KUVEMPU UNIVERSITY

Final Report on UGC Major Research Project

APPLICATION OF NANOSIZED METAL OXIDE PARTICLES AS PHOTOCATALYST IN THE DEGRADATION OF AZO DYES

F.No.39-330/2010 (SR), Dated 27th DEC 2010

Submitted to

University Grants Commission
Bahadur Shah Zafar Marg, New Delhi – 110002

By

Dr. K Yogendra

Principal Investigator, Department of Environmental Science
Kuvempu University, Jnanasahyadri, Shankaraghatta
Pin – 577 451 Shivamogga dist. Karnataka, India

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Principal investigator:**Dr. K Yogendra**

Project Fellow:**Ms. C Bhavya**

Annexure-III

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

Annual Report of the work done on the Major research Project

1.	Project report No	:	**Final**
2.	UGC Reference No	:	**F. No. 39-330/2010 (SR), 27.12.2010**
3.	Period of report	:	**10th February, 2011 to 10th February, 2014**
4.	Title of the research project	:	**"Application of nanosized metal oxide particles as photocatalyst in the degradation of azo dyes''**

5. a) Name of the Principal Investigator : **Dr. K. Yogendra**

b) Dept. and University/ College where work has progressed: **Department of Environmental Science, Kuvempu University, Shankaraghatta-577 451, Shimoga Karnataka, India.**

Effective date of starting of project : **10th February, 2011**

6. Grant approved and expenditure incurred during the period of the report:

a)	Total amount approved	:	**8,60,657/-**
b)	Total grant received	:	**7,84,371/-**
c)	Total expenditure	:	**7,64,080/-**

7. Report of the work done: (Please attach a separate sheet): **Enclosed**

i. Brief objective of the project

a. Synthesis of desire nanoparticles by simple and convenient route and their characterization by XRD and SEM.
b. Degradation of commercial azo dyes in laboratory conditions using nanoparticles
c. To evaluate the degradation rate of different dyes under laboratory condition, in presence synthesized new metal oxide nanoparticles under sun light irradiations.
d. To evaluate the result of these standardized protocols in degrading dyes at varying effective parameters such as pH, concentration of dye etc. against the conventional biological treatments.
e. Research publications/patents

ii. Work done so far and result achieved and publication, if any resulting from the work (give detail of the papers and names of the journal in which it has been published or accepted for publication):

1. **Solar Photocatalytic Degradation of Orange G (mono azo dye) and C.I. Direct Yellow 50 (di azo dye) by synthesized $CaZnO_2$ nanoparticle in aqueous solution.** International Journal of Universal Pharmacy and Life Sciences, Vol. 2 Issue 4, July-August 2012, 66-77.

2. **Synthesis and photocatalytic activity of ZnO nanoparticles against Coralene Red F3BS dye in presence of UV and solar radiation.** International Journal of Universal Pharmacy and Life Sciences, Vol. 2 Issue 4, July-August 2012, 16-25.

3. **Photocatalytic Degradation of Coralene Dark Red 2b Dye Using Calcium Aluminate ($CaAl_2O_4$) Catalyst.** Environmental Science: An Indian Journal, Vol. 6, (2011). 1-5.

4. **ZnO composite mediated photocatalyticdecolourization of Coralene red F3BS dye in presence of solar light.** Material Science: An Indian Journal, Vol. 7, No. 5, 2011. 16 (1): 97 - 102 (2011): ISSN-0972-6101.

5. **A comparative study of photocatalytic activities of two different synthesized ZnO composites against Coralene Red F3BS dye in presence of natural solar light.** International Journal of Environmental Sciences and Research, 2011, 1(1), 11-15.

6. **Photocatalytic degradation of Coralene Dark Red 2B azo dye using Calcium zincate nanoparticle in presence of natural sunlight: An aid to Environmental remediation.** International Journal of Chemical Engineering and Applications, Vol. 2, No. 4, August 2011.

7. **Photocatalytic activity of synthetic ZnO composite against Coralene red F3BS dye in presence of solar light.** International Journal of Environmental Science, Volume 1, No 5, 2011.

iii. Has progress been according to the original plan of work and towards achieving the objective? If not, state reason: **Yes, it is according to the original plan.**

iv. Please indicate any difficulties, if any, experienced in implementing the project: **No such difficulty experienced in implementing the project.**

v. If project has not been completed, please indicate the approximate time by which it is likely to be completed. A summary of the work done for the period (Annual basis) may please be sent to the commission on a separate sheet: **Project completed**

vi. If the project has been completed, please enclose a summary of the finding of the study. Two bound copies of the final report of the work done may also be sent to the commission: **Project completed**

vii. Any other information which would help in evaluation of work done on the project. At the completion of the project, the first report should indicate the output, such as (a) Manpower trained (b) Ph. D., awarded (c) Publication of result (d) Other impact, If any:

A Project fellow has been registered for Ph.D., degree under the project and the thesis will be submitted to KuvempuUniversity for the award of the Ph.D., degree.

Signature of the Principal Investigator

Dr. YOGENDRA K. Ph.D.,
Principal Investigator
UGC Sponsored Major Research Project
Department of Environmental Science
Kuvempu University SHANKARAGHATTA - 577 451

7/7/14

Registrar

Registrar
Kuvempu University
Jnana Sahyadri
Shankaraghatta-577 451
Shimoga Dist. Karnataka India

Annexure – IV

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002.

Utilization Certificate

Certified that the grant of Rs.7,64,080/- (Rupees Seven lakh sixty four thousand eightyonly) received from the University Grants Commission under the scheme of support for Major research Project entitled: **“Application of nanosized metal oxide particles as photocatalyst in the degradation of azo dyes’’**, vide UGC letter No **F. No. 39-330/2010 (SR) dated 27.12.2010** has been fully utilized for the purpose for which it was sanctioned and in accordance with the terms and conditions laid down by the University Grants Commission.

Signature of the
Principal Investigator

Dr. YOGENDRA K. Ph.D.,
Principal Investigator
UGC Sponsored Major Research Project
Department of Environmental Science
Kuvempu University SHANKARAGHATTA 577 451

Registrar
Registrar
Kuvempu University
Jnana Sahyadri
Shankaraghatta-577 451
Shimoga (Dist.) Karnataka (State)

Finance Officer
Kuvempu University
Shankaragatta-577 451

Auditor
g. s. yogisnappa
Government Auditor.
KUVEMPU UNIVERSITY
B. R. PROJECT
Shimoga [illegible]

Annexure – V

UNIVERSITY GRANTS COMMISSION, BAHADUR SHAH ZAFAR MARG NEW-DELHI – 110 002.

STATEMENT OF EXPENDITURE IN RESPECT OF MAJOR RESEARCH PROJECT

1. Name of the Principal Investigator: **Dr. K. Yogendra**
2. Dept. And University/ College : **Department of Environmental Science, KuvempuUniversity, Shankaraghatta-577 451, Shimoga, Karnataka.**
3. UGC approval No. and Date : **F. No. 39-330/2010 (SR) dated 27.12.2010**
4. Title of the Research project : **"Application of nanosized metal oxide particles as photocatalyst in the degradation of azo dyes''**
5. Effective date of starting of project: **10th February, 2011**
6. a) Period of Expenditure : **February, 2011 to February, 2014**
7. b) Details of Expenditure

	Expenditure Incurred		**Amount Approved (Rs.)**	**Expenditure Incurred (Rs.)**
1	**Books and Journal**	**1st installment**	NIL	NIL
		2nd installment	NIL	NIL
2	**Equipment**	**1st installment**	50,000.00	50,000.00
		2nd installment	NIL	NIL
3	**Contingency**	**1st installment**	25,000.00	25,000.00
		2nd installment	20,000.00	20,000.00
4	**Field work/travel**	**1st installment**	25,000.00	24,709.00
		2nd installment	20,000.00	00,000.00
5	**Hiring Services**	**1st installment**	25,000.00	25,000.00
		2nd installment	20,000.00	20,000.00
6	**Chemical and Glassware**	**1st installment**	45,000.00	45,000.00
		2nd installment	36,000.00	36,000.00
7	**Overhead**	**1st installment**	47,800.00	
		2nd installment	NIL	NIL
8	**Any other item (Please specify)**	**1st installment**	NIL	NIL
		2nd installment	NIL	NIL
	Total		3,13,800.00	2,93,509.00

Total = 2, 93,509/-

Date of Appointment: 10.02.2011

Sl.No	Expenditure Incurred	Installment	Amount Approved (Rs.)	Expenditure Incurred (Rs.)
1	Project fellow consolidated salary @Rs. 14000/-p.m from10-02-2011 to 10-02-2013 and @Rs. 16000/-p.m from 11-02-2013 to 10-02-2014	1st installment	1,44,000.00	1,44,000.00
		2nd installment	3,26,571.00	3,26,571.00
			4,70,571.00	**4,70,571.00**

Total amount = 4, 70,571/-

Total= Rs.2, 93,509.00 +Rs. 4, 70,571.00 = Rs7, 64,080/-

1. It is certified that the appointment(s) have been made in accordance with the terms and conditions laid down by the Commission.
2. If as a result of checks or audit objective, some irregularly is noticed, later date, action will be taken to refund, adjust or regularize the objected amounts.
3. Payment @ revised rates shall be made with arrears on the availability of additional funds.
4. It is certified that the grant of **Rs.7, 64,080.00** (Rupees Seven lakh sixty four thousand eightyonly) received from the University Grants Commission under the scheme of support for Major Research Project entitled **"Application of nanosized metal oxide particles as photocatalyst in the degradation of azo dyes''** vide UGC letter NO. **F. No. 39-330/2010 (SR) dated 27.12.2010** has been utilized for the period and purpose for which it was sanctioned and accordance with the terms and conditions laid down by the University Grants Commission.

Signature of the Principal Investigator

Dr. YOGENDRA K. Ph.D.,
Principal Investigator
UGC Sponsored Major Research Project
Department of Environmental Science
Kuvempu University SHANKARAGHATTA-577451

7/2/14

Registrar

Registrar
Kuvempu University
Jnana Sahyadri
Shankaraghatta-577 451
Shimoga Dist. Karnataka India

UNIVERSITY GRANTS COMMISSIONAnnexure IX
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002.

PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE FINAL REPORT OF THE WORK DONE ON THE PROJECT

1	Name and Address of the Principal Investigator	:	**Dr. K. Yogendra** Assistant Professor, Dept ofP.G Studies and Research inEnvironmental Science, Kuvempu University, Shankaraghatta- 577451, Shimoga District, Karnataka State, India.
2	Name and address of the institution	:	DeptofP.G Studies and Research inEnvironmental Science, Kuvempu University, Shankaraghatta- 577451, Shimoga District, Karnataka State, India.
3	UGC approval No. and Date	:	**F. No. 39-330/2010 (SR) dated 27.12.2010**
4	Date of implementation	:	10-02-2011
5	Tenure of the Project	:	**Three years**
6	Total grant allocated	:	**8,51,667/-**
7	Total grant received	:	**7,84,371/-**
8	Final expenditure	:	**7,64,080/-**
9	Title of the project	:	**Application of nanosized metal oxide particles as photocatalyst in the degradation of azo dyes**
10	Objective of the project	:	a. Synthesis of desire nanoparticles by simple and convenient route and their characterization by XRD and SEM. b. Degradation of commercial azo dyes in laboratory conditions using nanoparticles c. To evaluate the degradation rate of different dyes under laboratory condition, in presence synthesized new metal oxide nanoparticles under sun light irradiations. d. To evaluate the result of these standardized protocols in degrading dyes at varying effective parameters such as pH, concentration of dye etc. against the conventional biological treatments. e. Research publications/patents

11	Whether objective were achieved	:	YES
12	Achievements of the project	:	➢ Published Five research papers in an International journal ➢ Published Two Publications in National journal ➢ Presented research findings in Four national conference ➢ One best paper presentation award was received ➢ One candidate has been enrolled for Ph.D.
13	Summary of the findings	:	Present work deals with the degradation of azo dyes using metal oxide nanoparticles as photocatalysts. As we all know about the importance of water, it is of great concern to protect water source from getting contaminated. Textile industry is one of the main causes for water pollution as it consumes enormous amount of water for different processes, especially for dying the fabrics. During dying process, the unbound dyes washed away and reach the nearby water source resulting in pollution or contamination of water. There are many numbers of factors which indicates water pollution. Among them colour is the one indicator which can be visible to our eyes. Since a very less quantity of dye can impart colour to the water body, it is very important to remove the colour either by degradation or adsorption, as it hinders the light penetration in turn decreasing the photosynthetic activity of aquatic flora. With this concern, our main intention was to remove the colour imparted due to the dyes in textile waste water. Since majority of the dyes used in textile industry are the azo dyes, our work mainly focuses on the degradation of azo dyes. We used various metal oxide nanoparticles and number of azo dyes in order to carry out the degradation experiments.

The details of nanoparticles synthesized and model dyes used for degradation were given below:

Sl. No	**Name of the Dye**	**Metal oxide**	**Starting material**	**Fuel**
1	Coralene red F3BS	Zinc Oxide	Zinc Chloride	Hydrazine Hydrate
2	Coralene red F3BS	Zinc Oxide	Zinc Nitrate	Sugar
3	Coralene red F3BS	Zinc Oxide	Zinc Nitrate	Hydrazine Hydrate
4	Coralene Dark Red 2B	Calcium Aluminate	Calcium and Aluminium Nitrate	Acetamide
5	Coralene Dark Red 2B	Calcium Zincate	Calcium and Zinc Nitrate Zinc Nitrate	Acetamide
6	Coralene Violet 3R	Calcium Aluminate	Calcium and Aluminium Nitrate	Urea
7	Violet GL2B	Calcium Aluminate	Calcium and Aluminium Nitrate	Urea
8	Textile Effluent	Calcium Zincate	Calcium and Zinc Nitrate Zinc Nitrate	Acetamide

All the above mentioned nanoparticles were prepared in our laboratory and characterized by SEM and XRD techniques. The reported nanoparticles have shown degradation efficiency to a greater extent.

Azo dye Coralene red F3BS was selected as model dye for the three degradation experiments. The dye was coupled with three different nanoparticles to check the degradation efficiency of different nanoparticles on the Coralene red F3BS dye solution.

Degradation experiment for Coralene red F3BS using ZnO I reveals that, the prepared nanoparticle was highly efficient in degrading the selected dye in an aqueous solution at all the concentrations (50ppm, 75ppm and 100ppm concentrations 99.65%, 99.02% and 99.80% of degradation) at pH 7.

Similarly, ZnO II and ZnO also proved to be effective photocatalysts at pH 12 as the degradation efficiency was found to be 99% and 99.17% respectively.

			Coralene Dark Red 2B, the azo dye was coupled with two different nanoparticles, namely, Calcium aluminate and Calcium zincate. 90% and 100% degradation was recorded for calcium aluminate and Calcium zincate respectively at pH 12. The same calcium zincate nanoparticle was used to degrade the selected textile effluent and the highest degradation was found to be 95.61% at pH 5. Coralene Violet 3R and Violet GL2B azo dyes were degraded using Calcium aluminate nanoparticle and the degradation efficiency was found to be 92.98% at pH 3and 96.07% at pH 10after 120minutes respectively. Chemical oxygen demand was reduced to a considerable extent whereas the same is not true with the reduction in Total organic carbon for all the selected dyes in the present study. Thus all the reported nanoparticles were found to be very useful, effective and efficient catalyst for decolourization of azo dyes.
14	Contribution to the Society	:	The study will bring out the ideal method for the removal of colour using metal oxide nanoparticles. Previous researches have shown the degradation of many numbers of dyes by various methods but they are having their own limitations. In our present study, the degradation was mainly based on the advanced oxidation processes which are highly efficient, cost effective and the most important is they can be applied in large scale. Thus the protocol developed may be useful in cleaning waste waters containing dyes which are of great concern in the present scenario as this provides water for reutilization for different activities in day today life.
15	Whether any Ph.D., Enrolled/ Produced out of project	:	One Candidate Enrolled for Ph.D.,
16	No of Publication out of the project	:	07 ➢ Five Publications in an International journal ➢ Two Publications in an National journal

Signature of the Principal Investigator

Dr. YOGENDRA K. Ph.D.,
Principal Investigator
UGC Sponsored Major Research Project
Department of Environmental Science
Kuvempu University SHANKARAGHATTA-577 451

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Jnana Sahyadri
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Shimoga Dist. Karnataka India

LIST OF ABBREVIATIONS

AOP’s	Advanced Oxidation Processes
CB	Conduction band
COD	Chemical Oxygen Demand
$CaAl_2O_4I$	Calcium aluminate – urea
$CaAl_2O_4$ II	Calcium aluminate - acetamide
$CaZnO_2I$	calcium zincate– urea
$CaZnO_2$ II	calcium zincate - acetamide
Conc	Concentrated
Dil	Dilute
eV	Electron Volts
$FeSO_4$	Ferrous sulphate
FAS	ferrous Ammonium Sulphate
g	Gram
g/L	Gram per liter
HH	Hydrazine Hydrate
H_2SO_4	Sulphuric acid
H_3PO_4	Phosphoric acid
$K_2Cr_2O_7$	Potassium dichromate
L	Liter
mg	Milligram
min	Minute
mg/L	Milligram per liter
OC	Organic carbon
$OH^{\bullet}$	Hydroxyl Radical

ppm	Parts per million
SEM	Scanning Electron Micrograph
TOC	Total Organic Carbon
UV	Ultraviolet light
Vis	Visible light
VB	Valence band
XRD	X ray Diffraction
ZnO	Zinc Oxide
ZnO-I	Zinc Oxide Composite-I
ZnO-II	Zinc Oxide Composite-II

Contents

Chapter 1

INTRODUCTION

Chapter - 1

INTRODUCTION

The limited availability of fresh water is a global crisis. The growing consumption of fresh water by anthropogenic activities has taken its toll on available water resources. An anthropogenic activity that produces large volumes of concentrated effluent is the process of dyeing. Whether applied to fabric, paper, pulp, leather etc., the processes involved in dyeing generate effluents that are rich in colorants. Unfortunately, water bodies are still used as sinks for wastewater from domestic and industrial sources. However, in recent times, the need to replenish our water resources has been receiving increasing attention. This has led to the development of strategies to return water to its source in the least toxic form possible, to enable reutilization of water. These strategies and processes may be collectively termed as 'wastewater treatment'.

1.1Dyes

A dye is defined as a substance used to impart colour to a substance from a solution or fine dispersion. It is remained in the substance by adsorption, solution and mechanical retention or by ionic or covalent chemical bonds. Dyes are commercially available as liquids, pastes and powders. Dyes are classified by a variety of schemes. Classes based on usage or method of application, are of greatest value to the dyer, classes based on chemical composition are more use to the chemist.

The first human-made (synthetic) organic dye mauveine, was discovered by William Henry Perkin in 1856. Approximately 10,000 dyes are currently manufactured (ChengchengZhang*et al.*, 2012) and it is estimated that at least 15% of these are released into the environment (Chantal Guillard*et al.*, 2005). Synthetic dyes quickly replaced the traditional natural dyes as they cost less, they offered a vast range of new colours, and they imparted better properties to the dyed materials. Dyes are now classified according to how they are used in the dyeing process.

1.2 Classification of dyes

1.2.1 Acid dyes are water-soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fiber. Acid dyes are not substantive to cellulosic fibers. Most synthetic food colours fall in this category.

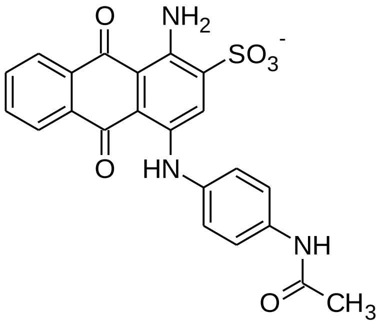


Fig. 1: Acid Blue 40

1.2.2 Basic dyes are water-soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. Basic dyes are also used in the colorization of paper.

