of dye is sensitive to the solution temperature with the activation energy of 20.7 kJ/mol.

Barka et al. (2010) found the activation energy as 32.95 kJ/mol for the photocatalytic oxidation of RY 84 with the TiO_2 catalyst.

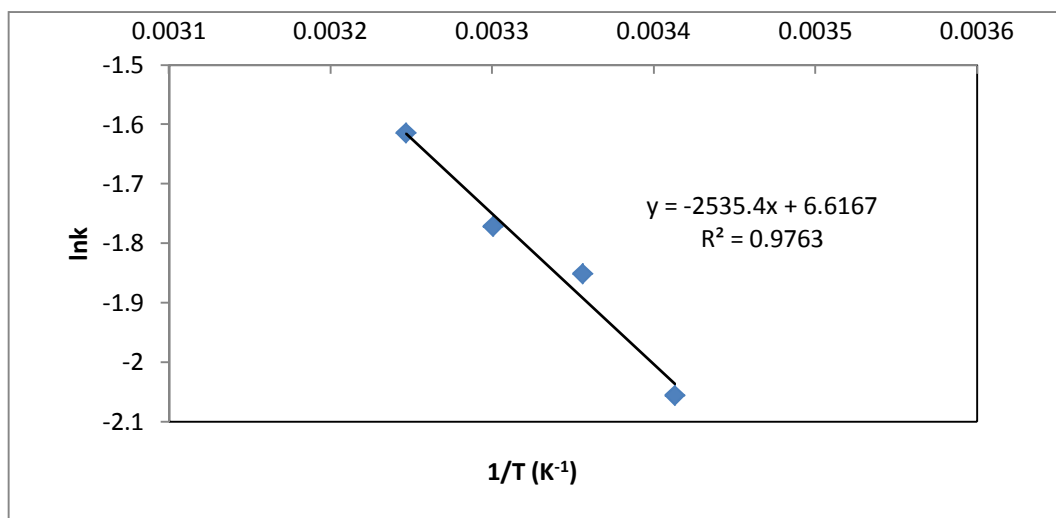


Figure 3.48. Plot of $\ln k$ versus $1/T$

3.5.5 Effect of catalyst loading on the sonophotoFenton oxidation of RY 84

The effect of catalyst loading on the degradation of RY 84 in the sonophotoFenton reaction was studied with different loadings of 0.25 g/L, 0.5 g/L and 1.0 g/L to find out the optimum catalyst amount for maximum efficiency while maintaining all other parameters constant. (25°C, 5mM H_2O_2 , initial RY 84 concentration of 25 mg/L, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6). Results are presented in Figure 3.49.

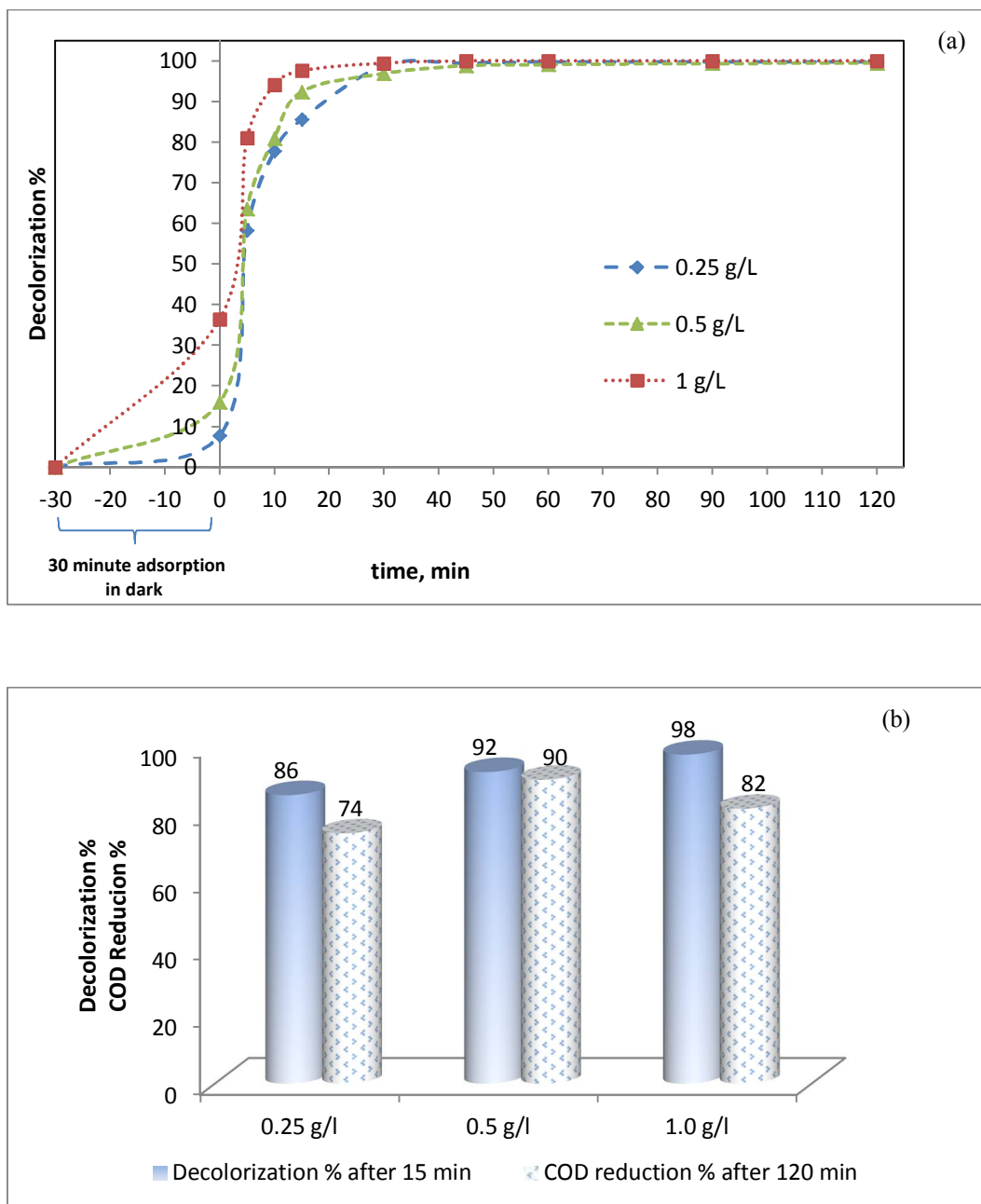


Figure 3.49. Effect of catalyst loading on the sonophotoFenton oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization, % in 15 min and COD removal % in 120 min

(25°C, 5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6).

As seen from the Figure 3.49, as the catalyst loading increases the adsorption of RY 84 on the catalyst increases. So the initial color removal is faster with the 1.0g/L catalyst amount, however there was so much turbidity during oxidation with this loading. It causes a decrease in UV light penetration, so the amount of formed OH• radicals are negatively affected (Kansal et al., 2007). COD reduction decreased from 90% to 82% while increasing the catalyst amount from

0.5 g/L to 1.0 g/L, respectively. On the other hand, COD reduction increased from 74% to 90% while increasing the catalyst amount from 0.25g/L to 0.5g/L, respectively. Increase in catalyst loading increases the adsorption capacity and active surface of the catalyst. It is suggested that the higher rated formation of cavities due to the nuclei in the pores of the catalyst improves the efficiency (Zhong et al., 2011 and references therein). However it can be concluded that an excess of catalyst results in a decrease of the catalytic efficiency. According to Zhong et al. (2011), this decrease may be due to the decrease in formation of active radicals in the solution.

The highest COD reduction was obtained with 0.5g/L catalyst amount. For this reason, this catalyst loading was selected as the optimum loading.

The apparent first order rate constants, k_{app} , of the degradation were calculated from the linear regression $-\ln(C/C_0)$ versus time plots. The results are shown in Figure 3.50. The apparent first order rate constants (k_{app}) and regression coefficients at different catalyst loadings are listed in Table 3.14. Figure 3.50 shows that sonophotoFenton degradation obeys the pseudo-first-order kinetics with respect to catalyst loading.

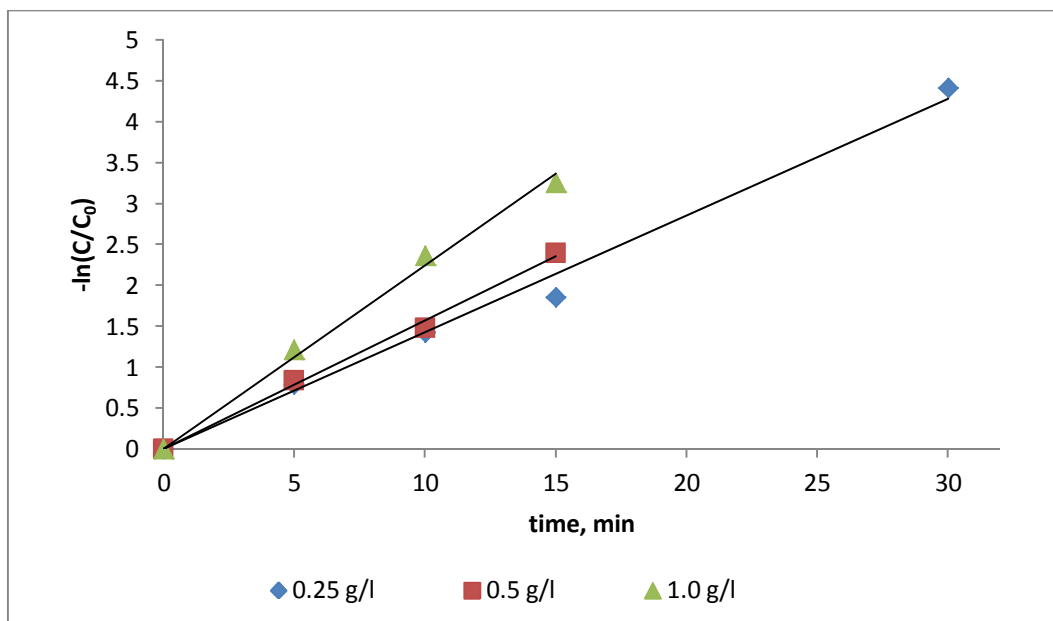


Figure 3.50. Pseudo-first-order kinetics for the sonophotoFenton degradation of RY 84 at different catalyst amounts

(25°C, 5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6).

Table 3.14. The apparent first order rate constants (k_{app} , min⁻¹) and regression coefficients (R^2) for sonophotoFenton degradation of RY 84 at different catalyst amounts

(25°C, 5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 40W ultrasonic power, 4+4 W UV-C lamps, initial dye pH of 6).

Catalyst amount, (g/L)	k_{app} , min ⁻¹	R^2
0.25	0.143	0.9904
0.5	0.157	0.9960
1.0	0.225	0.9943

3.5.6 Effect of ultrasonic power on the sonophotoFenton oxidation of RY 84

The effect of ultrasonic power on the degradation of RY 84 in the sonophotoFenton reaction was studied with the different US powers of 40W, 80W and 100W to find out the optimum ultrasonic power for maximum efficiency while maintaining all other parameters constant. (25°C, 5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6). Results are presented in Figure 3.51.

