



MEDRC Series of R & D Reports
MEDRC Project: 14-CoE-015

**Treatment of organic pollutants in water by nano particles embedded
on polymer**

M.Sc. Thesis By

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A Thesis Submitted in Partial Fulfillment of the
Requirements for
the **Degree of Master** in Water and Environment science

MEDRC Water Research

Muscat

Sultanate of Oman

06/08/2018



Al-Azhar University-Gaza

Deanship of Postgraduate Studies and Scientific Research

Institute of Water and Environment

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Al-Azhar University - Gaza

Palestine

2018

DECLARATION

I, the undersigned hereby, declare that the thesis titled:

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Al-Azhar University -Gaza
Deanship of Postgraduate Studies and Scientific
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By
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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

(وَاتَّقُوا اللَّهَ
وَيَعْلَمْكُمْ
اللَّهُ وَاللَّهُ بِكُلِّ شَيْءٍ
عَلِيمٌ)

صدق الله العظيم

سورة البقرة

282



Dedication

To My Father, Mother,

To My Husband

My daughter Salma

My son Sami

My Sisters and Brothers

To prof. Naji Al dwahidi

To the soul of my supervisors Prof. Dr. Farid

R. Zaggout,

To all

Who helped me

Throughout my studies

ACKNOWLEDGEMENTS

Praise be to Allah who enable me to complete this work. Thanks and deepest appreciation to The soul of my supervisors Prof. Dr. Farid R. Zaggout, for his guidelines, support and great help throughout this research, and Prof. Dr. Naji Al dwahidi for his encouragement, and continuous help. Many thanks for the external examiner Prof. Hazem Abu Shawish and the internal examiner Prof. Naser abu Ghalwa for their great efforts.

I am greatly indebted to them for all the efforts they have put in for the successful completion of this thesis and their great and continuous help encouragement and guidance during the research course.

I also extend my profound thanks to the department of chemistry at Al-Azhar University-Gaza and to the staff of the department of chemistry at Al-Azhar University for making the facilities available for me ,also Financial support for this project from MEDRIC

Alaa S. Baraka

List of Contents

Dedication	I
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Acknowledgements	II
List of Content	III
List of Table.....	VII
List of Figure.....	IX
Abstract.....	XIII
الملخص بالعربية.....	XVI
Key words.....	XVII
Chapter (1) Introduction.....	1
Introduction	2
1.1 Overview.....	2
1.2 Semiconductor Photocatalysis.....	3
1.2.1 Tin Dioxide (SnO ₂) Semiconductors.....	5
1.2.2 Ferric Oxide (Fe ₂ O ₃) Semiconductors.....	7
1.3 Photocatalytic reactions mechanism.....	9
1.4 Sensitization.....	11
1.5 Objectives.....	18
Chapter (2) Experimental.....	19
A.2 Tartrazine and Levofloxacin Photocatalytic degradation.....	20
A.2.1 Materials and Methods	20
A.2.2 Solutions preparation.....	20

A.2.2.1 Preparation of ($1 \times 10^{-3}M$) Tartrazine stock solution.....	20
A.2.2.2 Preparation of ($1 \times 10^{-3}M$) Levofloxacin stock solution.....	21
A.2.2.3 Tartrazine ($1 \times 10^{-5}M$) and Levofloxacin ($10 \times 10^{-5}M$) solutions of different pH values.....	21
A.2.2.4 Tartrazine and Levofloxacin solutions of different H_2O_2 concentrations.....	21
A.2.2.5 Preparation of Tartrazine and Levofloxacin solutions containing 200 ppm salts (NaF , $NaNO_3$, Na_2SO_4 , $NaHCO_3$).....	21
A.2.3 Photocatalysts membrane preparation.....	21
A.2.3.1 SnO_2/PVC preparation.....	22
A.2.3.2 $SnO_2/Eosin$ preparation.....	22
A.2.4 Equipment	22
A.2.5 Photocatalytic reactor.....	23
A.2.6 Tartrazine and Levofloxacin Photocatalytic degradation experiments.....	23
Chapter (3) Results and Discussion.....	24
A: Tartrazine Degradation.....	25
A.1 Photocatalytic activity of different metal oxides in degradation of Tartrazine.....	25
A.2 Effect of UV radiation and nano SnO_2/PVC membrane as photocatalyst system.....	26
A.3 Operational parameters :Investigation and optimization.....	30

A.3.1 Effect of Irradiation time.....	30
A.3.2 Effect of initial Tartrazine concentration.....	32
A.3.3 Effect of pH.....	34
A.3.4 Effect of H ₂ O ₂ concentration.....	37
A.3.5 Effect of energy of radiation.....	42
A.3.6 Effect of co-occurring ions.....	44
A.4 Reusability of SnO ₂ /PVC membrane photocatalyst.....	45
B:Levofloxacin degradation.....	47
B.1.1 Photocatalytic activity of Levofloxacin degradation under utilizing different metal oxides.....	47
B.1.2 Photocatalytic degradation of Levofloxacin using SnO ₂ /PVC membrane photocatalyst.....	48
B.2 Effect of presence of UV radiation and SnO ₂ /PVC membrane as catalyst.....	48
B.3 Comparison between different supports to metal oxide in term of photocatalytic activity in Levofloxacin degradation.....	51
B.4 Operational parameters :Investigation and optimization.....	52
B.4.1 Effect of irradiation time.....	52
B.4.2 Effect of initial concentration of Levofloxacin.....	53
B.4.3 Effect of solution pH.....	55
B.4.4 Effect of H ₂ O ₂ concentration.....	57
B.4.5 Effect of energy of radiation.....	60

B.4.6 Effect of co-occurring ions.....	62
B.5 Reusability of SnO ₂ /PVC photocatalyst membrane.....	63
C: Effect of a sensitizer	65
C.1 Dye sensitizers of SnO ₂ in Tartrazine degradation.....	66
C.2 Dye sensitizers of SnO ₂ in levofloxacin degradation	66
References.....	70

Table No.	List of Tables	Page No
3.1	Percent of photodegradation activity of Tartrazine using different metal oxide after 120 minutes exposure to UV radiation at 254nm.	25
3.2	Percent degradation and degradation rate of 1×10^{-5} M Tartrazine after 120 minutes under different degradation conditions.	28
3.3	%Degradation of different concentrations of Tartrazine dye after 120 minutes of the reaction.	33
3.4	Degradation percentage and degradation rate of 1×10^{-5} M Tartrazine after 120 minutes using SnO ₂ under different radiation wavelengths.	44
3.5	%Degradation of 1×10^{-5} M Tartazine after 120 minutes of photocatalytic reaction under UV254 nm in the presence of 120 ppm of NaF, NaNO ₃ , NaHCO ₃ , Na ₂ SO ₄ using SnO ₂ /PVC membrane.	45
3.6	Degradation percent of Levofloxacin after 120 minutes by using different catalysts membrane under the same condition of radiation(UV of 254 nm)	47
3.7	Percent degradation and degradation rate of 10×10^{-5} M Levofloxacin after 120 minutes under different degradation conditions.	50
3.8	%Degradation of Levofloxacin after 120 minutes by using different catalysts using 254 nm UV light.	51
3.9	%Degradation of Levofloxacin of different concentrations after 180 min of photocatalytic degradation by SnO ₂ /PVC membrane.	54
3.10	%Degradation of 10×10^{-5} M Levofloxacin after 120 minutes of photocatalytic reaction under UV254 nm in the presence of 120 ppm of NaF, NaNO ₃ , NaHCO ₃ , Na ₂ SO ₄ using SnO ₂ /PVC membrane at pH 7.5.	62

3.11	Percent of photodegradation activity of Tartrazine using SnO ₂ sensitized with Eosin under different radiation after 120 minutes all after exposure to UV at 254nm.	66
3.12	Degradation percent of Levofloxacin after 120 minutes by using different catalysts membrane under the same condition of radiation(UV of 254 nm)	68

Fig. No.	List of Figures	Page No.
1.1	Rutile structure of SnO ₂ .	6
1.2	Crystal structure of α-Fe ₂ O ₃ .	8
1.3	Mechanism of photocatalytic degradation of organic compounds utilizing metal oxide semiconductor as a photocatalyst.	10
1.4	Mechanism of dye-sensitized photocatalytic of metal Oxides.	12
1.5	Structural formula for Eosin Y.	13
1.6	Tartrazine chemical structure.	15
1.7	Levofloxacin chemical structure.	17
3.1	UV-Vis absorption spectra of 1×10 ⁻⁵ M Tartrazine decomposed upon different degradation conditions after 120 minutes of the reaction (a: with SnO ₂ membrane and no UV, b: with UV at λ=254nm) and no SnO ₂ membrane , c: with both SnO ₂ membrane and UV(254nm) radiation).	27
3.2	Effect of presence of UV radiation and SnO ₂ photocatalyst membrane on 1×10 ⁻⁵ M Tartrazine degradation as a function of the exposure time.	28
3.3	Calibration curve of Tartrazine.	30
3.4	UV-Vis absorption spectrum of 1×10 ⁻⁵ M Tartrazine before exposure to UV radiation and SnO ₂ photocatalyst membrane.	31
3.5	Gradual color removal of 1×10 ⁻⁵ M Tartrazine upon photocatalytic degradation process using SnO ₂ /PVC membrane after (a:0 min, b:60 min, c:90 min, d:120 min, e:180 min).	32
3.6	Effect of concentration on the photocatalytic degradation efficiency of Tartrazine using SnO ₂ /PVC membrane.	33

3.7	Effect of pH on the color removal of 1×10^{-5} M Tartrazine using SnO ₂ /PVC membrane.	35
3.8	Effect of pH on % remaining of 1×10^{-5} M Tartrazine after 120 minutes of photocatalytic degradation process utilizing SnO ₂ /PVC membrane.	36
3.9	Effect of H ₂ O ₂ concentration on photocatalytic degradation of 1×10^{-5} M Tartrazine by using SnO ₂ /PVC membrane.	39
3.10	UV-Vis absorption spectra after 120 minutes of photodegradation of 1×10^{-5} M Tartrazine by SnO ₂ membrane with addition of different H ₂ O ₂ concentrations (a:0 M, b:0.2M, c:0.05M, d:0.15M, e:0.1M).	40
3.11	Remaining% of 1×10^{-5} M Tartrazine after 120 min of photocatalytic degradation process at different H ₂ O ₂ concentrations.	40
3.12	Absorption spectra of 1×10^{-5} Tartrazine after 120 minutes of photocatalytic degradation utilizing SnO ₂ under different radiation wavelengths (a: dark, b:UV365 nm, c:solar, d:UV 254 nm).	43
3.13	Effect of radiation wavelength on photocatalytic degradation of 1×10^{-5} M Tartrazine by SnO ₂ .	43
3.14	The effect of reusability of SnO ₂ membrane on the photodegradation of Tartrazine dye.	46
3.15	Catalytic efficiency of SnO ₂ membrane in degradation of 1×10^{-5} M Tartrazine after 120 minutes of five consecutive usage times.	47
3.16	Calibration curve of Levofloxacin.	48
3.17	UV-Vis absorption spectra of 10×10^{-5} M Levofloxacin decomposed upon different degradation conditions after 120 minutes of the reaction (a: with SnO ₂ /PVC and no UV, b: with	49

	UV and no SnO ₂ /PVC, c: with both SnO ₂ /PVC and UV radiation).	
3.18	Effect of presence of UV radiation and SnO ₂ photocatalyst on 10×10 ⁻⁵ M Levofloxacin degradation.	50
3.19	UV-Vis absorption spectrum of Levofloxacin before exposure to UV radiation and SnO ₂ /PVC membrane.	52
3.20	Gradual removal of 10×10 ⁻⁵ M Levofloxacin upon photocatalytic degradation process using SnO ₂ membrane (after-a:0 min, b:60 min, c:180 min).	53
3.21	Effect of concentration of Levofloxacin on the removal efficiency upon photocatalytic degradation using SnO ₂ /PVC photocatalyst membrane.	54
3.22	Effect of pH on removal of 10×10 ⁻⁵ M Levofloxacin by photocatalytic degradation using SnO ₂ /PVC membrane.	56
3.23	%Remaining of 10×10 ⁻⁵ M Levofloxacin after 120 minutes of photocatalysis process utilizing SnO ₂ /PVC membrane.	57
3.24	Effect of H ₂ O ₂ concentration on removal efficiency of 10×10 ⁻⁵ M Levofloxacin by photocatalytic degradation process using SnO ₂ /PVC.	58
3.25	UV-Vis absorption spectra after 90 minutes of 10×10 ⁻⁵ M Levofloxacin removal by SnO ₂ /PVC membrane upon addition of different H ₂ O ₂ concentrations (a:0 M, b:0.2M, c:0.15M, d:0.1M, e:0.05M).	59
3.26	%Remaining of 10×10 ⁻⁵ M Levofloxacin after120 minutes of photocatalytic reaction at different H ₂ O ₂ concentrations.	59
3.27	Absorption spectra of 10×10 ⁻⁵ M Levofloxacin after 120 minutes of photocatalytic degradation using SnO ₂ /PVC membrane under	61

	different radiation wavelengths (a: dark, b:UV365 nm, c:solar, d:UV 254 nm.	
3.28	Effect of reusability of SnO ₂ /PVC membrane as photocatalyst for four consecutive times on removal efficiency of 10×10 ⁻⁵ M Levofloxacin.	64
3.29	Catalytic efficiency of SnO ₂ /PVC membrane in degradation of 10×10 ⁻⁵ M Levofloxacin after 120 minutes of four consecutive usage times.	64
3.30	Absorption spectra of 10×10 ⁻⁵ M Levofloxacin after 180 minutes of photocatalytic degradation using SnO ₂ /Eosin membrane under (a: λ=254 nm, b: sun light).	67
3.31	Effect of Eosin Y as sensitizer in levofloxacin photodegradation.	68

Abstract

Treatment of organic pollutants in water by nano particles embedded on polymer membrane

Water treatment methods followed in recent years, must guarantee the removal of contaminants to the allowable limit. The choice of treatment depends on the type of organic pollutants, their concentration and volume of the effluents treated and cost of treatment. Several studies conducted on the effectiveness of the use of photocatalytic degradation using different metal oxides such as Titanium dioxide (TiO_2) and tin oxide (SnO_2) in water treatment of some persistent organic pollutants, and this way have had a clear impact and successful, as has the focus of attention for researchers to water treatment. This research study is concerned with using semiconducting nanoparticles include tin oxide (SnO_2) and iron oxide (Fe_2O_3) in the form of a thin membrane for the photodegradation of Tartazine dye and levofloxacin, where the membrane containing tin oxide has proved highly efficient in breaking them. It was conducted several experiments on membrane-containing catalysts and its showed a good results that enable the reuse of these membranes for several consecutive times while maintaining the efficiency of the photocatalytic. There are several factors and conditions were tested such as the concentration of organic pollutant, the time of exposure of the membrane catalyst to radiation, the type and energy of radiation used, the pH, the type and concentration of receptors of electrons, and to include contaminants within the real samples and observe the effect of inorganic ions. In addition of that, to the first time a photosensitizer such as Eosin Y was attached on the surface of the catalyst semiconducting nanoparticles to check the degradation performance under solar radiation instead of UV irradiation.

