
CONTENTS

DESCRIPTION	PAGE NO
Abbreviations	xv - xvi
List of Figures	xvii - xxi
List of Tables	xxiii
Preface	xxv - xxviii
CHAPTER-1	1-25
1.1 Photocatalysis	1
1.2 Heterogeneous Semiconductor Photocatalysts	2
1.2.1 Mechanisms of Semiconductor Photocatalysts	2
Light Absorption	2
Recombination	2
Separation of excited charges	2
Utilization of excited charges	3
1.3 Strategies for efficient charge separation	4
1.3.1 Metal deposition	4
1.3.2 Metal or non-metal doping	5
1.3.3 Surface dye sensitization	5
1.3.4 Semiconductor composites or heterostructures	7
1.4 p-n heterojunction	9
1.5 Z-scheme mechanism	12
1.6 Iron Oxides	12
1.7 Synthesis strategies	15
1.7.1 Deposition-Precipitation method	16
1.7.2 Hydrothermal/solvothermal method	16
1.7.3 Other methods	17
1.8 Methods for investigating the p-n heterojunction mechanism	17

1.9 Literature review of p-n heterojunction photocatalysts	18
1.9.1 Fe ₃ O ₄ based p-n heterojunctions	19
1.9.2 α-FeOOH based p-n heterojunction photocatalysts	21
1.9.3. β-FeOOH based p-n heterojunction photocatalysts	21
1.10 Objectives of the thesis	22
1.10.1 Photocatalytic production of H ₂ O ₂	23
1.10.2 Photo- Fenton degradation of PNP and MO	24
CHAPTER-2	26-42
2.1 Introduction	26
2.2 Chemicals	26
2.3 Synthesis of iron oxide-based p-n heterojunction photocatalysts	27
2.3.1 Synthesis of starch functionalized Fe ₃ O ₄ /Ag/Ag ₂ O nanostructures	27
2.3.2 Synthesis of starch functionalized Fe ₃ O ₄ /Cu ₂ O nanostructures	28
2.3.3 Synthesis of starch functionalized α-FeOOH/β-FeOOH nanocomposites	28
2.3.4 Synthesis of starch functionalized α-FeOOH/β-FeOOH/Cu ₂ O nanostructures	29
2.4 Photocatalytic Experiment	29
2.4.1 Design of photocatalytic chamber	29
2.4.2 Photocatalytic production of H ₂ O ₂ on starch functionalized Fe ₃ O ₄ /Ag/Ag ₂ O nanostructures	29
2.4.3 Photo-Fenton PNP degradation	30
2.4.4 Photo-Fenton MO degradation	30
2.5 Techniques used for photocatalysts characterization	30
2.5.1 UV-Visible spectrophotometer	31
Principle	31
2.5.2 UV-Vis diffuse reflectance spectroscopy (UV- DRS)	33
Working principle	33

2.5.3 X-ray Diffraction (XRD)	34
Principle	35
2.5.4 Fourier Transform Infrared Spectroscopy (FT-IR)	36
Principle	36
2.5.5 Transmission Electron microscopy (TEM)	37
Principle	37
2.5.6 Magnetic property measurement system (MPMS)	39
Principle	39
2.5.7 X-ray photoelectron spectroscopy (XPS)	40
Principle	40
2.5.8 Electrochemical workstation/analyzer	41
Principle	42
CHAPTER-3	43-69
3.1 Introduction	43
3.2 Experimental	46
3.2.1 Preparation of starch functionalized magnetite nanoparticles	46
3.2.2 Synthesis of Fe ₃ O ₄ / Ag /Ag ₂ O nanocomposite	46
3.2.3 Photocatalytic Activity	47
3.2.4 Hydrogen peroxide determination	47
3.2.5 Analysis	47
3.3. Results and discussion	48
3.3.1 Characterization	48
3.3.2 Catalytic activity	62
3.3.2.1 Photocatalytic production of H ₂ O ₂	62
3.3.2.2 Catalyst Recyclability	63

3.3.2.3 H ₂ O ₂ production in the presence of an electron donor	64
3.3.2.4 H ₂ O ₂ production in different controlled conditions	65
3.3.3 Mechanism of photocatalytic H ₂ O ₂ production	66
3.4. Conclusions	68
CHAPTER-4	70-88
4.1 Introduction	70
4.2 Experimental	72
4.2.1 Preparation of starch functionalized magnetite nanoparticles (SMNPs)	72
4.2.2 Synthesis of SMNPs/ Cu ₂ O (CF) nanocomposites	72
4.2.3 Photocatalytic degradation of PNP over CF nanocomposites	73
4.2.4 Photocatalytic degradation of MO over CF nanocomposites	73
4.2.5 Analysis	73
4.3. Results and discussion	74
4.3.1 Characterization	74
4.3.2 Optical band determination	78
4.3.3 Visible light photo-Fenton degradation of PNP and MO by CF nanocomposites	80
4.3.4 Recyclability test	86
4.3.5 Proposed photocatalytic mechanism	87
4.4 Conclusions	88
CHAPTER-5	89-112
5.1 Introduction	89
5.2. Experimental Methods	92
5.2.1 Synthesis of S1 and S2 nanocomposites	92
5.2.2 Catalytic degradation of PNP over S1 and S2	93