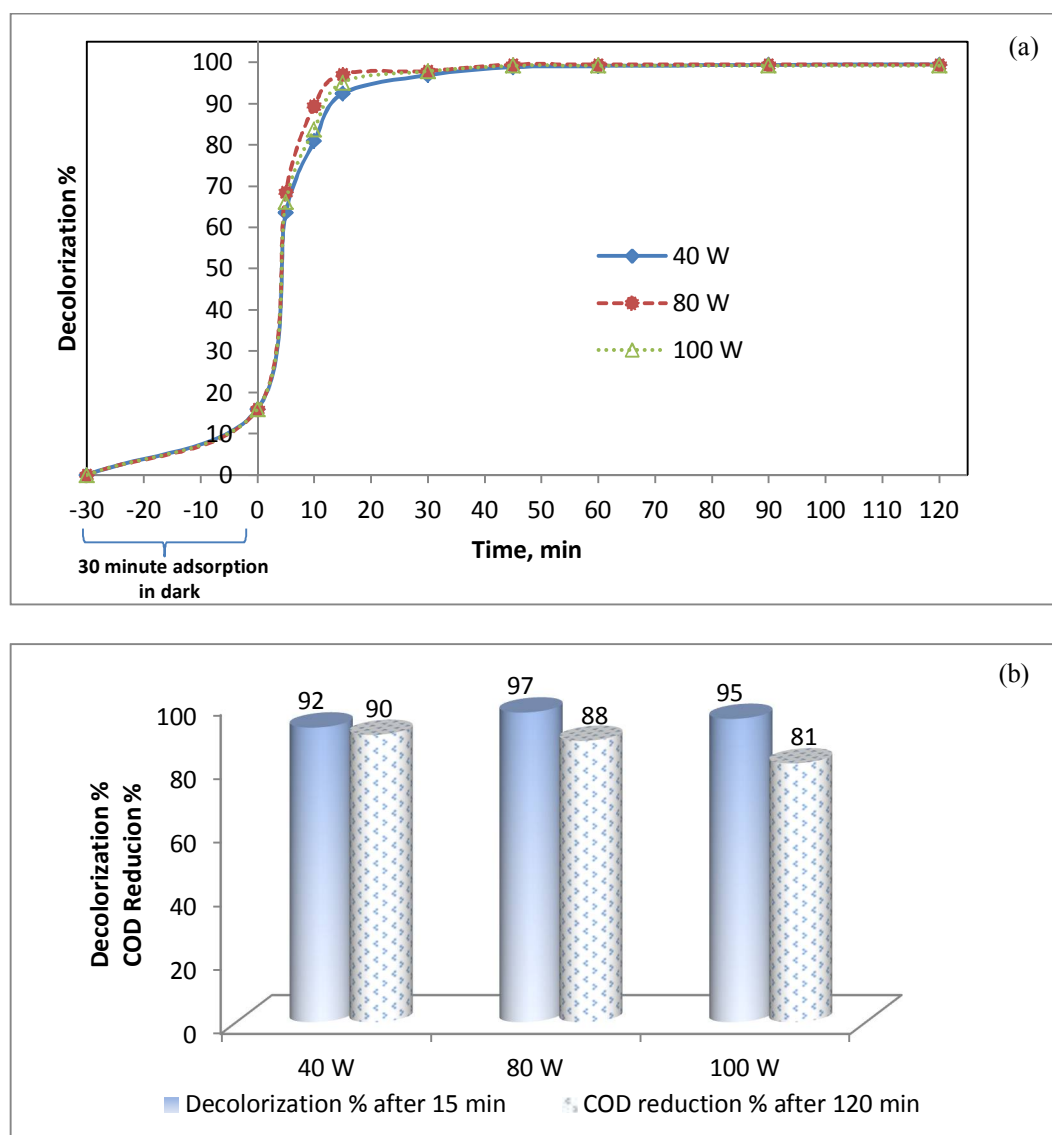


Figure 3.51. Effect of ultrasonic power on the sonophotoFenton oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization,% in 15 min and COD removal% in 120 min

(25°C, 5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6).

As seen from the Figure 3.51, the increase in ultrasonic power from 40 to 80 W slightly enhances the decolorization efficiency. Decolorization increased from 92% to 97% after 15 min of oxidation. For heterogeneous Fenton-like process, accessible surface of the catalyst and mass transfer between the solution and catalyst surface affect the catalytic efficiency (Ramirez et al., 2007b; Zhong et al., 2011). In addition to a continuously cleaning of the catalyst surface for photoFenton reactions, ultrasound breaks up the catalyst particles resulting in a larger reactive area and decrease in the mass transfer limitations. On the contrary, further increase in US to 100W didn't improve the efficiency but caused a decrease in COD reduction. High ultrasonic power may cause insufficient collapse of the cavitation bubbles. Also during the experiment turbidity was observed with the increase in the ultrasonic power especially to 100W power. So this turbidity may reduce the penetration of UV light resulting in a decrease in the process efficiency.

In the light of this discussion, ultrasonic power of 40W was selected as the optimum power. The highest COD removal (90%) was obtained at this US power.

The apparent first order rate constants, k_{app} , of the degradation were calculated from the linear regression $-\ln(C/C_0)$ versus time plots shown in Figure 3.52. The apparent first order rate constants (k_{app}) and regression coefficients at different ultrasonic powers are listed in Table 3.15. Figure 3.52 shows that sonophotoFenton degradation obeys the pseudo-first-order kinetics with respect to ultrasonic power.

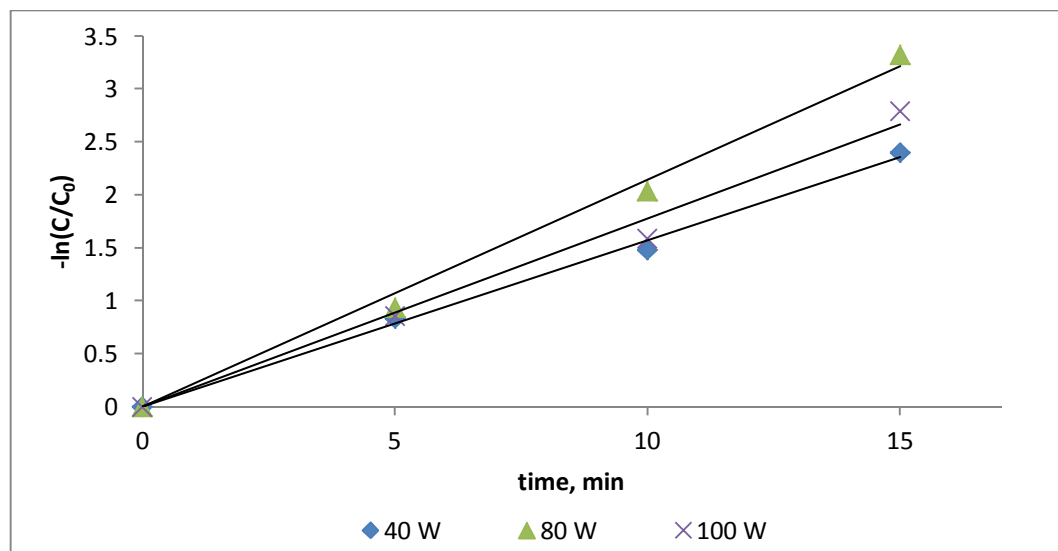


Figure 3.52. Pseudo-first-order kinetics for the sonophotoFenton degradation of RY 84 at different ultrasonic power

(25°C, 5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6).

Table 3.15 The apparent first order rate constants (k_{app} , min⁻¹) and regression coefficients (R^2) for sonophotoFenton degradation of RY 84 at different ultrasonic powers

(25°C, 5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6).

Ultrasonic power	k_{app} , min ⁻¹	R^2
40 W	0.157	0.9960
80 W	0.214	0.9933
100 W	0.177	0.9876

3.5.7 Optimum conditions

Based on the results of the effects of tested parameters on the decolorization and COD reduction efficiency in sonophotoFenton oxidation of RY 84, the optimal operating conditions were obtained as 25°C, initial RY 84 concentration of 25 mg/L, H₂O₂ concentration of 5 mM, 1%Fe/TiO₂ (IW) 300°C catalyst addition of 0.5 g/L, ultrasonic power of 40W, pH of dye of 6, Figure 3.51. The degradation of RY 84 in terms of COD removal and TOC removal by sonophotoFenton process was performed under the optimal conditions. After 45

min reaction, 55% COD removal and 38% TOC removal were achieved while the decolorization efficiency reached 100%. COD removal was more efficient than TOC reduction throughout the catalytic process. 90% of COD removal was obtained after the 120 min of reaction time. The corresponding TOC removal was obtained to be 57%. The low TOC removal rates may be explained by the production of small organic molecular fragments that are not completely mineralized under these oxidation conditions (Dukkanci et al., 2010a; Neamtu et al., 2004).

It can be concluded that, RY 84 could be effectively removed by the sonophotoFenton process, but the more aggressive conditions and prolonged reaction times are required to achieve a complete degradation of RY 84 which is in accordance with the literature (Zhong et al., 2011).

3.5.8 Catalyst Stability at the optimum conditions

Stability of the catalyst was tested for the sonophotoFenton degradation of RY 84. The catalyst was separated after each run by filtration, washed thoroughly with pure water and ethanol and dried at 120°C for 3 h and then calcined at 300°C for 3 h. The calcined catalyst was reused for the next run. Figure 3.53 shows the degradation of RY 84 using the same 1%Fe/TiO₂ catalyst with treatment after each run for 3 consecutive runs. About 100% dye removal was obtained after 45 min in the first and second runs and after 60 min in the last run. 90% COD removal took place at 120 min in the first run. Even after second run, 87% COD removal was achieved in the third run. However, initial decolorization rate decreased with the number of the reuse of the catalyst. Particularly a sharp decrease in the initial decolorization rate was measured in the third run. These observations deduce the stability and reusability of the catalyst.

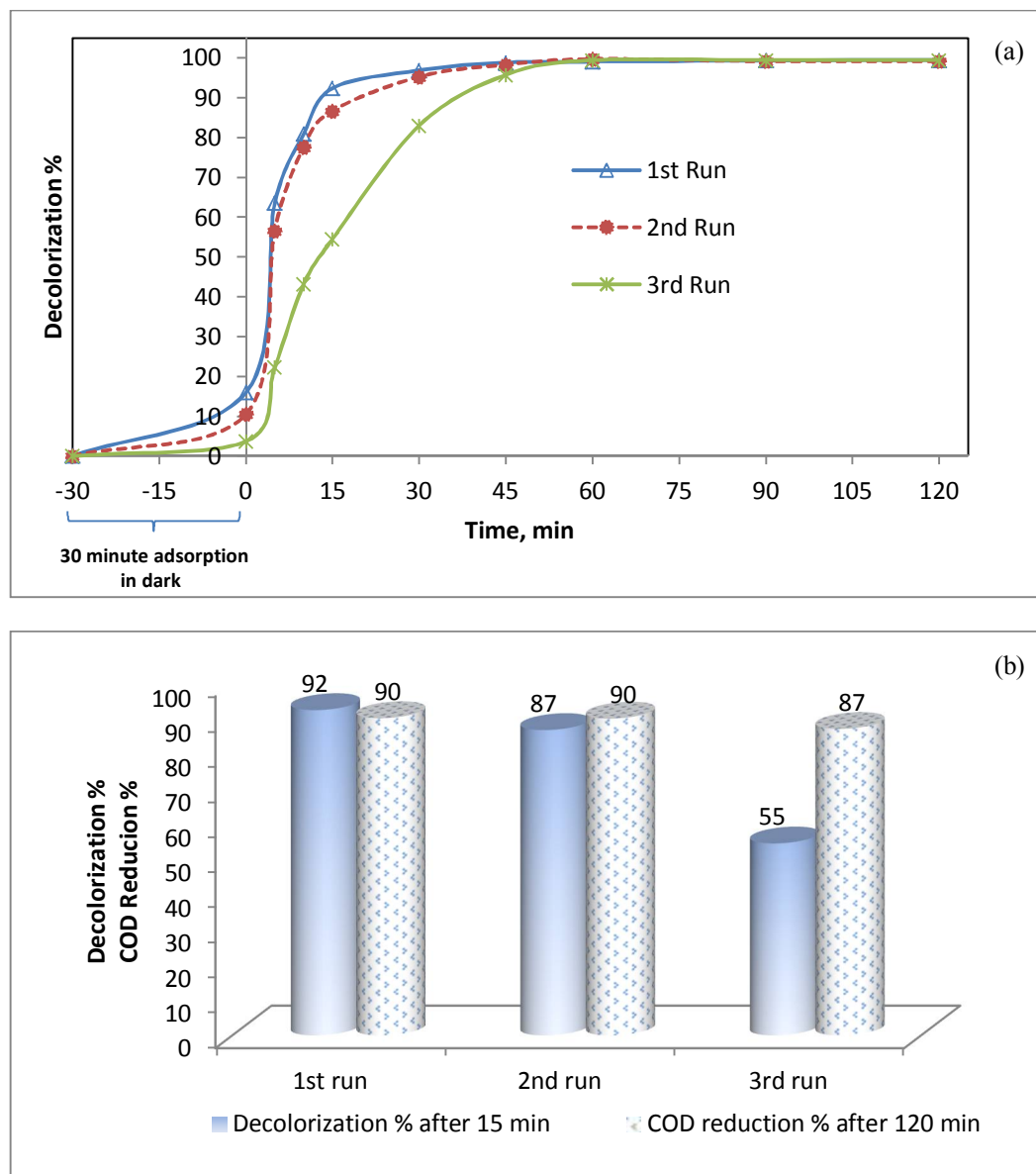


Figure 3.53. Effect of reusability of catalyst at optimum conditions (a) Time dependency of decolorization (b) Decolorization, % in 15 min and COD removal % in 120 min

(25°C, 5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 40W, 4+4 W UV-C lamps, initial dye pH of 6).