Results of this study has shown that the best degradation of Tartazine dye and antibiotic levofloxacin as an examples of organic pollutants will be at the optimum conditions of the following:

Maximum efficiency of photodegradation process with higher degradation rate for Tartazine dye and antibiotic levofloxacin were achieved by using the UV wavelength at 254 nm with a catalyst membrane based tin oxide (SnO₂) nanoparticles. It is found that the greater the duration of exposure to radiation and catalytic membrane together will increase the effectiveness of the degradation process. The smaller the concentration of the Tartazine dye and antibiotic levofloxacin resulted in an increase of the efficiency of the reaction of the degradation. The pH value of the solution was optimized to be acidic with a value of 3 for the Tartazine dye degradation and to be neutral with a value of 7 for Levofloxacin antibiotic referring to more electrostatic interaction between the dyes and the surface of the semiconducting photocatalyst. The ideal electron acceptor that used in this work was the hydrogen peroxide which is added with optimum concentration of 0.1 mol/ L for the highest photodegradation for both Tartazine dye and antibiotic levofloxacin, where it is expected more electron-hole pairs were generated resulted in more efficient radicals. It is exhibited that less photodegradation efficiency was obtained under the existence of inorganic ions. A high efficiency of degradation for Tartazine dye and antibiotic levofloxacin was found by using the membrane catalyst based on Eosin Y dye sensitized the tin oxide nanoparticles under the exposure of solar energy instead of using a harmful UV irradiation. This positive effect is interest, where it stimulates and promotes the research of the photodegradation under solar energy instead of UV treatment, where cost effective and safe process can be achieved.

الملخص بالعربية

معالجة الملوثات العضوية في المياه عن طريق جزيئات نانو مغموسة في غشاء من البوليمر.

العديد من الدراسات التي أجريت على فاعلية استخدام التحفيز الضوئي لأكاسيد المعادن المختلفة مثل ثاني أكسيد القصدير SnO_2 في معالجة المياه من بعض الملوثات العضوية كان لها أثر واضح وناجح، حيث أصبحت محط أنظار للباحثين لمعالجة المياه. وتتضمن هذه الدراسة البحثية استخدام ثاني أكسيد القصدير (SnO_2) وأكسيد الحديد (Fe_2O_3) على صورة غشاء رقيق حيث أثبت الغشاء المحتوي على أكسيد القصدير كفاءة عالية في تحطيم صبغة الترترازين والمضاد الحيوي ليفوفلاكسين. تم اجراء العديد من التجارب على الأغشية المحتوية على الحفازات وأظهرت نتائج جيدة تمكن من استخدام هذه الأغشية لعدة مرات متتالية مع الحفاظ على كفاءة عملية التحطم الضوئي تحت تأثير الأشعة. تم اختبار الظروف المثالية للعوامل المؤثرة في عملية التحطم الضوئي للملوثات العضوية وتم العمل على ضبطها والتحكم بباقي الظروف كثوابت ومتغيرات لحين الحصول على اكثر الظروف مناسبة مع إعطاء أكفاً نسبة تحطم وحفز ضوئي للملوثات العضوية , حيث تم دراسة عدة عوامل أهمها : التركيز الابتدائي للملوث العضوي , زمن تعرض الغشاء المحفز للأشعة , نوع وطاقة الأشعة المستخدمة, درجة حموضة الوسط المحتوي على الملوثات , نوع وتركيز مستقبلات الالكترونات في وسط التحطم والتفاعل. تضمن الملوثات ضمن عينات حقيقية وملاحظة أثر الأيونات الغير عضوية. أظهرت نتائج الدراسة والبحث أن أفضل تحطم لصبغة الترترازين و ليفوفلاكسين يكون عند الظروف المثالية المتمثلة بما يلي:

- الغشاء المحتوي على ثاني أكسيد القصدير كحفاز كان الأكثر كفاءة في عملية تحطم المضاد الحيوي ليفوفلاكسين وصبغة الترترازين.

- تزداد فعالية ونسبة التحطم كلما زادت مدة التعرض للغشاء الحفاز وللأشعة معا.
- كلما قل التركيز الابتدائي للملوث العضوي فان كفاءة تفاعل التحطم تزداد.
- اعلى كفاءة تحطم لصبغة الترترازين و ليفوفلاكسين وجدت عند استخدام غشاء محفز بثاني أكسيد القصدير مع الأيوسين باستخدام الطاقة الشمسية.
- درجة الحموضة المثلى لتحطم الترترازين عند باقي الظروف المثالية كانت في وسط حامضي عند 3 بينما كانت لتحطم المضاد الحيوي هي 7.
- التركيز المثالي لفوق أكسيد الهيدروجين المستخدم خلال عملية تحطيم صبغة الترترازين هو 0.1 مول/لتر بينما 0.05 مول/لتر كانت لليفوفلاكسين.
- تقل كفاءة عملية تحطم صبغة الترترازين و ليفوفلاكسين عند الظروف المثالية بوجود أيونات غير عضوية.
- أفضل كفاءة لعملية التحطم كانت باستخدام الأشعة فوق البنفسجية عند الطول الموجي 254 نانومتر مع غشاء محفز بثاني أكسيد القصدير.
- إضافة الأيوسين الي غشاء التحفيز له أثر إيجابي في تحفيز عملية التحطم وباستخدام الطاقة الشمسية.
- أفضل مادة استخدمت في صناعة الغشاء وقد أعطت فعالية تحطم جيدة هي بولي فينيل كلوريد.

Key words	
UV	Ultraviolet
AOPs	Advanced oxidation processes
PV	photovoltaic
V_B	valence band
C_B	conduction band
MO	methyl orange
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
$h\nu$	Light energy
PVC	Poly vinyl chloride
PMMA	Poly methyl methacrylate

Chapter (1)

Introduction

Introduction

1.1 Overview

Water is considered as an essential component for living beings on the earth for vital and many activities. It is a big sorrow that the quality of water resources is deteriorating continuously due to geological and environmental changes, geometrical growth of population, industrialization, civilization, domestic, and agricultural activities (Ali I.,2012). Dyes and pharmaceutical waste adversely affect the quality of water, inhibit sunlight penetration and reduce photosynthetic reactions. In addition, some dyes are either toxic or carcinogenic (Welderfael T., 2013) and very small amounts of pharmaceuticals present in everyday food may causes strains of resistant microorganisms in human and other organisms (Augugliaro et al., 2006). Dyes and pharmaceutical waste may pollute water bodies which are not only toxic but also biodegradable in overall time. When natural organic breakdown these compounds, dissolved oxygen level in the water become drops below the critical value, and the aquatic life such as fish and microorganisms will be dead. Therefore these conditions can prevent or disturb the growth of aquatic plant and animals. Removal of dyes and pharmaceuticals from wastewater has become a difficult issue due to their stability under hard condition and their biodegradation resistance state, dye decolorization received an increasing attention. Dye pollutants are currently removed via traditional physical techniques (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins, etc.). Nevertheless, they are non-destructive, that will transfer organic compound from water to another phase, and thus causing secondary pollution. Consequently, regeneration of the adsorbent materials and post-treatment of solid-wastes, which are

expensive operations, are needed (Puzyn and Mostrag 2012; Konstantinou and Albanis 2004 ; Rajamohan 2009 ; Sharma 2013). During the last decade, Advanced oxidation processes (AOPs) have been growing since they have the ability to deal with the problem of dye destruction in aqueous systems in a beneficial environment ways. The base of AOPs are physicochemical processes that produce in situ powerful transitory species, principally hydroxyl radicals ($\text{HO}\cdot$), by using chemical and a forms of energy, and have a high oxidation efficiency for organic matter (Augugliaro et al., 2006). Among AOPs, heterogeneous photocatalysis using semiconductor oxides that has demonstrated to be very effective to treat pollutants both in gas and in liquid (Kansal et al 2009).

Common photoassiated AOPs are UV/Fenton process, UV/Ozone, UV/ H_2O_2 and photocatalyst. Chemical treatment of wastewaters by AOPs can result in the complete mineralization of the pollutants to a harmless and simple end products such as carbon dioxide, water and inorganic salts. Ideally, a semiconducting photocatalyst should be chemically and biologically inert for the purification of water, photocatalytically active, easy to produce and use, and activated by UV or sunlight(Konstantinou and Albanis 2004 ; Rajamohan 2009). AOPs have been studied under a broad range of experimental conditions in order to reduce the color and organic component of dye containing effluent wastewaters (Mohsin et al., 2013 ; Giwa et al.,2012; Prabha and Lathasree, 2013; Šíma and Hasal ,2013).

1.2 Semiconductor Photocatalysis

Sunlight is the principal energy source for earth and sustains life on earth. The most important natural method for utilization of solar energy is the photosynthesis process by plants to produce carbohydrates and oxygen gas (O_2) by utilizing carbon dioxide (CO_2) and water (H_2O). Most of our daily

energy requirements are being met by fossil fuels. However, the limited availability of these non-renewable sources of energy has motivated researchers to find a new different techniques to use solar energy as an alternative for future energy needs. The most common method to directly converting of solar energy into electric energy is photovoltaic (PV), and this process utilizes semiconductors which generate electron–hole pairs upon illumination with visible light, thereby producing electric power in solar cells. However, the utility of photovoltaic cells is limited by poor conversion efficiency. To overcome these problems, a suitable methods to produce hydrogen (H₂) from photocatalysis of H₂O using sunlight have been tried to find by new researchers, which can be used in fuel cells for power generation (Mishra and Chun, 2015). A semiconductor is a material that has an electrical conductivity between a conductor and an insulator, the highest occupied energy band that is the valence band (VB) which is completely filled with electrons and the empty next band is the conduction band (CB). The resistivity of the semiconductor can be altered by up to 10 orders of magnitude (Ateeq,2012). To control the conductivity of the semiconductors under light or heat or by doping, an electric or magnetic field can be used.

The aim of semiconductor photocatalysis is to effectively detoxify noxious organic pollutants. UV or visible light is used to create electron-hole pairs in the semiconductor, then the electrons react with oxygen in the sample to form O₂^{•-} and holes react with surface hydroxyl groups to form OH radicals. The radical species then attack the organic molecules which are eventually oxidized to CO₂, H₂O and other mineral acids. There are many known semiconductors, such as TiO₂, ZnO, ZrO₂, V₂O₅, WO₃, Fe₂O₃, SnO₂, CdSe, GaAs, GaP and metal sulphides (CdS and ZnS) that have established their effectiveness in pollutant degradation and eventually complete

mineralization(Baruah et al.,2012; Chen et al.,2011; Elamin and Elsanousi,2013; Umar and Abdul Aziz,2013; Siuleiman et al.,2013; Mehra and Sharma,2012 ; Ameta et al., 2013).

One of the more interesting advanced oxidation process treatments is Heterogeneous photo-catalysis performed with irradiated semiconductor dispersions and it is able, in most cases, to complete the mineralization of the organic harmful species. Hence, one of the major advantages of photocatalytic processes over the existing technologies is that there is no need for further secondary treatments. The process can be summarized as follows:



Semiconductors differ from metals in their electrical properties. In metals the valence band of electron energy levels overlaps with the conduction band. In semiconductors, there is a large energy gap between the top of the valence band and the bottom of the conduction band. This results in a relatively low electronic conductivity since the number of electrons which have enough thermal energy to bridge the gap and provide current carriers is relatively low. Two types of current carriers found in semiconductors: the first is the conduction band electrons (electrons free to move through the crystal lattice) and the second is the valence band holes (electrons missing from covalent bonds). Each electron that bridges the energy gap produces one hole and one electron current carrier. The product of the concentrations of holes and electrons is a constant at a given temperature (Turner).

1.2.1 Tin Dioxide (SnO₂) Semiconductors

Tin dioxide is an inorganic compound with the chemical formula SnO₂. It mainly occurs in the mineral cassiterite, and crystallizes with a tetragonal structure as shown in Fig (1.1). It is a colorless, amphoteric and diamagnetic solid state that is usually thought of as an oxygen deficient n-type

semiconductor. It is insoluble in water, but dissolves in alkalis and acids. Purification of Tin dioxide can be performed by reduction of the metal and burning tin in air. The irradiation of SnO₂ particle with photons of energy equal or greater than its band-gap (3.6eV) (Suhail et al.,2012; Wang et al.,2007; Patil et al.,2012; Robertson and Ginley,2010; Drake,2003; Chowdhury et al.,2011) and this results in the transition of electrons from the valence band (VB) to the conduction band (CB). The result of this process is a region of positive charge termed a hole (h⁺) in the VB, and a free electron (e⁻) in the CB. Moreover, SnO₂ possesses a high electron mobility (~100–200 cm² V⁻¹s⁻¹), indicating a faster transport of photoexcited electrons (Xu et al., 2014).

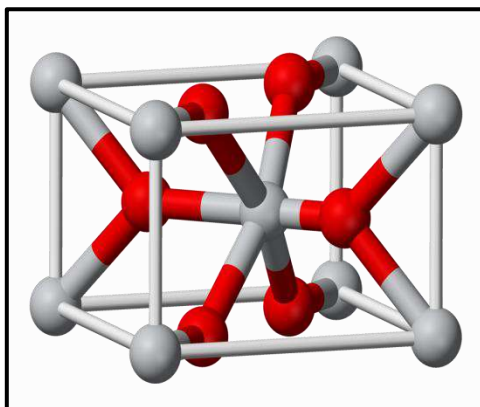


Fig (1.1):Rutile structure of SnO₂

These properties make tin oxide suitable for many applications, particularly as an electrode material in solar cell, light emitting diodes, transparent electromagnetic shielding materials and oxidation catalyst (Manificier et al., 1977; Li et al.,2012; Chua et al.,2009).