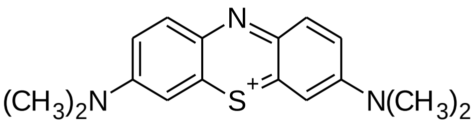


Fig. 2: Basic Blue 9

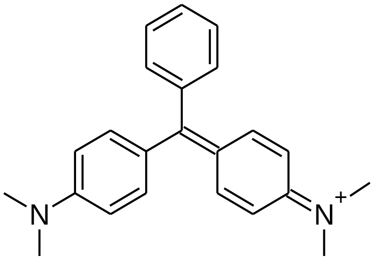


Fig. 3:Basic Green 4

1.2.3 Mordant dyes require a mordant, which improves the fastness of the dye against water, light and perspiration. The choice of mordant is very important as different mordant can change the final colour significantly. The most important mordant dyes are the synthetic mordant dyes, or chrome dyes, used for wool; these comprise some 30% of dyes used for wool, and are especially useful for black and navy shades. The mordant, potassium dichromate, is applied as an after-treatment. It is important to note that many mordants, particularly those in the heavy metal category, can be hazardous to health and extreme care must be taken in using them.

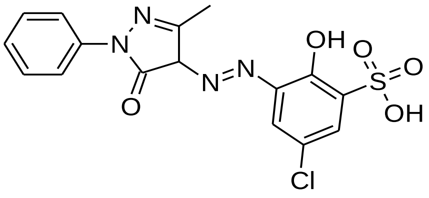


Fig. 4:Mordant Red 19

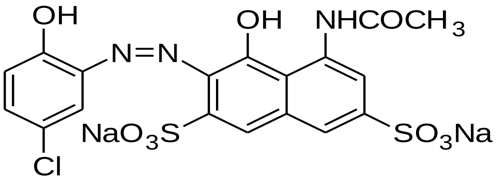


Fig. 5: Chrome blue 2K

1.2.4 Vat dyes are essentially insoluble in water and incapable of dyeing fibers directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile fiber. Subsequent oxidation reforms the original insoluble dye. The colour of denim is due to indigo, the original vat dye.

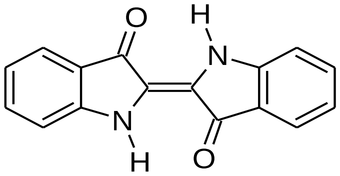


Fig. 6: Indigo

1.2.5 Reactive dyes utilize a chromophore attached to a substituent that is capable of directly reacting with the fiber substrate. The covalent bonds that attach reactive dye to natural fibers make them among the most permanent of dyes. "Cold" reactive dyes, such as Procion MX, Cibacron F and Drimarene K are very easy to use because the dye can be applied at room temperature. Reactive dyes are by far the best choice for dyeing cotton and other cellulose fibers at home or in the art studio.

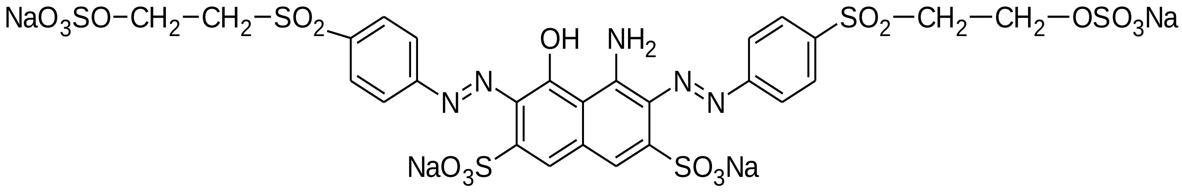


Fig. 7: Reactive Black 5

1.2.6 Disperse dyes were originally developed for the dyeing of cellulose acetate, and are water insoluble. The dyes are finely ground in the presence of a dispersing agent and sold as a paste, or spray-dried and sold as a powder. Their main use is to dye polyester but they can also be used to dye nylon, cellulose triacetate, and acrylic fibers. In some cases, a dyeing temperature of 130°C is required, and a pressurized dye bath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fiber. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.

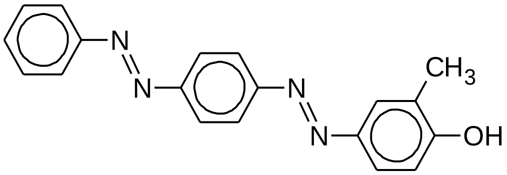


Fig. 8: Disperse Yellow 7

1.2.7 Azoic dyeing is a technique in which an insoluble azo dye is produced directly onto or within the fiber. This is achieved by treating a fiber with both diazoic and coupling components. With suitable adjustment of dye bath conditions the two components react to produce the required insoluble azo dye. This technique of dyeing is unique, in that the final colour is controlled by the choice of the diazoic and coupling components. This method of dyeing cotton is declining in importance due to the toxic nature of the chemicals used.

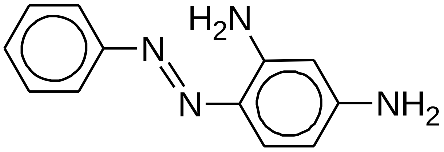


Fig. 9: Chrysoidine dye

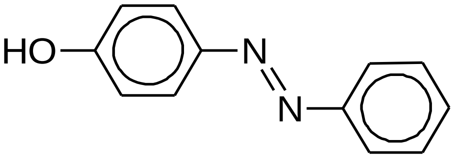


Fig. 10: Yellow Azo

1.2.8 Sulfur dyes are two part "developed" dyes used to dye cotton with dark colours. The initial bath imparts a yellow colour; this is after treated with a sulfur compound in place to produce the dark black.

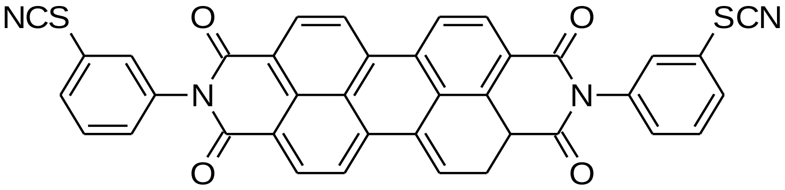


Fig. 11: CI Sulphur Red 14

1.2.9 Direct or **substantive dyeing** is normally carried out in a neutral or slightly alkaline dye bath, at or near boiling point, with the addition of either sodium chloride (NaCl) or sodium sulfate (Na_2SO_4). Direct dyes are used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.

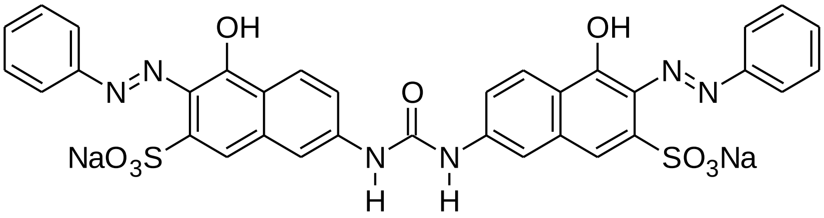


Fig. 12: Direct Orange 25

Among all dyes, azo dyes are the largest and most versatile class of compounds due to the outstanding coloring properties, brilliance of shades, very good leveling power with excellent light and wash fastness. They are used in dying and printing wool, polyamides, silk and other fabric materials (Golka*et al.,* 2004). The fixation degree of azo dyes to fabrics is not complete, resulting in the contamination of the effluents in wastewater (Chatzisymeon*et al.,* 2013; MontiraLeelakriangsak*et al*., 2012).

Azo dyes are characterized by the existence of nitrogen nitrogen(-N=N-) double bonds and the bright colour is due to the azo bonds and chromospheres (ElisangelaFranciscon*et al.,* 2012). Furthermore, azo dyes also affect photochemical activities in aquatic systems by reducing light penetration. The removal of azo dyes is important because many azo dyes are toxic to aquatic organisms (Sharrna*et al.*, 2007).

Azo dyes are one of the oldest industrially synthesized organic compounds and these are designed to be recalcitrant under typical product service conditions (WamikAzmi*et al.,* 1998; Ogawa*et al.*, 1990). The azo dye production in the United States in 1985 amounted to over 108 kg, which was used by textile, printing, drug and pharmaceutical industries (United States International Trade Commission 1986). Approximately 10,000 dyes are currently manufactured (Zollinger1987) and it is estimated that at least 15% of these are released into the environment (Vaidya*et al.,* 1982). They occur in industrial effluent, groundwater, contaminated soils and sediments. These compounds are of concern because some of the dyes, dye precursors or their biotransformation products, such as the aromatic amines, have been shown to be carcinogenic (Donlon*et al.,* 1997; Kamaljit Singh and Sucharita Arora 2011).

Dyes used in the textile industry are difficult to remove by conventional wastewater treatment methods, since they are stable to light and oxidizing agents and are resistant to aerobic digestion. The discharge of highly colored wastewater impedes light penetration, which disturbs the various biological reactions within a stream. Dyes can cause allergic dermatitis, skin irritation, cancer, genetic mutation etc. Removal of color from wastewater is most challenging task in the present scenario. Chemical precipitation and biological methods are the two commonly used processes for treatment of coloured wastewater. But, these methods have some disadvantages like sludge disposal and long-term biodegradation process.

1.3 Processes and sources of effluents in textile industry

1.3.1 Sizing

It is the process by which warp thread is sized with starch to give necessary tensile strength and smoothness required for weaving. Effluent from this process contains starch and softeners. Though, the volume is slowly replaced by carboxyl methyl cellulose and polyvinyl alcohol which reduce the BOD of the effluent by 40– 90%.

1.3.2 Desizing

This process is employed to remove the sizing materials present in the grey cloth to make it suitable for dying and further processing. There are two methods of desizing.

1.3.2.1 Desizing with acid

The grey cloth has to be treated with dilute sulfuric acid (0.5%) and washed well.

1.3.2.2 Desizing with enzymes

The cloth is steeped in baths containing enzymes or malt which hydrolyzes the starch and converts it to readily soluble substances. Then the clothes are subjected to mild acid treatment.

Effluents arise mainly from the washing and contain the products of hydrolysis and other sizes in dissolved and colloidal form. The pH of effluents is usually in natural range and it has a high BOD and dissolved solids. The suspended solids content is appreciable.

1.3.3 Kier boiling

To remove natural impurities such as greases, waxes, fat and other impurities, the designed cloth are subjected to kier boiling. They are boiled with the aid of stream in an alkaline solution containing caustic soda (1-3%), soda ash, sodium silicate and sodium peroxide with small amounts of detergents for several hours.

1.3.4 Dyeing

Dyes are used over fabrics to enhance the aesthetic quality and make potential dying. It is carried out with varied types of dyes like direct dyes, basic dyes, Sulfuric dye, vat dye, naphtol dye, developing dye etc.

1.3.5 Yarn dyeing

In some mills, yarn itself is dyed after souring and bleaching.

1.3.6 Printing

It is carried out normally in roller machines; the dye is as a thick paste along with starch or printing gums and mordents for fixation of dyes. The fabrics are then thoroughly washed to remove the unfixed dyes.

1.3.7 Finishing

Starches dextrin, natural and synthetic waxes and synthetic resins are used for finishing which is done after dying and printing to impart smoothness and resistance to adhere only a part of the processed fabrics. Finishing is done according to the requirements.

1.4 Need for dye removal from effluents

Synthetic dyes are preferred for use over natural dyes due to their superior performance. As compared to natural dyes, synthetic dyes impart brighter colors, show better light-fastness and are more resistant to washing. Also, synthetic dyes offer a wider variety of colors (Michelle Reis da Silva*et al.*, 2010). Wastewater or effluents from industries that manufacture paints, pigments and color cosmetics contain a variety of synthetic dyes.

Industries involved in dyeing of textile, paper, leather and plastics, release effluents that are highly colored (Abo-Farah 2010). Azo dyes feature among the most widely used synthetic dyes in industry globally. The fixation of azo dyes (on textile) is quite low and often, up to 50% of the applied dye may be lost in the wash stream (Zille*et al.*, 2004). The presence of dyestuffs in industrial effluent is more than just an aesthetic problem. The chromophores of dyes strongly absorb sunlight (Michelle Reis da Silva*et al.*, 2010; Abo-Farah2010). When the effluent reaches the receiving water body, the dyes hinder photosynthesis by the aquatic flora. The presence of dyes in the water body increases the Chemical and Biological Oxygen Demand (COD and BOD respectively) (Kagalkar*et al.*, 2010). Additionally, effluent containing dyestuffs are found to have a large concentration of suspended solids (Abedin 2008). These factors upset the ecological balance of the receiving water body. Several dyes have been found to be potentially toxic (Zille*et al.*, 2004).

Thus, the presence of synthetic dyes is a serious environmental concern. Evidently, it is necessary to remove colorants from the effluent before it is discharged into a water body.

1.5 Causes of recalcitrance of pollutants

The removal of coloring matter from effluent is a major problem faced by industries. In general, the chemical structure of dyes contains conjugated double bonds and aromatic rings (Zille*et al.,* 2005). Many synthetic dyes tend to persist in the environment due to the inherent stability of their molecular structure. Azo dyes for example, have a characteristic azo (-N=N-) linkage which is electron withdrawing in nature. The presence of this linkage decreases the susceptibility of azo dyes to oxidative reactions (Maddhinni*et al.*, 2006) thus making them resistant to conventional degradation methods. Complex pollutants that resist degradation and tend to persist in the environment for long durations are considered to be recalcitrant pollutants (Mohapatra2006). Recalcitrance of a given pollutant may sometimes be attributed to unusual substitutions with halides (Cl^- or Br^-), very large molecular size, and presence of unusual bonds or highly condensed aromatic rings. The presence of tertiary and quaternary carbon atoms also contributes to recalcitrance (Jogdand 2006).

1.6 Conventional processes for removal of dyes from effluent

The conventional methods used in the textile industry for color removal from effluents include physico-chemical methods like coagulation/flocculation and activated carbon adsorption. Both flocculation and adsorption generate large amounts of sludge and waste, which require separate treatment before disposal (Michelle Reis da Silva*et al.,* 2010). An effective means of decolorization of dye containing effluent is the application of the Advanced Oxidation Processes (AOPs). These processes are based on the generation of highly reactive species like the hydroxyl radicals ($^{\bullet}$OH) that have a strong oxidative potential ($E_0 = + 2.8$ V). These radicals can rapidly oxidize a broad range of organic pollutants in a non-selective manner. The common AOPs include Fenton and Fenton-like oxidation, ozonation, photochemical oxidation, electrochemical oxidation, photolysis using H_2O_2 and O_3, Corona Process, TiO_2 photolysis, radiolysis, wet oxidation and the use of electronic beams or γ-beams (Abo-Farah 2010). Ozonation is a method used to treat dyes in effluent. Although it effectively decolorizes dyes, it does not reduce COD adequately. It may produce exhausted ozone in the wastewater and increase the cost of treatment.

The Fenton process requires Fe^{2+}/Fe^{3+} and H_2O_2. It is commonly used since it is relatively inexpensive and can be easily operated. This method is capable of cleaving the azo (-N=N-) linkage, thereby bringing about the partial or complete degradation of azo dyes. The major disadvantages of the Fenton treatment are that it operates in the acidic pH range of 2-5 and that the Fe^{2+}/Fe^{3+} need to be regenerated at the end of the treatment. The conventional treatment processes have several shortcomings such as being unsuitable for use when the effluent contains high concentrations of the target pollutants, high running cost and low efficiency of removal (Stanisavljevic*et al.*, 2004).

1.7 Photocatalytic Oxidation or Photocatalytic Degradation

Photocatalytic Oxidation harnesses photon energy to destroy many toxic organic compounds that are hazardous to human health and the environment. The key to photocatalytic oxidation is the photocatalyst. A photocatalyst is a chemical compound that becomes highly reactive when exposed to various wavelengths of UV light. In the presence of organic pollutants, such as hydrocarbons, chlorinated solvents, alcohol, ketones and aromatic compounds, the active photocatalyst attacks the pollutants chemical bond, converting the toxic compounds into benign constituents, such as water and carbon dioxide. Photocatalytic systems have the ability to convert toxic carbon monoxide, at room temperature, to non-harmful carbon dioxide. This is a major development because carbon monoxide often is a cause of sick-building syndrome and it cannot be removed from the air with any type of absorption media. In this type of advanced oxidation process, nanoparticles are used for the treatment of textile industrial wastewater.

The two main factors involved in photocatalysis are the solar/UV-light irradiation and a semiconductor where it needs light energy for its activation. But degradation does not occur in the absence of oxygen. Heterogeneous photocatalysis is a promising method among advanced oxidation processes, which can be used for degradation of various organic pollutants in water and wastewater. In photocatalysis systems a combination of semiconductors (such as TiO_2, ZnO, F_2O_3, CdS and ZnS) and UV or visible lights can be used. Upon irradiation, valence band electrons are promoted to the conduction band leaving a hole behind. These electron hole pairs can either recombine or interact separately with other molecules. The holes at the valence band, having an oxidation potential of +2.6 V versus normal hydrogen electrode (NHE) at pH=7, can oxidize water or hydroxide to produce hydroxyl radicals. The limitation of the rate of photocatalytic degradation is attributed to the recombination of photo generated electron-hole (e^-/h^+) pairs. Various attempts have been made to reduce e^-/h^+ recombination in photocatalytic processes. Recently, much attention has been paid to photocatalytic methods for dye containing sewage decolourization using nano catalysts TiO_2, ZnO, etc (Tangand Chen 2004).

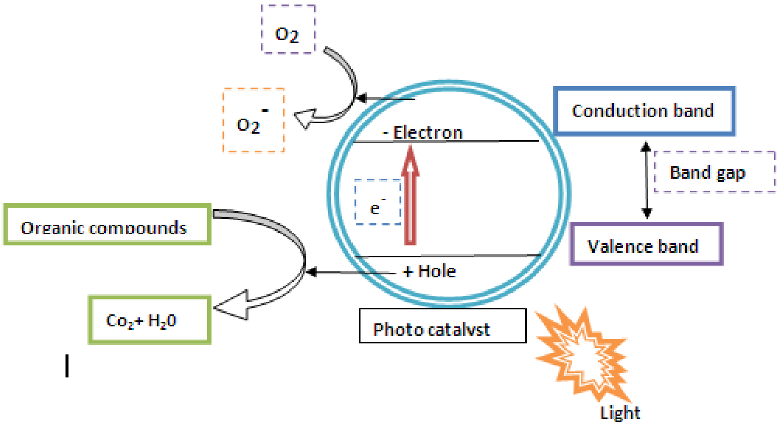


Fig. 13: Diagrammatic representation of photoinduced charge separation (electron and hole) upon illumination of a semiconductor particle with light of energy higher than the band gap.

1.8 GeneralMechanism of dye degradation

$\text{Metal oxide nanoparticle} + h\nu \rightarrow (e^-_{CB} + h^+ VB)$ …… (1)

$e^-_{CB} + O_2 \rightarrow O^{2\bullet-}$……… (2)

$H_2O + O_2^{\bullet-} \rightarrow OOH^\bullet + OH^-$…… (3)

$2OOH^\bullet \rightarrow O_2 + H_2O_2$ …… (4)

$O_2^{\bullet-} + \text{dye} \rightarrow \text{dye-OO}^\bullet$…………(5)

$OOH^\bullet + H_2O + e^-_{CB} \rightarrow H_2O_2 + OH^-$…… (6)

$H_2O_2 + e^-_{CB} \rightarrow OH^\bullet + OH^-$……..(7)

$H_2O_2 + O_2^{\bullet-} \rightarrow OH^\bullet + OH^- + O_2$ ….(8)

$OH^\bullet / O_2^{\bullet-} / \text{MONP} + \text{dye} \rightarrow$Dye degradation… (9)

The mechanism of photocatalytic activity of metal oxide nanoparticle can be predicted as above. Under sunlight irradiation nanoparticles get excited and transfer electron to the conduction band (Eq 1). Electron in the conduction band of a nanoparticle can reduce molecular oxygen and produce the super oxide radical (Eq 2). This radical may form hydrogen peroxide or organic peroxide in the presence of oxygen and organic molecule (Eq 3, 4, 5). Hydrogen peroxide can be generated in another path (Eq 6). Hydrogen peroxide can form hydroxyl radicals which are powerful oxidizing agents (Eq 7, 8). The radicals produced are capable of attacking dye molecules and degrade them (Eq 9).

With this strong background, the present work is focused on the efficient degradation of azo dyes using photocatalytic activity of synthesized metal oxide nanoparticles under solar irradiation.