The apparent first order rate constants, k_{app} , of the degradation were calculated from the linear regression of $-\ln(C/C_0)$ versus time plots and the results are shown in Figure 3.54. The apparent first order rate constants (k_{app}) and regression coefficients (R^2) with fresh and reused catalysts are listed in Table 3.16.

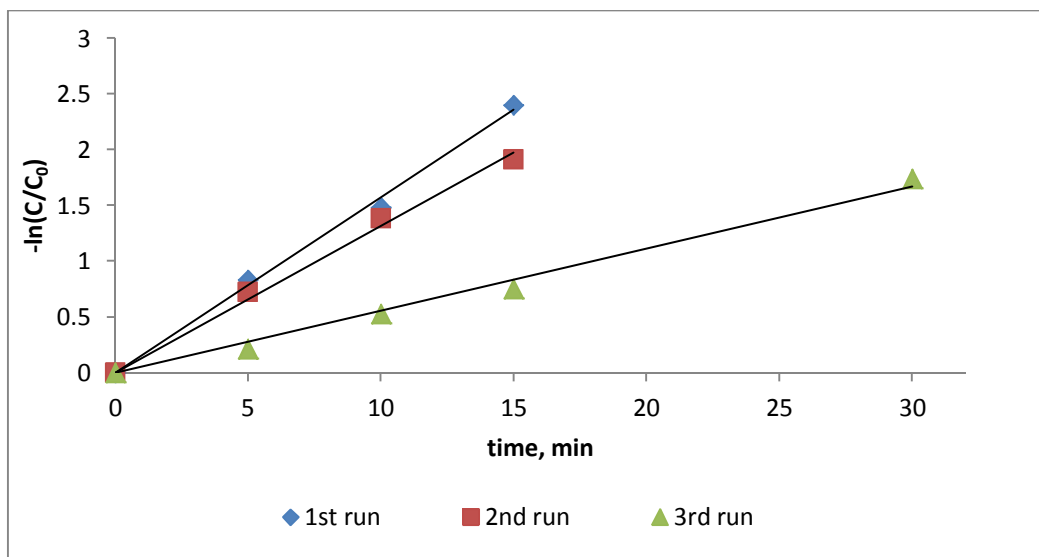


Figure 3.54. Pseudo-first-order kinetics for the fresh and reused catalysts at the optimum conditions

(25°C, 5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 40W, 4+4 W UV-C lamps, initial dye pH of 6).

Table 3.16. First order rate constants, k_{app} , and the regression coefficients (R^2) for the sonophotoFenton degradation of RY 84 with fresh and reused catalysts at the optimum conditions

(25°C, 5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 40W, 4+4 W UV-C lamps, initial dye pH of 6).

# of run	k_{app}, min^{-1}	R^2
1 st Run	0.157	0.9960
2 nd Run	0.132	0.9934
3 rd Run	0.056	0.9909

As seen in Figure 3.54 and Table 3.16 initial color removal rate was slower after second run. The lowest decolorization rate constant was obtained in the third usage of the catalyst. The iron leaching into the solution was determined to be 0.56mg/L (12%), 0.1mg/L (2.2%) and 0.1mg/L (2.2%) at the first, second and third runs, respectively. The decrease in color removal rate may be due to the decrease in the amount of iron in the catalyst structure.

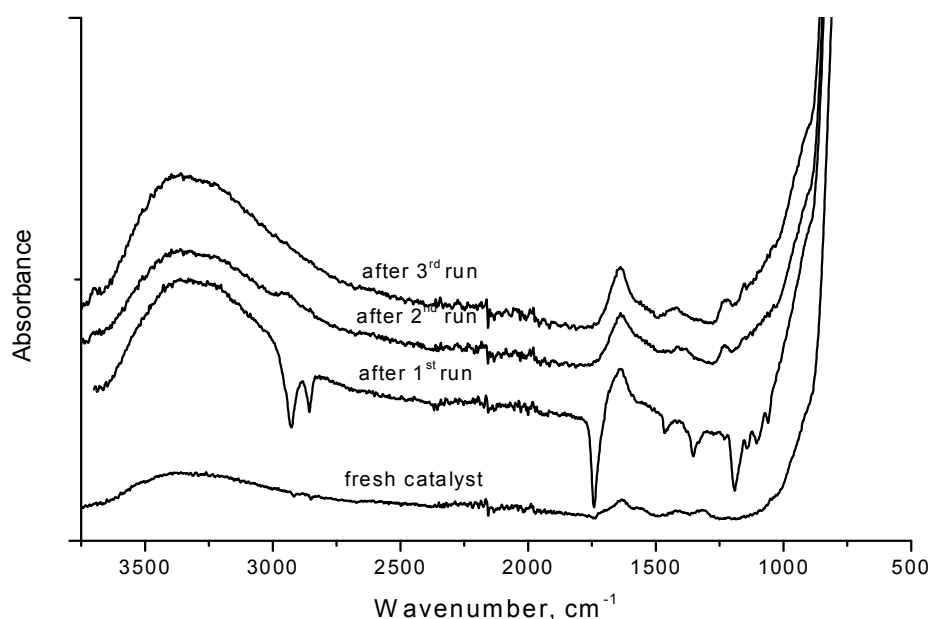


Figure 3.55. FTIR spectra of the fresh and reused catalysts.

Figure 3.55 shows the FTIR spectra of the catalyst before and after three cycles of the sonophotoFenton oxidation of RY 84. FTIR spectra of fresh catalyst were similar to those for used catalysts. The spectra of used catalyst did not show additional bands which may arise from the possible intermediates compared to the spectra of fresh catalyst. Bands are common after each use: the broad band at $3600\text{--}2800\text{ cm}^{-1}$ and narrow band at 1640 cm^{-1} were assigned to the hydroxyl group. Intensity of these bands increased with the use of catalyst. However, the weak band formed at around 2800 cm^{-1} after the first run disappeared with the number of reuse of the catalyst. This band may be attributed to the stretching vibrations of O-H.

3.5.9 Further experiments at the optimum conditions

As a further study, 15 mg/L and 75 mg/L of initial dye concentrations were tested in the sonophotoFenton reaction at the optimum conditions in order to compare with the 25 mg/L which is the optimum condition of initial dye concentration. (25°C , $5\text{ mM H}_2\text{O}_2$, 0.5 g/L catalyst, 40 W ultrasonic power, $4+4\text{ W}$ UV-C lamps, initial dye pH of 6). Results are presented in Figure 3.56.

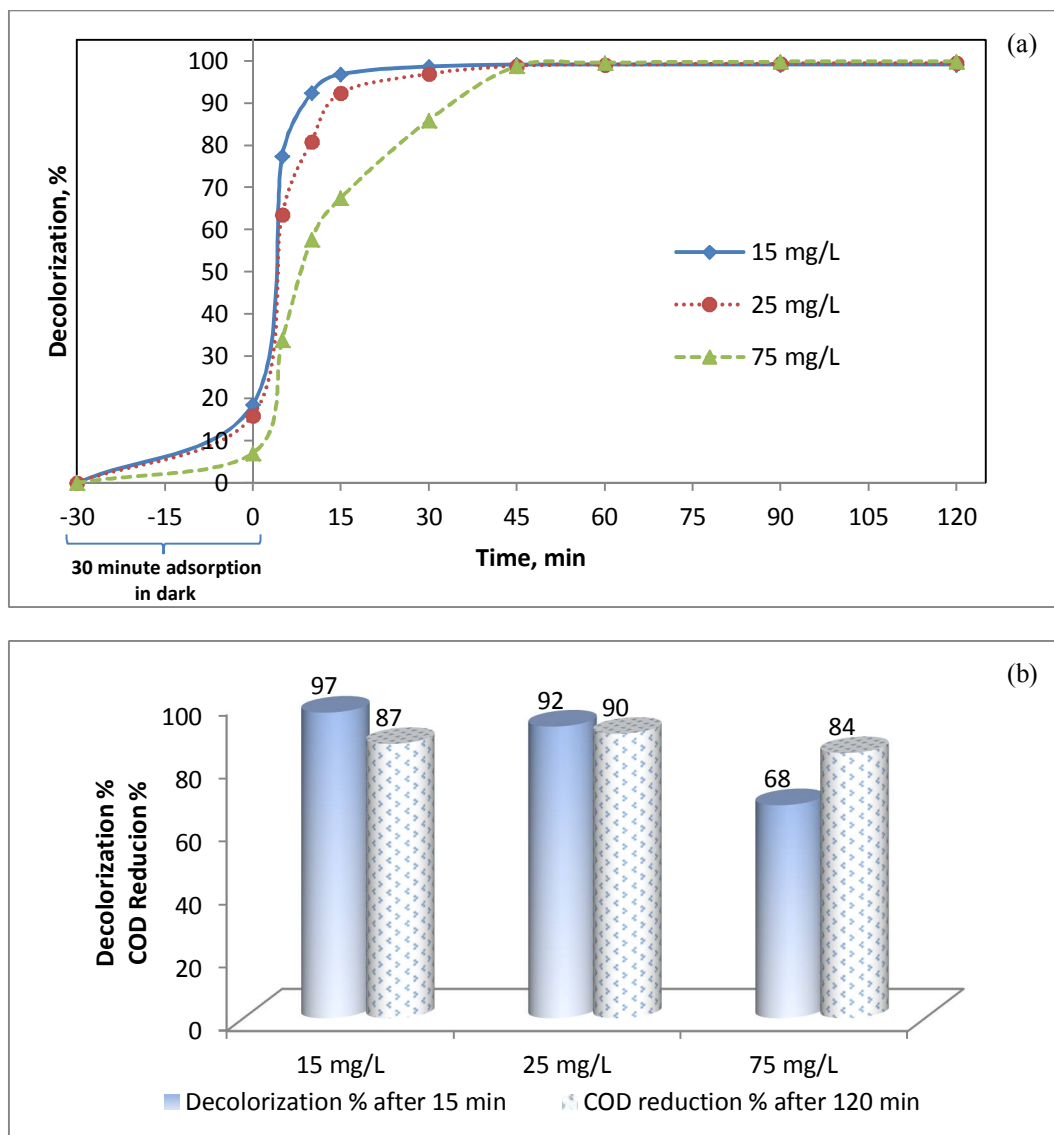


Figure 3.56. Effect of initial dye concentration on the sonophotoFenton oxidation of RY 84 at the optimum conditions (a) Time dependency of decolorization (b) Decolorization, % in 15 min and COD removal % in 120 min

(25°C, 5mM H₂O₂, 0.5 g/L catalyst, 40W, 4+4 W UV-C lamps, initial dye pH of 6).

As seen from the Figure 3.56, initial decolorization efficiency in 15 min decreased from 97% to 92% and to 68% with increasing the initial dye concentration from 15mg/L to 25mg/L and 75mg/L at the optimum conditions. COD reduction at the end of the 2h oxidation was not so much affected when the initial dye concentration increased from 15mg/L to 25mg/L. As expected, COD reduction efficiency negatively affected from the initial dye concentration increase. COD reduction decreased from 90% to 84% with increasing the initial dye concentration from 25mg/L to 75mg/L at the optimum conditions.

The apparent first order rate constants, k_{app} , of the degradation were calculated from the linear regression of $-\ln(C/C_0)$ versus time plots and the results are shown in Figure 3.57. The apparent first order rate constants (k_{app}) and regression coefficients at different initial dye concentrations at optimum conditions (25°C, 5mM H₂O₂, 0.5 g/L catalyst, 40W, 4+4 W UV-C lamps, initial dye pH of 6) are listed in Table 3.17.

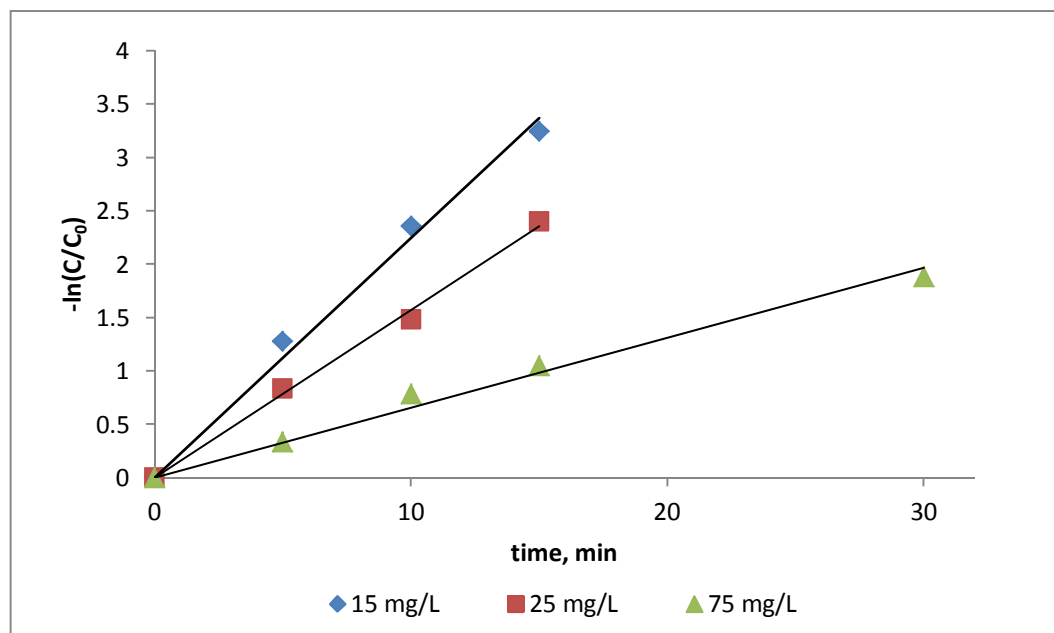


Figure 3.57. Pseudo-first-order kinetics for the sonophotoFenton degradation of RY 84 at different initial dye concentrations at optimum conditions

(25°C, 5mM H₂O₂, 0.5 g/L catalyst, 40W, 4+4 W UV-C lamps, and initial dye pH of 6).