In the last decade, SnO₂ has been studied as a promising material with many unique surface properties including luminescence and photocatalytic activity (Abdelkader et al., 2016) and it has been studied for the treatment or degradation of environmental pollutants (Jia et al.,2012; Cheng et

al.,2011). SnO₂ hollow microspheres possess excellent photocatalytic performance for the degradation of methylenblue dye, about 95% of the dye was degraded in 25min (Xiao et al.,2016). Tin dioxide (SnO₂) nanoparticles have been expected to be a powerful photocatalyst material for the degradation of organic pollutants in aqueous solution which possesses an excellent properties, such as transparency, low cost, environmental friendliness, good chemical and biological inertness, easy production, nontoxicity, high photosensitivity, photostability, and thermodynamic stability SnO₂ nanoparticles were found to exhibit approximately 3.8 times higher activity than bulk SnO₂ in the photodegradation of methylene blue and the maximum photodegradation achieved was 79% after an irradiation time of 180 min (Kima et al.,2016). SnO₂ with TiO₂/nanoporous composite as powder prepared and the photocatalytic performance for Bisphenol A destruction was studied, and the performance of the prepared composite was compared with that of commercial TiO₂. The SnO₂ TiO₂/nanoporous composite showed better Bisphenol A degradation than pure TiO₂, with 10 ppm of Bisphenol A being removed 75% after 24 hours(Kim et al.,2011). The photocatalytic activities of tin dioxide nanoparticles as suspension using methyl orange (MO) as a model organic pollutant was studied (Yuan and XU,2010). The influences of photocatalysts concentration, doping of different metal ions and pH of MO solution were studied. It showed that well-crystalline SnO₂ with the particle size of 30-40 nm can be prepared by constant temperature hydrolysis sintered at 800 °C, and 97%of MO removed within 120 min.

1.2.2 Ferric Oxide (Fe₂O₃) Semiconductors

Hematite or Fe₂O₃,with its narrow band gap of about 2.2 eV is one of the promising candidate for photocatalytic applications. Furthermore, hematite absorbs light up to 600 nm, it can collects up to 40% of the solar

spectrum energy, stable in most aqueous solutions ($\text{pH} > 3$) and is one of the cheapest semiconductor materials available (Rio, 2011). Fe_2O_3 is a promising photoanode material for photoelectrochemical water splitting as a result of which Fe_2O_3 is capable of absorbing large portion of the visible solar spectrum (absorbance edge 600nm) (Elamin N. and Elsanousi, 2013; Hassena, 2016; Sharma et al., 2014; Reddy et al., 2010; Fujishima et al., 2000). Also its good chemical stability in aqueous medium, low cost, abundance and nontoxic nature makes it a promising material for photocatalytic water treatment and water splitting applications. Except these advantages the usage of Fe_2O_3 has been restricted by many anomalies such as higher (e^-h^+) recombination effect, low diffusion length and valence band positioning (VB is positive with respect to H^+/H_2 potential) (Choi et al., 2012; Benćina, 2013; Mishra and Chun, 2015).

Fig. (1.2) shows the crystal structure of Hematite .

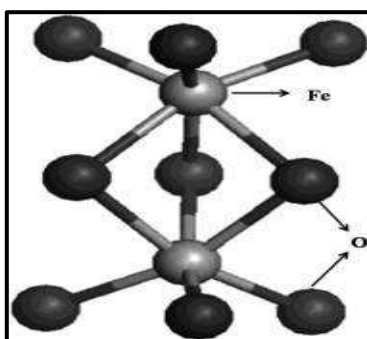


Fig. (1.2): Crystal structure of $\alpha\text{-Fe}_2\text{O}_3$.

$\alpha\text{-Fe}_2\text{O}_3$ is also a good photocatalyst for aniline to azobenzene (Karunakaran and Senthilvelan, 2006) and acrylamide polymerization (Stroyuk et al., 2007). Photopolymerization reaction is the mechanism of acrylamide formation, which starts with the formation of holes in the valence band of $\alpha\text{-Fe}_2\text{O}_3$ molecules followed by the formation of acrylamide radicals. The

step is followed by the subsequent recombination of the growing macro-radicals. Nano-sized ferric oxide particles with average crystal size of 35 and 150 nm were used to completely degradation of Congo red dye with and without irradiation with no pronounced effect of radiation on the catalytic degradation (Khedr,2009). Ferric oxide nanoparticles modification with titanium dioxide was achieved a high photodegradation percentage of phenol by using a low concentration (0.2g/L), which contributes to the cost effectiveness of the photodegradation process (Herrera et al.,2016).

Ferric oxide nanoparticles are suitable for the degradation of anthracene under UV irradiation. The decay profiles of anthracene follow first-order kinetics with half-lives of anthracene were 3.2 and 4.4 h on α -FeOOH and Fe₃O₄, respectively (Gupta et al.,2017). The synthesized ferric oxide nanoparticless exhibited mono dispersity with the particles size of 64 nm and the photocatalytic degradation of CV dye under UV illumination reached to 86.69% within 210 min (Ahmed et al.,2016).

1.3 Photocatalytic reactions mechanism

Heterogeneous photocatalysis is based on adsorption of photons with high energy resulting in initiating excitation related to charge separation event (gap band). Generation of excited high-energy states of electron and hole pairs occurs when wide band gap semiconductors are irradiated higher than their band gap energy.

Fig.(1.3) illustrates the mechanism of electron–hole pairs generation when the semiconductor particle is irradiated with sufficient light energy ($h\nu$). It results in the promotion of an electron in the conductive band (e_{CB}^-) and formation of a positive hole in the valence band (h_{VB}^+). The h_{VB}^+ and e_{CB}^- are powerful oxidizing and reducing agents, respectively. The h_{VB}^+ reacts with organic compounds resulting in their oxidation producing CO₂ and

H₂O as end products. The h_{VB}⁺ can also oxidize organic compounds by reacting with water to generate OH[•]). The OH[•] can non-selectively oxidize almost all electron rich organic molecules due to its electrophilic nature (electron preferring, eventually converting them to CO₂ and water).

Generally, mechanism of heterogeneous photocatalysis on the surface of the semiconductor has four essential steps as the following:

1. charge carrier generation.
2. charge carrier trapping.
3. charge carrier recombination.
4. photocatalytic degradation of organic pollutants.

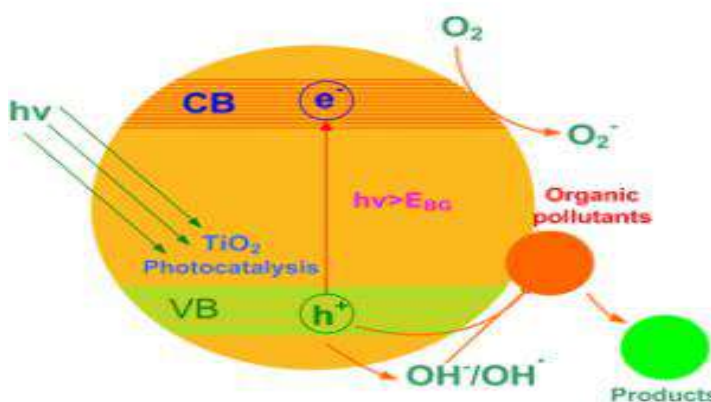
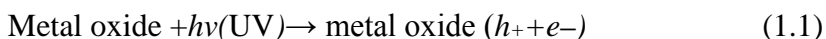
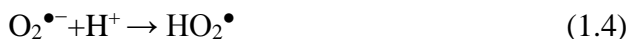


Figure (1.3): Mechanism of photocatalytic degradation of organic compounds using metal oxide semiconductor as a photocatalyst



On the other hand, it is important for the electron in the conduction band (CB) to be scavenged by an electron acceptor to suppress its recombination with the trapped hole. Molecular oxygen (O₂) is one of the efficient electron

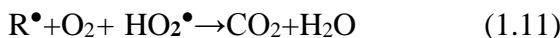
acceptors, while reactive superoxide radical anions $O_2^{\bullet-}$ are produced. Together with other oxidizing species such as hydroperoxyl radicals HO_2^{\bullet} and hydrogen peroxide (H_2O_2) are also subsequently formed. The additional OH^{\bullet} radicals are generated through the following mechanism (Lam et al., 2012):



During the process, there is the opportunity that both $e-h+$ pair recombination and trapped carrier recombination happen.

Essentially OH^{\bullet} , HO_2^{\bullet} and $O_2^{\bullet-}$ radicals as well as photogenerated hole ($h+$) are highly reactive intermediates that will be attacked organic pollutants and lead to complete mineralization and degradation of them.

The role of OH^{\bullet} , $h+$ and $e-$ as oxidative reductive species illustrate in the following reactions (Rasul et al., 2011):



1.4 Sensitization

Photosensitization can be achieved by a photosensitizer which absorbs light energy, transforms the light energy into chemical energy, and transfers it under favorable conditions to otherwise photochemically unreactive substrates (Larson et al., 1992).

Metal oxides have a wide band gap, with limited photo-catalytic applications to shorter wavelengths (it demands UV light), so metal oxides

performance under solar light must be improved. Using small band gap semiconductors instead is not an alternative, because they are unstable, in order to improve metal oxide properties as photocatalyst under solar light; studies have been made to sensitize metal oxides by adding another element or compound with the certain character.

Dye sensitization is used in widely manner to utilize visible light for energy conversion. Some dyes having redox property and visible light sensitivity can be used in solar cells as well as photocatalytic systems. Under illumination by visible light, the excited dyes can inject electrons to CB of semiconductors to initiate the catalytic reactions as illustrated in Fig (1.4).

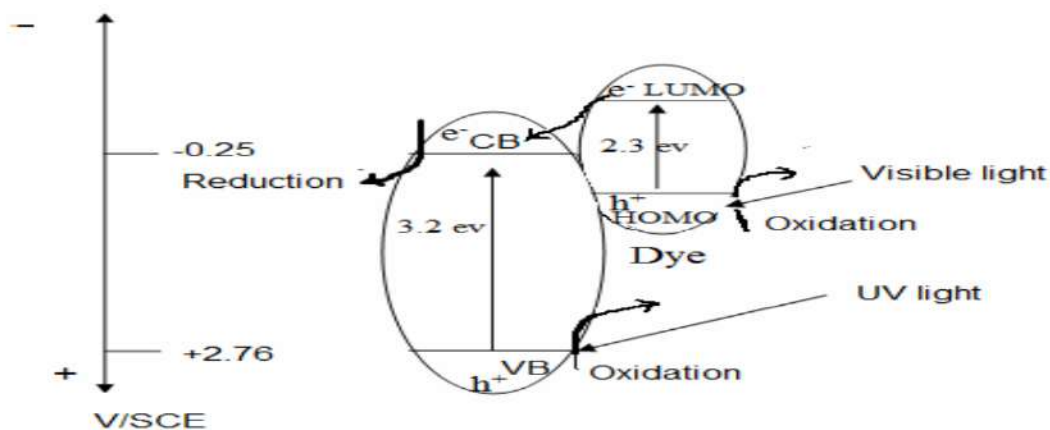


Figure (1.4): Mechanism of dye-sensitized photocatalytic of metal Oxides

In the last years, plentiful organic dyes such as eosin Y (Chakrabarti et al.,2008; Jin et al.,2007) riboflavin(Cui et al.,2001), rose Bengal (Whitehead and Hedges,2005), cyanine(Guo et al.,2005) cresyl violet (Liu et al.,1997), hemicyanine(Chen et al.,2005) and merocyanine(Abe et al.,2002) got particular attention and had been tested as photosensitizers, However, the stability of pure organic dyes is a notable problem which should be solved emergently (Vinodgopal et al.,1996).

In this study, Eosin Y was selected to be used as a sensitizer, where it is a popular organic pigment with excellent light harvesting property, low cost,

and often used as a fluorescent dye in biological research, has been used in dye sensitized solar cells(Zhang et al.,2014). Fig (1.5) shows the structural formula for Eosin Y molecule.

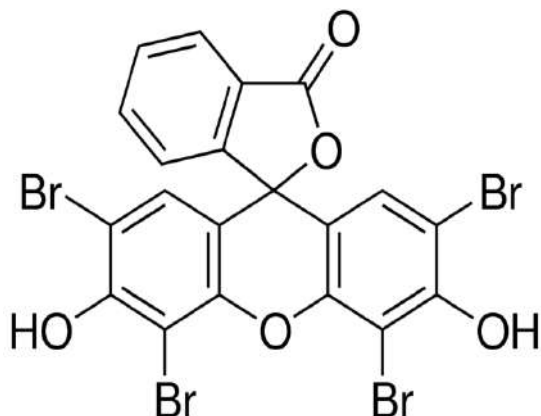


Figure (1.5): Structural formula for Eosin Y.

Under appropriate circumstances, photosensitizer can be adsorbed at the semiconductor surface by an electrostatic, hydrophobic, or chemical interaction that, upon excitation, injects an electron into its conduction band. Only the one layer of adsorbed dye molecules would attach to the semiconductor particle surface, so that the light harvesting efficiency is expected to be small quantity, but the effective surface area in the powder semiconducting material is relatively large enough to compensate. This led to prefer sensitized nanoparticle semiconductor in experimental work than the bulk counterparts (Zyoud,2009). Sensitization process involves enhanced the excitation of the dye molecules from ground state to an excited state by absorption of a photon. Using Eosin Y as a dye that have a large π conjugated system, allowing π - π^* transitions at low energy, i.e., in the visible part of the spectrum. In molecular terminology, an electron jumps from Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO) and this is followed by relaxation through electron loss to metal oxides conduction band and the dye left as a

surface-adsorbed cation. The dye positive charge convey to redox species that maybe an organic contaminant molecule. The electrons in the conduction band of the semiconductor spontaneously will reduce species like O₂. There are two prerequisites for such heterogeneous semiconductor systems to function efficiently: (1) the band gap of the sensitizer should be near the appropriate value for optimum utilization of solar radiant energy and (2) its conduction band edge should be higher than that of semiconductor and this allowing electrons transferring from the sensitizers to semiconductor (Jing and Guo,2007). The electron can be injected during the relaxation process when the energy level of the LUMO is higher than the conduction band edge of metal oxides and the HOMO lower than the reduction potential of the organic pollutants(Gaetzel and McEvoy,2004). The Peculiar molecular properties of the dyes, and the possibilities of related technological applications, are directly related to (a) the energetic spectrum that determines the optical absorption and emission characteristics, (b) the efficiency in electron injection from the excited state to the semiconductor, and (c) after the electron injection, a fast and efficient regeneration of the dye cation occur (Hazebroucq et al.,2008).

In this study, Tartrazine and levofloxacin will be used as an organic pollutant:

A: Tartrazine

Tartrazine is a synthetic lemon yellow azo dye used as food colorants, in cosmetic and in textile industry .Tartrazine is water soluble and has a maximum absorbance in an aqueous solution at 427 ± 2 nm, out of azo dyes , tartrazine seems to cause the most allergic and intolerance reactions, particularly among asthmatic patients and those with aspirin intolerance (Alvarez et al., 1981). Fig (1.6) show Tartrazine chemical structure .