Chapter 2

Review of Literature

Chapter - 2

REVIEW OF LITERATURE

Ronghua Wang *et al*., 2004, synthesized Silver ions doped ZnOnanocrystalline using Ag-doped Zn5 (CO3)2(OH)6 as precursor. Synthesis involved the application of hybrid induction and laser heating (HILH) techniques. The physical properties of prepared nanoparticles were characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and UV-Vis methods. The results of the photocatalytic degradation of methylene blue (MB) and phenol in aqueous suspensions showed that silver ions doping greatly improved the photocatalytic efficiency of ZnO nanocrystallites. Thus, the investigation throws light on the enhanced the photocatalytic activity due to increase in the amount of silver ions resulted in increased lattice deficiency.

Feng Peng*et al*., 2006, successfully prepared the zinc oxide thin films on aluminum foil by sol–gel method with methyl glycol as solvent. The film was characterized by means of XRD, TG, UV–vis, SEM and AFM, which shows that, the ZnO/Al film is formed by a layer of ZnOnano-sized particles with average diameter of 52.2 nm. Experimental studies revealed that the prepared photocatalyst is a promising visible light responded photocatalyst for the activation of O_2 at room temperature to degrade organic pollutants.

Chien-Tsung Wang *et al*., 2007, reported on the degradation of Disperse Blue 79 azo dye in water under ultraviolet light illumination using nano gold/iron oxide (maghemite) aerogels as photocatalysts. Characterization of nanoparticles was done by diffuse reflection spectroscopy (DRS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy. Maximum degradation was recorded when the experiments were conducted in an alkaline media or in the presence of hydrogen peroxide. In the photocatalysis system, metallic gold particles serve to facilitate the transfer of surface electrons, and hydroxyl radicals near the catalyst surface act as the main oxidative species to attack dye molecules. At high catalyst concentrations, the use of ultrasound and light irradiation improved the activity declined by catalyst particle aggregation. Results demonstrate the feasibility of aero gel powders as a model photocatalyst for dye decontamination in textile wastewater.

Pardeshi and Patil2008, examined the effectiveness of zinc oxide-mediated solar photocatalytic degradation of phenol. Degradation experiments were conducted for various parameters such as concentration of substrate, amount of photocatalyst, pH and irradiation time. Chemical Oxygen Demand (COD) reduction experiment was conducted to check the demineralization of substrate. They found that the photocatalytic degradation of phenol was more effective under solar light in comparison to artificial visible light irradiation and also photodegradation of phenol was favorable in weakly acidic or neutral solutions. This work envisages great potential that sunlight mediated photocatalysis has in the removal of phenol from waste water.

Rajeshwar*et al*., 2008, reviewed the heterogeneous photocatalytic treatment of organic dyes in air and water. They used many number of semiconductor photocatalysts such as titanium dioxide (TiO_2), ZnO, CdS, WO_3, and Fe_2O_3 for decolorizing and decomposing the organic dye to mineralized products. The review includes historical aspects, dark adsorption of the dye on the semiconductor surface and its role in the subsequent photoreaction, semiconductor preparation details, photoreactor configurations, photooxidation kinetics/mechanisms and comparison with other Advanced Oxidation Processes (e.g., UV/H_2O_2, ozonation, UV/O_3, Fenton and photo-Fenton reactions), visible light-induced dye decomposition by sensitization mechanism, reaction intermediates and toxicity issues, and real-world process scenarios.

TianTan*et al*., 2008, presented a two-step method to synthesize metal–semiconductor heterostructurephotocatalyst. They synthesized Ag/TZnOheterostructure by RF magnetron sputtering method in this two-step preparation technique based on the tetrapod-like zinc oxide (T-ZnO) deposited by thermal evaporation. Detailed study of the structure and the photocatalytic properties of the Ag/T-ZnOreveal that the Ag/T-ZnOheterostructure exhibits better photocatalytic activity than that of the pure T-ZnO and there is an optimum sputtering time and sputtering power for the heterostructure'sphotocatalytic activity. Thus the present study reveals the enhanced photocatalytic activity which indicates the feasibility of this novel two-step method which may be developed to a promising synthesis technique.

Yinhua Jiang *et al*., 2008, reported on the preparation of nanosized, bicomponent TiO_2-ZnO powders of varying Ti/Zn ratio using an ultrasonic precipitation method and their crystalline structure and surface area were determined using X-ray diffraction and N_2 physical adsorption. They conducted the decolorization of C.I. Basic Blue 41 in water under solar irradiation using prepared TiO_2-ZnO powders and the highest photocatalytic activity was recorded for 1:1 molar ratio of Ti/Zn. The effects of various parameters such as photocatalyst loading, initial solution pH, initial dye concentration and irradiation time on decolorization rate were systematically investigated. Results revealed that, approximately 100% color removal was achieved in about 1 hour.

Su *et al*., 2008, prepared Quantum-sized ZnO using sol–gel method with zinc acetate dihydrate ($Zn(CH_3COO)_2$ $2H_2O$) and lithium hydroxide monohydrate ($LiOH.H_2O$) as raw material. Characterization of ZnO was done by X-ray diffraction (XRD), Infrared absorption spectroscopy (IR) and UV–vis spectroscopy. The degradation rate of reactive brilliant blue X-BR in aqueous solution was used to evaluate the photocatalytic performance of the quantum-sized

ZnO. The experimental results indicated that the photocatalytic property of the ZnO was excellent.

Sobana*et al.*, 2008, worked on the photocatalytic degradation of Direct Red 23 (DR23) by nano-Ag doped TiO_2 under different conditions. They reported that the photo deposition of 1.5% Ag on the surface of TiO_2 enhanced its photo activity in DR23 degradation. The study was carried out for various optimal experimental conditions such as catalyst amount, pH and dye concentration. It was found that, addition of some inorganic oxidizing species such as H_2O_2, (NH_4) S_2O_8 and $KBrO_3$ up to a certain concentration increased the rate of degradation. The higher photoactivity of Ag-TiO_2 than TiO_2 under UV irradiation can be ascribed to the effect of silver deposits acting as electron traps on the Ag-TiO_2 surface.

Abdullah M. Asiri*et al.*, 2010, studied the Photo degradation of Rhodamine 6G and phenol red by nanosized Titanium dioxide (TiO_2) under solar irradiation. The study was involved different parameters such as the effect of the anchoring groups on the catalyst, concentration of the n-TiO_2 semiconductor. They have synthesized n-TiO_2 by a sol–gel process and characterized by SEM. The rate of degradation was estimated spectrophotometrically.

Pouretedal*et al.*, 2010, studied the photodegradation of methylene blue catalyzed by CeO_2 under UV and solar irradiation. They synthesized CeO_2nanocrystals by simple precipitation method and calcinations at 600°C. Cerium (IV) nitrate $(NH_4)_2Ce\ (NO_3)_6$ and ammonia were used as precursors for the synthesis of CeO_2. Characterization was done by X-ray diffraction, Fourier transform infrared spectroscopy, transmission electron microscopy, and N_2 adsorption. The highest degradation obtained with 1.0g/L CeO_2 at pH 11 within 125min for methylene blue.

Yogendra*et al*., 2011, conducted degradation study of red F3BS using photoactive Zinc oxide (ZnO) composite. ZnO composite was prepared by simple solution combustion method. The study was mainly focused on the degradation of dye at different ZnO composite dosage and pH. The study reveals that, prepared ZnO composite was very effective in removing the color (~ 99 %) at pH 12.9 in 45 min.

Madhusudhana*et al*., 2011, studied the photocatalytic degradation of Coralene Dark Red 2B Azo Dye using Calcium Zincate ($CaZnO_2$) nanoparticle in presence of natural sunlight. $CaZnO_2$ was prepared by simple solution combustion method and characterized by SEM and XRD. Degradation studies were carried out at different pH, and photocatalyst dosages. They have reported that $CaZnO_2$ as an effective photocatalyst for the degradation of Coralene Dark Red 2B in the presence of sunlight.

Literatures related to present study have been referred during literature survey reveals that number of research works has been done related to the dye degradation using nanoparticles as photocatalysts. With this background the present research work focuses on the degradation of azo dyes by using various metal oxide nanoparticles.

Chapter 3

Materials and methods

Chapter – 3

MATERIALS AND METHODS

3.1 Chemicals and Instruments for photocatalytic activity

The commercially available water soluble azo dyes such as Coralene Red F3BS, Coralene Dark Red 2B, Coralene Violet 3R and Violet GL2B were collected from Colourtex Limited, Surat, Gujarat, India, and all the chemicals required for the experiments were procured from S D fine-chem limited, Mumbai, India, JobalChemie, Mumbai, India and Hi-media chemicals, Mumbai and used as received. The textile effluent was obtained from textile industry Himatsingka Linens, Hassan.

The details of the azo dyes, starting materials and the fuels used for the synthesis of nanoparticles are given below:

Sl. No.	**Name of the Dye**	**Metal oxide**	**Starting material**	**Fuel**
1	Coralene red F3BS	Zinc Oxide	Zinc Chloride	Hydrazine Hydrate
2	Coralene red F3BS	Zinc Oxide	Zinc Nitrate	Sugar
3	Coralene red F3BS	Zinc Oxide	Zinc Nitrate	Hydrazine Hydrate
4	Coralene Dark Red 2B	Calcium Aluminate	Calcium and Aluminium Nitrate	Acetamide
5	Coralene Dark Red 2B	Calcium Zincate	Calcium and Zinc Nitrate	Acetamide
6	Coralene Violet 3R	Calcium Aluminate	Calcium and Aluminium Nitrate	Urea
7	Violet GL2B	Calcium Aluminate	Calcium and Aluminium Nitrate	Urea
8	Textile Effluent	Calcium Zincate	Calcium and Zinc Nitrate	Acetamide

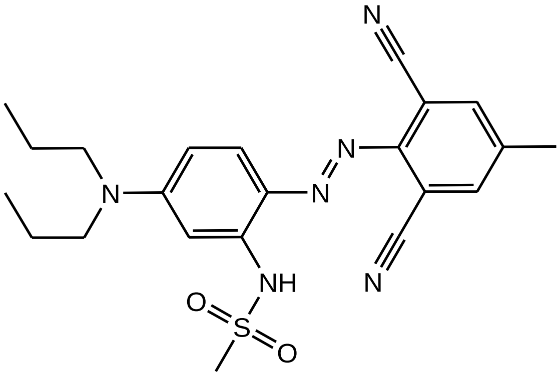


Fig. 14: Coralene Red F3BS

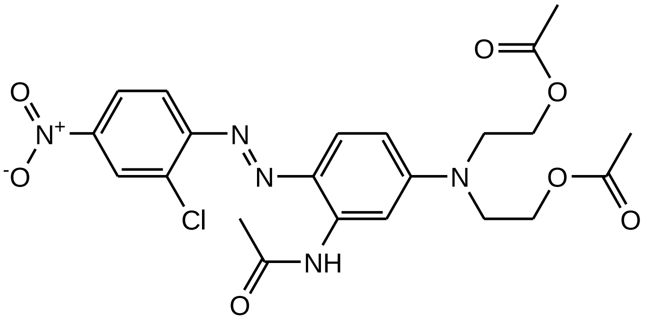


Fig. 15: Coralene Dark Red 2B

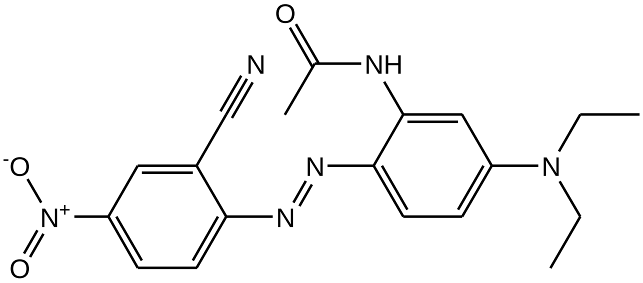


Fig. 16: CoraleneViolet 3R

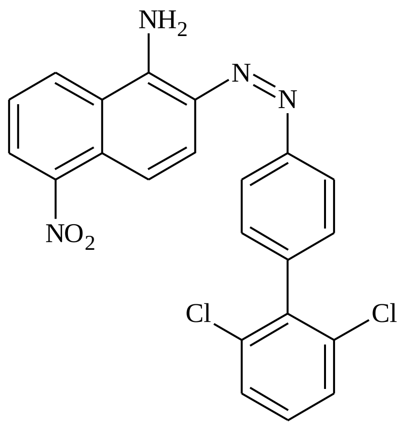


Fig. 17: Violet GL2B

UV-vis Spectrophotometer (Systronics) was used for recording the absorbance and λ_{max} (wavelength of light at which maximum absorbance have been recorded for the selected model azo dyes, namely Coralene Red F3BS, Coralene Dark Red 2B, Coralene Violet 3R and Violet GL2B).

3.2 Synthesis of the metal oxide nanoparticles

3.2.1Synthesis of ZnO Composite-I

Aliquot of hydrazine hydrate was used as fuel and added drop wise at room temperature to zinc chloride in 1:1 molar ratio under vigorous stirring. The obtained white precipitate after complete combustion of $ZnCl_2$ with $N_2H_4.H_2O$ was suspended in 50ml of distilled water for hydrolysis and heated to 50° C with constant stirring for 2hours in order to achieve destruction of the agglomerates and re-dispersion into primary particles. The residue was the filtered and dried in hot air oven at 100°C for 3 hours and characterized. The photocatalyticdecolourization of Coralene Red F3BS dye in presence of natural sunlight was investigated by using nanosizedZnO composite-I.

3.2.2 Preparation of ZnO Composite-II

ZnO composite-II was prepared by drop wise addition of 5.02g hydrazine hydrate (99%) to the beaker containing 11.88g of zinc nitrate with vigorous stirring. The obtained white precipitate was diluted to 50ml by distilled water and stirred for one hour. After centrifugation at 2000 rpm and washing with water several times the product was dehydrated at 100-120°C in hot air oven for 2-3 hours. The final white powder was then crushed manually and stored for further use.

3.2.3Synthesis of ZnO-I nanoparticles

The ZnO-I nanoparticle was prepared by solution combustion method using zinc nitrate and sugar (as fuel). The stoichiometric amounts of zinc nitrate and fuel sugar were calculated using the total oxidizing and reducing valencies of the compounds which serve as numerical coefficients for stoichiometric balance. Initially $Zn(NO_3)_2.4H_2O$ (14.135g) and sugar (3.470g) were dissolved in minimum quantity of water in a silica crucible. The crucible was introduced to the muffle furnace and then muffle furnace was heated from room temperature to 500°C. The solution boils and undergoes dehydration followed by decomposition along with the release of certain amounts of gases; it froths and swells forming foam which ruptures with a flame.

The product formed after combustion is a voluminous and foamy ZnO-I. After the complete combustion, crucible was taken out and allowed to cool. According to the propellant chemistry, the following reaction takes place during combustion.

$$48\ Zn(NO_3)_2 + 10\ C_{12}H_{22}O_{11} \rightarrow 48\ ZnO + 120\ CO_2 + 110\ H_2O + 48\ N_2$$

3.2.4Synthesis of $CaAl_2O_4$II

Ca $(NO_3)_2.4H_2O$ (6.49g) and Al $(NO_3)_3.9H_2O$ (20.63g) were dissolved in a minimum quantity of water along with acetamide (5.90g) in a silica crucible (with a volume of 100 cm^3). The resulting mixture was introduced into the muffle furnace which was preheated to 600°C. The combustion reaction for the synthesis of $CaAl_2O_4$ by the redox mixture method can be written as:

$11Ca\,(NO_3)_2 + 22Al\,(NO_3)_3 + 40CH_3\,CONH_2 11CaAl_2O_4 + \rightarrow 80CO_2 + 100H_2O + 64\,N_2$

3.2.5Synthesis of $CaZnO_2$II

The Calcium zincate nanoparticle was prepared by solution combustion method. The procured calcium nitrate, Zinc nitrate, and Acetamide as fuel were used for the synthesis of nanoparticle**.** A mixture of stoichiometric amounts of Calcium nitrate (8.65g), Zinc nitrate (10.89g), and Acetamide (3.93g) was dissolved in a small quantity of distilled water in a silica crucible (100 cm^3 capacity). The solution mixture in the crucible was introduced into the muffle furnace, which was preheated to 500°C. The solution undergoes dehydration and catches fire by spreading throughout the mass, finally yielding Calcium zincate. The obtained Calcium zincate is crushed in a mortar to make it amorphous. Thus Calcium zincate nanoparticle is formed by the complete combustion of the calcium nitrate and zinc nitrate with acetamide as fuel. According to the principle used in propellant chemistry the reaction is as shown below.

$$11\,Ca\,(NO_3)_2 + 11\,Zn\,(NO_3)_2 + 20\,CH_3CONH_2 \rightarrow 11\,CaZnO_2 + 40\,CO_2 + 50\,H_2O + 32\,N_2$$

3.2.6 Synthesis of $CaAl_2O_4$ nanoparticle I

The Calcium aluminate nanoparticle was prepared by solution combustion method, using procured Calcium nitrate, Aluminium nitrate, and Urea as fuel. Stoichiometric amounts of Calcium nitrate, Aluminium nitrate, and fuel Urea were calculated using the total oxidizing and reducing valencies of the compounds which serve as numerical coefficients for stoichiometric balance. Initially Ca $(NO_3)_2.4H_2O$ (3.54g) and Al $(NO_3)_3.9H_2O$ (11.225g) were dissolved in minimum quantity of water along with Urea (24g) in a silica crucible. The crucible was introduced into the muffle furnace which was preheated to 600˚C. The solution boils and undergoes dehydration followed by decomposition along with the release of certain amounts of gases it froths and swells forming foam which ruptures with a flame. The product formed after combustion is a voluminous and foamy $CaAl_2O_4$. The combustion product thus obtained is crushed in a mortar to make it amorphous. According to the propellant chemistry, the following reaction takes place during combustion.

$$3\ Ca(NO_3)_2 + 6\ Al(NO_3)_3 + 20\ NH_2CONH_2 \rightarrow 3\ CaAl_2O_4 + 20\ CO_2 + 40\ H_2O + 32\ N_2$$

3.3 Photocatalytic Experimental Procedure

3.3.1 Experimental Set Up 1: ZnO Composite I) + Coralene Red F3BS

Initially, the 50ppm, 75ppm and 100ppm Coralene Red F3BS dye solutions were prepared by dissolving 50mg, 75mg and 100mg of Coralene Red F3BS dye in 1000ml distilled water. The photocatalyticdecolourization experiment was carried out in the presence of ZnO composite-I with different dosages of catalyst, for each standard dye solutions. In the exploratory experiment , the reaction volume of 100ml of dye solution (of 50ppm dye concentration) was taken in clean beakers and various doses (0.5g, 0.1g, 0.15g, 0.2g, 0.25g, 0.3g, 0.35g, 0.4g) of ZnO composite-I particles were dispersed directly in to the beaker in presence of direct sunlight. The experiments were repeated for 75ppm and 100ppm dye solutions separately. Absorbance readings of the dye solution were recorded at regular intervals (15 minutes) by UV-vis Spectrophotometer. Further, the experiments were carried out at 3, 7 and 12 pH levels (adjusted by dilute hydrochloric acid and sodium hydroxide) to study the effect of pH on photodecolourization of various concentrations (50ppm, 75ppm and 100ppm) of Coralene Red F3BS aqueous solution.

3.3.2 Experimental Set Up 2: ZnO Composite II + Coralene Red F3BS

The photo decolourization of Coralene Red F3BS dye solution was studied in the presence of ZnO composite-II particles and solar radiation. Coralene Red F3BS is widely used azo dye in silk yarn dyeing industries and most of the textile industries. Photocatalytic reaction experiments were performed in presence of direct sunlight. Standard dye stock solution of 50ppm was prepared by dissolving 50mg of Coralene Red F3BS in 1000ml of distilled water and the initial absorbance was recorded at 521nm (λ_{max}). 100ml of this standard dye stock solution was taken in set (6 numbers including control sample) of Borosilglass beakers and prepared ZnO composite-II at various concentrations (0.1g, 0.2g, 0.3g, 0.4g, 0.5g) were directly dispersed to each beakers simultaneously. The absorbance readings at regular time intervals (15min) were compared with initial absorbance for the investigation of photocatalytic activity of prepared ZnO composite-II at different concentrations and pH (12.0, 7.0 and 3.0).