Table 3.17. The apparent first order rate constants (k_{app} , min⁻¹) and regression coefficients (R^2) for sonophotoFenton degradation of RY 84 at different initial dye concentrations at optimum conditions

(25°C, 5mM H₂O₂, 0.5 g/L catalyst, 40W, 4+4 W UV-C lamps, initial dye pH of 6).

Initial dye concentration, mg/L	k_{app} , min ⁻¹	R^2
15	0.225	0.9911
25	0.157	0.9960
75	0.067	0.9868

Figure 3.58 presents the effect of temperature on oxidation of RY 84 for 3 different initial dye concentrations. Figure 3.58 shows that, increase in temperature enhanced the initial rate at different initial dye concentrations.

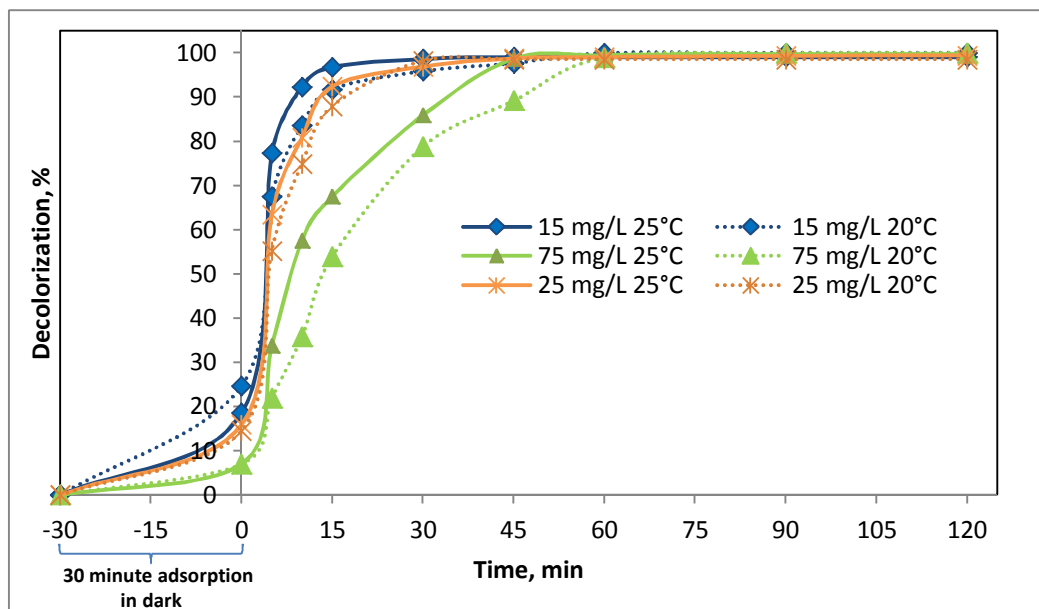


Figure 3.58. Effect of temperature on the sonophotoFenton oxidation of RY 84 at different initial dye concentrations

(5mM H_2O_2 , 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6).

As shown in Figure 3.59. 15mg/L and 75mg/L of initial dye concentrations were also studied at the US power of 80W keeping the other optimum conditions same (25°C, 5mM H_2O_2 , 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6). As we discussed before, increase in ultrasonic power slightly enhanced the color removal efficiency at the 25 mg/L initial concentration whereas at the initial concentration of 15 mg/L and 75 mg/L color removal was not affected by the ultrasonic power increase to 80W. On view of COD reductions, at lower concentration, increase in ultrasonic power negatively affects the reduction. The reason of this negative effect may be due to the turbidity of solution because at 80W ultrasonic power there was more turbidity when compared to the 40W at the same initial concentration of dye. No significant change in COD removal was observed at the 25mg/L and 75 mg/L with the increase in US power.

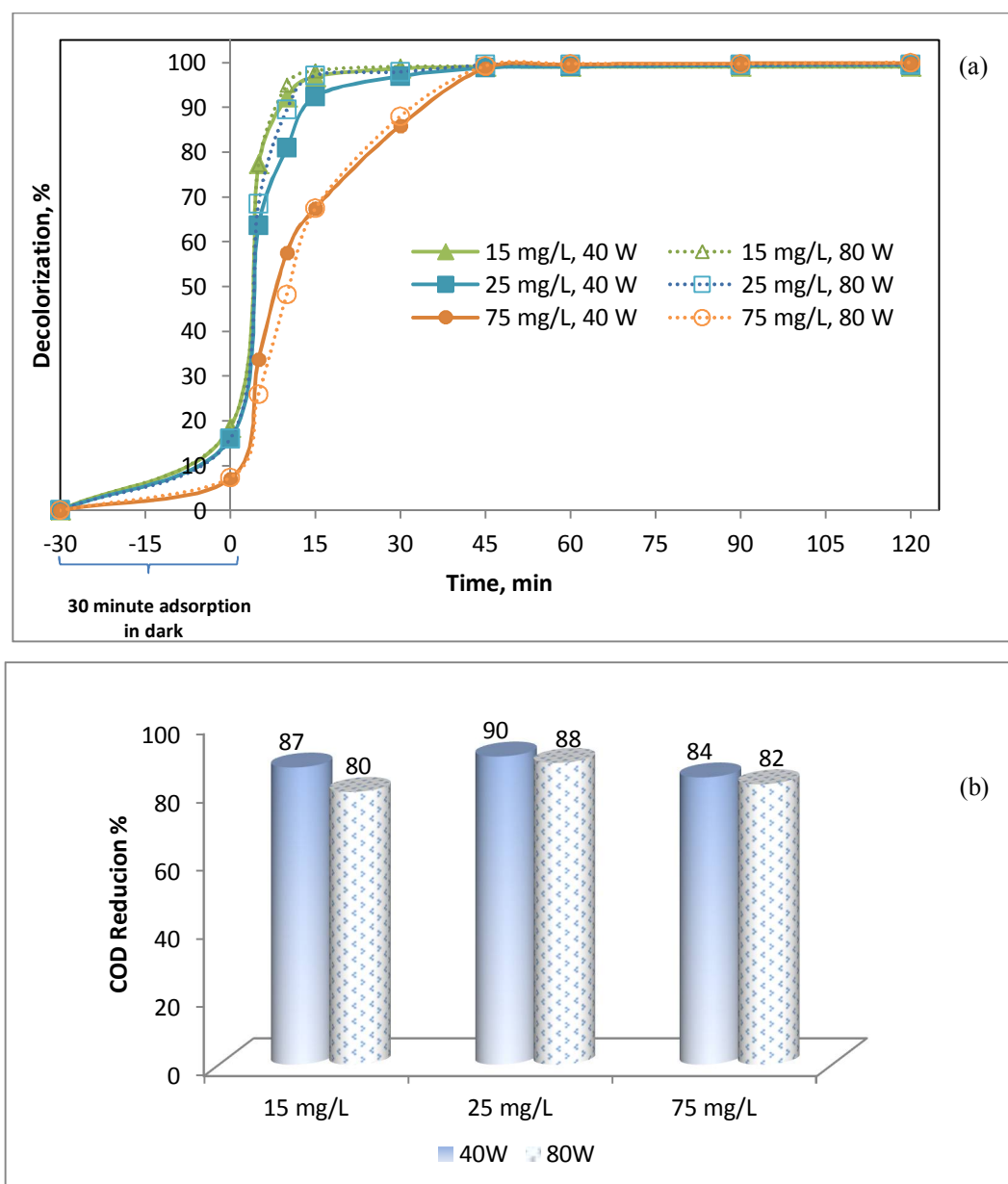


Figure 3.59. Effect of US power on the sonophotoFenton oxidation of RY 84 at different initial dye concentrations (a) Time dependency of decolorization (b) COD removal% in 120 min

(25°C, 5mM H₂O₂, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6).

3.6 Economical Evaluation

For the systems including UV power and particularly ultrasonic power, electric energy can represent a significant fraction of the operating costs. Simple economical comparison of the different oxidation treatments (Figure 3.32) studied is shown in Table 3.18 and Table 3.19 by means of the calculation of electric energy per mass (E_{EM}) which is defined as the electric energy in kilowatts hours (kWh) required to degrade a unit of mass of contaminant in polluted water.

Calculations were made according to the literature (Segura et al., 2009). The E_{EM} value (kWh kg^{-1}) can be calculated as follows:

$$E = (P * t)/60 \quad (3.16)$$

$$E_{EM} = \frac{E.10^6}{(C_0 - C).V} \quad (3.17)$$

where E is the electric energy consumption in each system (kWh), P is the power (kW) of the AOP system, t (min) is the time in which the power is supplied to the dye waste water, V is the volume (L) of dye waste water treated, and C_0 and C are the initial and final concentrations of RY 84, respectively. In order to compare energy consumption by means of COD reduction, in the eqn. 3.17 instead of C_0 and C we use initial and final COD values. But firstly actual US power was determined.

3.6.1 Determination of actual US power

To find the experimental power of US, calorimetric measurements were performed (Dukkanci and Gunduz, 2013). In a pure liquid, it is assumed that almost all the mechanical energy produces heat and so, via calorimetry, some estimate of the acoustic power entering the system can be obtained. For this purpose, the temperature (T) was recorded against time (t), using a thermocouple placed into the reaction cell. The ultrasonic power actually entering the system was obtained according to equation:

$$\text{Power} = \left(\frac{dT}{dt}\right) c_p m \quad (3.18)$$

Where, c_p = heat capacity of water ($4.187 \text{ kJ kg}^{-1} \text{K}^{-1}$ at 20°C) and m= mass of water used.

From the slope of the Figure 3.60 we get the dT/dt then by using the eq.3.18 we calculate the actual power of US as 23W.

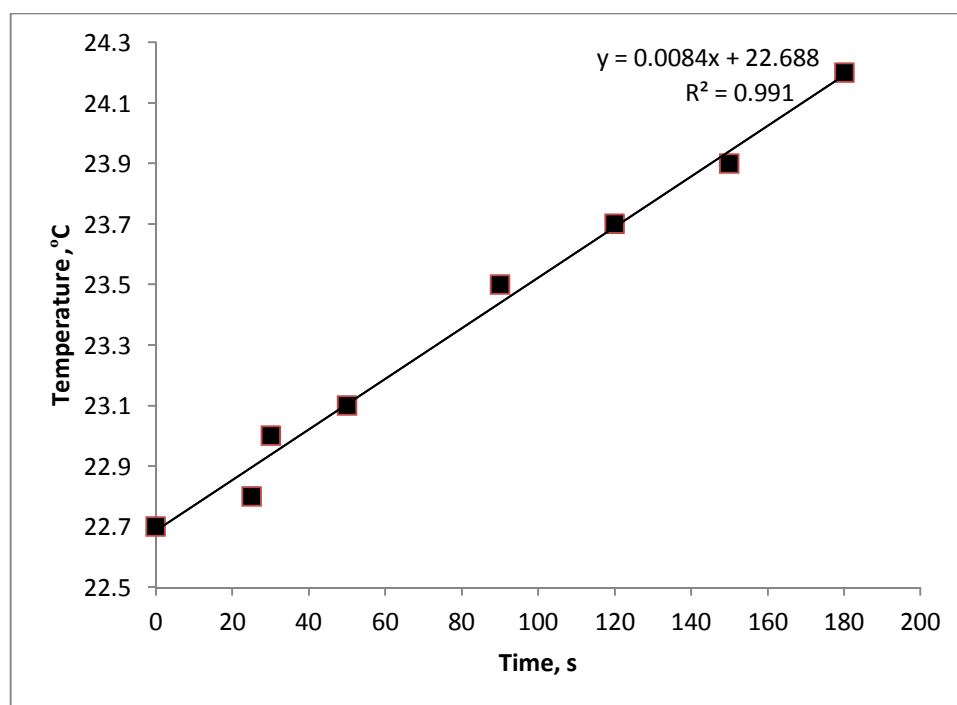


Figure 3.60. Calorimetric measurement for actual US power

3.6.2 Economical evaluation of different AOPs

Energy requirement (kWh) for different advanced oxidation combinations used in this study, given in Figure 3.32, was calculated by the eqs. (3.16) and (3.17), in per unit mass of COD reduction and in per unit mass of dye decolorized. Results are presented in Tables 3.18 and 3.19.