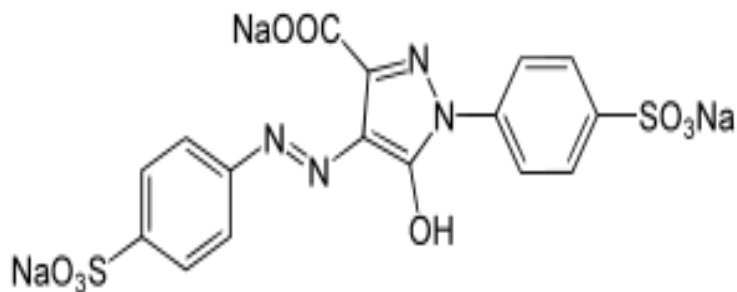


Figure (1.6): Tartrazine chemical structure.

Many foods contain tartrazine in varying proportions, depending on the manufacturer or person preparing the food. When in food, tartrazine is typically labelled as "color", "tartrazine", or "E102". Products containing tartrazine commonly include processed commercial foods that have an artificial yellow or green color, or that consumers expect to be brown or creamy looking. The foods that may contain tartrazine as some of desserts, candies, soft drink, condiment and breakfast cereals .

Azo dyes , they are resistant to biodegradation under aerobic condition (Pagga and Taeger, 1994) , the toxic concentration of tartrazine on humans has been reported to be 7.5 mg/kg as European Food Safety Authority publish. Tartrazine , as an azo dye has been chosen for this study due to its extensive use as a colorant in food, cosmetics, pharmaceuticals and textile industry , as well as its high stability against biodegradation and conventional wastewater treatment procedures after disposal from industrial effluent. Several studies have demonstrated that Tartrazine could be degraded employing AOPs like: ozonation , electrochemical oxidation , photo Fenton oxidation , UV/HO, photolytic , and photocatalytic oxidation. The heterogeneous photo-Fenton process for the removal of Tartrazine on structured catalysts. In particular, LaFeO_3 or Pt/LaFeO_3 perovskite supported on honeycomb monoliths have been tested by Giuseppina Iervolino et. al, and the results showed that the process is effective both for

discoloration and mineralization of the dye, after 180 min the degradation of Tartrazine reached to 45% and 65% using LaFeO_3 or Pt/LaFeO_3 respectively. Using the solar-reactor with a heterogeneous photocatalysis process (TiO_2/UV) gives a high degradation efficiency of Tartrazine reached to 99% after 200 min although the expensive apparatus that used (Chekir et al.,2017). The effect of Microwaves ($\text{UV}/\text{H}_2\text{O}_2/\text{MW}$) on the color removal of Tartrazine reached approximately 92% in 24 min of irradiation, however no mineralization occurred and the biodegradability and ecotoxicity remained approximately the same (Parolin et al.,2013).

Salem and Gemeay(2000) examine the oxidation kinetics of tartrazine with peroxydisulfate in the presence and absence of Ag(I) and Fe(III) catalysts and observed higher tartrazine conversion in alkaline media. Fragoso et al, (2009) investigated the degradation of tartrazine by oxidation with H_2O_2 in alkaline solution ,Oancea and Meltzer(2013) investigated using a laboratory scale photoreactor equipped with a low pressure mercury lamp ,the total disappearance of tartrazine by photo-Fenton process and the total organic carbon removal 80% indicate the presence of some small organic molecules in solution. (Aldawery,2013) show that the maximum rate of tartrazine degradation is $3.4 \times 10^{-3} \text{ min}^{-1}$ in a solution of 500mg/L titanium dioxide with UV lamp.

B: Levofloxacin

levofloxacin ,chiral fluorinated carboxyquinolone, is a broad spectrum antibiotic that belongs to fluoroquinolone class and is known for its broad spectrum activity against gram positive bacteria (staphylococcus aureus, streptococcus pneumoniae , staphylococcus epidermidis) and gram negative bacteria(Escherichia Coli , Haemophilus influenza, Klebsiella pneumoniae)(Nasuhoglu et al., 2012). Its empirical formula is

$C_{18}H_{20}FN_3O_4 \cdot \frac{1}{2} H_2O$ and its molecular weight is 370.38. Levofloxacin crystal or crystalline powder is a light yellowish-white to yellow-white. Levofloxacin is rapidly and essentially completely absorbed after oral administration. Peak plasma concentrations are usually attained one to two hours after oral dosing. Fig (1.7) shows Levofloxacin chemical structure.

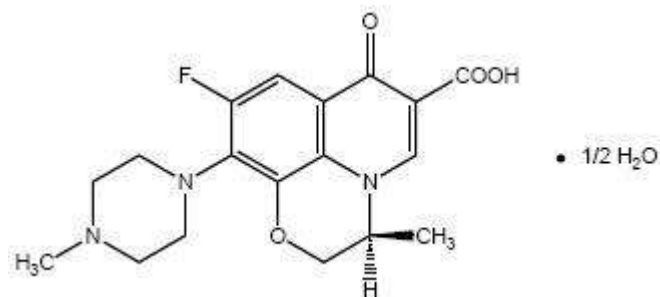


Figure (1.7) Levofloxacin chemical structure.

Although the antibiotics discharge into the domestic water have no direct toxicity, the potential hazard of residual antibiotics might enhance resistance to harmful bacteria, which were untimely metabolized by animal or incompletely treated by wastewater treatment plants with active sludge (Fu et al., 2015). A well crystalline TiO_2 nanoparticles synthesized using sol-gel technique and under UV-illumination achieved 90% degradation of Levofloxacin after 120 min (Kansal et al.,). A dimensionally stable anode with modified cathode using hydrazine hydrate and ethanol for electro-Fenton show degradation decay of Levofloxacin to be 0.2883 min^{-1} (Liu et al., 2017). The combination of ultrasound and CCl_4 show a positive effect on Levofloxacin degradation as the biodegradability enhanced as BOD_5/COD ratio from 0 to 0.41 (Guo et al., 2010).

Levofloxacin aqueous solutions were successfully mineralized by hydroxyl radical generated in electro-Fenton process, maximum mineralization rate of Levofloxacin reached to 91% COD removal (Yahya et al., 2015).

1.5 Objectives

The main goal of this work is to find safe and economic methods for removal textile dyes and pharmaceutical wastes by photocatalytic degradation using UV irradiation as well as solar irradiation under the existence of metal oxides (SnO_2 and Fe_2O_3) nanoparticles and a photosensitizer adsorbed on the surface of the nanoparticles. The semiconducting nanoparticles will be immobilized in a polymeric substrate. Evaluation the efficiency of the photodegradation process with different parameters will be investigated as in the followings:

- Purification of water from Tartrazine and Levofloxacin by photodegradation by sensitized SnO_2 and Fe_2O_3 photocatalyst immobilized in polymer using UV irradiation as well as visible irradiation.
- Study the factors and parameters that affect the degradation efficiency of Tartrazine and Levofloxacin including the initial concentration of pollutants, pH of solution, effect of different radiation source, at different wave lengths, effect of presence of peroxides, and competing and interfering ions present in natural water.
- Studying the possibility of multiple use of the photocatalyst membrane (recovering and reusing the photocatalyst for multiple times in photo-degradation process).
- Studying the effect of using photosensitizers to investigate the performance of solar irradiation as an alternative of UV irradiation.

Chapter (2)

Experimental

Experimental Work

A.2 Tartrazine and Levofloxacin Photocatalytic degradation

A.2.1 Materials and Methods :

- Tin oxide (SnO_2) and iron oxide (Fe_2O_3), Commercial SnO_2 (nanoparticles) were obtained from (Hefei Quantum Quelle Nano Science And Technology Co., Ltd), and Fe_2O_3 were obtained , Pure PVC, PMMA , Eosin as sensitizer, THF, HCl and NaOH was purchased from Aldrich and used as received, Tartrazine (E102) dye was obtained from Aldrich , pure grade Levofloxacin was provided by Pharmaceutical Co.(Memphise), salts (NaF , NaNO_3 , Na_2SO_4 , NaHCO_3) were purchased from Aldrich and used as received.

A.2.2 Solutions preparation:

The following solutions were prepared and used:

- Tartrazine stock solution (1×10^{-3} M)
- Levofloxacin stock solution (1×10^{-3} M)
- Tartrazine (1×10^{-5} M) and Levofloxacin (10×10^{-5} M) solutions of different pH values (3 , 5 , 7 ,9 ,11).
- Tartrazine (1×10^{-5} M) and Levofloxacin (10×10^{-5} M) solutions of different H_2O_2 concentrations(0 M, 0.05 M, 0.1 M, 0.15Mand0.2M).
- Tartrazine (1×10^{-5} M) and Levofloxacin (10×10^{-5} M) solutions containing 190 ppm salts (NaF , NaNO_3 , Na_2SO_4 , NaHCO_3).

A.2.2.1 Preparation of (1×10^{-3} M) Tartrazine stock solution:

Tartrazine powder of 0.134g was dissolved in distilled water then completed with to 250ml to get (1×10^{-3} M) Tartrazine stock solution , then the different standard solutions of (1×10^{-4})M and (1×10^{-5})M were prepared by dilution using distilled water.

A.2.2.2 Preparation of (1×10^{-3} M) Levofloxacin stock solution:

A 0.09g of levofloxacin was dissolved in distilled water then completed with to 250ml to get (1×10^{-3} M) levofloxacin stock solution , then the different standard solutions of(1×10^{-4})M and (1×10^{-5})M were prepared by dilution using distilled water.

A.2.2.3 Tartrazine (1×10^{-5} M) and Levofloxacin (10×10^{-5} M) solutions of different pH values:

By using acid and base a solution of (1×10^{-5} M) Tartrazine and (10×10^{-5} M) Levofloxacin were prepared with different pH values by adding a suitable volumes of 0.05M NaOH solution and 0.05 M HCl solution to obtain the desired pH values of (3 , 5 , 7 , 9 , 11). pH meter (HM-40V) was used to measure the pH of the solutions .

A.2.2.4 Tartrazine and Levofloxacin solutions of different H₂O₂ concentrations:

To obtain the desired concentrations of H₂O₂ in solutions, 100 mL of Tartrazine and Levofloxacin solutions were prepared by adding a 0.5ml, 1ml, 1.5ml, 2ml of (32% H₂O₂, d=1.18g/cm³) respectively to got a solutions of H₂O₂ of (0.05M, 0.1M, 0.15M and 0.2M) respectively.

A.2.2.5 Preparation of Tartrazine and Levofloxacin solutions containing 200 ppm salts (NaF, NaNO₃, Na₂SO₄, NaHCO₃) :

0.02 g of each of the following salts (NaF, NaNO₃, Na₂SO₄, and NaHCO₃) added to 100 mL of Tartrazine and Levofloxacin solutions separately.

A.2.3 Photocatalysts membrane preparation:

- SnO₂/PVC membrane.
- Fe₂O₃/PVC membrane.
- SnO₂/PMMA membrane.

- Fe₂O₃/PMMA membrane.
- PVC membrane.
- SnO₂/Eosin/PVC membrane.
- Fe₂O₃/Eosin/PVC membrane.

All these membranes were prepared in the same manner as the following as an example:

A.2.3.1 SnO₂/PVC preparation: 0.2 g of the membrane base (that is poly vinyl chloride) was gradually added in a glass petri dish 250mm diameter that contains 10 ml of a PVC solvent (THF) with continuous stirring with a glass rod until all PVC particles dissolved. Then gradually add 0.05g metal oxide nanoparticle (to prepare SnO₂/PVC) with continuous stirring of the mixture. Let the mixture dry for 24 hours at room temperature, and then the dry membrane can be used.

A.2.3.2 SnO₂/Eosin preparation:

1g of SnO₂ was mixed with 5ml Eosin solution (containing 0.4g Eosin) and 5ml deionized distilled water and stirred magnetically for 30 minutes at room temperature. The mixture was then covered and left overnight to precipitate. Suction filtration was performed on SnO₂/Eosin and the solid powder was collected and washed with distilled water then dried in air to be used in preparation of SnO₂/Eosin/PVC membrane.

A.2.4 Equipments:

UV-Vis spectrophotometer:

A Shimadzu (UV-2450) model UV-VIS 3101-PC Spectrophotometer was used for absorbance measurement of Tartrazine and Levofloxacin to monitor the degradation process of them.

Light source:

Different light sources were used in the degradation process of the pollutants such as UV lamp (4W-365nm, 4W-254 nm), Halogen spot Lampe and direct solar radiation was used.

pH meter:

pH meter (HM-40V) was used to adjust pH of the used solutions as desired at specific values.

A.2.5 Photocatalytic reactor:

To avoid exposure to a harmful UV radiation, a black box was used , a vessel of reaction that containing organic material to be degraded, other reaction mixture and photocatalytic membrane was placed in the box at fixed distance from the irradiation source.

A.2.6 Tartrazine and Levofloxacin Photocatalytic degradation experiments:

The photocatalyst embedded on polymer (the membrane) was placed in the reaction beaker in which 100 ml of pollutant of known concentration was present photocatalytic reactor irradiated by UV-radiation at 254nm and 365nm and intensity of 8W or halogen lamp at room temperature also the experiment performed outdoor to full exposure to solar radiation (in June and July from 11am to 3pm) ,5mL of reaction solution were withdrawn at various time intervals. The pollutant was analyzed using UV-VIS spectrophotometer through out the degradation process to monitor the degradation and the efficiency of the photocatalytic degradation reaction.

Chapter (3)

Results and Discussion

Results and Discussion

A: Tartrazine Degradation

A.1 Photocatalytic activity of different metal oxides nanoparticles

Heterogeneous photocatalysis that based on a semiconductor nanoparticles have been used as a catalyst, which is activated by UV radiation with energy equal to or higher than the gap energy of the metal oxides in order to excite electrons from valence band to conduction band (Lam et al.,2012). The activity of photocatalyst depends on surface and structural properties of semiconductor such as crystal composition, surface area, particle size distribution, porosity, band gap and surface hydroxyl density (Rasul et al.,2011). Different nanostructured metal oxides particles were used as a photocatalytic membrane. Table(3.1) shows the percentage of photodegradation activity of Tartrazine using SnO₂, Fe₂O₃ nanoparticles as a photocatalyst. The data was carried out after the exposure to UV radiation at wavelength $\lambda = 254\text{nm}$ for 120 min. It is clear from the data that the maximum degradation of Tartrazine dye was achieved by utilizing SnO₂ nanopowder as photocatalyst with degradation percentage of 85% followed by 57% for the Fe₂O₃ photocatalyst.