3.3.3 Experimental Set Up 3: ZnOI Nanoparticle + Coralene Red F3BS

The series of photocatalytic experiments were carried out in batch mode using glass reactors of 100ml capacity. For UV/ZnO-I and solarlight/ZnO-I experiments, the experiments were conducted in UV chamber at short wavelength of 365nm and direct sunlight respectively. The reactors were ensured with enough supply of oxygen in the reaction solution. Initially 50ppm dye solution was prepared by dissolving 50mg of Coralene Red F3BS in 1000ml distilled water and transferred to six glass reactors including control sample. The solution containing photocatalyst at different catalyst dosages (0.05g to 0.25g) was magnetically stirred in darkness for 5minutes to establish adsorption–desorption equilibrium prior to photoreaction. After each 15minute interval of irradiation time, an aliquot (~2ml) of the reaction volume was taken, centrifuged and concentration of Coralene Red F3BS was monitored spectro-photometrically by recording absorbance of supernatant at a wavelength of 521nm (λ_{max}). The reaction mixture was regularly stirred after each sampling time throughout the reaction to keep the mixture in suspension. Similarly, the experiments were repeated for 75ppm and 100ppm solutions in both irradiations. To study the effect of pH the experiments were conducted at different pH levels (pH 3, pH 7 and pH 12) at optimum catalyst dosage. Further, the experiments were repeated at optimum catalyst dosage and pH level for standard 50ppm dye solution to study the effect of addition of H_2O_2 (2ml/100ml of reaction volume).

3.3.4 Experimental Set Up 4: Calcium aluminate II + Coralene Dark Red 2B

The known concentration of dye solution was prepared by dissolving 30mg of Coralene Dark Red 2B dye in 1000 ml distilled water and it was used for the degradation. Initially 300 ml of 30 mg/L dye sample was tested with different catalyst dosage such as 300, 600, 900, 1200 and 1500mg in presence of direct sunlight. After the photocatalytic degradation, the extent of decolorization was estimated by recording absorbance of the dye solution with respective to 30min time interval. The experiments were repeated for different pH of 2, 5, 9 and 12 for the same standard solution.

3.3.5 Experimental Set Up 5: Calcium aluminate I + Coralene Violet 3R and Violet GL2B

The known concentration of dye solution was prepared by dissolving 30mg of Coralene Violet 3R dye in 1000ml distilled water and it was investigated for its decolorization in the presence of Calcium aluminate nanoparticle at different catalyst dosages and pH levels. Initially, 10ml of 30 mg/L dye sample was tested with different catalyst dosage (from 0.01g to 0.1g) in presence of direct sunlight. After the photocatalyticdecolorization, the extent of decolorization was estimated by recording absorbance of the dye solution using UV-VIS spectrophotometer 169 in order to get the optimum catalyst dose. The experiments were repeated at different pH levels (from 2 to 11) for the 100ml of same standard dye solution with the optimum catalyst dose.

The photocatalyticsuspensions of 100mg, 200mg, 300mg, 400mg and 500mg were tested on the dye samples. The suspension pH values were adjusted by using NaOH/HClsolutions using pH meter. Before irradiation, photocatalystsuspension was stirred in the dark to ensure the adsorption equilibrium and it was kept in sunlight for thephotocatalyticdegradation. The suspension was sampled at regular time intervals of 30minutes and centrifuged using (EBA-Hetlich) at 2500rpm for 10min to remove photocatalystparticles. The residual concentration of the solution samples was monitored by using UV-VIS spectrophotometer169 (Systronics) at 545 nm. The violet GL2B experiments were conducted at pH range of 2.5 to 9.5 in order to study the efficiency of the nanoparticle on acidic, alkaline and neutral conditions.

3.3.6 Experimental Set Up 6: Calcium zincate II + Coralene Dark Red 2B and Textile Effluent

The known concentration of dye solution was prepared by dissolving 30mg of Coralene Dark Red 2B dye in 1000ml distilled water and it was investigated for its decolorization in presence of Calcium zincate nanoparticle at different catalyst dosages. Initially, 300ml of 30mg/L dye sample was tested with different catalyst dosage (300, 600, 900, 1200 and 1500mg) in presence of direct sunlight. After the photocatalyticdecolorization, the extent of decolorization was estimated by recording absorbance of the dye solution taken at each 30minute time interval, using UV-Vis spectrophotometer 169 (Systronics). The experiments were repeated at different pH levels (2, 5, 9 and 12) for the same standard dye solution, with the same catalytic dosages.

100mL of 5%Textile effluent solution was taken in 100ml Borosil beakers was investigated for its decolorization in the presence of Calcium zincate nanoparticle at different catalyst dosages and pH levels. Initially, 10ml of 5% effluent sample was tested with different catalyst dosage (from 0.01g to 0.1g) in presence of direct sunlight. After the photocatalyticdecolorization, the extent of decolorization was estimated by recording absorbance of the effluent solution using UV-VIS spectrophotometer 169 in order to get the optimum catalyst dose. The experiments were repeated at different pH levels (from 2 to 11) for the 100ml of same standard effluent solution with the optimum catalyst dose.

3.3.7 Calculations

The percentage of decolourization was calculated by using the following equation,

$$D = [(A_0 - A_t)/A_0] \text{ X } 100$$

Where, $A_0$is the initial absorbance of dye solution and $A_t$is absorbance at time‘t’.

3.4 Chemicals and Instruments for Chemical Oxygen Demand (COD) analysis

Chemicals required for the COD analysis such as potassium dichromate, Sulphuric acid, ferrous ammonium sulphate (FAS), Mercuric Sulphate, 1, 10-phenanthroline monohydrate were obtained from Hi-Media chemicals, Mumbai. All chemicals are used as received.

Ferroin indicator was prepared by dissolving 1.485g of 1, 10-phenanthroline monohydrate and 695 mg of $FeSO_4.7H_2O$ in distilled water and made up to 100mL.

COD digester (The Timber Glassware Co., AmbalaCantt) was used to analyze the COD content of both initial and final stage of dye samples.

3.4.1 COD Experimental Procedure

COD of the samples were analyzed by Open Reflux method (Std. Analytical Procedure, May 1999). Add 20ml of dye solution (both initial dye sample and the degraded sample), 10ml 0.025N potassium dichromate solution and 30ml of concentrated sulphuric acid to the COD reflux tubes. Then place the tubes in COD digester for about 2 hours at 150^{o} C. Take out the tubes and dilute the digested samples to 150mL. Titrate the resultant sample against 0.01N FAS.

3.4.2 Calculations

The amount of COD was calculated by using the following equation,

$$\text{COD} = \frac{(Blanktitervalue - sampletitervalue) \times NormalityofFAS \times 8 \times 1000}{mLofsampletakenfordetermination}$$

3.5 Chemicals and Instruments for Total organic Carbon (TOC) analysis

- 0.1N potassium dichromate ($K_2Cr_20_7$): Dilute 49.04 g of potassium dichromate to 1 liter in a volumetric flask with distilled water.
- 0.5N ferrous sulphate ($FeS0_4.7H_20$): Dilute 140g of reagent grade of $FeS0_4.7H_20$ in distilled water, add 40mL of conc. Hp4, cool and dilute to 1 liter. Standardize by titrating against 10mL of 0.1N $K_2Cr_20_7$ solution.
- Barium diphenylamine sulphonate indicator solution: Dissolve 0.16g/100mL distilled water.
- Sulphuric acid
- Phosphoric acid

3.5.1 TOC Experimental Procedure

TOC of the samples were analyzed by Wet Oxidation method (Walkley and Black 1934).

3.5.1.1 Digestion

- Measure 0.1 to 2.0mL of samples into a 1000mL beaker and add 10mL of 1.0N $K_2Cr_20_7$ solution.
- Add 20mL of concentrated H_2SO_4 rapidly, directing stream into solution. This should be done in a fume hood since strong acid fumes are evolved.
- Immediately swirl vigorously by hand for 1minute and then let beaker stand on a sheet of asbestos for 30 minutes. If the solution has a green colour, add more $K_2Cr_20_7$ and H_2SO_4 keeping the same proportions 1:2.

3.5.1.2 Titration

- Add 500mL distilled water, 10mL H_3PO_4 and 1.0mL of barium diphenylamine sulphonate indicator solution.
- Stir with a magnetic stirrer and from a burette; add $FeSO_4$ rapidly until liquid in beaker is purple or blue, then more slowly until the color flashes to green.
- If end point is passed, add a small volume (0.5-lmL) of 1.0 N $K_2Cr_20_7$solution and complete the titration.
- Standardize the ferrous sulphate solution by titrating against 10mL of the 1N $K_2Cr_20_7$ solution.

3.5.2 Calculations

$$\% \text{ TOC} = \frac{(Blanktitervalue - Sampletitervalue) \times NormalityofFAS \times 0.003 \times 100}{Volumeofsampletaken}$$

Chapter 4

Results and Discussion

Chapter – 4

RESULTS AND DISCUSSION

4.1 X-Ray Diffraction and Scanning Electron Micrographs of Synthesized nanoparticles

4.1.1 ZnO Composite-I

The x-ray diffraction pattern of the synthesized ZnO composite-I was recorded. According to x-ray diffraction report, the crystallite size of the ZnO composite-I particles calculated by using Scherrer's formula was found between 18nm to 82nm. The scanning electron micrograph images of composite samples have shown the typical texture and morphology of ZnO composite-I. It also indicated the presence of some vestigial inorganic byproduct from the combustion media and starting material. The x-ray diffraction and scanning electron micrograph images of synthesized ZnO composite-I is as shown in Fig 18.

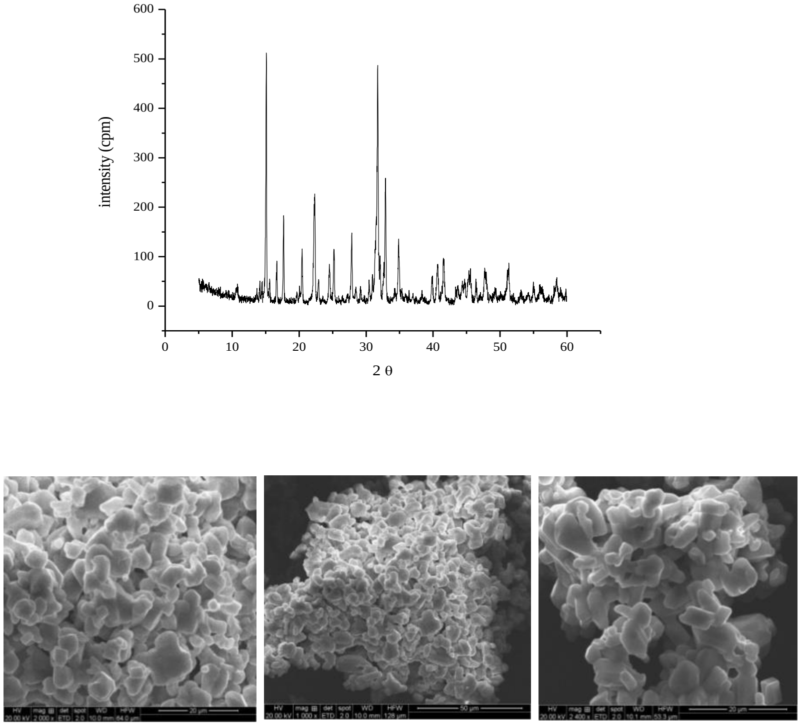


Fig. 18: X-ray diffraction and scanning electron micrograph images pattern of ZnO composite-I

4.1.2 ZnO Composite-II

The x-ray diffraction (Fig19) of the synthesized ZnO composite-II confirmed that, the obtained product under the current experimental conditions is a molecular composite containing photocatalystZnO. The scanning electron micrograph images of composite sample have shown the typical texture and morphology of ZnO composite-II. The x-ray diffraction results depicted the crystallite size of the ZnO composite-II particles were between 8 to 145nm respectively (DebyeScherrer’s formula). Hence, the new ZnO composite obtained in this chapter has been named as ZnO composite-II.

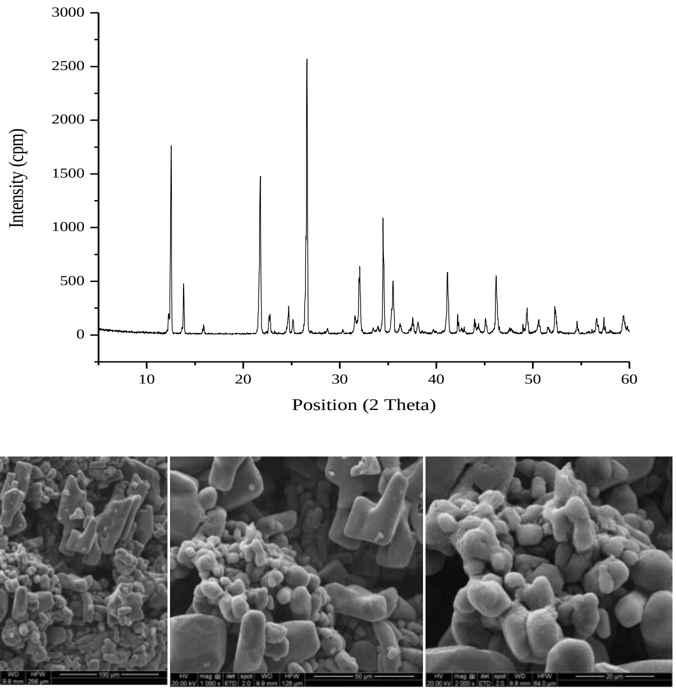


Fig. 19: X-ray diffraction spectra and scanning electron micrographs of ZnO composite-II

4.1.3 ZnO-I nanoparticles

The average crystallite size (D in nm) of synthesized ZnO-I particle was determined from x-ray diffraction pattern of the ZnO-I nano-powder. According to the Scherrer’s equation, i.e., D= k(λ/β cos θ) where k is a constant equal to 0.89, λ the X-ray wavelength equal to 0.154nm, β the full width at half maximum and θ the half diffraction angle. The x-ray diffraction studies depicted that synthesized ZnO precursor was in its purest form. The average crystallite size of ZnO-I nanoparticles was in the range of 31nm to 52nm.The scanning electron micrograph images of freshly synthesized compound has shown the morphology and texture of ZnO-I nanoparticles (Fig 20).

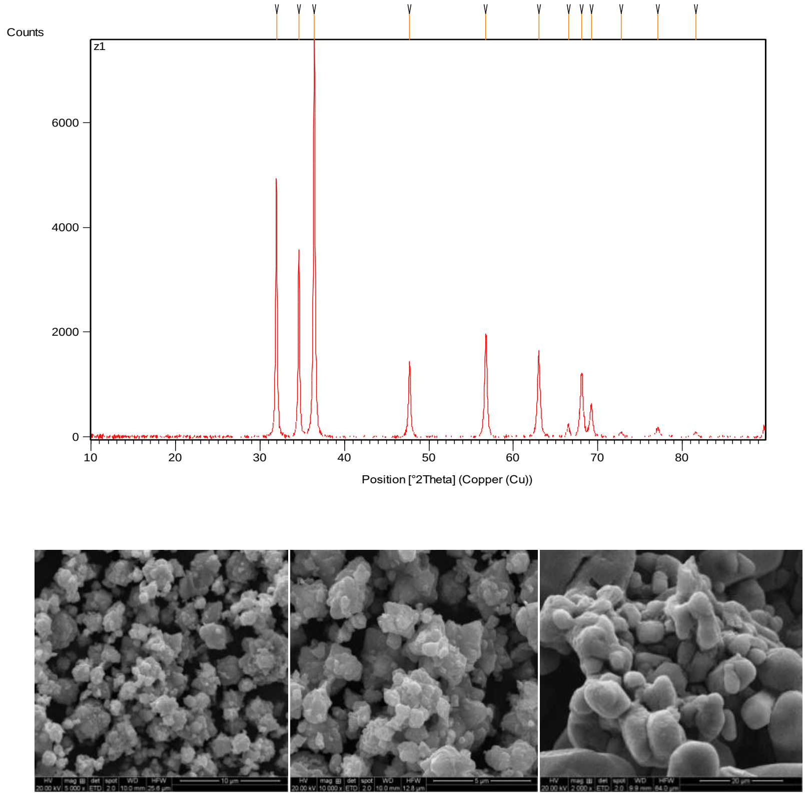


Fig. 20: X-ray diffraction pattern Scanning electron micrograph images of synthesized ZnO-I particles

4.1.4 $CaAl_2O_4$II

The XRD was performed by powder X-ray diffraction (Rigakudiffractrometer) using Cu-Kα radiation (1.5406 Å) in a θ-2θ configuration. The output from XRD analysis of the prepared Calcium aluminate nanoparticle sample yields a plot of intensity versus angle of diffraction as shown in Fig 21. Thus various reflections of Calcium aluminate nanoparticles are observed which indicate that the product is amorphous. In addition, the particle size is very small according to the Debye Scherer’s$D=K\lambda/\beta\cos\theta$, where K is the Scherrer’sconstant, λ the X-ray wavelength, β is the peak width at half-maximum and θ is the Bragg diffraction angle.. The average crystallite size D is 42nm. The SEM images of prepared Calcium aluminate nanoparticles have shown a typical texture and morphology. It shows both the mixtures of crystal and plate like morphology, which are placed at irregular intervals. The Fig21 has shown evenly distributed amorphous nature of the Calcium aluminate in the SEM images.

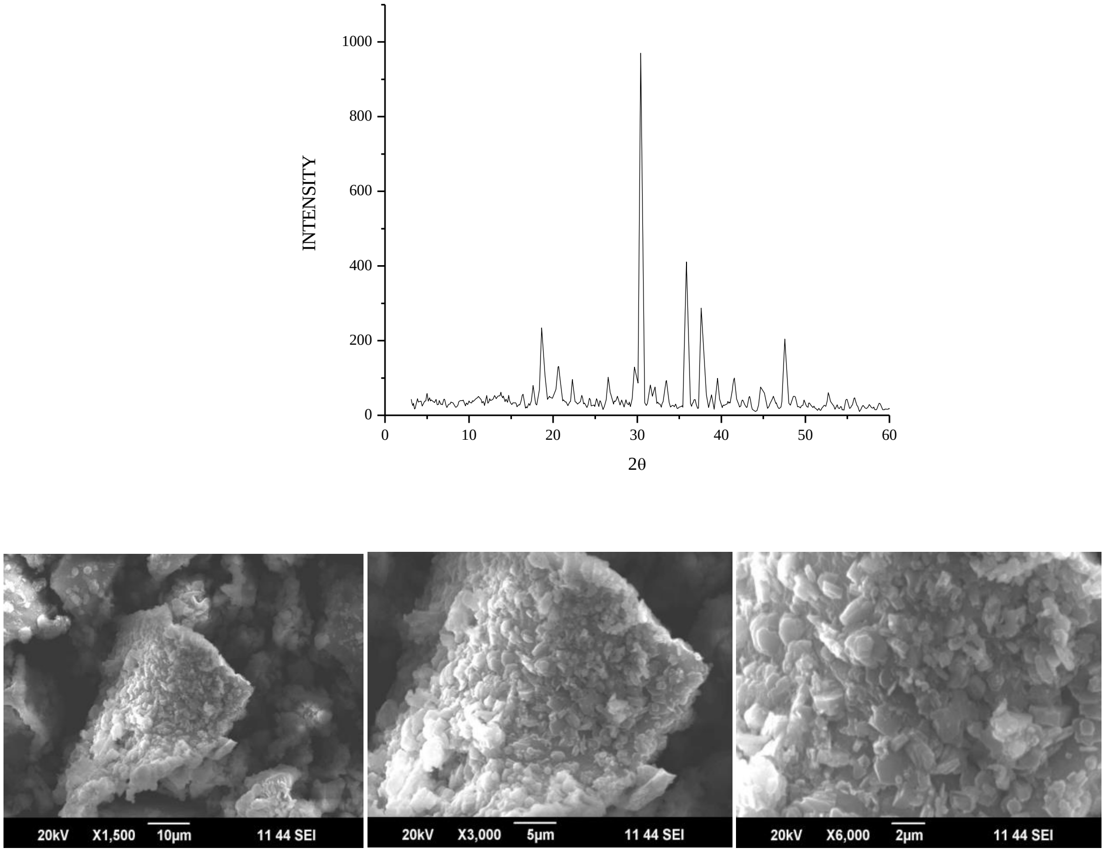


Fig. 21: X-ray diffraction and SEM photograph of $CaAl_2O_4$

4.1.5 $CaAl_2O_4$ I

XRD analysis was carried out on fresh sample to assess the purity of the expected phasesand the degree of crystallization, i.e., size, composition and crystal structure.XRDwas performed by Rigakudiffractometerusing Cu-K$_\alpha$ radiation (1.5406Å) in a θ-2θ configuration. The XRD pattern of the prepared CaAl$_2$O$_4$nanoparticle was as shown in Fig22. According to the Debye–Scherrer'sformula D=Kλ/βcosθ, where K is the Scherrer's constant, λ the X-ray wavelength, β is the peak width at half-maximum and θ is the Bragg diffraction angle. The average crystallite size D is 38.55nm.