Table 3.18. Electric energy estimated for the COD reduction of RY 84 by different treatment methods after 2 h

(20°C, initial RY 84 concentration of 25 mg/L, according to the combination; 35 mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

	power (kW)	V (L)	(COD ₀ -COD) mg/L	E (kWh)	E _{EM} (kWh kg ⁻¹)	COD red.%
UV	0.008	0.65	0.1	0.016	246153.8	0
US+UV+catalyst	0.031	0.65	94	0.062	1014.6	17
UV+H ₂ O ₂	0.008	0.65	205	0.016	120.1	37
US+UV+H ₂ O ₂	0.031	0.65	266	0.062	358.6	48
UV+catalyst+H ₂ O ₂	0.008	0.65	266	0.016	92.5	49
US+UV+catalyst+H ₂ O ₂	0.031	0.65	310	0.062	307.7	56

Table 3.19. Electric energy estimated for 100% decolorization of RY 84 with different oxidation systems

(20°C, initial RY 84 concentration of 25 mg/L, according to the combination; 35 mM H₂O₂, 0.5 g/L catalyst, 40W ultrasonic power, 4+4 W UV-C lamps)

	power (kW)	V (L)	time (min)	(C ₀ -C) mg/L	E (kWh)	E _{EM} (kWh kg ⁻¹)
US+UV+catalyst+H ₂ O ₂	0.031	0.65	32	25	0.005	1017.4
UV+catalyst+H ₂ O ₂	0.008	0.65	90	25	0.012	738.5

According to Table 3.18, from the COD reduction point of view, the ordering of electric energy estimated can be given as follows:

$$E_{EM(UV+cat.+H_2O_2)} < E_{EM(UV+H_2O_2)} < E_{EM(US+UV+cat.+H_2O_2)} < E_{EM(US+UV+H_2O_2)} < E_{EM(US+UV+cat.)} < E_{EM(UV)}$$

As can be seen from the Table 3.19, to obtain the 100% color removal of RY 84 the E_{EM} for the UV+catalyst+H₂O₂ system is lower than that obtained for sonophotoFenton system.

As shown in Figure 3.32 heterogeneous sonophotoFenton process demonstrated a much higher decolorization and COD removal efficiency but UV+catalyst+H₂O₂ system is more cost effective than the sonophotoFenton system.

3.7 Further Investigation of UV+catalyst+H₂O₂ Oxidation of RY 84

Since UV+catalyst+H₂O₂ oxidation of RY 84 is obtained to be more cost effective, the effects of H₂O₂ concentration, initial pH of solution, initial dye concentration, catalyst amount were studied on the degradation of RY 84 by UV+catalyst+H₂O₂ oxidation with 1%Fe/TiO₂ catalyst which was prepared by incipient wetness impregnation method and calcined at 300°C, and compared with the sonophotoFenton oxidation.

3.7.1 Effect of H₂O₂ concentration on the UV+catalyst+H₂O₂ oxidation of RY 84

Effect of hydrogen peroxide concentration on the UV+catalyst+H₂O₂ oxidation of RY 84 was studied with the H₂O₂ concentrations of 2.5 mM, 5 mM, while maintaining all other parameters constant. (25°C, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6). Results are presented in Figure 3.61.

Initial color removal within the 15 min increases from 91% to 94% when the H₂O₂ concentration increases from 2.5 mM to 5 mM, respectively. Also, COD reduction after 120 min of oxidation time, increases from 76% to 87% with increasing the H₂O₂ concentration from 2.5 mM to 5mM, respectively. As we discussed before corresponding COD reduction was 49% and initial color removal within the 15 min was 88% when 35mM H₂O₂ was used at 20°C (initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 4+4 W UV-C lamps and initial dye pH of 6), Figure 3.31. It is well known that photocatalytic oxidation is not temperature dependent and an optimum H₂O₂ concentration exists in Fenton's oxidation. Decrease in color removal efficiency and COD reduction with the increase in H₂O₂ concentration from 5mM to 35mM is due to the scavenging effect of H₂O₂ at high concentrations, the excess of hydrogen peroxide reacts with OH• radicals and lowers the OH• radicals concentration (Kritikos et al., 2007; Muruganandham and Swaminathan, 2004; Zhong et al., 2011).



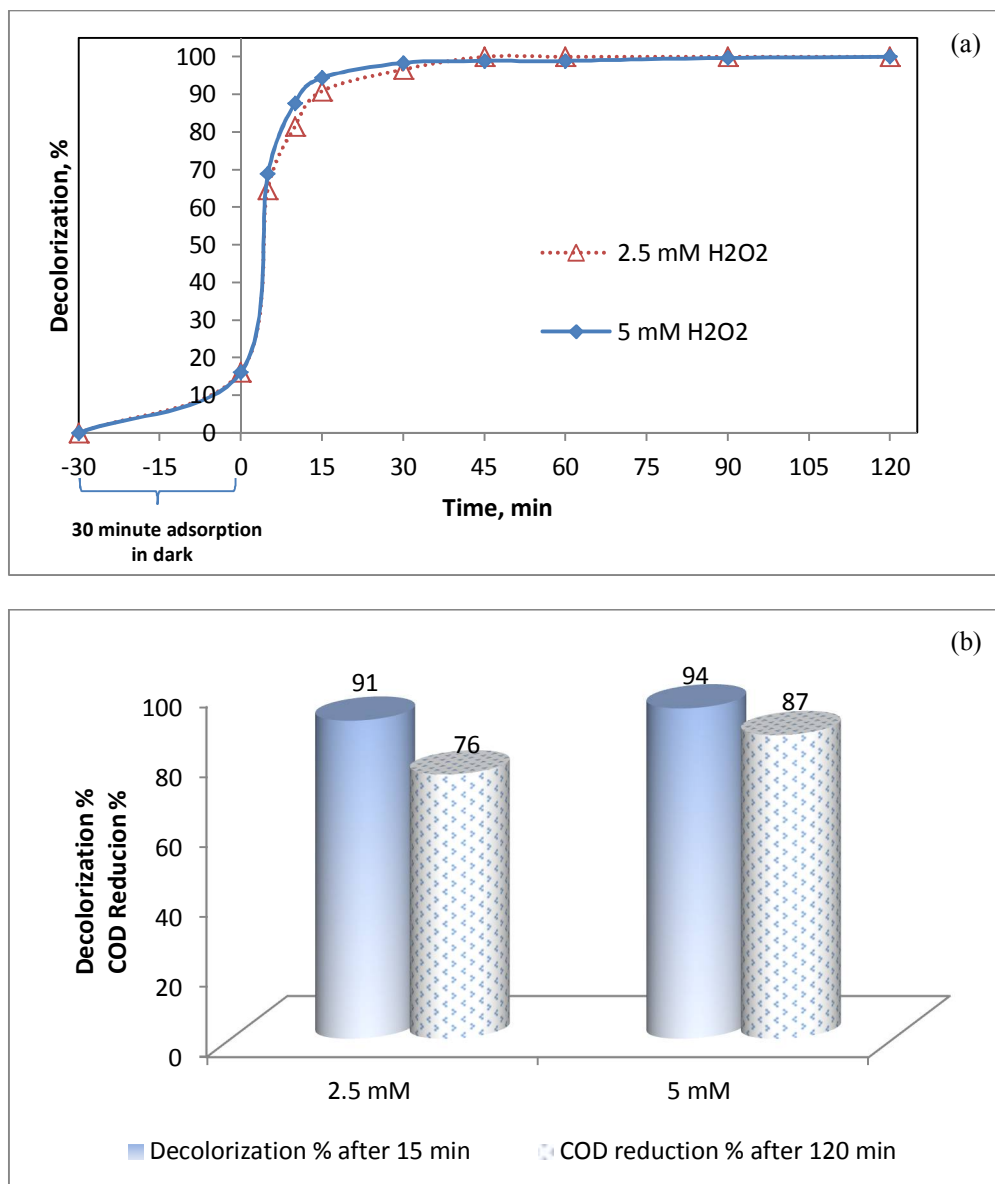


Figure 3.61. Effect of H_2O_2 concentration on the UV+catalyst+ H_2O_2 oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization, % in 15 min and COD removal % in 120 min

(25°C, 25 mg/L of initial dye concentration, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6).

UV+catalyst+ H_2O_2 oxidation of RY 84 followed the pseudo-first-order kinetics (Figure 3.62). The correlation coefficients (R^2) and reaction rate constants (k_{app}) are given in Table 3.20.

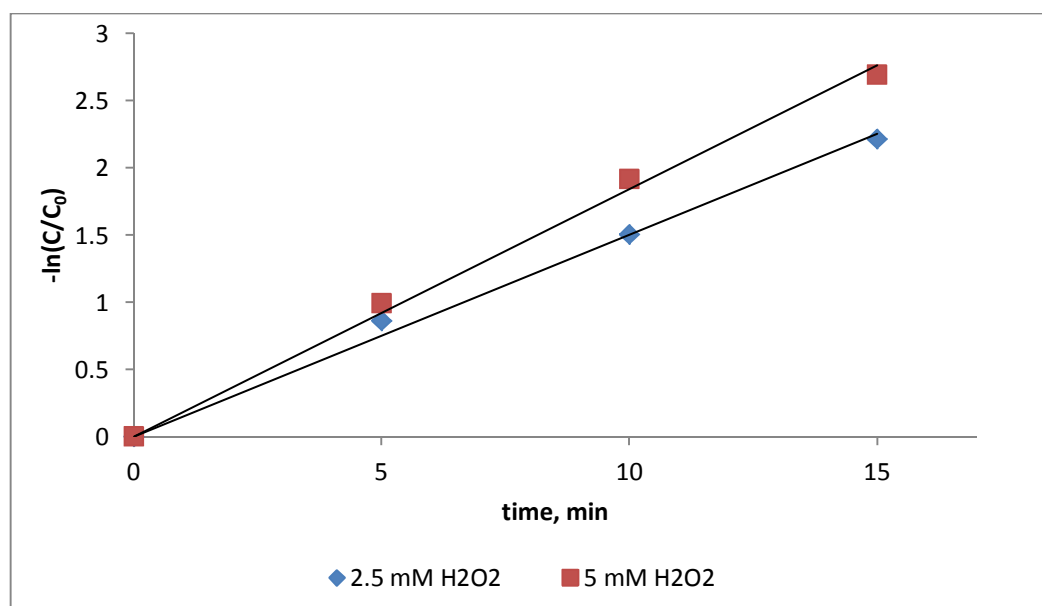


Figure 3.62. Pseudo-first-order kinetics for the UV+catalyst+H₂O₂ degradation of RY 84 at different H₂O₂ concentration

(25°C, 25 mg/L of initial dye concentration, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6).

Table 3.20 The apparent first order rate constants (k_{app} , min⁻¹) and regression coefficients (R^2) for UV+catalyst+H₂O₂ degradation of RY 84 at different H₂O₂ concentration

(25°C, 25 mg/L of initial dye concentration, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6).

H ₂ O ₂ concentration, mM	k_{app} , min ⁻¹	R^2
2.5	0.151	0.9945
5	0.184	0.9961

In addition to the result that initial decolorization rate with 5mM H₂O₂ is faster than that of 2.5mM H₂O₂, almost 100% color removal was obtained with both H₂O₂ concentrations within 30 min of reaction time and since the COD removal efficiency with 5mM H₂O₂ (87%) was higher than 2.5mM H₂O₂ (76%), 5mM H₂O₂ seems to be the best adaptation for degradation of RY 84 with UV+catalyst+H₂O₂ oxidation. This H₂O₂ amount is the same with the sonophotoFenton oxidation of RY 84.