Table(3.1): Percent of photodegradation activity of Tartrazine using different metal oxide after 120 minutes exposure to UV radiation at 254nm:

Catalyst type	Degradation percent after 120 minutes
SnO ₂	85
Fe ₂ O ₃	57

SnO₂ was selected to be the proper photocatalyst membrane for Tartrazine degradation. It is anticipated that this is attributed to the strong adsorption of Tartrazine dye molecules onto SnO₂ surface than the adsorption onto Fe₂O₃. The strong adsorption is referred to the high electrostatic interaction between the Tartrazine molecules and the SnO₂ nanoparticle surface.

A.2 Effect of UV radiation and nano SnO₂/PVC membrane as photocatalyst system

The optimization of the best condition for the degradation of the Tartrazine dye using UV irradiation exposure and the photocatalyst membrane were carried out. Figure (3.1) depicted the UV-VIS absorption spectrum of three samples, which treated using the SnO₂ photocatalyst membrane without exposure to UV irradiation, the exposure of UV irradiation ($\lambda=254$ nm) without the existence of the photocatalyst membrane, and in the presence of UV irradiation in addition to SnO₂ photocatalyst membrane, respectively. The exposure time of Tartrazine solution was 120 minutes. As shown in these UV-VIS absorption spectra, the presence of both the UV irradiation and the SnO₂ photocatalyst membrane is the optimum condition to results in an effective degradation of the Tartrazine dye. The characteristics absorption peak of Tartrazine is reduced significantly by using both the UV exposure and the SnO₂ photocatalyst.

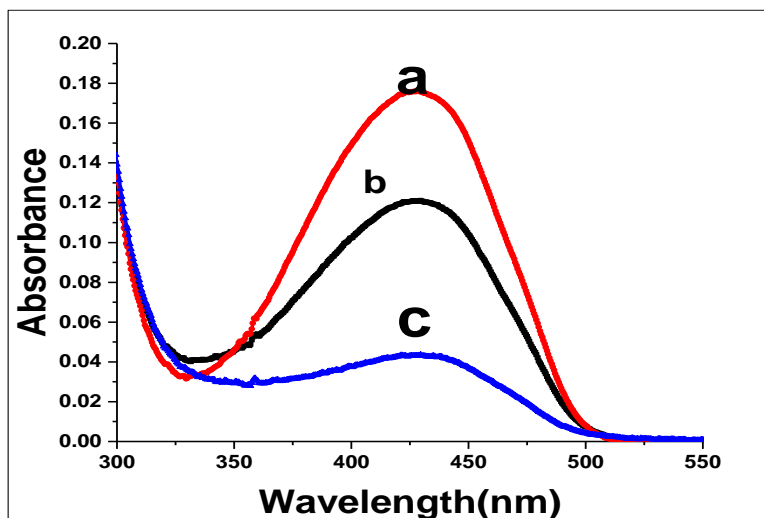


Figure (3.1): UV-Vis absorption spectra of $1 \times 10^{-5} \text{M}$ Tartrazine decomposed upon different degradation conditions after 120 minutes of the reaction (a: with SnO_2 membrane and no UV, b: with UV at $\lambda=254 \text{nm}$) and no SnO_2 membrane, c: with both SnO_2 membrane and UV(254nm) radiation).

According to the previous results, the optimization parameters for the best degradation was carried out using the SnO_2 photocatalyst membrane and under the presence of UV irradiation at wavelength $\lambda=254 \text{ nm}$, which is the optimum condition for creating radicals capable of destroying the bonding of the pollutant.

Figure (3.2) shows the effect of the exposure time of the experiment using the previous conditions, where the significant sharp drop of the dye remaining is noticed after 30 min for the sample treated using both the photocatalyst and the UV irradiation, and then the remaining decreased gradually up to 210 min, where after that no significant degradation was observed.

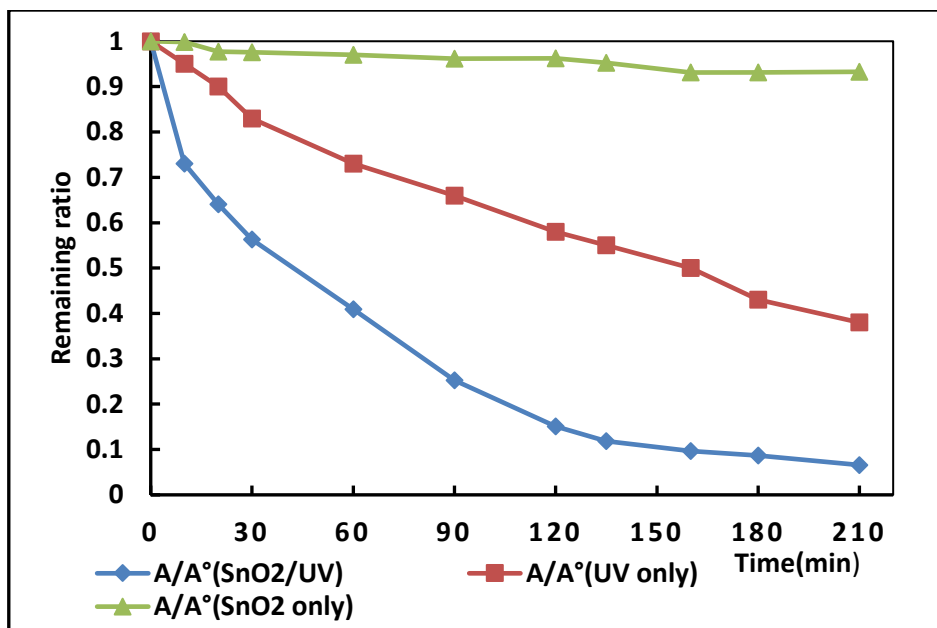


Fig (3.2): Effect of presence of UV radiation and SnO₂ photocatalyst membrane on 1×10⁻⁵ M Tartrazine degradation as a function of the exposure time.

Table (3.2) illustrates a summary of the results obtained from this study about the effect of the presence of UV radiation and SnO₂ on the efficiency of degradation process as well as the degradation rate for each process. The optimum degradation of the Tartrazine dye was 85 %, which was correlated with the highest degradation rate of 0.71 Mmin⁻¹.

Table (3.2): Percent degradation and degradation rate of 1×10⁻⁵ M Tartrazine after 120 minutes under different degradation conditions.

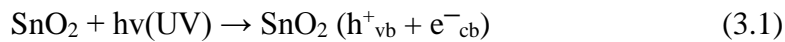
Samples	%Degradation	Degradation rate (M min ⁻¹)
SnO ₂ membrane+Tartrazine +H ₂ O ₂ +No UV radiation(Dark catalysis)	4%	0.03

Tartrazine+H ₂ O ₂ +UV radiation and No SnO ₂ membrane (photolysis)	42%	0.35
SnO ₂ membrane + Tartrazine+ H ₂ O ₂ + UV radiation at λ=254 nm (photocatalytic degradation)	85%	0.71

Degradation rate=molarity/time

The basis of photocatalysis is the photo-excitation of a semiconductor that is a result of the absorption of electromagnetic radiation. A mechanism that explains how the photocatalytic degradation performed the degradation of pollutants can be simplified in few steps including the following (Munter,2001):

1. Absorption of efficient photons can form electrons -hole pairs.



2. Oxygen adsorption leading to O₂^{•-} free radicals formation.



3. Formation of HO[•] radical by photoholes.



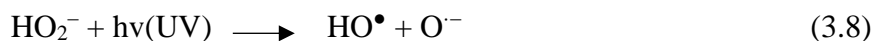
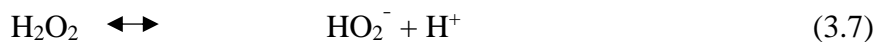
4. Oxidation of organic species R by HO[•] radical or holes



On the other hand the direct photolysis of hydrogen peroxide leads to the formation of HO[•] radicals, whereas,



Also HO₂⁻, which is in acid–base equilibrium with H₂O₂, absorbs the UV radiation of the wavelength 254 nm:



Different concentrations (1×10^{-5} M, 3×10^{-5} M, 5×10^{-5} M and 10×10^{-5} M) of Tartrazine dye were prepared to test the photodegradation by using nano SnO₂/PVC photocatalyst membrane as a function of the concentration. Fig (3.3) illustrates calibration curve of Tartrazine plotted including the prepared solutions, where a linear relationship is found between the absorbance and the dye concentration.

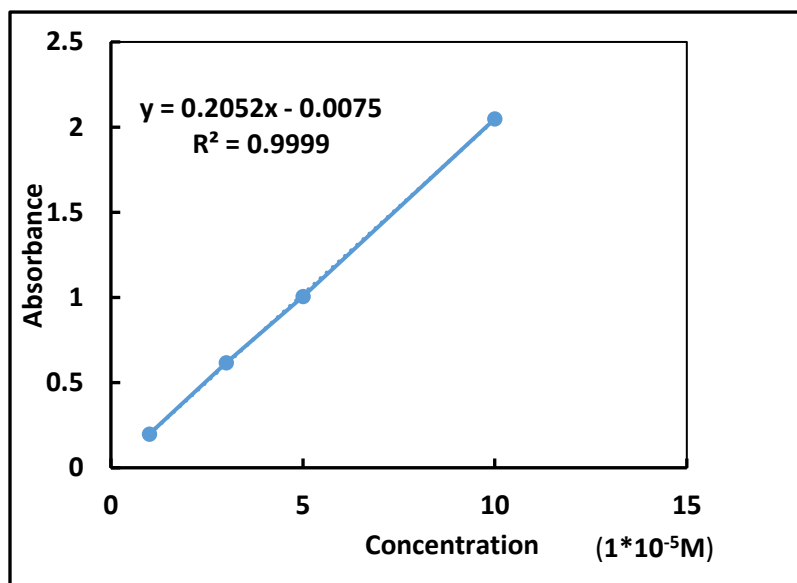


Figure (3.3): Calibration curve of Tartrazine.

A.3 Operational parameters :Investigation and optimization

A.3.1 Effect of Irradiation time:

Figure (3.4) shows the absorption of 1×10^{-5} M Tartrazine solution before the degradation measured at the range (200-800) nm. The characteristic absorption peak of Tartrazine is the highest peak at 425nm. This observed peak is located in visible region which may be assigned to the aromatic ring bearing the substituent groups (OH and SO₃) which are called auxochromes. The photocatalytic degradation set cause the absorption intensity spectrum

of Tartrazine to decrease with time until it completely disappeared, this maybe the destruction of chromophoric structure.

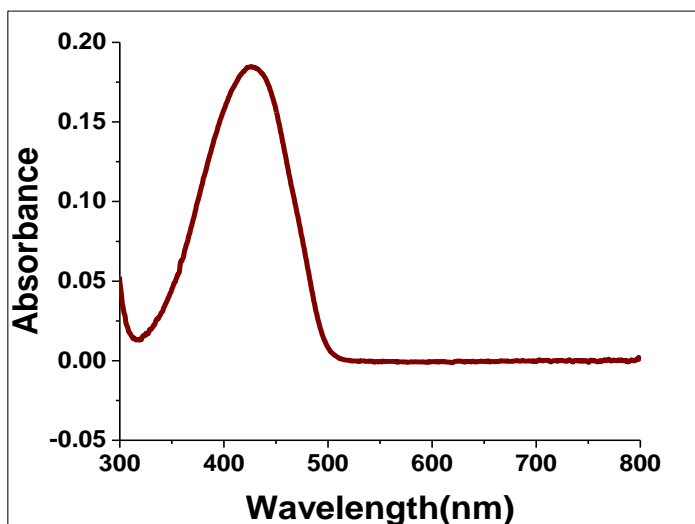


Figure (3.4): UV-Vis absorption spectrum of 1×10^{-5} M Tartrazine before exposure to UV radiation and SnO_2 photocatalyst membrane .

The yellow-orange color of Tartrazine solution completely disappeared after **180** minutes of the exposure reaction. It was observed that the color intensity and the absorbance of dye continues decreasing with the increasing of the irradiation time, where the dye may be degraded due to further oxidation process that's lead to further degradation of tartrazine dye molecules and turn over to mineral salts and some gases. This can explain the importance of the presence of both sufficient energy radiation from UV lamp at 254 nm and the SnO_2/PVC membrane as a catalyst. Absorbance of 1×10^{-5} M tartrazine was measured at different time intervals (from 0 min until color removed at 180 min) by UV-Vis spectrophotometer in the range from (200 to 800 nm) in order to give wide space to notice the color of the dye and monitor the color removal. The spectra are shown in figure (3.5).

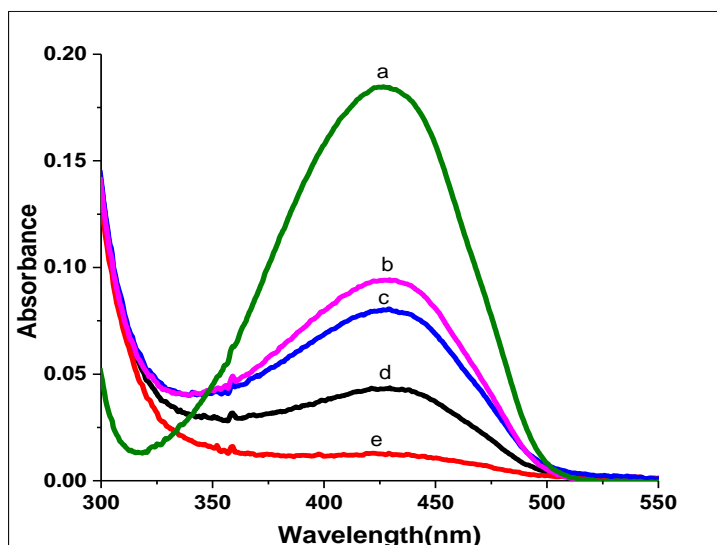


Figure (3.5): Gradual color removal of 1×10^{-5} M Tartrazine upon photocatalytic degradation process using SnO₂/PVC membrane after (a:0 min, b:60 min, c:90 min, d:120 min, e:180 min)

A.3.2 Effect of initial Tartrazine concentration:

The influence of UV radiation utilizing SnO₂ on the initial concentration of Tartrazine solution and the rate of degradation was studied. The concentrations of tartrazine solution were used varied from (1 to 10) $\times 10^{-5}$ M. Percent degradation after 120 minutes of photocatalytic degradation for different concentrations of Tartrazine is shown in Table (3.3). As the Table shows, increasing in the dye concentration is followed by increasing in the remaining ratio which mean a decreasing in the degradation rate. When the concentration was 1×10^{-5} M, 87% of Tartrazine degraded and removed after 120 minutes, however this degradation percentage decreased to 65% when the concentration increased to 5×10^{-5} M and then decreased to less extent when the dye concentration reached 10×10^{-5} M. This behavior indicates that the efficiency of Tartrazine photodegradation decreases with increasing concentration, which indicates that the decomposition rate is strongly dependent on the initial pollutants concentration.