The SEM images of prepared CaAl$_2$O$_4$nanoparticle have shown the typical texture and morphology. SEM images obtained were depicted that the synthesized nanoparticles were crystal like structures.

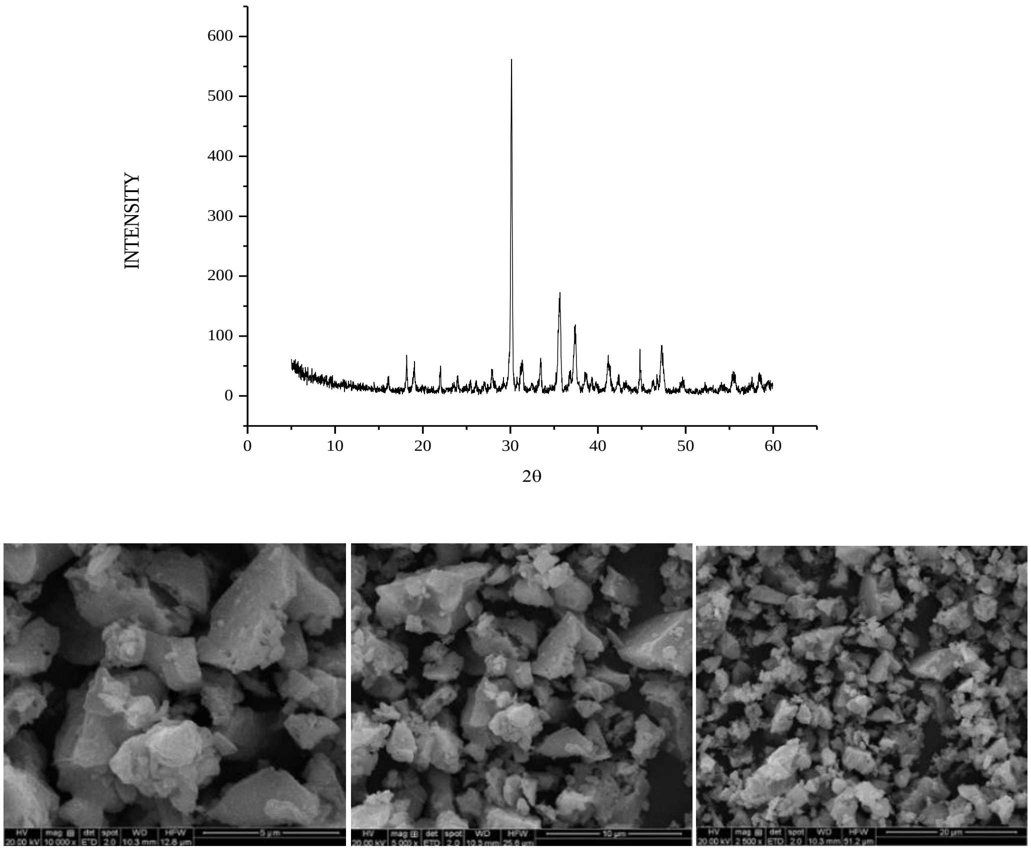
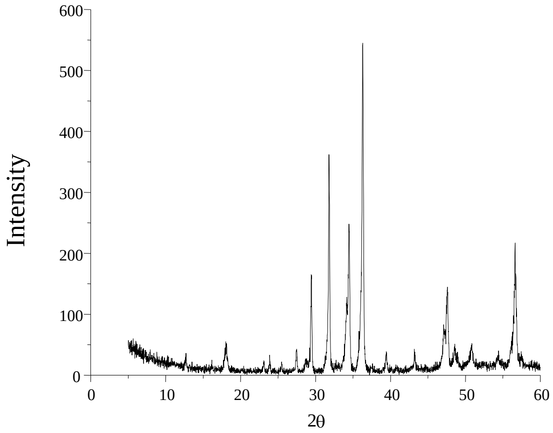


Fig. 22: X-ray diffraction and SEM micrographs of CaAl$_2$O$_4$ nanoparticle

4.1.6 $CaZnO_2$ II

XRD analysis was performed on fresh sample, to assess the presence and purity of the expected phases and to evaluate their degree of crystallization. XRD is normally used to obtain the structural parameters of the materials, such as size, composition and crystal structure. In order to know the crystal properties of the prepared Calcium zincate ($CaZnO_2$) nanoparticle, the XRD was performed by powder X-ray diffraction (Rigakudiffractometer) using Cu-Kα radiation (1.5406 Å) in a θ-2θ configuration. The output from XRD analysis of the prepared $CaZnO_2$ nanoparticle sample yields a plot of intensity versus angle of diffraction as shown in Fig 23. Thus various reflections of $CaZnO_2$ are observed which indicate that the product was well crystallized. Further, no peaks of impurity were observed, confirming that the obtained Calcium zincate was in its purest form. In addition, the peak was widened implying that the particle size was very small according to the Debye–Scherrer's formula $D = K\lambda/(\beta\cos\theta)$, where K is the Scherrer's constant, λ the X-ray wavelength, β is the full width of half-maximum, and θ is the Bragg diffraction angle calculated using the Debye–Scherrer's formula. The average crystallite size D is 43.59nm.



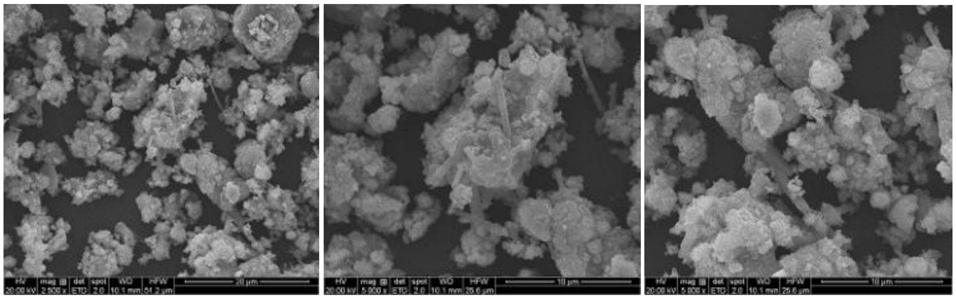


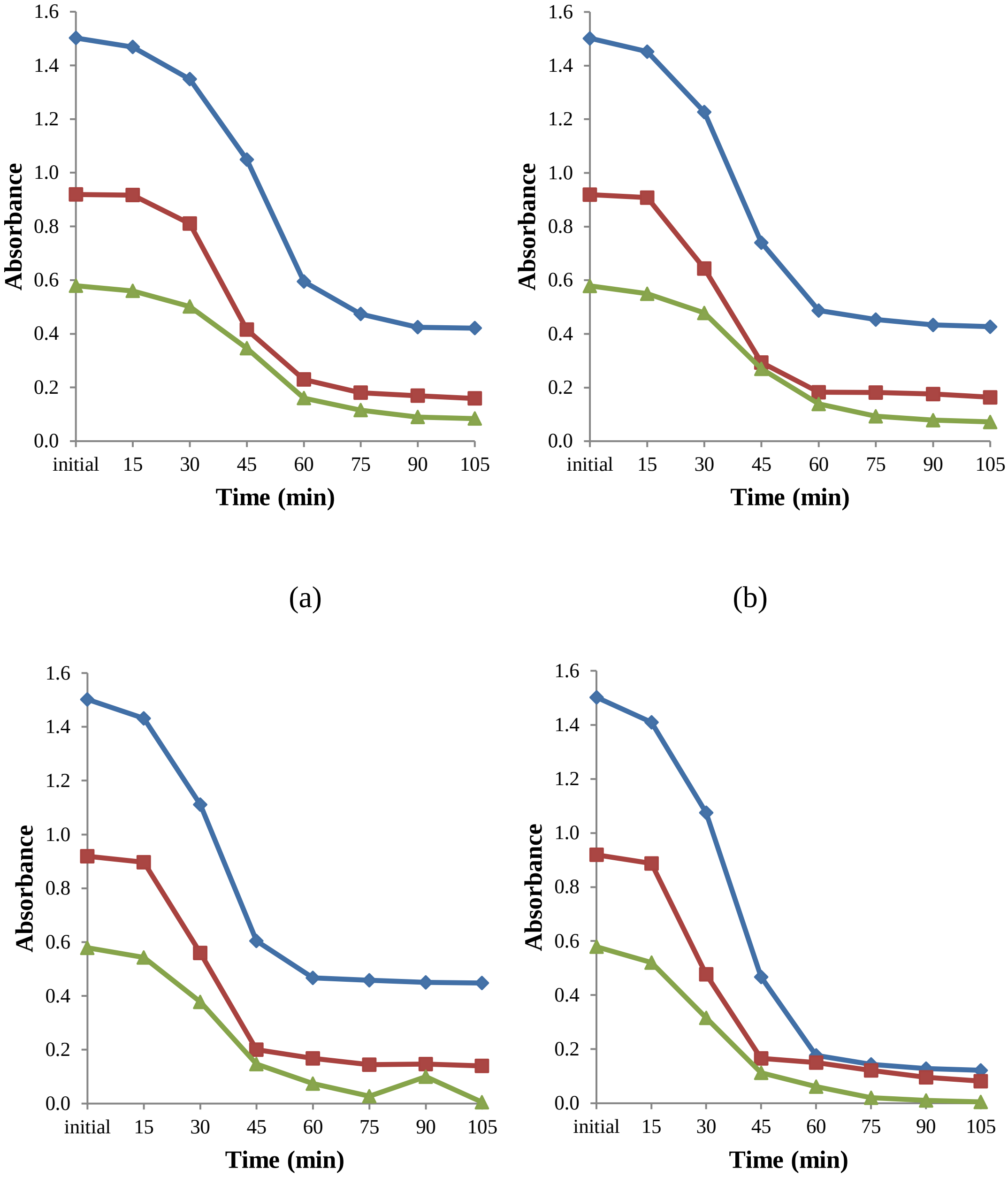
Fig. 23: X-ray diffraction and scanning electron micrograph images pattern of *$CaZnO_2$ Acetamide*

4.2 Photocatalytic activity of ZnO Composite I

4.2.1 Effect of Initial Dye Concentration

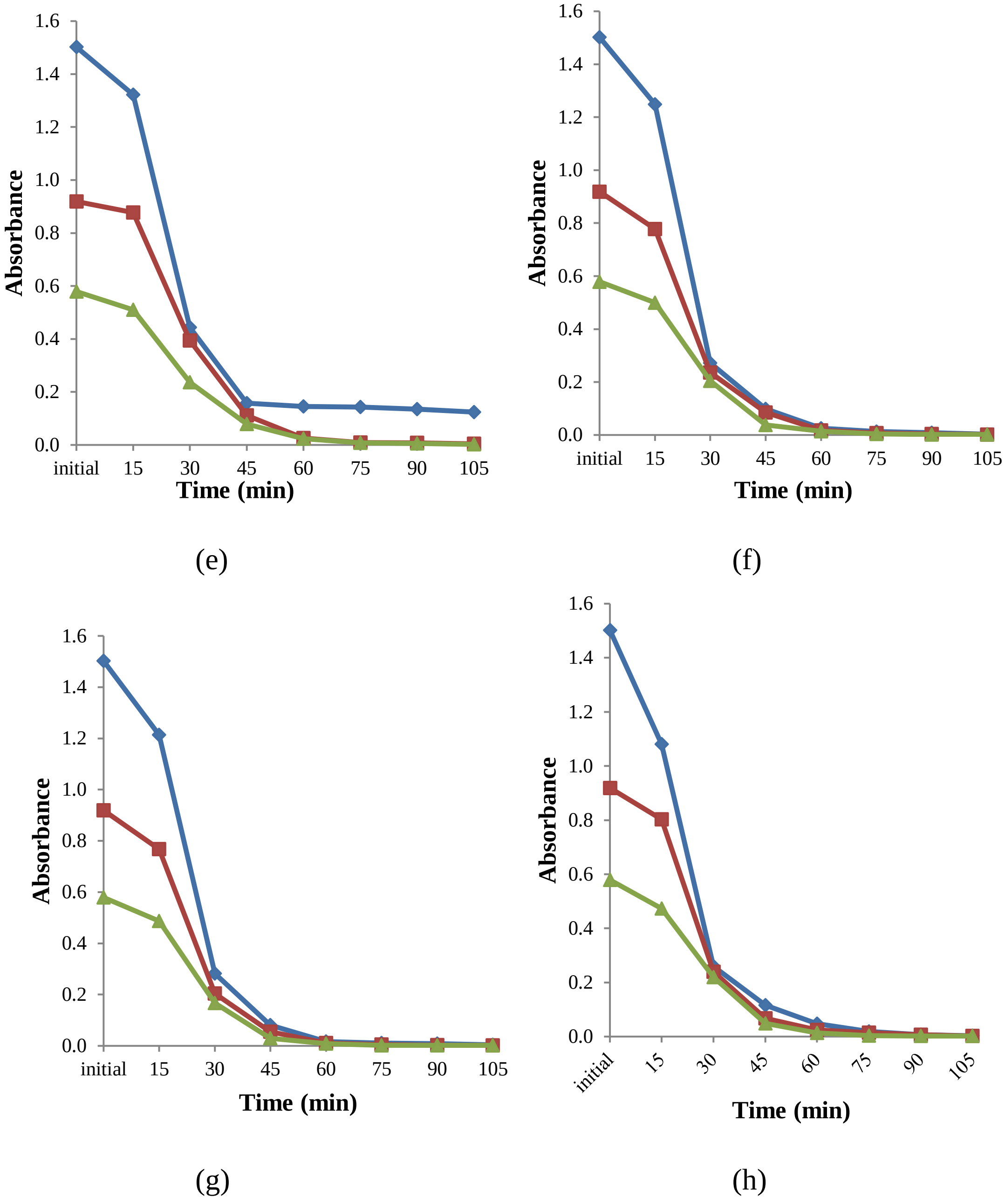
The effect of dye concentrations were investigated by varying the initial standard concentration (from 50ppm to 100ppm) and results obtained are shown in fig 24. Fig 24(a), 24 (b), 24(c), 24(d), 24(e), 24(f), 24(g) depicts the photocatalyticdecolourization efficiency of Coralene Red F3BS dye at ZnO composite-I dosage of 0.05g, 0.1g, 0.15g, 0.2g, 0.25g, 0.3g, 0.35g and 0.4g respectively, at 50ppm, 75ppm and 100ppm dye concentrations.

The maximum decolourization recorded after 105minutes of irradiation for 50ppm, 75ppm and 100ppm dye concentrations were 71.97%, 82.69%, 85.49% respectively for catalyst dosage of 0.05g/100ml; 71.57%, 82.15%, 87.56% respectively for catalyst dosage of 0.1g/100ml; 70.17%, 84.76%, 99.13% respectively for catalyst dosage of 0.15g/100ml; 91.87%, 91.07%, 99.13% respectively for catalyst dosage of 0.2g/100ml; 91.74%, 99.56%, 99.65% respectively for catalyst dosage of 0.25g/100ml; 99.80%, 99.78%, 99.65% respectively for catalyst dosage of 0.3g/100ml; 99.73%, 99.78%, 99.65% respectively for catalyst dosage of 0.35g/100ml; 99.80%, 99.78%, 99.65% respectively for catalyst dosage of 0.4g/100ml. It is observed that, the rate of decolourization of Coralene Red F3BS dye was inversely affected by the concentration of dye, i.e., higher the dye concentration decreases the rate of decolourization process. The experimental results depicted that, the rate of photo decolourization was slow at 75ppm and 100ppm dye solutions in comparison with decolourization in 50ppm dye solution.



(a) (b)

(c) (d)



(e) (f)

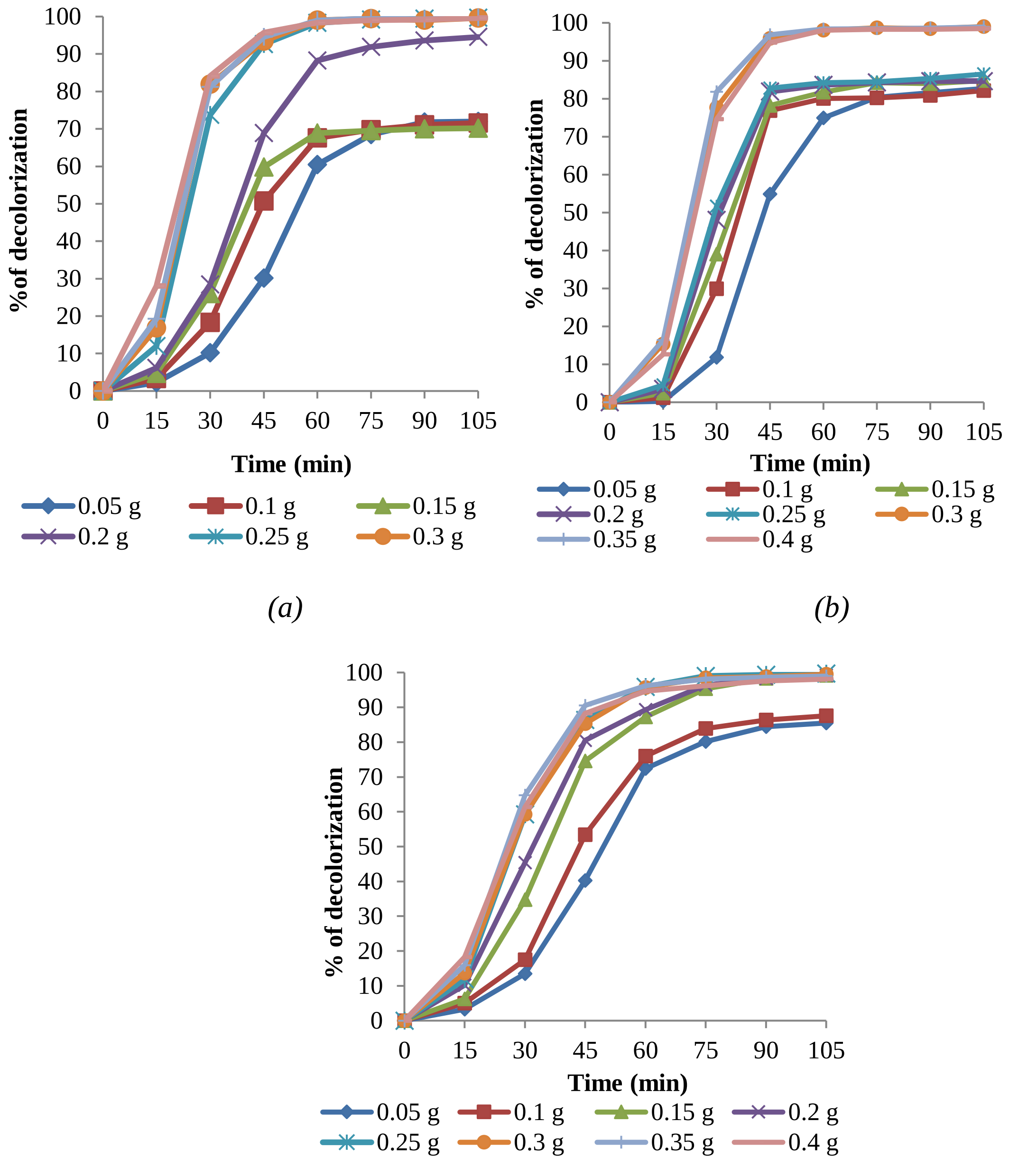
(g) (h)

Fig. 24: Effect of initial dye concentration (50ppm, 75ppm and 100ppm) on the decolourization of Coralene Red F3BS dye solution at pH 7.0 at differet catalyst load: (a) 0.05g, (b) 0.1g, (c) 0.15g, (d) 0.2g, (e) 0.25g, (f) 0.3g, (g) 0.35g and (h) 0.4g

4.2.2 Effect of Catalyst Loading

To determine the effect of the catalyst loading, a series of experiments were carried out by varying the amount of catalyst (from 0.05g/100ml to 0.4g/100ml) and decolourization is depicted in figure 25(a), 25(b), and 25(c). Decolourization efficiency was maximum at the high catalyst dosage from 0.25g/100ml to 0.4g/100ml when compared to lower loading levels from 0.05g/100ml to 2.0g/100ml.