5.2.3 Catalytic degradation of MO over S1 and S2	93
5.2.4 Characterization	93
5.3 Results and Discussion	94
5.3.1 Characterization of S1 and S2	94
5.3.2 Optical band gap	98
5.3.3 Fenton degradation of PNP by S1 and S2	101
5.3.4 Visible light photo-Fenton degradation of PNP over S1 and S2	102
5.3.5 Photo - Fenton degradation of MO by S1 and S2	105
5.3.6 Recyclability test	109
5.3.7 Photocatalytic mechanism	109
5.4 Conclusions	111
CHAPTER-6	113-128
6.1 Introduction	113
6.2 Experimental Methods	114
6.2.1 Synthesis of starch functionalized FeOOH (S2) nanocomposites	114
6.2.2 Synthesis of s-FeOOH/Cu ₂ O nanocomposites	114
6.2.3 Photo-Fenton degradation of PNP over CSP	115
6.2.4 Photo-Fenton degradation of MO over CSP	115
6.2.5 Characterization	115
6.3 Results and discussion	116
6.3.1 Characterization	116
6.3.2 Optical band determination	119

6.3.3 Photo-Fenton degradation of PNP and MO over CSP	122
6.3.4 Recyclability test	126
6.3.5 Photocatalytic mechanism	126
6.4 Conclusions	127
CHAPTER-7	129-134
7.1 Overview	129
7.2 Photocatalytic production of H ₂ O ₂ by starch functionalized Fe ₃ O ₄ /Ag/Ag ₂ O nanostructures	129
7.3 Photo-Fenton degradation of PNP	130
7.4 Photo-Fenton degradation of MO	132
7.5 Future scope of this work	133
REFERENCES	135-153

ABBREVIATION

NPs	Nanoparticles
SMNPs	Starch functionalized magnetite nanoparticle
Fe₃O₄/Ag/Ag₂O	Magnetite/silver/silver oxide nanostructures
Fe₃O₄/Cu₂O	Magnetite/ cuprous oxide nanostructures
α-FeOOH/β-FeOOH	Goethite/akageniite nanocomposites
α-FeOOH/β-FeOOH /Cu₂O	Goethite/akageneite/cuprous oxide nanostructures
PNP	<i>p</i> -nitrophenol
MO	Methyl orange
NaOH	Sodium hydroxide
HCl	Hydrochloric acid
VB	Valance Band
CB	Conduction Band
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
E_g	Band gap
LSPR	Localized surface plasmon resonance
t	time
t₀	zero time
A_t	Absorbance at time t
A₀	Absorbance at time t ₀
TOF	Turn over frequency

H₂O₂	Hydrogen Peroxide
OH[·]	Hydroxyl radical
OOH[·]	Peroxide radical
OH⁻	Hydroxide ion
UV-vis	Ultra violet visible Spectroscopy
UV-DRS	Ultra violet diffuse reflectance spectroscopy
XRD	X-ray diffractometer
FWHM	Full width half maximum
FTIR	Fourier transforms infrared spectroscopy
TEM	Transmission electron microscopy
MPMS	Magnetic property measurement system
XPS	X-ray photoelectron spectroscopy
MS	Mott Schottky