Table (3.3): %Degradation of different concentrations of Tartrazine dye after 120 minutes of the reaction.

Initial concentration(M)	Degradation %
1×10^{-5}	85
3×10^{-5}	79
5×10^{-5}	65
10×10^{-5}	60

Figure (3.6) depicts the evolution of photodegradation of Tartrazine dye for different concentration. The less concentrated dye is degraded more rapid compared with the high concentrated one. Figure (3.6) illustrates the remaining ratio under different concentrations of Tartrazine during photocatalytic degradation process.

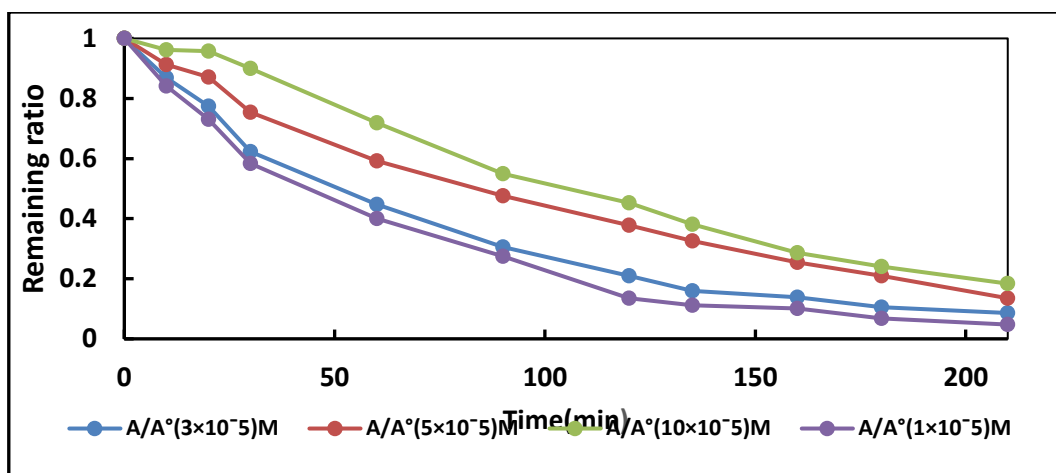


Figure (3.6): Effect of concentration on the photocatalytic degradation efficiency of Tartrazine using SnO₂/PVC membrane.

The increase in pollutant concentration decreases the path length of photon entering into the pollutant solution. At high pollutant concentrations, a significant amount of light radiation may be absorbed by the pollutant molecules rather than the photocatalyst and this reduces the photocatalytic efficiency (Rajamanickam et al., 2016). Thus less number of photons could

reached SnO₂ photocatalyst membrane surface, other amount of photons from UV radiation would be absorbed by Tartrazine molecules instead of the photocatalyst membrane. The surface adsorption process is of importance in controlling the degradation of pollutants. When the pollutant concentration is too high, the active sites will be occupied by intermediate products, from the photocatalyst surface can result in the deactivation of the active sites of SnO₂ photocatalyst. It can also be attributed to the reason of competition between the adsorbed Tartrazine molecules and H₂O molecules for photogenerated h⁺ resulting in reduction in the generation of the most reactive oxidative species OH[•] radical and other reactive species. So that more pollutant molecules are adsorbed on the surface of photocatalyst membrane in contrast, the relative number of OH[•] radical attacking the pollutant molecules decreases due to reaction conditions remain in the constancy state.

A.3.3 Effect of pH:

The pH of the initial dye solution largely affects the rate of photocatalysis, where the pH of solution is an effective parameter on the photodegradation process, since the surface charge of the semiconductor photocatalyst is controlled by the adjustment of the pH of the solution. Effect of pH on degradation rate depends on the ionization state of the organic substance to be degraded, especially acids and amines, as well as acid-base properties of the photocatalyst and can be explained on the basis of zero point charge "pzc". The photocatalyst is negatively charged at pH above its pzc, and below this point, its surface attains positive charge (Abdollahi et al., 2012; Meng and Juan, 2008). These characteristics can significantly influence the interaction and affinity between photocatalyst and dye pollutant with variation of solution pH. SnO₂ has pzc of 4.5, where below this point its surface is positively charged and is often negatively charged above 4.5.

Effect of pH on the degradation efficiency of Tartrazine under UV light radiation and the presence of SnO₂ photocatalyst membrane was studied at different pH values. Figure (3.7) represents the remaining (A/A_0) of Tartrazine dye along the reaction time at different pH values. Remaining ratio (A/A_0) increases as pH of Tartrazine solution increases and it is noticed that the maximum degradation efficiency was achieved when the pH of the dye was 3, while the least efficiency was observed at higher pH value (9-11).

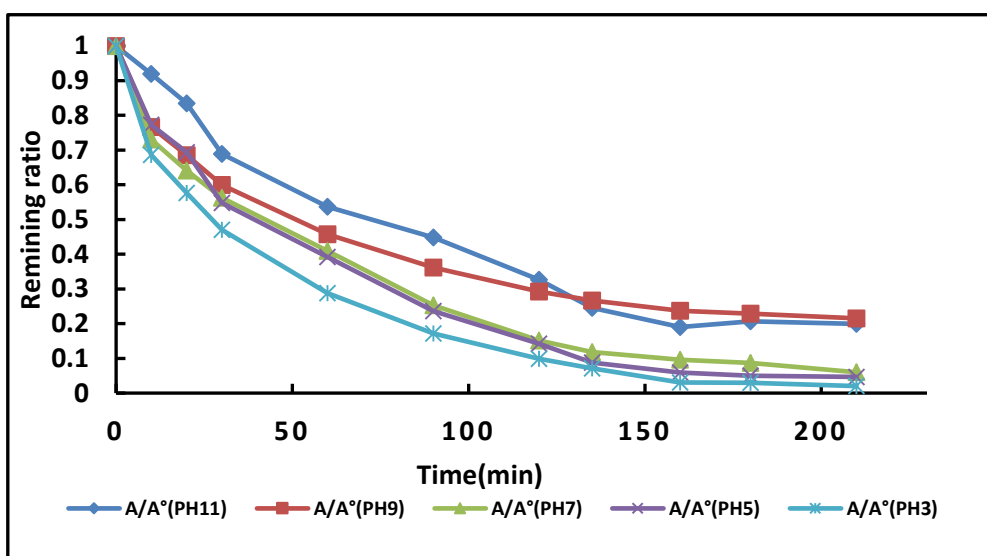


Figure (3.7): Effect of pH on the color removal of 1×10^{-5} M Tartrazine using SnO₂/PVC membrane.

A value of Percent remaining of 1×10^{-5} M Tartrazine solution after 120 minutes of the photocatalytic degradation reaction was calculated, Figure (3.8) shows the percent remaining of the Tartrazine dye as a function of pH in the specific time and at different pH values (3, 5, 7, 9 and 11), where a gradual increase of the remaining is observed by increasing the pH, which

were 9%, 14%, 15%, 29% and 33% respectively. The acidic medium is the optimum one to give effective degradation.

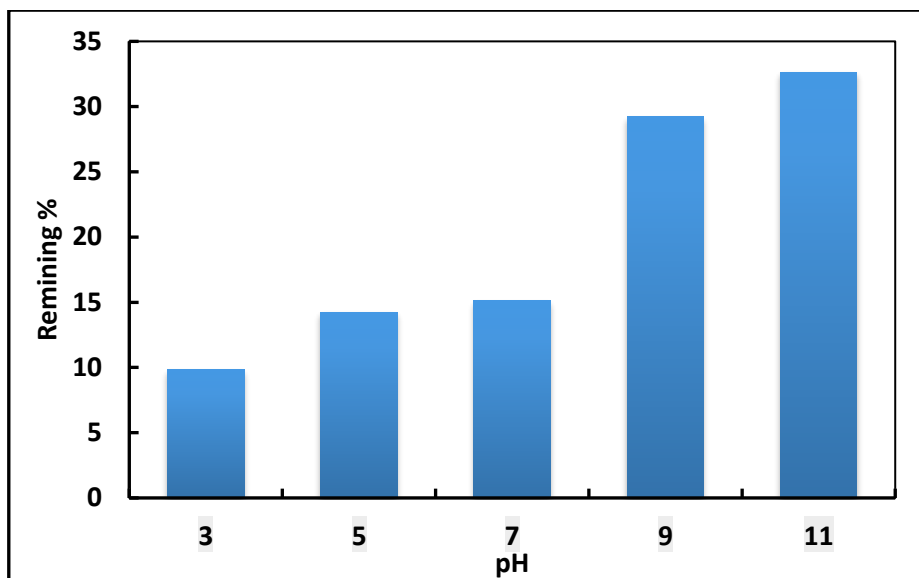


Figure (3.8): Effect of pH on % remaining of 1×10^{-5} M Tartrazine after 120 minutes of photocatalytic degradation process utilizing SnO_2/PVC membrane.

From the obtained results, it is confirmed that the degradation efficiency related to the pH of the solution that undergoes to be degraded, as it is depicted from the previous results that the effect of pH on Tartrazine solution degradation in the presence of SnO_2 membrane is illustrated by degradation efficiency as this order:

$$pH3 > pH5 > pH7 > pH9 > pH11$$

Depending on the ionic form of the organic molecule, at different pH, repulsion or attraction of the molecule with the SnO_2 membrane surface is observed and this accordingly either inhibits or improves the photodegradation efficiency. There are at least three phenomena in photocatalytic reaction that are affected by pH: catalyst surface charge (dependent on PZC), oxidation mechanism (positive holes or hydroxyl radicals) and behavior of the molecule (dependent of pKa) to be treated.

As the results shows the effect of pH on the photodegradation rate of Tartrazine, indicating that the degradation rate increases with the solution pH decreasing. This is mainly ascribed to the variations of surface charge properties of the photocatalyst. So, the maximum photodegradation obtained at acidic range at pH3.

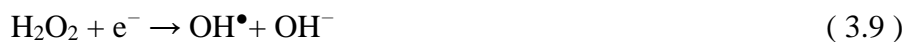
At pH3, SnO₂ is positively charged due to its pzc value, while Tartrazine is negatively charged which means that strong electrostatic interaction is resulted so that, which means strong adsorption of Tartrazine molecules takes place which makes them close to the center of the electron-hole pair generation. At low pH medium, positive holes are considered to be the predominant species in this condition, for this the degradation efficiency is highly improved (Lam et al.,2012). It can be concluded that the degradation rate efficiency decreases by increasing basicity of the Tartrazine solution as shown in figure, as the degradation rate continues to decrease in the range from 7 to 11, which may be explained by the ionization state of SnO₂ nanoparticle and the existence of the sulphonate group (SO₃⁻) of the anionic Tartrazine dye. This results can be interpreted as a result of the hydroxyl radical scavenging, thus they do not have the opportunity to react with the dye molecules. The inhibitory effect seems to be more pronounced at high pH. With these results, it can be confirmed that pH plays an important role in the photodegradation process of Tartrazine dye and to get and determine the optimum solution pH for high efficiency photocatalytic degradation. It is important to study the nature of the pollutants to be degraded and semiconductor photocatalyst surface properties to enhance the degradation performance.

A.3.4 Effect of H₂O₂ concentration:

Figure (3.9) shows the remaining of 1×10^{-5} M Tartrazine dye along 180 minutes of photocatalytic degradation utilizing SnO₂/PVC membrane under

UV radiation at 254 nm with the addition of different concentration of H₂O₂. As the Figure(3.9) shows the remaining ratio of 1×10⁻⁵M Tartrazine within 180 minutes of reaction and it illustrates the least remaining ratio that the degradation, which was obtained when the concentration of H₂O₂ is 0.1M. This means that a concentration of 0.1M of is the optimum H₂O₂ concentration that has to be added to get the best degradation and more efficiency of the Tartrazine dye photocatalytic degradation beside the other optimum operational conditions. Degradation performance becomes worse when the concentration of H₂O₂ increased, where the remaining ratio increased as H₂O₂ concentration increases up to 0.2M. However, the worst degradation was achieved when H₂O₂ was not added to the reaction solution. Hydrogen peroxide was a determining parameter for promoting the photocatalytic degradation, and in this study it was selected as an electron acceptor. To keep the efficiency of the added H₂O₂ at the maximum, it is necessary to choose the optimum concentration of H₂O₂ according to the type and concentration of the pollutants. The presence of hydrogen peroxide as an electron acceptor that have a high oxidation potential, can reduce the total time that needed for complete the degradation of Tartrazine dye. The influence of H₂O₂ on the degradation process can be explained in terms of the number of generated OH[•] radicals and the capture of OH[•] radicals. It is well known that H₂O₂ can trap photoinduced e⁻ to stabilize the paired e⁻,h⁺.

according to the following mechanism:



Additional OH^\bullet radicals could be yielded via the reaction between H_2O_2 and e^- or $\text{O}_2^{\bullet-}$ (1) and (2). As a result, the addition of H_2O_2 into the photocatalytic system was expected to promote the degradation of Tartrazine. Exceeding the optimum dosage, however, the excess H_2O_2 would trap the OH^\bullet radicals to form weaker oxidant HO_2^\bullet radicals. Accordingly, the capture of OH^\bullet radicals was occurred through (3) and (4). The decline in the OH^\bullet radical concentration, triggered by the higher H_2O_2 dosage, restrained the degradation of Tartrazine. So that because this important role that the $\cdot\text{OH}$ radicals play, it was added to the solution to be degraded (Tseng et al.,2012).

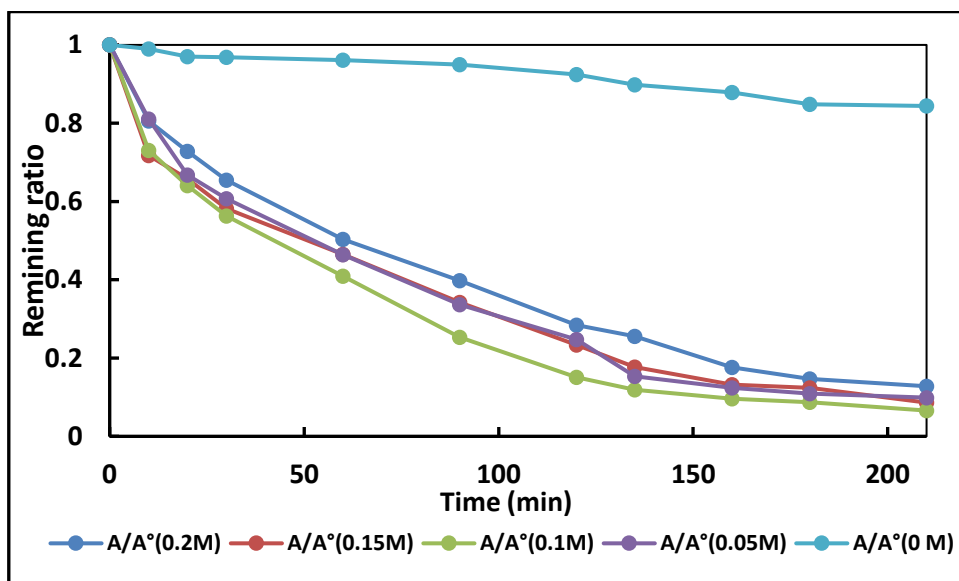


Figure (3.9): Effect of H_2O_2 concentration on photocatalytic degradation of 1×10^{-5} M Tartrazine by using SnO_2/PVC membrane.