The initial decolourization rate was very fast and decreases exponentially with time at all catalyst dosages for the prepared standard dye solutions. In the first rapid phase (45min), 40-80% decolourization was recorded for lower dosage (0.05g/100ml to 0.2g/100ml) of catalysts and 85-90% decolourization observed at higher dosages (0.25g/100ml to 0.4g/100ml). In the second phase of the reaction (from 45min to 105min), decolourization was increased by 19-40% and 12-14% at lower catalyst dosages and higher catalyst dosages respectively (Fig 25). The recorded experimental data depicted that, in all dye concentrations (50ppm, 75ppm and 100ppm) at pH 7.0 condition, catalyst dosage of 0.3g/100ml was found to be successful in achieving highest decolourization of 99.48%, 99.02% and 99.60% respectively.



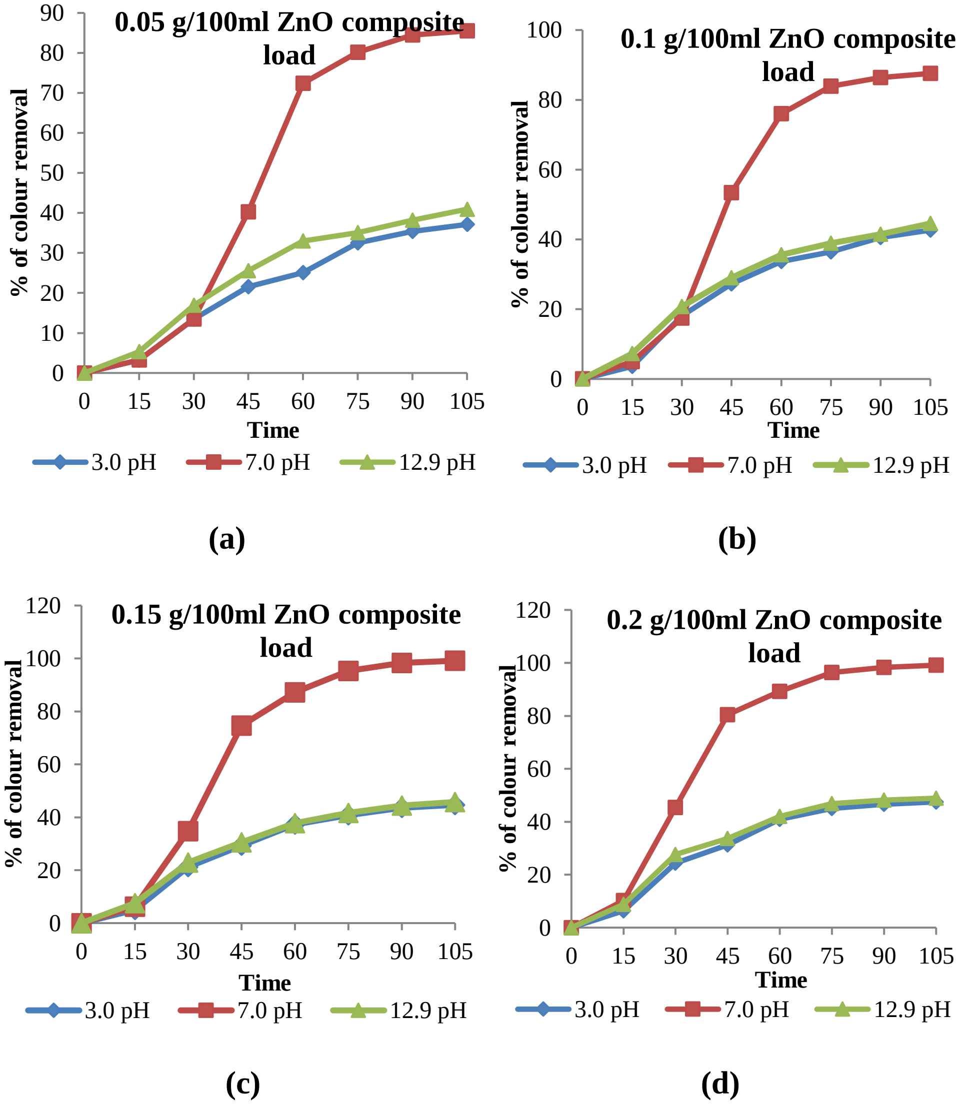
(a) *(b)*

(c)

Fig. 25: Effects of catalyst load on percentage of decolourization at dye concentrations (a) 50ppm, (b) 75ppm and (c) 100ppm with respect to time and catalyst load.

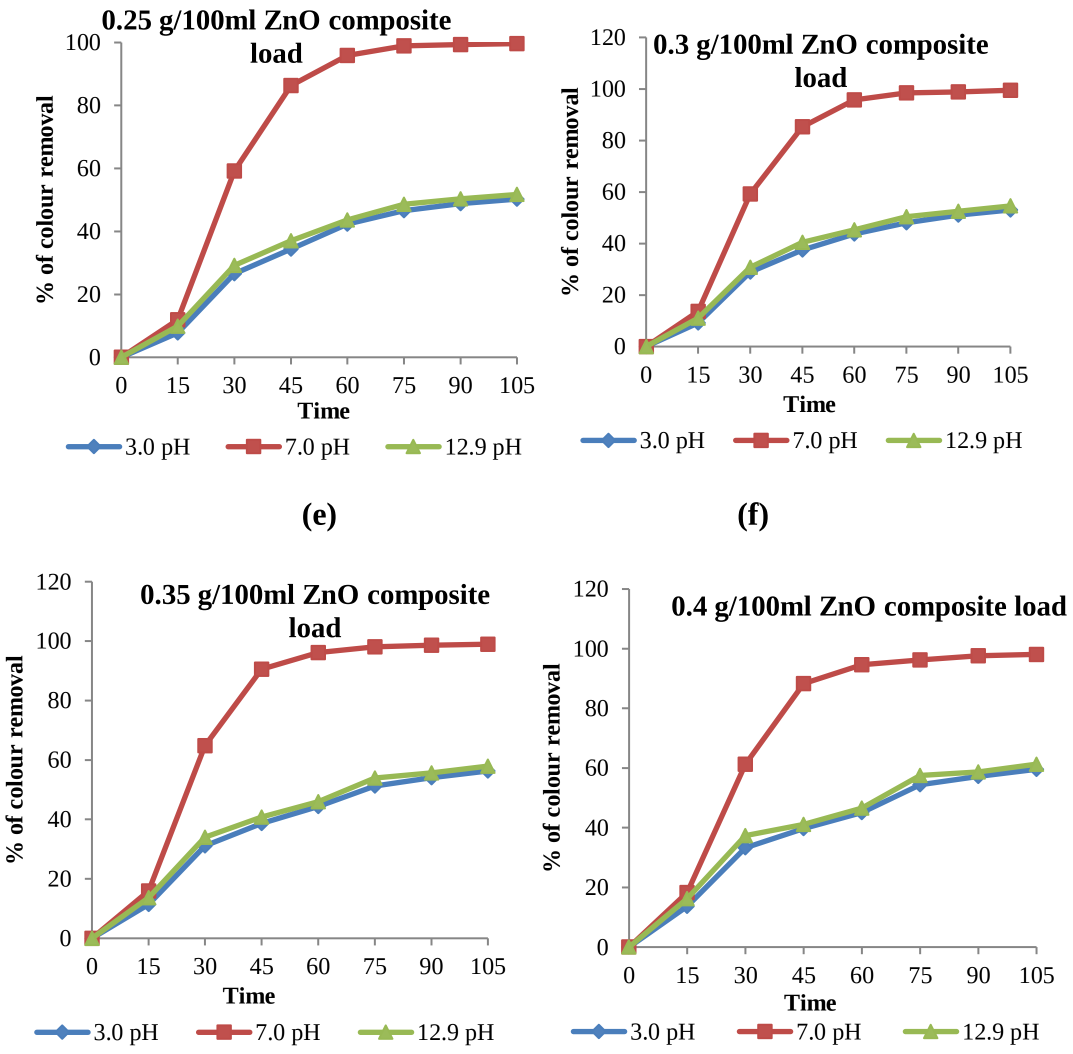
4.2.3 Effect of pH

The decolourization efficiency of Coralene Red F3BS by synthesized ZnO composite-I at different pH level has been analyzed in presence of solar light (Fig 26). It was found that, the decolourization of dye was negatively pH sensitive, i.e., at pH 12.9 (alkaline condition) and 3.0 (acidic condition) the decolourization was less (61.31 % and 59.59 % respectively) whereas at pH 7.0 (normal) the percentage of decolourization was 99.65 % which was too fast in 105 minutes for all the standard concentrations of dye solutions.



(a) (b)

(c) (d)



(e) (f)

(g) (h)

Fig. 26: Effect of pH of dye solution on percentage of decolourization of 50ppm Corelene Red F3BS dye solution at differet catalyst load; 0.05g, 0.1g, 0.15g, 0.2g, 0.25g, 0.3g, 0.35g and 0.4g

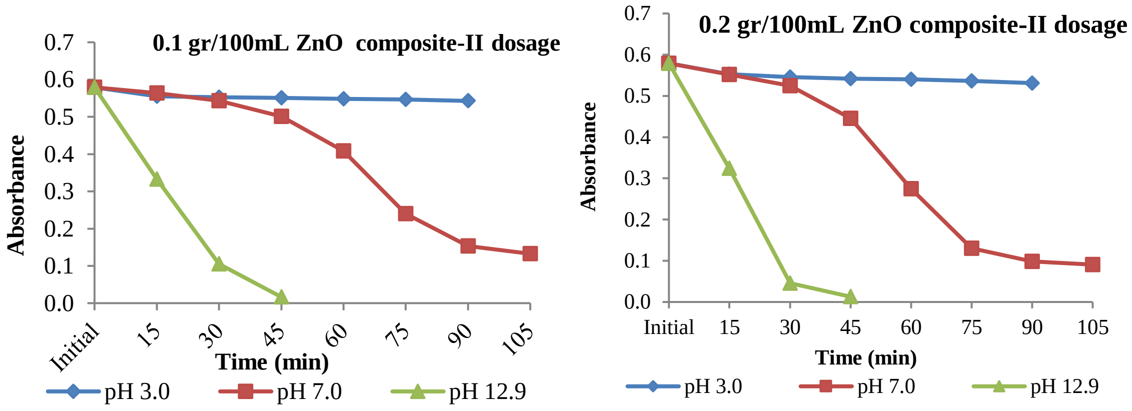
4.3 Photocatalytic activity of ZnO Composite II

4.3.1 Effect of pH on Degradation of Coralene Red F3BS

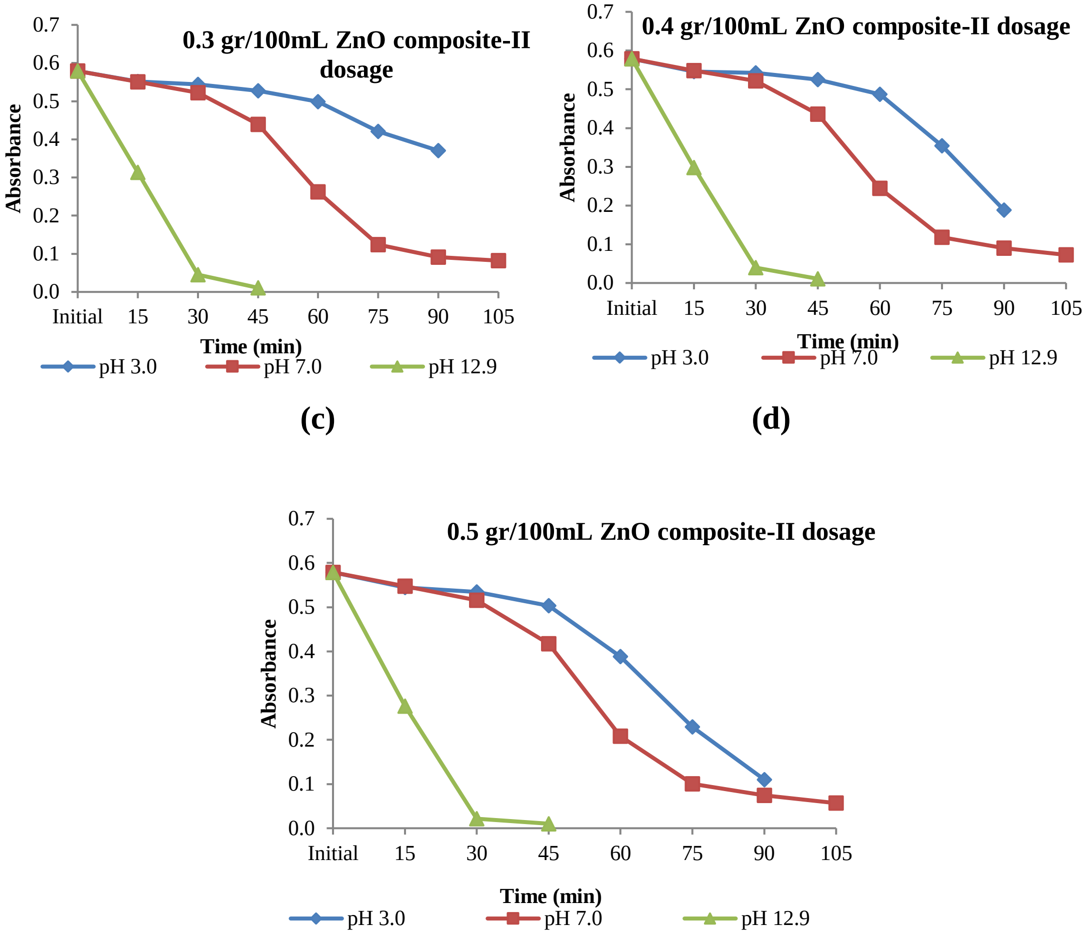
The decolourization of Coralene Red F3BS by synthesized ZnO composite-II at different pH levels with respect to amount of catalyst load is shown in Fig 27. The pH of dye solution (50ppm) was adjusted with dilute NaOH and HCl solutions. It was found that, the decolourization of selected dye solution was highly pH sensitive and achieves the maximum colour removal of 98% at pH 12.0 within 45min. At pH 3.0 (acidic condition), the decolourization was 10-15 times less at lower composite dosages and 1-2 times at higher dosages than that of pH 12.0 condition at maximum time interval of 105minutes.

The possible explanation for dependence of decolourization on pH of dye solution is that, as the pH increases the catalyst represents positive charge and thus promotes the adsorption of dye since dye contains negative sulphonate group. An additional explanation for the pH effects can be related to specifications of selected model azo dye, i.e., protonation or deprotonation of the dye can change its adsorption characteristics and redox activity.

Further, dependence of photocatalytic adsorption on pH is expected to rely on different reaction mechanism, such as hydroxyl radical attack, direct oxidation by positive hole and direct reduction by the electron in the conduction band can contribute to colour removal. All these reactions depend on nature of dye and pH of dye solution. In this study, the prepared ZnO composite-II was found to have optimal and rapid photocatalytic activity at pH 12.0 under the given experimental condition.



(a) **(b)**



(c)

(d)

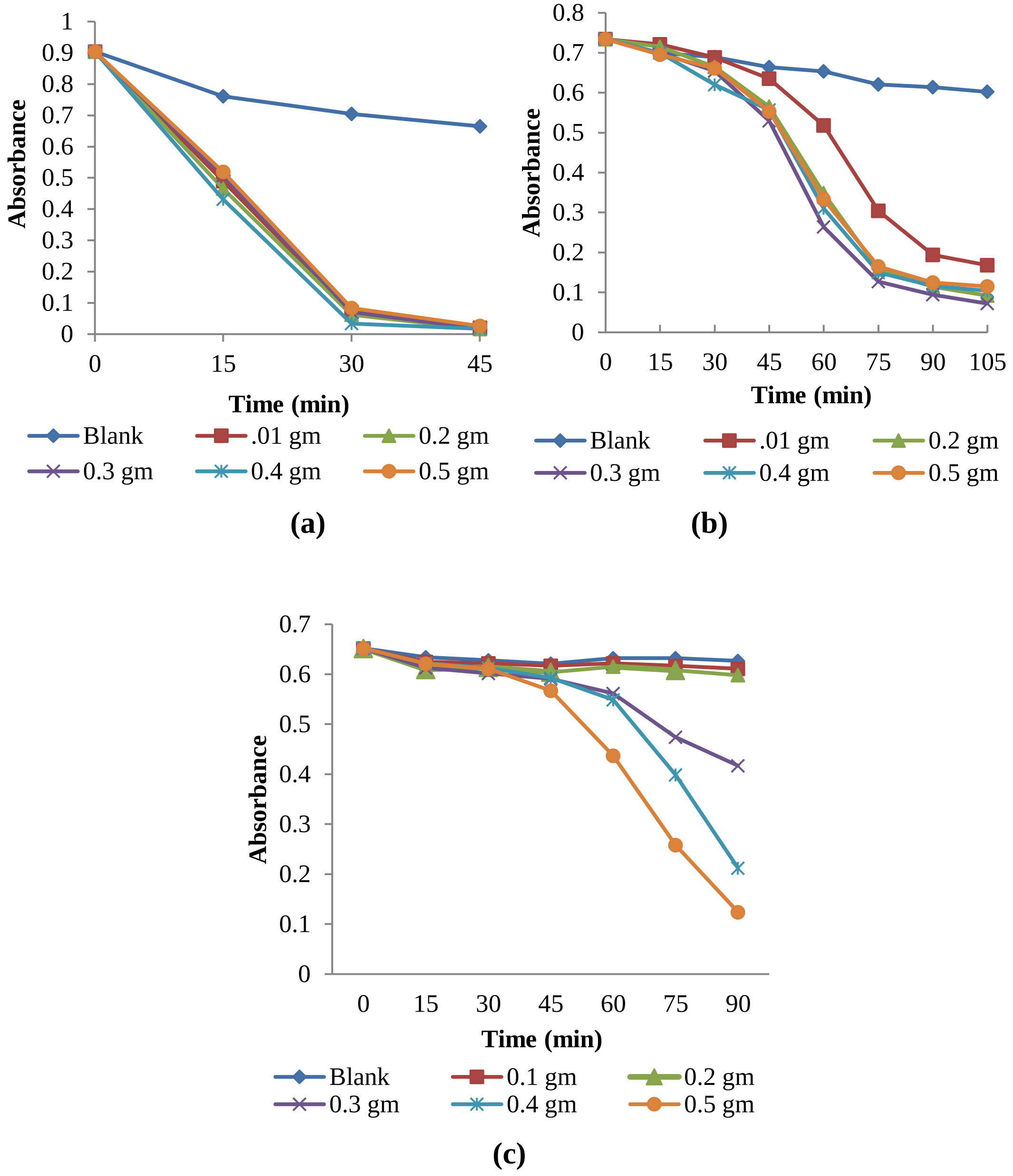
(e)

Fig. 27: Effect of pH of dye solution on percentage of decolourisation of 50ppm Corelene Red F3BS dye solution at differet catalyst load; (a) 0.1g, (b) 0.2g, (c) 0.3g, (d) 0.4gand (e) 0.5g

4.3.2 Effect of Catalyst Loading on Degradation of Coralene Red F3BS

To determine the effect of the catalyst loading, a series of experiments were carried out by varying the amount of catalyst from 0.1 to 0.5g/100ml. The decolourization is depicted in fig 28(a), 28(b) and 28(c). Maximum decolourization was recorded at the higher catalyst dosages of about 0.3 to 0.5g/100ml.

This extreme point results from the conflicting effects of catalyst load on the photocatalytic process; at lower loading levels, such as 0.05g/100ml, photonic adsorption controls the reaction extent due to the limited catalyst surface area, and an increase in catalyst loading greatly enhances the process performance. The initial decolourization rate was very fast and decreases exponentially with time. In contrast, at lower dosage the colour removal proceeds with uniform rate and reaches up to 73%.