3.7.2 Effect of initial pH of dye on the UV+catalyst+H₂O₂ oxidation of RY 84

The effect of pH on the degradation of RY 84 with UV+catalyst+H₂O₂ oxidation was studied with the different initial pH values of 3.5, ≈6 (which is the dye pH), while maintaining all other parameters constant. (25°C, initial RY 84 concentration of 25 mg/L, 5mM H₂O₂, 0.5 g/L catalyst, 4+4 W UV-C lamps). Results are presented in Figure 3.63.

The pH of the solution was adjusted before reaction and it was not controlled during the reaction.

Figure 3.63 indicates that in acidic medium the amount of dye adsorbed is higher and adsorption decreases with increasing the initial pH.

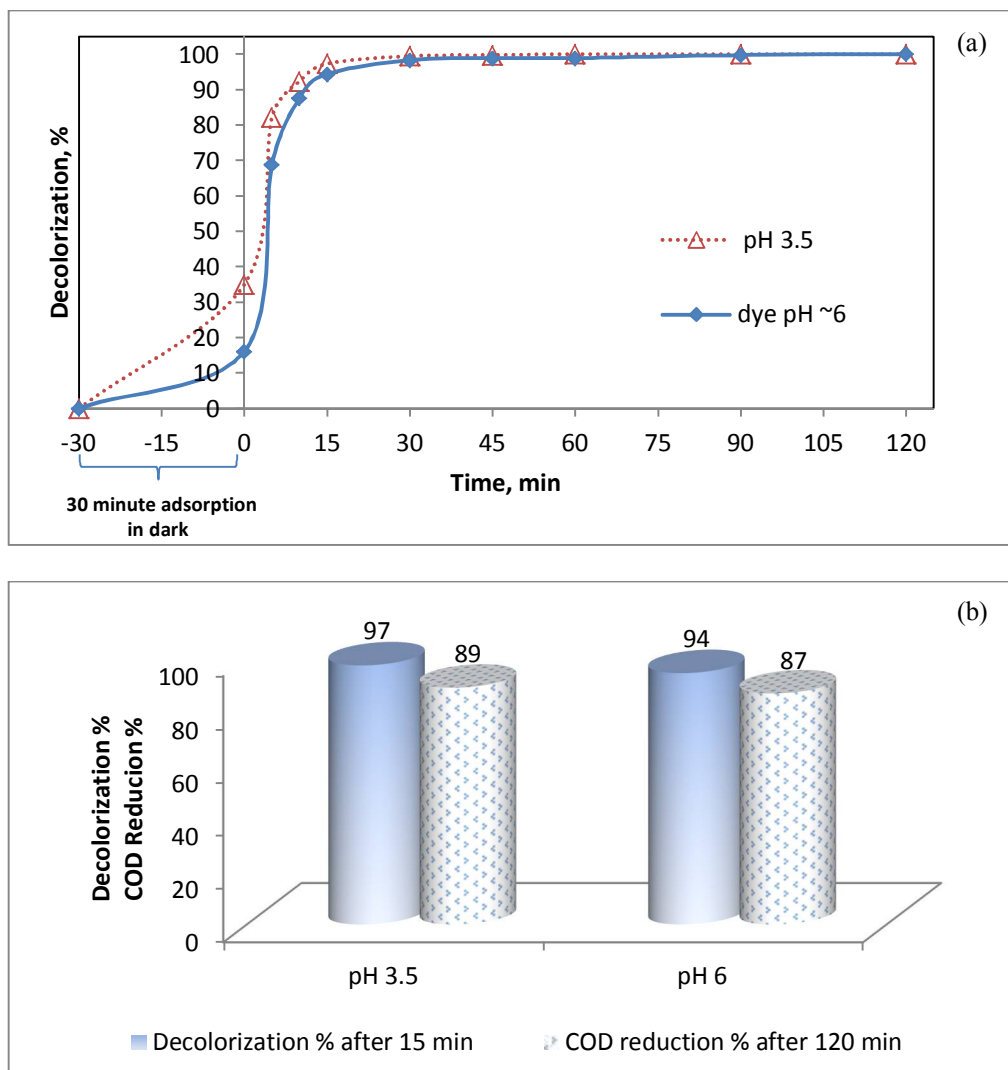


Figure 3.63. Effect of initial pH of dye on the UV+catalyst+H₂O₂ oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization, % in 15 min and COD removal % in 120 min

(25°C, 25 mg/L of initial dye concentration, 5 mM H₂O₂, 0.5g/L catalyst, 4+4 W UV-C lamps).

As seen from the Figure 3.63, change in the initial pH of the solution did not affect so much initial color removal and COD reduction after 120 min. Initial color removal after 15 min was 97% and 94% for the initial pH values of 3.5 and 6, respectively. COD reduction was 89% and 87% for the initial pH values of 3.5 and 6, respectively.

The apparent first order rate constants, k_{app} , of the degradation after 15 min at initial pH of 3.5 and 6 were calculated from the linear regression $-\ln(C/C_0)$ versus time plots and the results are shown in Figure 3.64. The apparent first order

rate constants (k_{app}) and regression coefficients at different pHs are listed in Table 3.21.

The high adsorption of the dye on the catalyst leads to a fast decrease of the dye concentration in acidic condition. It can be said from the results that, effect of initial pH on kinetics of degradation is due to the dye adsorption on the catalyst.

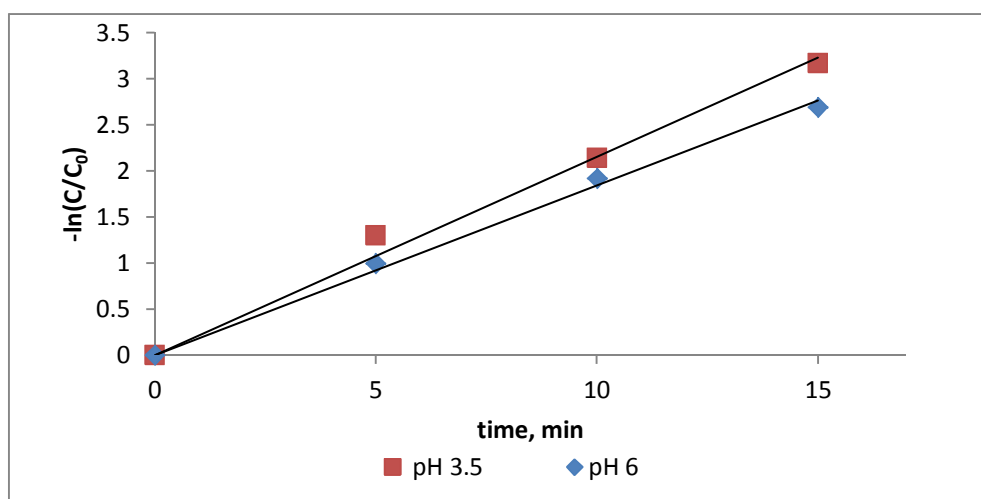


Figure 3.64. Pseudo-first-order kinetics for the UV+catalyst+H₂O₂ degradation of RY 84 at different initial pH

(25°C, 25 mg/L of initial dye concentration, 0.5 g/L catalyst, 5 mM H₂O₂, 4+4 W UV-C lamps).

Table 3.21. The apparent first order rate constants (k_{app} , min⁻¹) and regression coefficients (R^2) for UV+catalyst+H₂O₂ degradation of RY 84 different initial pH

(25°C, 25 mg/L of initial dye concentration, 0.5 g/L catalyst, 5 mM H₂O₂, 4+4 W UV-C lamps).

Initial pH	k_{app} , min ⁻¹	R^2
3.5	0.216	0.9902
Dye pH ($\approx$ 6)	0.184	0.9961

Since the color removal and COD reduction of UV+catalyst+H₂O₂ oxidation at the dye pH of 6 were not significantly different from the oxidation at acidic pH (pH 3.5) and to adjust the initial pH of the solution will bring extra cost, to use the

dye pH seems to be the suitable for UV+catalyst+H₂O₂ degradation of RY 84 which is the same result obtained with the sonophotoFenton oxidation of RY 84.

3.7.3 Effect of catalyst loading on the UV+catalyst+H₂O₂ oxidation of RY 84

The effect of catalyst loading on the degradation of RY 84 in the UV+catalyst+H₂O₂ reaction was studied with the different loadings of 0.25 g/L, and 0.5 g/L while maintaining all other parameters constant. (25°C, 5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 4+4 W UV-C lamps, initial dye pH of 6). Results are presented in Figure 3.65.

As seen from the Figure 3.65, as the catalyst loading increases the adsorption of RY 84 increases. The color removal efficiency didn't change significantly. Color removal after 15 min was decreased from 97% to 94% while COD reduction increased from 84% to 87% with the increase in the catalyst amount from 0.25g/L to 0.5g/L, respectively the corresponding COD values were 74% and 90% for the sonophotoFenton oxidation of RY 84 (Figure 3.49). Increase in catalyst loading increases the adsorption capacity and active surface of the catalyst. The highest COD reduction was obtained with 0.5g/L of catalyst amount. So, it was selected as the best catalyst loading which was similar with the sonophotoFenton system.

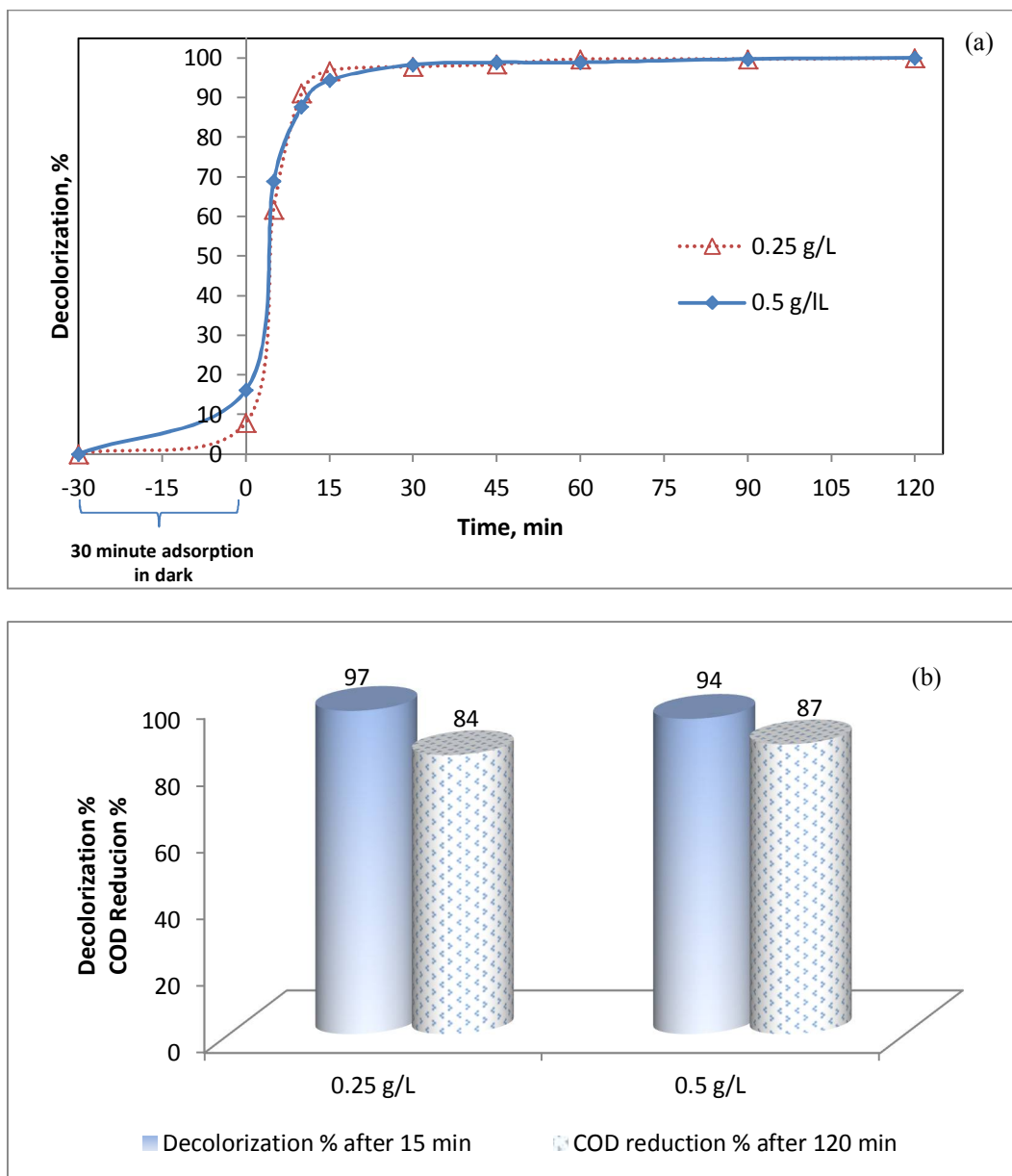


Figure 3.65. Effect of catalyst loading on the UV+catalyst+H₂O₂ oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization, % in 15 min and COD removal % in 120 min

(25°C, 25 mg/L of initial dye concentration, 5 mM H₂O₂, 4+4 W UV-C lamps, initial dye pH of 6).