As shown in the Figure above, by the absence of H_2O_2 less than 16% of Tartrazine dye degraded after 180 minutes under UV 254 nm compared to 90% when the optimum concentration of 0.1M was used.

Figure (3.10) shows UV-Vis absorption spectra of 1×10^{-5} M Tartrazine after 120 minutes of photocatalytic degradation reaction upon addition of different concentrations of H_2O_2 . The absorption intensity of Tartrazine increases significantly as the concentration of the H_2O_2 increases from 0.1 M to 0.2 M. The remaining ratio of Tartrazine was the highest when no H_2O_2 added to the photocatalytic reaction, and this represent the highest absorption intensity , where the remaining ratio increase as H_2O_2 increases from 0.1M to 0.2M.

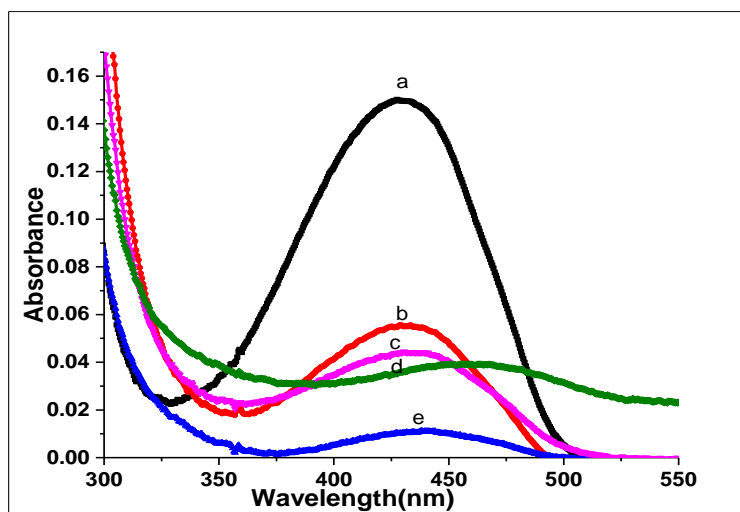


Figure (3.10): UV-Vis absorption spectra after 120 minutes of photodegradation of 1×10^{-5} M Tartrazine by SnO_2 membrane with addition of different H_2O_2 concentrations (a:0 M, b:0.2M, c:0.05M, d:0.15M, e:0.1M)

All the previous information and results are represented in the figure (3.11).

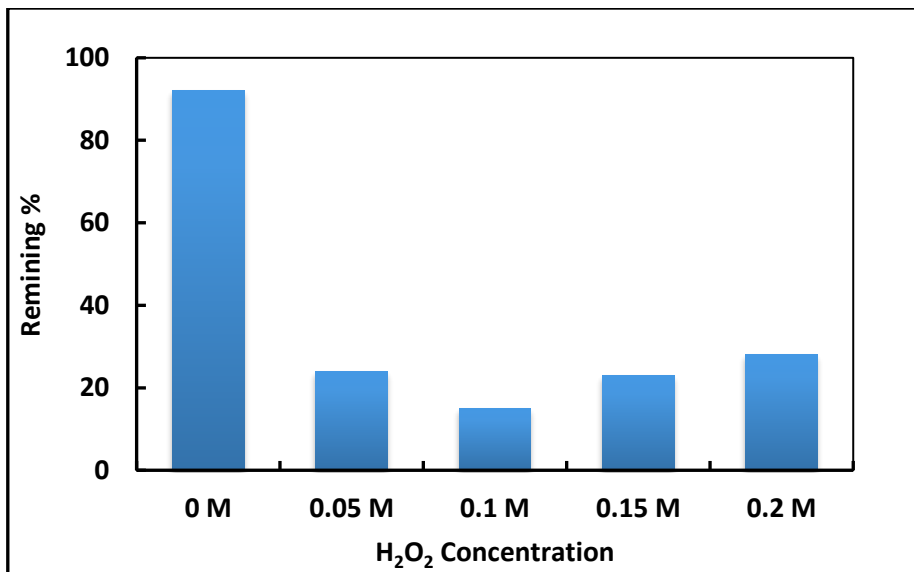
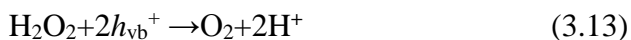


Figure (3.11): Remaining% of 1×10^{-5} M Tartrazine after 120 min of photocatalytic degradation process at different H_2O_2 concentrations.

The effect of H_2O_2 concentration in the photocatalytic degradation of 1×10^{-5} M of Tartrazine is as the following:

$$0.1M > 0.15M > 0.05M > 0.2M > 0M.$$

By increasing in H_2O_2 concentration, the OH^\bullet radical formation increases, that enhanced the photodegradation of Tartrazine and this lead to more mineralization for the organic dye. However the excess of H_2O_2 concentration, which is the main oxidative species, could act as OH^\bullet radical scavenger in the photocatalytic system, forming HO_2^\bullet which is less reactive than OH^\bullet



Moreover, the H_2O_2 may compete with Tartrazine for the active sites of SnO_2 particle and can be modified it ,so this could lead to inhabit the photocatalytic degradation of Tartrazine(Tseng et al.,2012). And In the

absence of H_2O_2 small amount of OH^\bullet radicals would be formed so that the degradation process.

A.3.5 Effect of energy of radiation:

Light intensity is a major factor in photocatalytic degradation because electron-hole pairs are produced by light energy. Radiation can generate the photons required for the electron transfer from the valence band (V_B) to conduction band (C_B) of a semiconductor photocatalyst. The energy of a photon is related to its wavelength, and the overall energy input to the photocatalytic process is light wavelength dependent. The effect of energy of irradiation on SnO_2 photocatalyst membrane was studied for UV irradiation using two different wavelengths of 365 nm and 254 nm during the degradation process, and in addition to the use of solar energy (Ohama and Gemert, 2011). The effect of irradiation wavelength on the degradation efficiency of 1×10^{-5} M of Tartrazine dye solution using SnO_2 membrane was illustrated in figure (3.12). It has been simplified to this figure through the remaining ratio formula as shown in the figure (3.13) as a function of the duration of exposure. It was depicted that the intensity of the characteristic absorption peak of Tartrazine dye is affected by the type of irradiation. By increasing the energy of the irradiation (shorter wavelength) the absorption peak is remarkably reduced. The exposure to the solar spectrum is more effective than the use of UV irradiation at wavelength of 364 nm, where the solar spectrum include part of the UV irradiation with higher energy. As it was observed, the decolorization efficiency after 120 minutes irradiation time under solar light reached to 66%, whereas in the presence of UV irradiation ($\lambda = 254$ nm) for the same duration, 86% decolorization efficiency was recorded. On the other hand only 17% degradation efficiency was observed when the wavelength of UV radiation

is 365nm, while the less efficiency of degradation that reached was observed under dark catalysis.

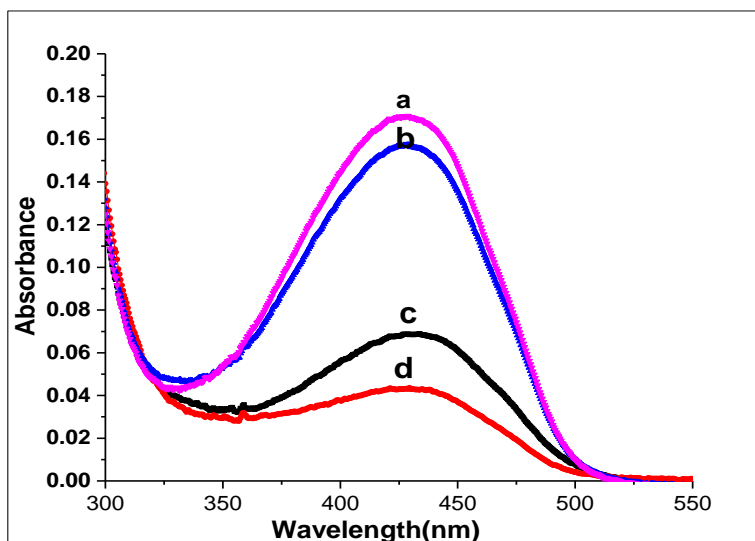


Figure (3.12): Absorption spectra of 1×10^{-5} Tartrazine after 120 minutes of photocatalytic degradation utilizing SnO_2 under different radiation wavelengths (a: dark, b:UV365 nm, c:solar, d:UV 254 nm).

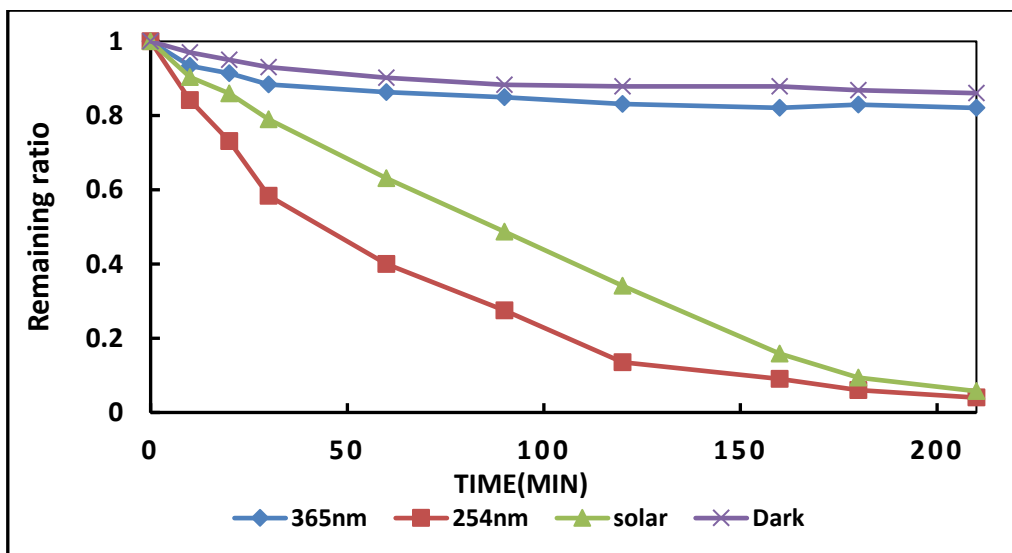


Figure (3.13): Effect of radiation wavelength on photocatalytic degradation of 1×10^{-5} M Tartrazine by SnO_2 .

Table (3.4) illustrates and summarizes the previous obtained results. The highest optimum degradation was corresponding to higher degradation rate of 0.7 Mmin^{-1} for the shortest wavelength.

Table (3.4): Degradation percentage and degradation rate of $1 \times 10^{-5} \text{ M}$ Tartrazine after 120 minutes using SnO_2 under different radiation wavelengths.

Radiation type	%Degradation	Degradation rate(M min^{-1})
Dark catalysis	12	0.1
Solar radiation	66	0.55
UV 254 nm	85	0.70
UV 365 nm	17	0.14

As discussed earlier, the best efficiency of degradation obtained by using the UV irradiation at $\lambda = 254 \text{ nm}$, which correspond to energy greater than the energy gap of SnO_2 $E_g = 3.6 \text{ eV}$, which is responsible of the enhanced charge transfer of electron from valence band to conduction band of the SnO_2 semiconductor, that is followed by OH^\bullet radical formation which is used in the oxidation process.

A.3.6 Effect of co-occurring ions

Since the body water obtained from the environmental sources contains a lot of organic and inorganic substances, thus the effect of co-occurring substances should be taken into consideration. In this work the effect of some ions such as NaF , NaNO_3 , NaHCO_3 and Na_2SO_4 on the degradation efficiency of Tartazine using SnO_2 membrane.

Percent degradation of $1 \times 10^{-5} \text{ M}$ Tartazine after 120 minutes of photocatalytic degradation by SnO_2 membrane in the presence of 200 ppm of NaNO_3 , NaHCO_3 , Na_2SO_4 and NaF were estimated and the obtained values were shown in table (3.5). Percent degradation of the dye under test

was slightly decreased in the presence of inorganic ions and act as inhibitor for the degradation of Tartazine.

Table (3.5): %Degradation of 1×10^{-5} M Tartazine after 120 minutes of photocatalytic reaction under UV254 nm in the presence of 120 ppm of NaF, NaNO₃, NaHCO₃, Na₂SO₄ using SnO₂/PVC membrane.

Co-occurring ion	%Degradation(after 120 min)
Pure Tartazine	85
Tap water as a real sample	73
NaF	78
NaNO ₃	77
NaHCO ₃	45
Na ₂ SO ₄	74

A.4 Reusability of SnO₂/PVC membrane photocatalyst:

The reusability of the catalyst in photocatalytic applications is an important parameter since it can contribute towards the lowering of the overall cost of the dye wastewater treatment. In order to evaluate photocatalytic stability of SnO₂ membrane many consecutive cycles of photocatalytic dye degradation were performed using the same photocatalyst membrane but fresh solution of dye every time. While studying reusability of photocatalyst , all parameters including irradiation time, Tartrazine concentration, pH of the medium and H₂O₂ concentration were kept at optimum condition. As the given results we have obtained that the SnO₂ membrane keep its effectiveness of photocatalytic activity at the same level after each continuous recycles. It is observed that the catalytic activity is slightly

decreased after subsequent reuse, so we can say that the SnO₂ showed stability and good reusability. The recovered catalyst membrane was reused for each consecutive runs. Figure (3.14) illustrates the remaining ratio (A/A₀) of 1×10⁻⁵ M Tartrazine within reaction time of photocatalytic degradation using SnO₂ membrane for five consecutive times. After the reaction finished, the photocatalyst membrane was recovered and washed with distilled water. The recovered catalyst was treated for the next degradation run.