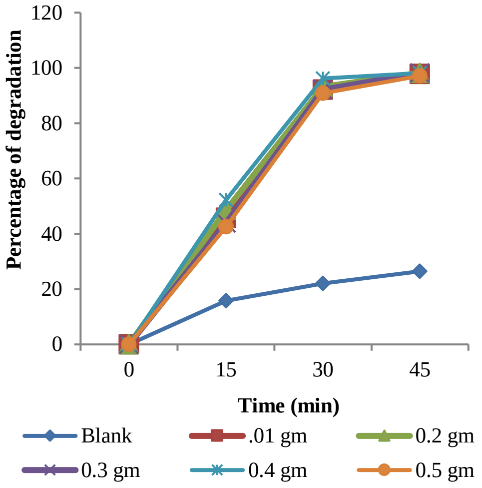
(a) **(b)**

(c)

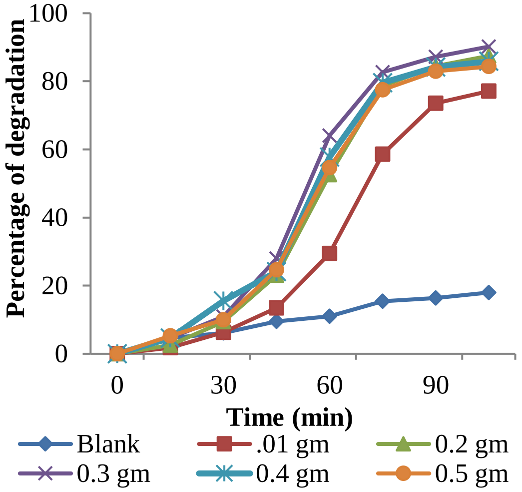
Fig. 28: Effect of catalyst load on the decolourization of 50ppm Coralene Red F3BS dye solution at different dosages at pH levels [(a) at pH 12.0, (b) at pH 7.0 and (c) at pH 3.0]

4.3.3 Effect of Reaction Time

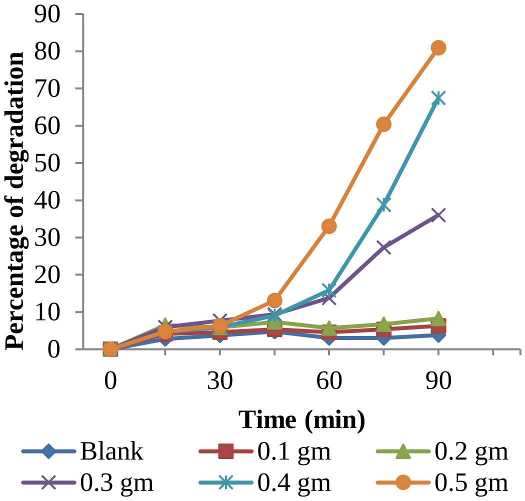
It can be seen that, the dye removal process using prepared ZnO composite-II as semiconductor photocatalyst was found to proceed with two phases at pH 3.0 and 7.0 [Fig 29(a) and Fig 29(c)]. At maximum catalyst dosage (0.5g/100ml), the first rapid phase was for the first 45min and found to comprise 13% and 27% adsorption respectively as shown in Fig 29**.** The removal thereafter attains saturation in 105 and 90min reaction time and finally increases to reach 87% and 80% adsorption (removal) at pH 3 and 7 respectively. The first rapid adsorption phase, i.e., 0-45min, at pH 3 and 7 respectively, may be due to an increased number of vacant sites available at the initial stage and as a result, the decrease in the concentration of dye in solution. As time proceeds, due to adsorption of dye molecules on vacant sites previously available adsorbent surface decreases and thus virtually saturation stage was perceived. At pH 12.0 [Fig 29(a)], reaction rate was at uniform speed even in initial 30minutes and 90% of decolourization in an average for all catalyst loads and attains the optimum saturation of 98% after 45min.



(a)



(b)



(c)

Fig. 29: Percentage of decolourization of Coralene Red F3BS dye solution (50 ppm) at different pH levels [(a) at pH 12.0, (b) at pH 7.0 and (c) at pH 3.0]

4.4 Photocatalytic activity of ZnO I nanoparticles

4.4.1 *Effect of Catalyst Load*

The effect of ZnO-I nanoparticle concentration on decolourization rate was investigated by varying its amount from 0 to 0.25g/100mL, keeping all other parameters identical (i.e., pH 7 and dye concentration 50ppm) and the results are presented in Fig 30.

The increase in the amount of catalyst increased the number of active sites on the photocatalyst surface, which in turn, increased the number of hydroxyl radicals. Further, it would hinder the transmission of UV light/solar light in the reaction volume can consequently decrease the decolourization rate. In the present study, the optimal catalyst concentration was 0.25g/L at pH 7 in presence of both UV and solar irradiations by achieving 79.05% and 99.17% respectively.

However the decolourization in the initial stages at lower catalyst dosages was faster compared to higher catalyst concentrations due to decrease in light penetration which hinders the creation of active species.

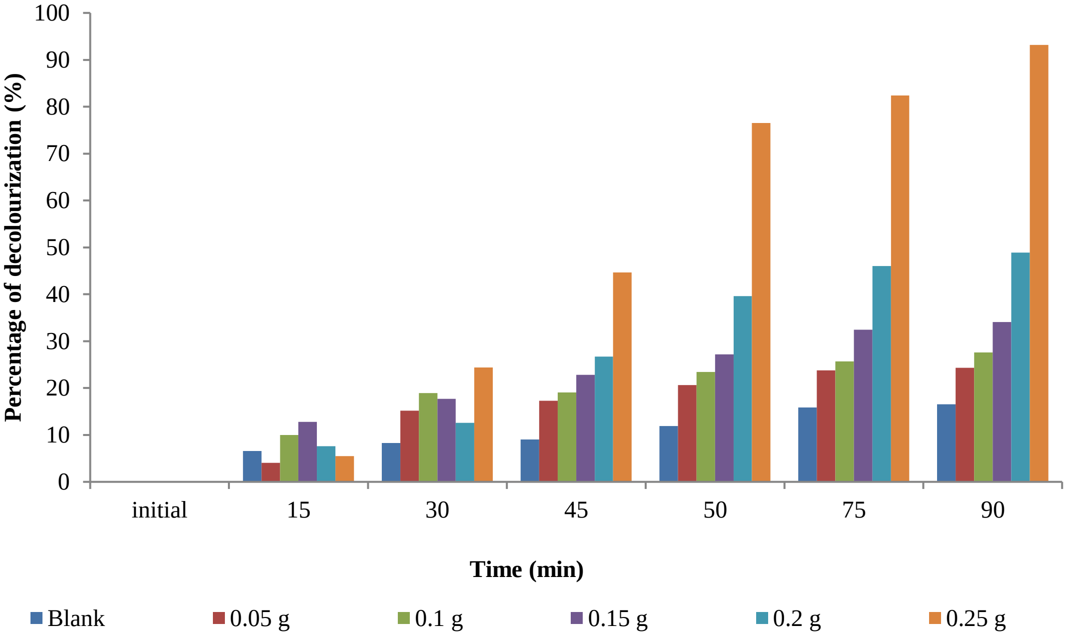


Fig. 30: Effect of ZnO-I catalyst dosage on the photodecolourization efficiency of Coralene Red F3BS dye under solar irradiation time of 90minutes. Dye concentration: 50ppm; pH 7.0

4.4.2 Effect of pH

To study the influence of dye solution pH on the decolourization rate, the experiments were conducted at different pH levels in the range of pH 3 to pH 12 keeping all other parameters constant (i.e., catalyst dosage 0.25g/100ml and 50ppm dye concentration). It has been observed that, decolourization was increasing with the increase in the pH of the dye solution in both UV and solar irradiations (Fig 31).

At pH 3, pH 7 and pH 12 the decolourization recorded after 90 min was 84.42%, 93.17% and 99.65% in presence of solar irradiation respectively. On the other hand, only 54.91%, 64.92% and 79.05% of decolourization was achieved in case of UV irradiation at pH 3, pH 7 and pH 12 respectively. This is because of the amphoteric property of ZnO-I semiconductor which influences the surface-charge property of the photocatalyst. In addition, pH of the dye solution influences the generation of hydroxyl radicals which in turn increases the percentage of decolourization.

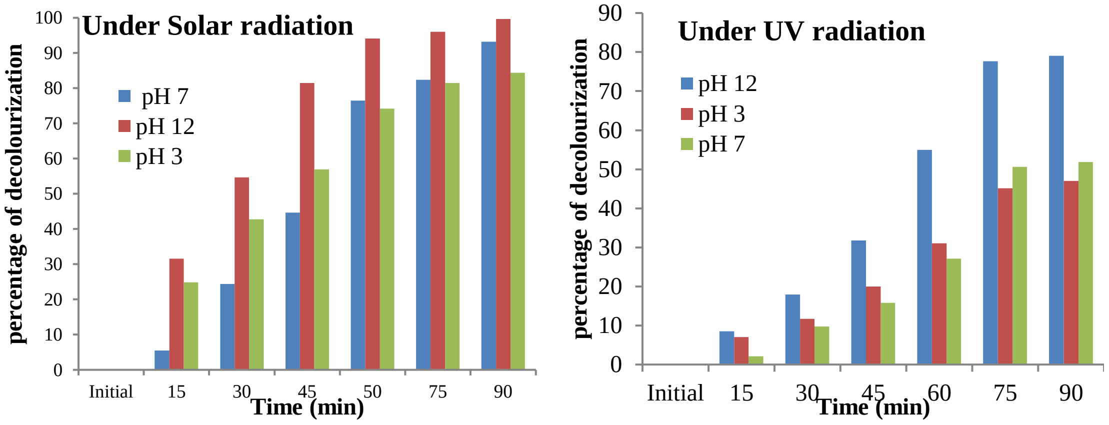


Fig. 31: Effect of pH on photocatalytic degradation of Coralene Red F3BS in presence of Solar and UV irradiation time of 90minutes. Dye concentration: 50ppm; Catalyst load: 0.25g/100ml.

4.4.3 Effect of Dye Concentration

The effect of initial dye concentration on the photocatalyticdecolourization efficiency using synthesized zinc oxide nanoparticles was investigated in the range 50-100mg/L dye concentration at pH 7 and catalyst dosage of 0.25g/100ml for 90min. The obtained results are shown in Fig 32.

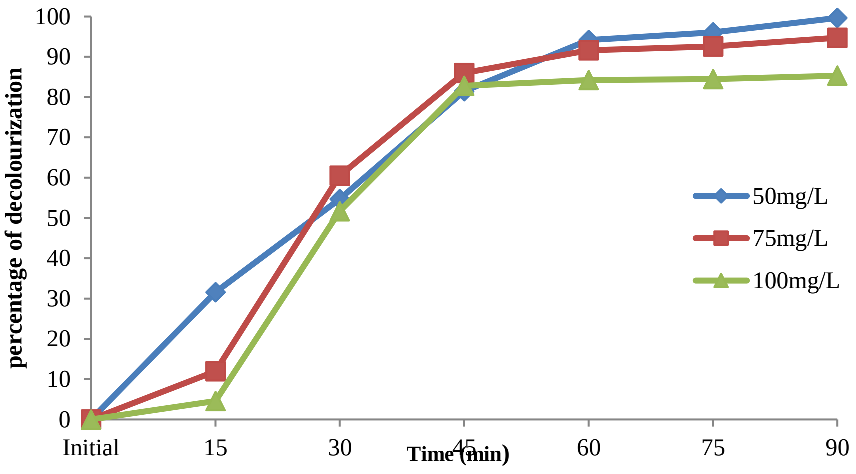
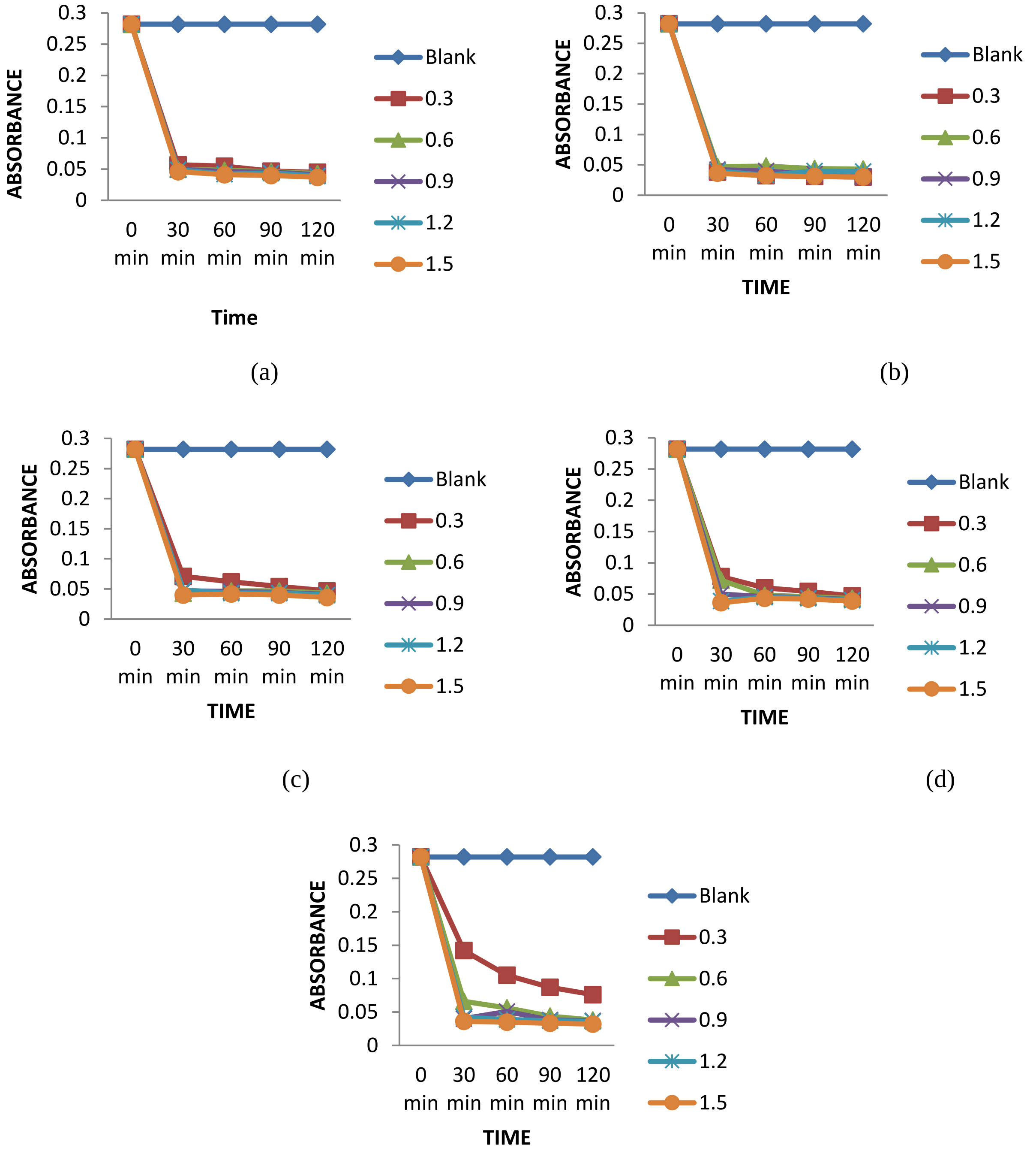


Fig. 32: Effect of initial dye concentration on photocatalytic degradation efficiency of Coralene Red F3BS. Catalyst concentration: 0.25/100ml; pH 12

4.5 Photocatalytic activity of Calcium aluminate II

4.5.1 Effect of Catalyst Load

The catalytic dosage was varied from 300mg, 600mg, 900mg, 1200mg and 1500mg for 30 (mg/L) of Coralene Dark Red 2B dye mg/L in the neutral condition. For the first 30min, it was 79.78% for minimum dosage and 83.68% for the maximum dosage decolorized, after 120 min it was degraded up to 84.04% for minimum dosage and 86.87% for maximum dosage. Decolorization efficiency was same and maximum for all the catalyst dosages of 300mg, 600 mg, 900mg, 1200mg and 1500mg/300ml. The catalyst loading levels in photonic adsorption has helped the reaction to a great extent, and the catalyst loading has significantly enhanced the degradation performance. In all the dosages the rate of decolorization is fast in the first 30min and slightly slow in the later one and half an hour or the initial decolorization rate is very fast and decreases exponentially with time (Fig 33).



(a) (b)

(c) (d)

Fig. 33: Effect of catalyst load on the decolorizationof Coralenedarkred 2B dyeatconcentration 30mg/L, On Neutral, pH2, pH5, pH9, and pH12.

4.5.2 Effect of pH

The rate of degradation was found to be less in neutral condition as compared to other pH ranges with the degradation of approximately 87% in 120 minutes. When the pH increased to 9 and 12, the rate of degradation was increased with the degradation of approximately 90% in 120 minutes. Also when pH decreased to pH 2 and 5, the degradation rate was high. Hence it is concluded that the degradation in acidic and basic medium is higher than that of neutral medium. The increase in rate of photocatalytic degradation may be due to the more availability of OH^- ions. In pH range between 2 to 12, more OH- radicals may be generated due to electronic excitation in catalyst. Formation of these hydroxyl radicals is responsible for the high photocatalytic degradation (Fig 34).

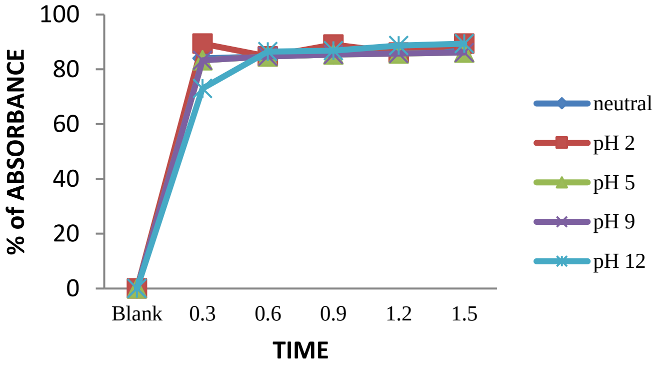


Fig. 34: Effect of pH on decolorization efficiency of $CaAl_2O_4$ against Coralene dark red 2B dye

4.6 Photocatalytic activity of Calcium aluminate I

4.6.1 Coralene Violet 3R Azo dye

4.6.1.1 Optimum Catalyst Dose

To study the effect of catalyst load, calcium aluminate dosage was varied from 0.01g to 0.1g for 30 mg/L of Coralene Violet 3R dye solution keeping all other parameters constant and the results are presented in Fig 35. On exposure of reaction volume to sunlight after adding the catalyst, the dye color started to fade showing the visible signs of decolorization. The highest degradation (85.52%) was recorded for 0.3g/100ml of catalyst which was sufficient to degrade the Coralene Violet 3R dye solution within 120min.

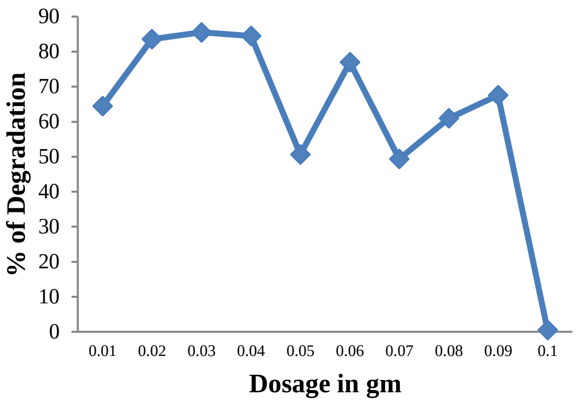


Fig. 35: Effect of catalyst load on the decolourization of Coralene Violet 3R dye at concentration 30mg/L, at pH 7 with respect to time interval of 120minutes

4.6.1.2 Optimum pH

The photocatalytic experiments were conducted at different pH from 2 to 11 by keeping the catalyst dose constant (0.3g/100ml) for 30 mg/L of Coralene violet 3R dye solution. pH of the solution was adjusted by using 0.2 N HCl/NaOH solution and the results are presented in Fig 36. On exposure of reaction volume to sunlight, the highest degradation (87.93%) was recorded at pH 3 which was optimum to degrade the Coralene Violet 3R dye solution within 120minutes.