The apparent first order rate constants, k_{app} , of the degradation were calculated from the linear regression of $-\ln(C/C_0)$ versus time plots and the results are shown in Figure 3.66. The apparent first order rate constants (k_{app}) and regression coefficients at different catalyst loadings are listed in Table 3.22.

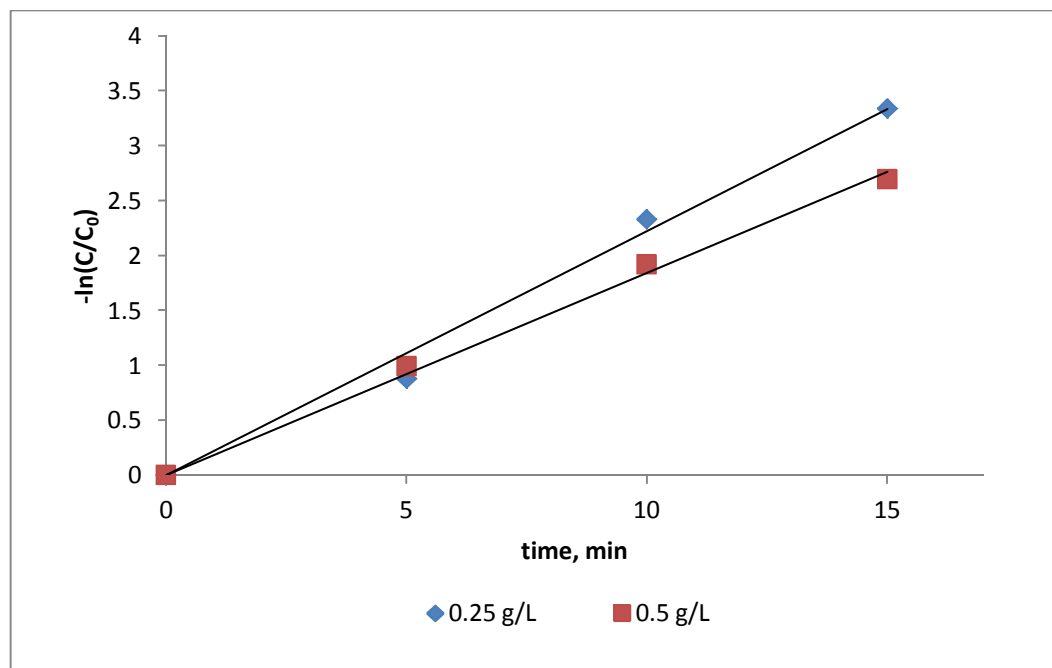


Figure 3.66. Pseudo-first-order kinetics for the UV+catalyst+H₂O₂ degradation of RY 84 at different catalyst loading

(25°C, 25 mg/L of initial dye concentration, 5 mM H₂O₂, 4+4 W UV-C lamps, initial dye pH of 6).

Table 3.22. The apparent first order rate constants (k_{app} , min⁻¹) and regression coefficients (R^2) for UV+catalyst+H₂O₂ degradation of RY 84 at different catalyst loading

(25°C, 25 mg/L of initial dye concentration, 5 mM H₂O₂, 4+4 W UV-C lamps, initial dye pH of 6).

Catalyst loading (g/L)	k_{app} , min ⁻¹	R^2
0.25	0.223	0.9901
0.5	0.184	0.9961

3.7.4 Effect of initial dye concentration on the UV+catalyst+H₂O₂ oxidation of RY 84

The effect of initial dye concentration on the degradation of RY 84 in the UV+catalyst+H₂O₂ reaction was studied with the different initial dye concentrations of 15, 25, and 75 mg/L while maintaining all other parameters constant. (25°C, 5mM H₂O₂, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6). Results are presented in Figure 3.67.

As seen from Figure 3.67, the initial decolorization efficiency in 15 min of reaction decreased from 98% to 94% and 69% with the increase in the initial dye concentration from 15 to 25 and 75 mg/L, respectively. Because the formed OH• radicals are not enough for oxidation with increasing concentration of dye. Another presumed reason is, at high concentrations the active sites of the catalyst covered by dye molecules so the generation of OH• radicals on the surface of the catalyst reduces. Also at high concentrations, a significant amount of UV may be absorbed by dye itself rather than the catalyst and that reduces the catalytic activity so the formation of OH• and O₂•⁻, too (Zhong et al., 2011) (Konstantinou and Albanis, 2004). At high concentration of dye the UV light penetration is also retarded. It is concluded that catalyst surface needed for the degradation also increases at high concentration. COD reduction decreased slightly. When the initial dye concentration increased from 15 mg/L to 25 mg/L and 75 mg/L, COD reduction decreased from 88% to 87% and 80%, respectively, where the corresponding results in the sonophotoFenton oxidation with the US power of 40W were 87%, 90% and 84%, Figure 3.56.

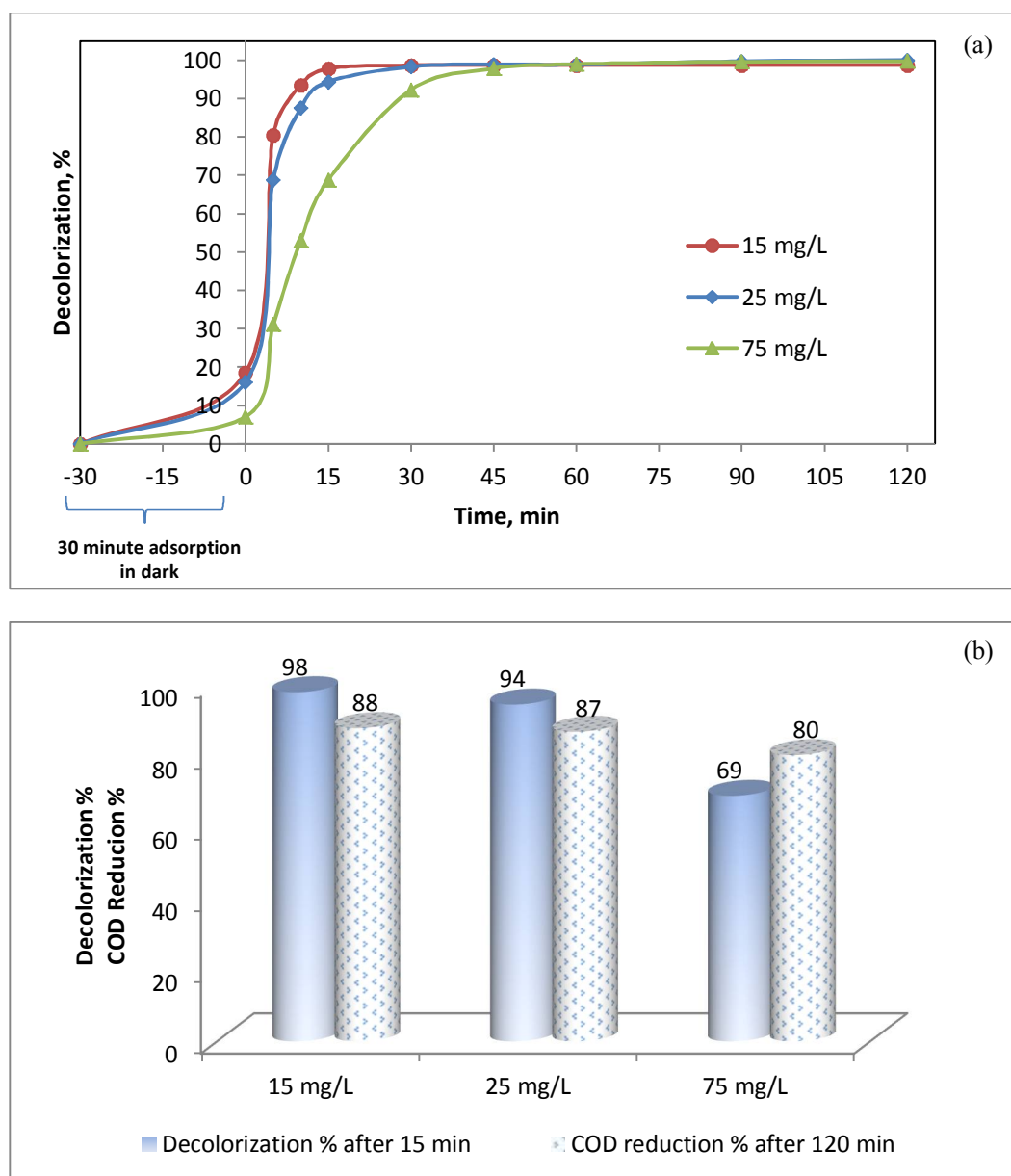


Figure 3.67. Effect of initial dye concentration on the UV+catalyst+H₂O₂ oxidation of RY 84 (a) Time dependency of decolorization (b) Decolorization, % in 15 min and COD removal % in 120 min

(25°C, 5mM H₂O₂, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6).

The apparent first order rate constants, k_{app} , of the degradation were calculated from the linear regression of $-\ln(C/C_0)$ versus time plots and the results are shown in Figure 3.68. The apparent first order rate constants (k_{app}) and regression coefficients at different initial dye concentrations are listed in Table 3.23.

Fe leached to the solution was below the 0.5 mg/L after 120 min of oxidation. To the contrary of sonophotoFenton oxidation, turbidity was not observed during the reactions. This is attributed to the absence of ultrasound in the system.

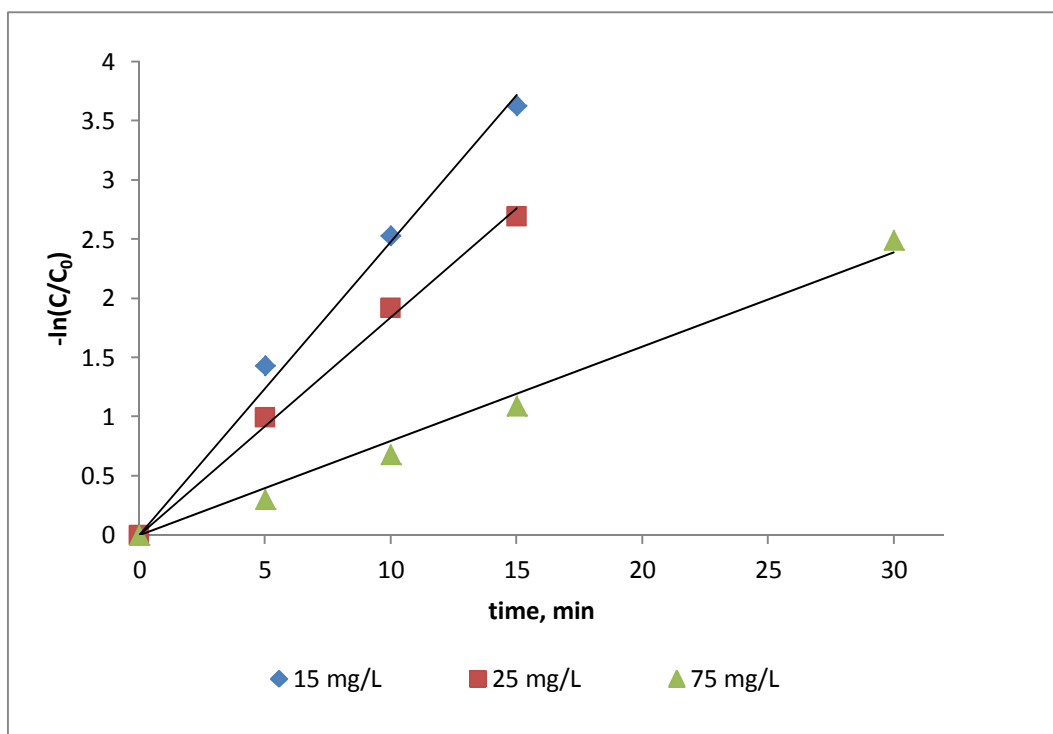


Figure 3.68. Pseudo-first-order kinetics for the UV+catalyst+H₂O₂ degradation of RY 84 at different initial dye concentrations

(25°C, 5mM H₂O₂, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6)

Table 3.23. The apparent first order rate constants (k_{app} , min⁻¹) and regression coefficients (R^2) for UV+catalyst+H₂O₂ degradation of RY 84 at different initial dye concentrations

(25°C, 5mM H₂O₂, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6)

initial dye concentration	k_{app} , min ⁻¹	R^2
15 mg/L	0.248	0.9935
25 mg/L	0.184	0.9961
75 mg/L	0.079	0.9884

3.8 Comparison of sonophotoFenton oxidation with oxidation of RY 84 by UV+catalyst+H₂O₂ combination

SonophotoFenton oxidation of RY 84 was compared with the UV+catalyst+H₂O₂ combination at the obtained optimum conditions of sonophotoFenton (25°C, 5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6 and 40W US power for sonophotoFenton) from the point of COD and TOC reduction. Results are presented in Figure 3.69 and Table 3.24.