LIST OF FIGURES

Figure 1.1	Schematic presentation of steps involved in the mechanism of the semiconductor photocatalysis	3
Figure 1.2	Schematic presentation of the effect of metal doping on semiconductor photocatalysis	5
Figure 1.3	A schematic of the general mechanism of dye-sensitized semiconductor photocatalysis	6
Figure 1.4	Different types of composite semiconductor photocatalyst	7
Figure 1.5	The general mechanism involved in type I and type III composite semiconductor photocatalyst	8
Figure 1.6	The excitation mechanism of type II composite semiconductor photocatalysts	9
Figure 1.7	<p style="margin-left: 20px;">(a) Schematic representation of p-n junction formation</p> <p style="margin-left: 20px;">(b) Schematic illustration of the mechanism of a p-n heterojunction photocatalyst under light irradiation</p>	10-11
Figure 1.8	Different phases of iron oxides	13
Figure 2.1	UV-Visible spectrophotometer (Agilent Cary 60)	33
Figure 2.2	XRD diffractometer (Mini Flex 600)	34
Figure 2.3	Schematic explaining diffraction occurring as per Bragg's law	35
Figure 2.4	Transmission electron microscopy (FEI Technai-20 G ²).	38
Figure 2.5	X-ray photoelectron spectroscopy (Thermo fisher scientific make K-Alpha)	40
Figure 2.6	Schematic representation of the photoemission process	41
Figure 3.1	UV-Vis absorbance spectra of aqueous C1 and C2 dispersion	49
Figure 3.2	X-ray powder diffraction patterns of samples SMNPs, C1 and C2	50
Figure 3.3	TEM images (a, b) and the respective particle size distribution (c, d) of samples C1 and C2	51
Figure 3.4	HR-TEM micrograph of sample C1 showing Ag/Ag ₂ O quantum dots formed on SMNPs surface. The part of the manuscript describing the photograph gives the details	52
Figure 3.5	XPS analysis of C1 and C2 (a, b) survey spectrum (c, d) Fe 2p, (e, f) Ag 3d, and (g, h) O 1s	54
Figure 3.6	Magnetic moment versus magnetic field graph of SMNPs, C1, and C2	55

Figure 3.7	Schematic models of possible nanocomposite structures	57
Figure 3.8	Solid-state UV -Vis absorption spectra of (a) SMNPs (b) C1 and (c) C2 nanoparticles and their respective Tauc plots	58
Figure 3.9	Mott Schottky plot of (a) SMNPs (b)Ag ₂ O (c) C1 and C2 measured under the dark condition in 0.5M Na ₂ SO ₄ at 1 kHz	59
Figure 3.10	Band edges and band gap values of the semiconducting components constituting C1 and C2	61
Figure 3.11	Nyquist plot of EIS spectra for C1 and C2	62
Figure 3.12	H ₂ O ₂ production per gram of catalyst in one hour at different pH-values	63
Figure 3.13	Ten cycles C1 and C2 reusability results in histogram format for H ₂ O ₂ production	64
Figure 3.14	Schematic representation of the proposed mechanism	68
Figure 4.1	The X-ray powder diffraction pattern of SMNPs and CF powder samples	74
Figure 4.2	(a) Bright-field TEM image, (b) the size distribution plot, and (c) HR-TEM image of the CF nanostructure	75
Figure 4.3	XPS analysis of CF (a) survey spectrum (b) Fe 2p, (c) Cu 3d, and (d) O 1s	76
Figure 4.4	Magnetic moment versus magnetic field graph of SMNPs and CF	77
Figure 4.5	Tauc plot of pure Cu ₂ O and CF nanocomposite	78
Figure 4.6	Mott Schottky plot of (a) CF and (b)Cu ₂ O measured under the dark condition in 0.5M Na ₂ SO ₄ at 1 kHz and (c) the Nyquist plots of electrochemical impedance spectroscopy (EIS) for CF and SMNPs for the investigation of the electron transfer kinetics	79
Figure 4.7	of the catalysts Bandgaps and band edge positions of a) SM and Cu ₂ O pure materials b) CF nanocomposite.	80

Figure 4.8	Kinetics of PNP degradation photocatalyzed by CF at different pH	81
Figure 4.9	(a) UV-visible plots after regular intervals of the reaction time of photo Fenton degradation of PNP catalyzed by the CF nanocomposite (b) The plots of (A/A_0) [absorbance (A) measured at λ_{\max} 317 nm] versus time for PNP degradation reactions catalyzed by SMNPs and CF	82-83
Figure 4.10	(a) UV-visible plots of photo Fenton degradation of MO at regular intervals of reaction time (under visible light conditions) catalyzed by CF (b) The plots of (A/A_0) [absorbance (A) measured at λ_{\max} 505 nm] versus time for (MO degradation) reactions catalyzed by SMNPs and CF	83-84
Figure 4.11	Five cycles of CF reusability results in histogram format for PNP degradation for 1 hour	87
Figure 4.12	Schematic representation of the proposed mechanism	88
Figure 5.1	The XRD patterns of S2 and S1 powder samples	94
Figure 5.2	A comparison between FTIR plots of soluble starch, S1, and S2 samples	96
Figure 5.3	TEM images of (a) S1 and (c) S2. Corresponding HR-TEM images of (b) S1 and (d) S2	97
Figure 5.4	Solid-state UV-visible absorption spectra of samples S1 and S2	98
Figure 5.5	(a, b) Tauc plots of S1 and S2 (direct transitions)	99
Figure 5.6	Mott Schottky plots of (a) S1 and (b) S2 measured under the dark condition in 0.5M Na ₂ SO ₄ at 1 kHz. (c) The Nyquist EIS plots for S1 and S2 for investigating the electron transfer kinetics of the catalysts	100
Figure 5.7	Band edges and band gap values of S1 and S2	101