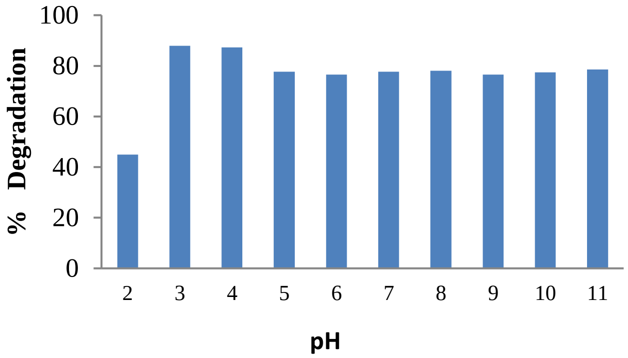


Fig. 36: Effect of optimum catalyst dose on the decolourization of Coralene Violet 3R dye at concentration 30mg/L, at different pH levels with respect to time interval of 120minutes

4.6.1.3 Degradation efficiency of $CaAl_2O_4$ at different dye concentrations

To study the effect of initial dye concentration on the photocatalytic efficiency of $CaAl_2O_4$ nanoparticle, the initial dye concentrations were varied from 30ppm to 60ppm, 90ppm and 120ppm and experiments were conducted at optimum catalyst dosage and pH. The highest degradation (92.98%) was recorded for the concentration of 30ppm dye solution. The experiment result depicts the decreased degradation rate with increase in the concentration of dye solution.

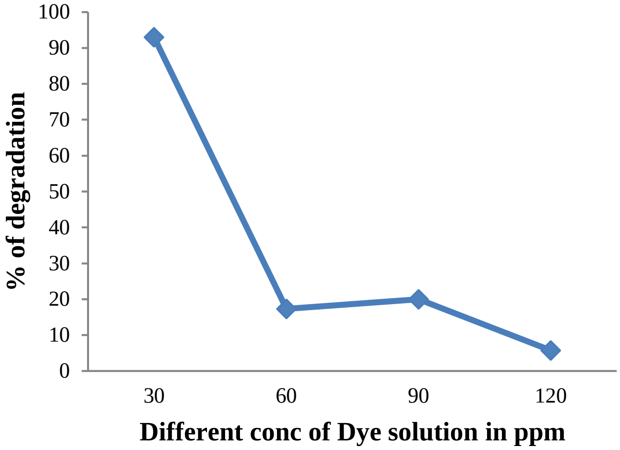


Fig 37: Effect of optimum catalyst dose and pH on the decolourization of Coralene Violet 3R dye at different concentrations (30ppm, 60ppm, 90ppm and 120ppm)

4.6.2 Violet GL2B

4.6.2.1 Effect of Catalyst Loading

The catalytic dosage was varied from 0.1g to 1.0g for 30ppm (30mg/L) against Violet GL2B at pH 7 and the results are presented in Fig 38. On exposure of reaction volume to sunlight after adding the catalyst, the dye color started to fade showing the visible signs of decolorization. The highest degradation (94.74%) was recorded for 0.5g/100ml of catalyst which was sufficient to degrade the Violet GL2B dye solution within 120min.

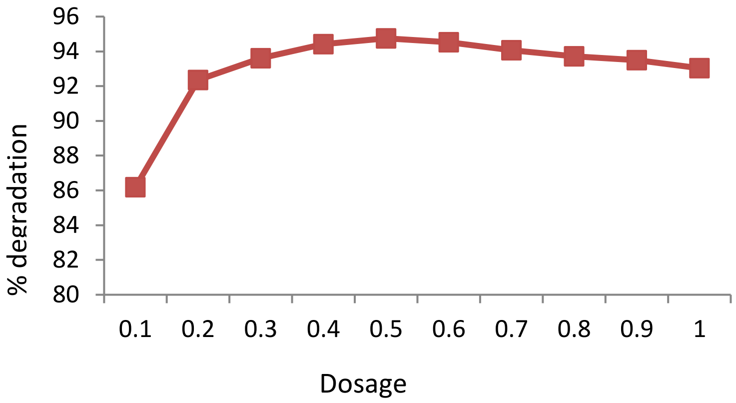


Fig. 38: Effect of catalyst load on the decolourization of Violet GL2B dye at concentration 30mg/L, at pH 7 with respect to time interval of 120minutes

4.6.2.2 Effect of pH on the dye samples

In order to study the effect of pH on the degradation efficiency of $CaAl_2O_4$ catalyst on photocatalyticdegradation of violet GL2B dye, experiments were carried out at varied pH ranging from 2to 11. As shown in fig39, maximum degradation forvioletGL2B (96.07%) was achieved at pH 10 at the end of 120min.The experimental data revealed that higher degradation rate of violet GL2B was observed in all the pH conditions. In alkaline medium, excess of hydroxyl ions facilitate photo generation of OH radicals which is accepted as primary oxidizing species responsible for photocatalytic degradation, resulting in enhancement of the efficiency of the process.

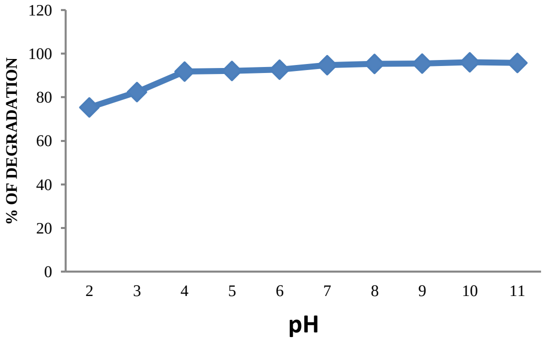


Fig. 39: Effect of optimum catalyst dose on the decolourization of Violet GL2B dye at concentration 30mg/L, at different pH levels with respect to time interval of 120minutes

4.6.2.3*Degradation efficiency of $CaAl_2O_4$ at different dye concentrations*

To study the effect of initial dye concentration on the photocatalytic efficiency of $CaAl_2O_4$ nanoparticle, the initial dye concentrations were varied from 30ppm to 60ppm, 90ppm and 120ppm and experiments were conducted at optimum catalyst dosage and pH. The highest degradation (96.07%) was recorded for the concentration of 30ppm dye solution. The experiment result depicts the decreased degradation rate with increase in the concentration of dye solution.

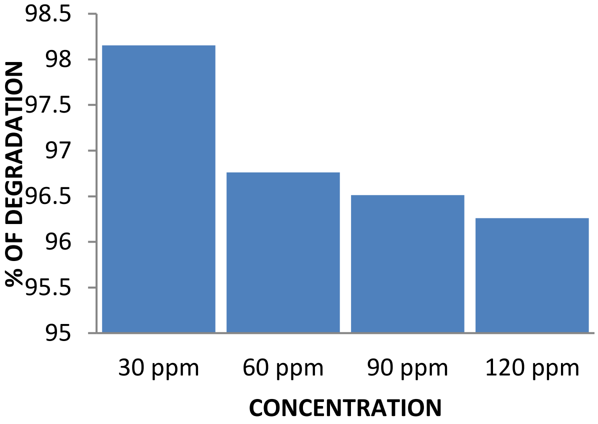


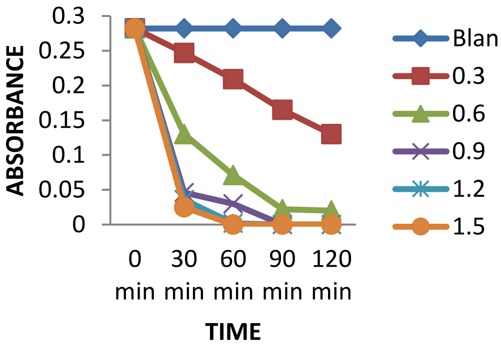
Fig. 40: Effect of optimum catalyst dose and pH on the decolourization of Coralene Violet 3R dye at different concentrations (30ppm, 60ppm, 90ppm and 120ppm)

4.7 Photocatalytic activity of Calcium zincate (Acetamide)

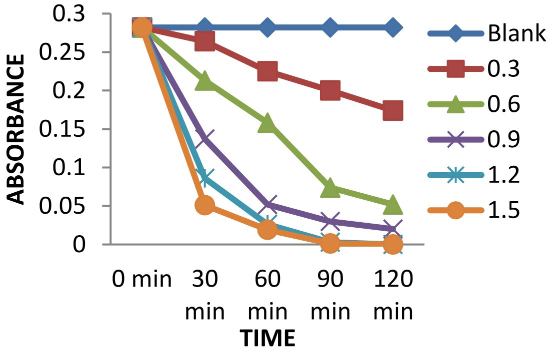
4.7.1 Coralene Dark Red 2B

4.7.1.1 Effect of Catalyst Loading

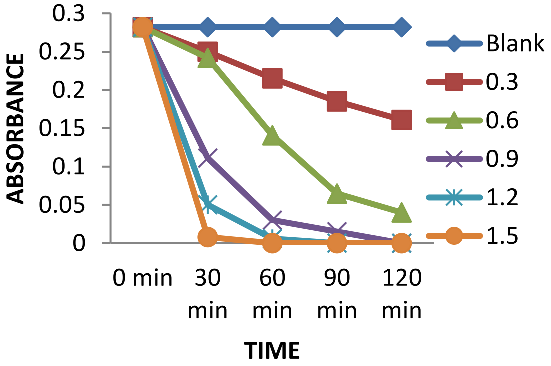
Catalyst loading is an important factor which can significantly influence the photocatalyticdecolorization rate of Coralene Dark Red 2B dye solution. To study the effect of catalyst load, calcium zincate dosage was varied from 300mg, 600mg, 900mg, 1200mg and 1500 mg for 30mg/L of Coralene Dark Red 2B dye solution keeping all other parameters identical and the results are presented in Fig 41. On exposure of reaction volume to sunlight after adding the catalyst, the dye color started to fade showing the visible signs of decolorization. In the first 30 minutes, percentage of decolorization recorded was 12.41 % for minimum dosage and 91.13% for the maximum dosage decolorized and after 120min, it was decolorized upto 53.90% for minimum dosage and ~100% for maximum dosage. Decolorization efficiency was more at the high catalyst dosage of 1500 mg/300ml. The increase in the amount of catalyst load increased the number of active sites on the photocatalyst surface, which in turn, increased the number of hydroxyl radicals. Further, increasing the loading of photocatalyst increased the catalyst surface area and as a result increased the decolorization rate. It may be assumed that, it would have hindered the transmission of sun light in the reaction container if catalyst dosage was increased more than 1500mg/300ml and consequently decreased the decolorization rate. However, at all the dosages, the rate of decolorization is fast in the first 30min and finally reaches to ~100% within 120min.



(c)



(d)



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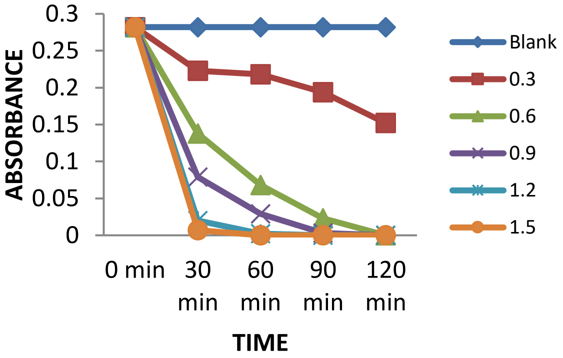

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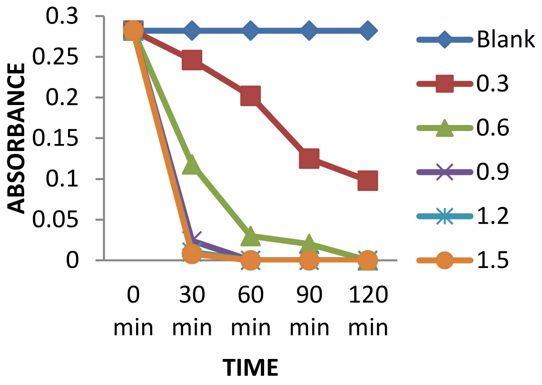

Fig. 41: Effect of catalyst dosage on the decolorizationof Coralene Dark Red 2B dyeatconcentration 30mg/L, on Neutral (a), pH2 (b), pH5 (c), pH 9 (d), and pH 12 (e) with respect t to time interval of 120minutes

4.7.1.2 Effect of pH on the dye samples

The photocatalytic experiments were conducted at acidic (pH 2 and PH 5), neutral (pH 7) and alkaline (pH 9 & pH 12) condition on Coralene Dark Red 2B dye solution (30mg/L). At pH 2 in the first 30min, degradation was 6.38% for minimum dosage and 81.91% for the maximum dosage and after 120min; it was decolorized up to 38.29% and ~100% respectively. The decolorization efficiency was higher at the high catalyst dosage of 1200mg/300ml and 1500mg/300ml. At pH 5, in the first 30min, decolorization was 11.34% for minimum dosage and 97.16% for the maximum dosage and after 120minutes it was decolorized upto 42.90% and ~100% respectively. At pH 7 (neutral), for the first 30min decolorization was 12.41 % for minimum dosage and 91.13% for the maximum dosage and after 120 minutes, it was decolorized up to 53.90% and ~100% respectively. The decolorization efficiency was maximum (~100%) at higher dosages of 900 mg/300ml, 1200mg/300ml and 1500mg/300ml at both pH 5 and pH 7 levels. At pH 9, for the first 30minutes the decolorization was 20.92% for minimum dosage and 97.51% for the maximum dosage and after 120min, it was decolorized up to 46.09% and ~100 %respectively. At pH 12, for the first 30minutes the decolorization was 12.76% for minimum dosage and 97.16% for the maximum dosage and after 120min, it was degraded up to 65.24%

and ~100% respectively. The decolorization efficiency of Calcium zincate nanoparticle was maximum at higher dosages of 600mg/300ml, 900mg/300ml, 1200mg/300ml and 1500mg/300ml at both pH 9 and pH 12 levels. The decolorization is mainly attributed to the variation of surface charge properties of the photocatalyst at different pH values. The ~100% decolorization was observed irrespective of pH variation at different catalytic dosages from 600mg/300ml to 1500mg/300ml (Fig 42).

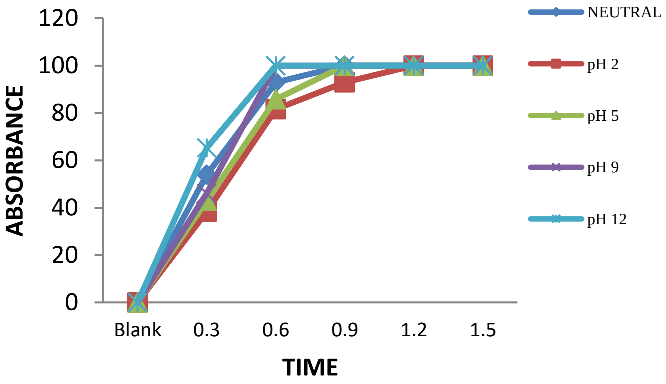

Fig. 42: Effect on Coralene Dark Red 2B dye at different pH on the decolorization efficiency of Calcium zincate nanoparticle.

4.7.2 Textile Effluent

4.7.2.1 Optimum Catalyst Dose

To study the effect of catalyst load, Calcium zincate dosage was varied from 0.01g to 0.1g for 5% of textile effluent solution keeping all other parameters constant and the results are presented in Fig 43. On exposure of reaction volume to sunlight after adding the catalyst, the effluent color started to fade showing the visible signs of decolorization. The highest degradation (95.17%) was recorded for 0.4g/100ml of catalyst which was sufficient to degrade the textile effluent solution within 120min.

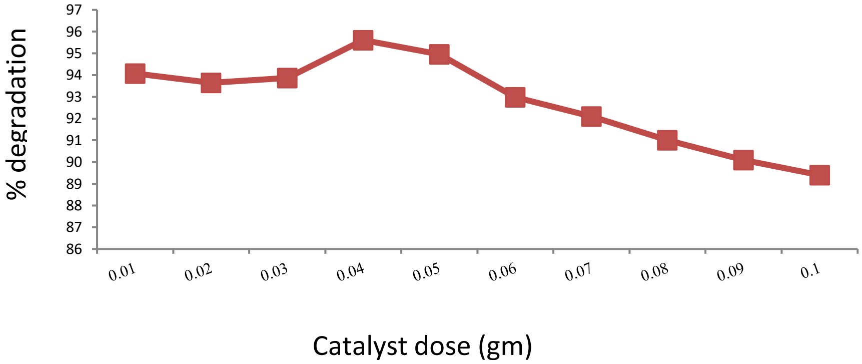

Fig. 43: Effect of catalyst load on the decolourization 5% textile effluent at pH 7 with respect to time interval of 120minutes

4.7.2.2 Optimum pH

The photocatalytic experiments were conducted at different pH from 2 to 11 by keeping the catalyst dose constant (0.4g/100ml) for 5% of effluent solution. pH of the solution was adjusted by using 0.2N HCl/NaOH solution and the results are presented in Fig 44. On exposure of reaction volume to sunlight, the highest degradation (95.61%) was recorded at pH 5 which was optimum to degrade the effluent solution within 120min.

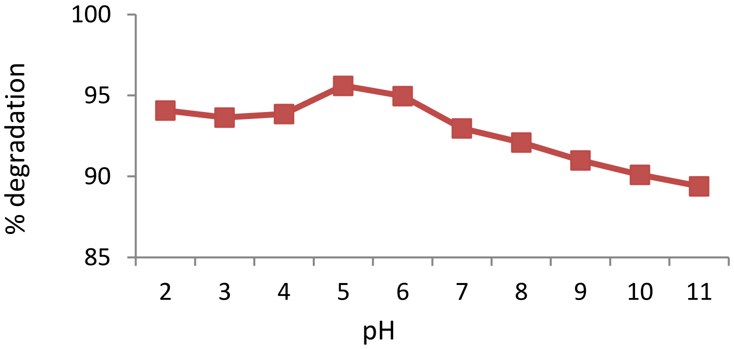

Fig. 44: Effect of optimum catalyst dose on the decolourization of 5% textile effluent at different pH levels with respect to time interval of 120minutes

4.7.2.3 Degradation efficiency of $CaZnO_2$ at different dye concentrations

To study the effect of initial effluent concentration on the photocatalytic efficiency of $CaZnO_2$ nanoparticles, the initial dye concentrations were varied to 10%, 15%, 20% and experiments were conducted at optimum catalyst dosage and pH. The highest degradation (95.61%) was recorded for the concentration of 5% effluent solution. The experiment result depicts the slight decrease in the degradation efficiency with the increase in effluent concentration.

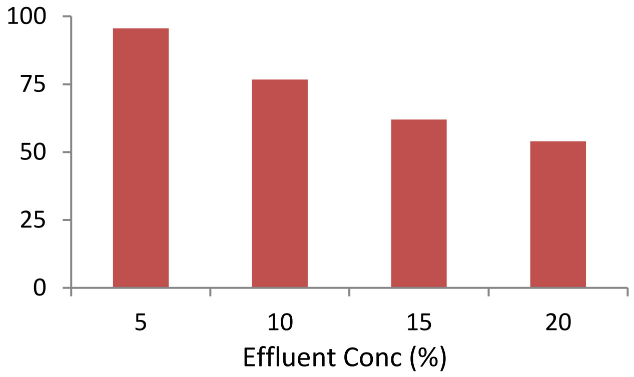

Fig. 45: Effect of optimum catalyst dose and pH on the decolourization of textile effluent at different concentrations (5%, 10%, 15% and 20%)

4.8 COD and TOC of all the selected dyes

Nanoparticle	Azo dye	COD		TOC	
		Initial value (mg/L)	Final value (mg/L)	Initial value (%)	Final value (%)
Zinc Oxide Composite I	Coralene Red F3BS	65.24	34.72	15.4	14.8
Zinc Oxide Composite II		65.24	37.84	15.4	14.7
Zinc Oxide Nanoparticles		65.24	41.52	15.4	15.2
Calcium Aluminate	Coralene Dark Red 2B	53.62	25.84	15.0	14.4
Calcium Aluminate	Coralene Violet 3R	56.24	27.84	14.9	14.6
	Violet GL2B	39.9	34.3	14.9	14.6
Calcium Zincate	Coralene Dark Red 2B	58.64	30.84	15.2	15.0
	Textile Effluent	62.4	26.04	27.5	14.8

All the photocatalysts can reduce the chemical oxygen demand to a considerable extent compared to total organic carbon for all the selected azo dye solutions except for textile effluent as for the effluent both COD and TOC values get reduced to half of the original values.

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