It was possible to achieve 99% color removal, 62% COD reduction, and 48% TOC reduction after 45 min of UV+catalyst+H₂O₂ oxidation at 25°C, initial dye pH of 6, 5mM H₂O₂ with an initial RY 84 concentration of 25 mg/L and 0.5 g/L catalyst under 4+4 W UV-C lamps. Addition of 40 W ultrasonic power to the same conditions (sonophotoFenton process), 99% color removal, 55% COD, and 38% TOC reductions were obtained after 45 min of oxidation. At the end of the 120 min of oxidation, COD reduction increased to 87% and 90% with UV+catalyst+H₂O₂ and sonophotoFenton oxidation, respectively. On the other hand TOC reduction kept constant after 45 min with UV+catalyst+H₂O₂ combination system whereas TOC reduction reached to the 57% with the sonophotoFenton oxidation. That means that complete mineralization may be possible by using sonophotoFenton oxidation but needs long time. Molecular weights of the organic intermediates as decomposition products of dye are thought to be decreased gradually but it is difficult to complete mineralization in short reaction time (Maezawa et al., 2007). Hence, the degradation rate of TOC is slow. In the study of Maezawa et al. (2007), in the sonophotocatalytic oxidation of Acid Orange 52 after 120 min of reaction organic intermediates which have small molecular weights decompose to the inorganic compounds and the TOC degradation rate becomes much higher with using the hybrid system of sonophotocatalyst than that of sonolysis and photocatalysis. Also Stock et al. (2000) have reported that sonication promotes the rapture of azo bond and photocatalysis promotes the oxidation of reaction intermediates.

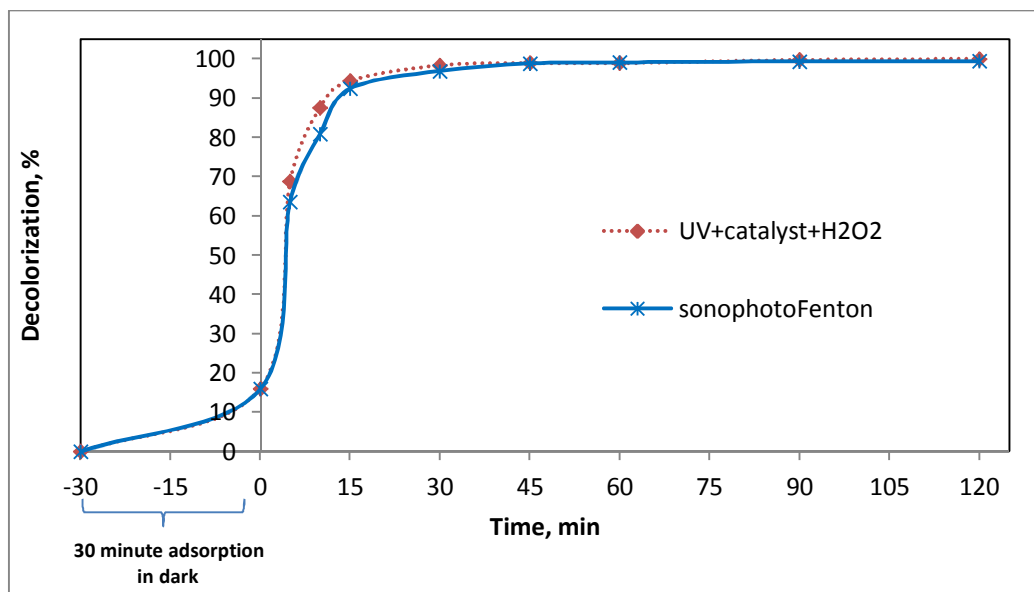


Figure 3.69. Comparison of UV+catalyst+H₂O₂ with sonophotoFenton of RY 84

(25°C, 5mM H₂O₂, initial RY 84 concentration of 25 mg/L, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6 and 40W US power for sonophotoFenton)

Table 3.24. Evaluation of degradation performance of UV+cat.+H₂O₂ and sonophotoFenton hybrid system

	COD red.% after 45 min	COD red.% after 120 min	TOC red.% after 45 min	TOC red.% after 120 min	Fe leached mgL ⁻¹ / %*
UV+cat.+H ₂ O ₂	62	87	48	48	0.5 / 11
sonophotoFenton	55	90	38	57	0.56 / 12

* With respect to the initial amount of iron in the catalyst

3.9 Toxicity Measurement

Toxicity measurements were done with 75 mg/L of untreated RY 84 and treated RY 84 after oxidations with sonophotoFenton and UV+catalyst+H₂O₂ combinations at the obtained optimum conditions. (25°C, 5mM H₂O₂, 0.5 g/L catalyst, 4+4 W UV-C lamps, initial dye pH of 6 and 40W US power for sonophotoFenton) (Figure 3.70).

Experiment was done according to the modified method given by Arambasic et al. (1995). *Lepidium Sativum* L. (Garden cress) seeds were used to evaluate the toxicity of 75 mg/L RY 84 solution prior to and after 120 min of treatment with sonophotoFenton or UV+catalyst+H₂O₂ combination. 25 seeds of

cross were placed in 9 cm glass petri dish, on filter paper moistened with 5 mL of the test solution. Closed petri dishes were placed in the dark for 120 hours at room temperature. At the end of 120 hours root lengths of seeds were measured. (Arambasic et al., 1995) Test was based on the root length grow of the treated and untreated RY 84 solution. The root length growth% was calculated according to the eqn 3.21:

$$\text{Root length grow, \%} = \frac{\text{root length}_{\text{treated sample}} - \text{root length}_{\text{untreated sample}}}{\text{root length}_{\text{treated sample}}} \times 100 \quad (3.21)$$

Root length growth,% was obtained 46% and 37% for the samples treated with sonophotoFenton and UV+catalyst+H₂O₂ combination, respectively. This result clearly indicates that higher reduction in toxicity of RY 84 is achieved by sonophotoFenton oxidation than that by combined system of UV+catalyst+H₂O₂.

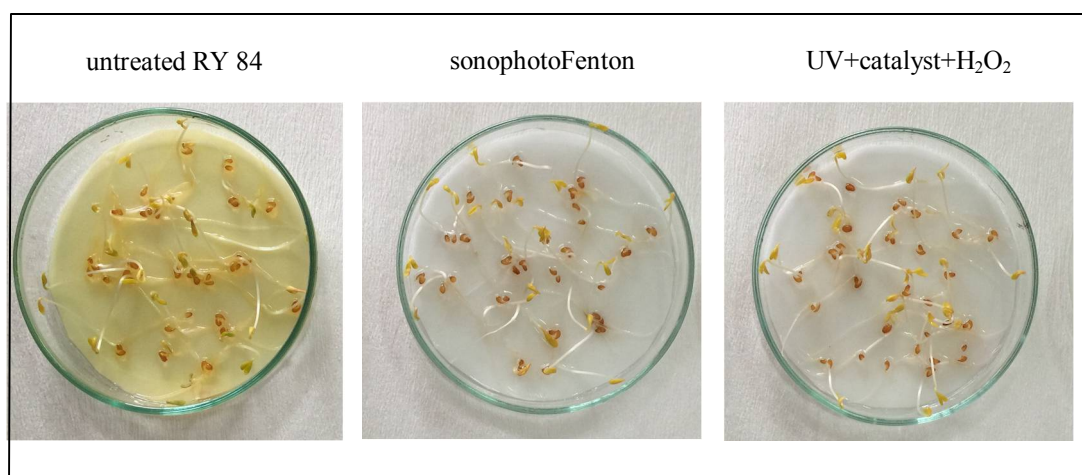


Figure 3.70. Toxicity test for RY 84.

(25°C, 5mM H₂O₂, 0.5 g/L catalyst, 75 mg/L initial concentration, 4+4 W UV-C lamps, initial dye pH of 6 and 40W US power for sonophotoFenton).

4. CONCLUSION

In the first part of the study; ultrasonic degradation of Reactive Yellow 84, was investigated in two different ultrasonic systems that are ultrasonic bath (indirect sonication) and ultrasonic reactor (direct sonication). High frequency ultrasound and low initial concentration without H_2O_2 addition was found adequate for decolorization of RY 84. Our findings show that direct sonication method gives more effective results than those with indirect sonication on decolorization of dye solution. Optimum decolorization degree (38.1 %) was obtained by 250 mL of 10 mg/L RY 84 aqueous solution in ultrasonic reactor at a power of 75 W, without H_2O_2 addition under 3.7 acidic pH. However, no COD removal could be obtained for these optimum conditions.

Catalysts were prepared by incipient wetness impregnation and sol-gel methods with different Fe loadings. Prepared catalysts were characterized and tested in sonophotoFenton oxidation of RY 84. 1wt%iron-containing TiO_2 catalyst prepared by incipient wetness impregnation method and calcined at 300°C behaves as efficient catalyst for the heterogeneous sonophotoFenton degradation of RY 84. The catalytic activity of the catalyst depends on the percentage of anatase phase in the TiO_2 . At the experimental conditions of 650 mL of 25 mg/L RY 84 solution, 35 mM H_2O_2 , 0.5 g/L of catalyst, 20°C reaction temperature, an ultrasonic power of 40 W with 20 kHz, UV-C lamp at 4W+4W, a color removal of 100 %, and a COD removal of 56 % could be achieved after 120 min of reaction.

The combinations of US+UV+ H_2O_2 and UV+catalyst+ H_2O_2 have been found to be effective, especially considering the COD removal. For these combinations, at the above conditions color removal of 89% and 99% and COD removal of 48% and 49% were obtained respectively, at the end of 120 min of oxidation.

In the second part of the study, dye degradation carried out over heterogeneous sonophotoFenton system and found that degradation is sensitive to the initial dye pH, hydrogen peroxide concentration, catalyst loading, and

temperature as well as to the applied ultrasonic power. Increasing the H_2O_2 concentration from 2.5mM to 5mM enhances the decolorization and COD reduction whereas further increase in H_2O_2 concentration negatively affects the efficiency. Adsorption of RY 84 was high at the initial pH of 3.5. Color removal rate and COD reduction were low at high initial pH. The increase in initial RY 84 concentration decreases the color removal and COD reduction efficiencies. High ultrasound power decreased the catalyst particle size resulting in turbidity in the solution. This turbidity made difficult the measurement of dye absorbance. The rate of the sonophotoFenton degradation was sensitive to the solution temperature with activation energy of 20.7 kJ/mol. The study of such reaction parameters allowed us to determine the optimum experimental conditions for efficient RY 84 degradation, 25°C, 5mM H_2O_2 , 0.5 g/L catalyst, 25 mg/L initial concentration, initial dye pH of 6 and US power of 40W. Under these conditions, 99% color removal, 55% COD, and 38% TOC reductions were obtained after 45 min of sonophotoFenton oxidation. On the other hand 99% color removal, 62% COD reduction, and 48% TOC reduction were obtained after 45 min of UV+catalyst+ H_2O_2 oxidation. Although UV+catalyst+ H_2O_2 found to be more effective at the conditions of 20°C, initial RY 84 concentration of 25 mg/L, 35 mM H_2O_2 and 0.5 g/L catalyst, at the optimum conditions, TOC reduction kept constant after 45 min with UV+catalyst+ H_2O_2 combination system whereas TOC reduction reached to the 57% with the sonophotoFenton oxidation after 120 min. COD reduction at 120 min, increases to 87% and 90% with UV+catalyst+ H_2O_2 and sonophotoFenton oxidation, respectively.

On the other hand, it has been found that, heterogeneous sonophotoFenton degradation can be explained in terms of Langmuir–Hinshelwood kinetic model.

The toxicity measurements showed that the root length growth of cress seeds was 46% and 37% for the treated and untreated 75 mg/L RY 84 solution samples by using sonophotoFenton and UV+catalyst+ H_2O_2 oxidation processes under the optimum conditions determined.

In future studies, it is recommended to do experiments on degradation of RY 84 by sonophotoFenton process for longer reaction time than 2 hours, in order to enhance the TOC removal from 57% to higher values.

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