Figure 5.8	UV-visible plots of Fenton degradation (in the dark) of PNP at regular intervals of reaction time catalyzed by (a) S1 and (b) S2 samples	102
Figure 5.9	UV-visible plots of photo Fenton degradation of PNP at regular intervals of reaction time (under visible light conditions) catalyzed by (a) S1 and (b) S2 samples. (c) The plots of (A/A_0) [absorbance (A) measured at λ_{\max} 317 nm] versus time for (PNP degradation) reactions catalyzed by S1 and S2	103
Figure 5.10	UV-Visible plots for the Fenton degradation of MO on (a) S1 and (b) S2 samples, respectively	106
Figure 5.11	UV-Visible plot for the photodegradation of MO as a function of reaction time under the optimum reaction conditions by (a)S1 and (b) S2 catalytic sample (c) Photo Fenton kinetics (A/A_0) [absorbance (A) measured at λ_{\max} 506 nm] versus time plots of reactions carried over S2 and S1	107
Figure 5.12	Five cycles of S2 reusability for PNP degradation reaction	109
Figure 5.13	Schematic representation of the mechanism proposed for explaining the photo- Fenton degradation of organic pollutants	111
Figure 6.1	The X-ray powder diffraction pattern of S2 nanocomposite and CSP nanostructure powder samples	116
Figure 6.2	(a) Bright-field TEM image and (b) HR-TEM image of the CSP nanostructure.	117
Figure 6.3	XPS analysis of CF (a) survey spectrum (b) Fe 2p, (c) Cu 3d, and (d) O 1s	118
Figure 6.4	(a) solid state UV vis spectra of CSP nanostructure and (b) their respective Tauc plot	120
Figure 6.5	(a) Mott Schottky plot of CSP measured under the dark condition in 0.5M Na ₂ SO ₄ at 1 kHz and (b) the Nyquist plots of electrochemical impedance spectroscopy (EIS) for CSP and S2	121

for the investigation of the electron transfer kinetics of the catalysts

- Figure 6.6** Band edges and band gap values of components of CSP before and after the formation of p-n-p heterojunction **122**
- Figure 6.7** (a, c) UV-Visible plot for the Fenton degradation (dark condition) of PNP and MO as function of reaction time under the optimum reaction conditions by CSP catalytic sample (b,d) rate kinetics plots of PNP and MO degradation using CSP catalyst **123**
- Figure 6.8** (a, c) UV-Visible plot for the photo-Fenton degradation of PNP and MO as function of reaction time under the optimum reaction conditions by CSP catalytic sample (b,d) rate kinetics plots of PNP and MO degradation using CSP catalyst **124**
- Figure 6.9** Five cycles of CSP reusability results in histogram format for PNP degradation for 1 hour **126**
- Figure 6.10** Schematic representation of the mechanism proposed for explaining the photo- Fenton degradation of organic pollutants **127**

LIST OF TABLES

Table No	DESCRIPTION	Page No
2.1	Names, chemical formula, molecular weights, manufacturer's name, and physical appearances of the reagents used.	26
3.1	Visible light photocatalytic H ₂ O ₂ production at pH 3 (under different reaction conditions.	65
4.1	Comparison of TOF values for Photo-Fenton degradation of PNP over different photocatalysts studied earlier in literature with the one investigated in this work.	85
4.2	A comparison of the TOF values of various photocatalysts for photo-Fenton degradation of MO over CF nanoparticles	86
5.1	Comparison of TOF values for Photo-Fenton degradation of PNP in the presence of different catalysts studied earlier in literature with ones investigated in this work.	104
5.2	Comparison of MO photodegradation TOF values on different nanocomposites studied earlier in literature with ones investigated in this work.	108
6.1	Comparison of TOF values for Photo-Fenton degradation of PNP in the presence of different catalysts studied earlier in literature with ones investigated in this work.	125
6.2	Comparison of TOF values for photodegradation of MO in the presence of different catalysts studied earlier in literature with ones investigated in this work.	125
7.1	Comparison of photocatalytic H ₂ O ₂ generation result of various heterostructure photocatalyst studied earlier in literature with the one investigated in this work.	130
7.2	Comparison of TOF values using the different catalyst for photo-Fenton PNP degradation	131
7.3	Comparison of TOF values using the different catalyst for photo-Fenton PNP degradation	132-133