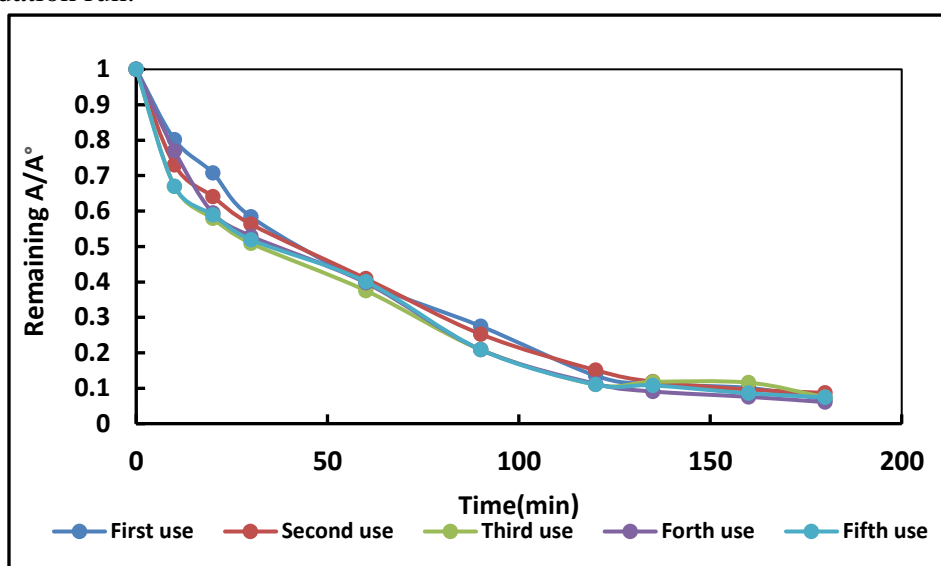


Figure (3.14): The effect of reusability of SnO₂ membrane on the photodegradation of Tartrazine dye.

In total, after several uses more than five times, it is observed that the degradation rate is approximately constant, as shown in the figure (3.15) it shows that the degradation rate after 120 minutes of the start of the reaction, then noted the similarity in the performance and effectiveness of the membrane in the degradation every time it is used.

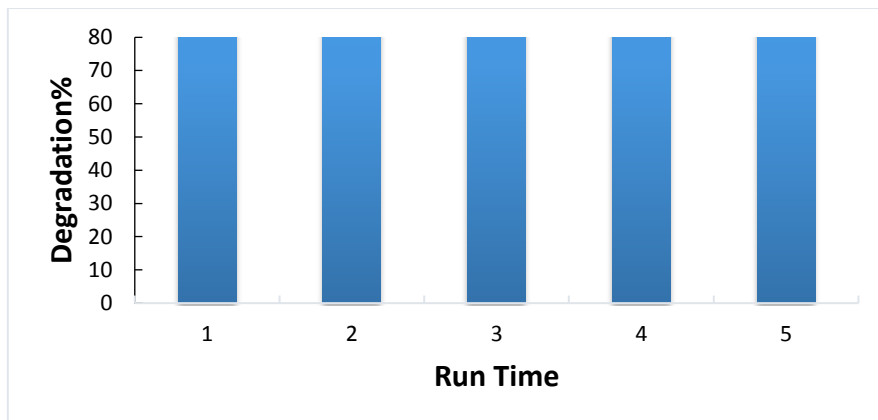


Figure (3.15): Catalytic efficiency of SnO₂ membrane in degradation of 1×10⁻⁵ M Tartrazine after 120 minutes of five consecutive usage times.

B:Levofloxacin degradation

B.1.1 Photocatalytic activity of Levofloxacin degradation under utilizing different metal oxides

Levofloxacin degradation using SnO₂, Fe₂O₃, under UV radiation source was performed to confirm activity of each membrane in the photocatalytic degradation process. Comparison between these photocatalyst membranes was shown in Table (3.6) in term of degradation percent after 120 minutes of UV exposure. It is shown that a maximum degradation percent to Levofloxacin solution was observed using the SnO₂ photocatalyst membrane and the minimum degradation percent was achieved when Fe₂O₃ was used. This may be attributed to the stronger electrostatic interaction between the Levofloxacin and the surface of the tin oxide nanoparticles.

Table (3.6): Degradation percent of Levofloxacin after 120 minutes by using different catalysts membrane under the same condition of radiation(UV of 254 nm) .

Catalyst membrane	Degradation percent after 120 min
SnO ₂	62%
Fe ₂ O ₃	49%

B.1.2 Photocatalytic degradation of Levofloxacin using SnO₂/PVC membrane photocatalyst:

Levofloxacin solutions of different concentrations, 5×10^{-5} M, 10×10^{-5} M and 15×10^{-5} M was tested for photodegradation by using SnO₂/PVC photocatalyst membrane. Figure (3.16) illustrates the calibration curve of Levofloxacin plotted including the prepared solutions, where the absorption behaves linearly with the concentration. The main absorption peak of Levofloxacin is located in the UV region, which is observed at $\lambda = 288$ nm (Figure 3.19).

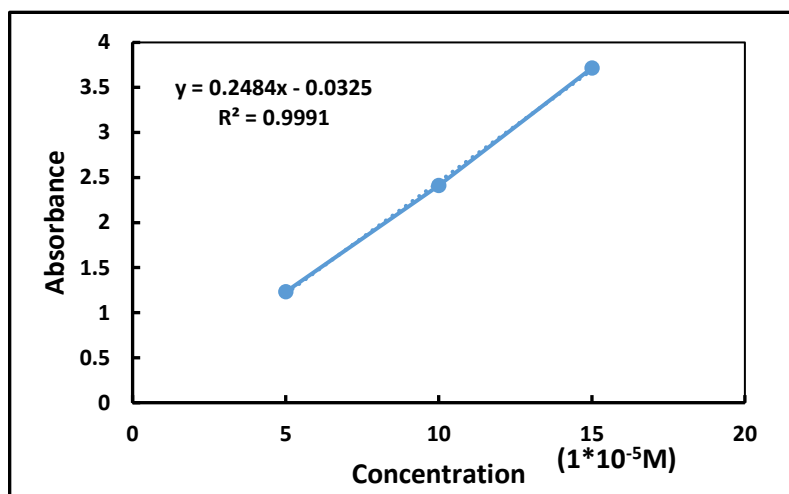


Figure (3.16): Calibration curve of Levofloxacin.

B.2 Effect of presence of UV radiation and SnO₂/PVC membrane as catalyst

Irradiation type has a significant effect in the photodegradation process, where UV lamp with different wavelengths (365nm and 254nm) was used for the photodegradation process. Figure (3.17) shows the absorbance of the

Levofloxacin treated with different conditions. The treatment of Levofloxacin under UV illumination using SnO₂ membrane as photocatalyst represents the optimum treatment. Without using UV or the presence of SnO₂ membrane, slight degradation was observed. The minimum degradation is obtained by using SnO₂ photocatalyst membrane without the radiation. This is a confirmation that both SnO₂ photocatalyst and UV irradiation are important for the removal of Levofloxacin from water.

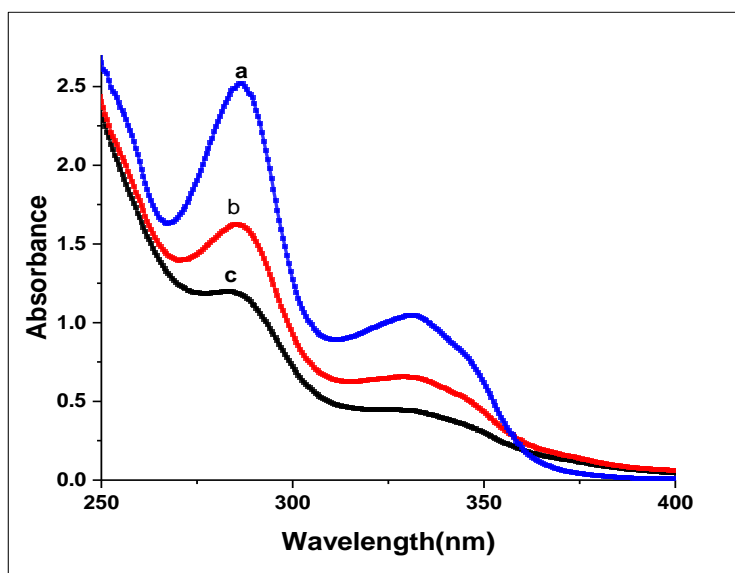


Figure (3.17): UV-Vis absorption spectra of 10×10^{-5} M Levofloxacin decomposed upon different degradation conditions after 120 minutes of the reaction (a: with SnO₂/PVC and no UV, b: with UV and no SnO₂/PVC, c: with both SnO₂/PVC and UV radiation).

Figure (3.18) show the remaining ratio of 10×10^{-5} M Levofloxacin degradation under the effect of presence of UV radiation and SnO₂ photocatalyst as a function of the exposure duration. A significant degradation was observed during the first 30 min under the optimum condition, where a gradual degradation was noticed up to 180 minutes.

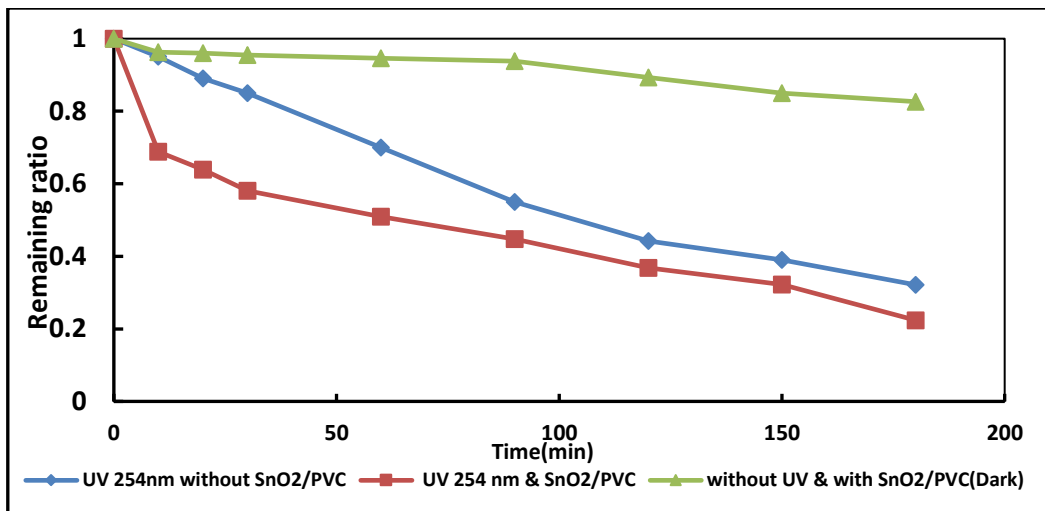


Figure (3.18):Effect of presence of UV radiation and SnO₂ photocatalyst on 10×10⁻⁵ M Levofloxacin degradation.

Table (3.7) summarized the degradation percent and degradation rate after 120 minutes of 10×10⁻⁵ M Levofloxacin which was estimated 62% of the Levofloxacin in the presence of both UV irradiation and the SnO₂ membrane, while the percentage decreased to 56% in the case of photodegradation process using UV irradiation alone and the minimum degradation percentage (11%) was achieved in the absence of both UV radiation (Dark catalysis).

Table (3.7): Percent degradation and degradation rate of 10×10⁻⁵ M Levofloxacin after 120 minutes under different degradation conditions.

Samples	%Degradation	Degradation rate(M min ⁻¹)
Levofloxacin +SnO ₂ (Dark catalysis, adsorption)	11	0.091

Levofloxacin +UV254nm (Photodegradation)	56	0.46
Levofloxacin+SnO ₂ +UV254nm (Photocatalytic degradation).	62	0.51

B.3 Comparison between different supports to metal oxide in term of photocatalytic activity in Levofloxacin degradation.

Changing the supporting material that is used to construct the membrane as PVC and PMMA was studied. It is found that by using PVC as a support material of the metal oxide, the degradation process is better than using the PMMA. Table (3.8) shows that the degradation efficiency of Levofloxacin by using the PVC as a support for both SnO₂ and Fe₂O₃ nanopowders which is more effective than that by using PMMA. The SnO₂ membrane supported over the PVC shows a photodegradation of 62% of a Levofloxacin after 120 min comparing with 32% when PMMA is used, and in the same manner, when Fe₂O₃ is used , 49% of Levofloxacin degraded with PVC and 28% of Levofloxacin degraded when the support material is PMMA. This can be attributed to the flexural strength and compression strength of PVC that is higher than PMMA (Govindaraj et al.,2012).

Table (3.8): %Degradation of Levofloxacin after 120 minutes by using different catalysts using 254 nm UV light.

Catalysts	% Degradation (after 120 min)
SnO ₂ /PVC	62
SnO ₂ /PMMA	32
SnO ₂ /Eosin/PVC	54
Fe ₂ O ₃ /PVC	49
Fe ₂ O ₃ /PMMA	28

B.4 Operational parameters :Investigation and optimization

B.4.1 Effect of irradiation time

Figure (3.19) represents the absorption spectra of the Levofloxacin solutions before degradation. The main absorption peak of Levofloxacin is observed at $\lambda=288$ nm. As the spectrum shows, intensity of absorption peak increases as concentration increases. The UV-Vis spectra measured during the photodegradation of the Levofloxacin is shown in the Figure (3.20). Absorbance of 10×10^{-5} M of Levofloxacin during photocatalytic degradation was measured at different time treatment duration by UV-Vis spectrophotometer in the range (200-400) nm to monitor the degradation process .It is indicated from the continuous decrease in absorbance intensity that Levofloxacin was gradually decomposed due to further oxidation-reduction processes and this leading to further degradation of Levofloxacin into smaller fragments which was achieved during the time of the treatment by the influence of both UV radiation and SnO₂ photocatalyst. Levofloxacin disappeared completely after 180 min of the reaction.

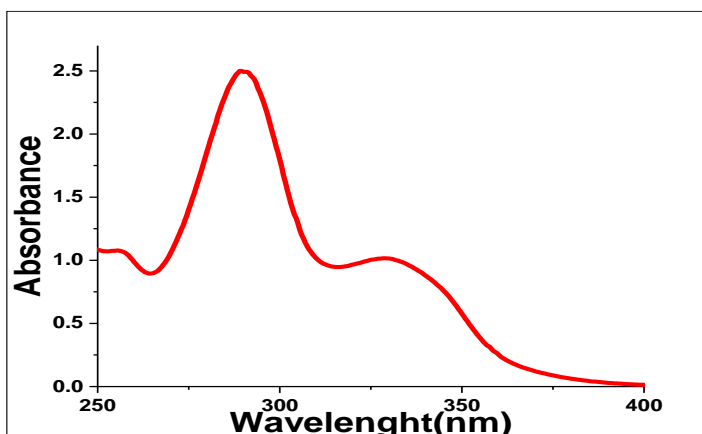


Figure (3.19):UV-Vis absorption spectrum of Levofloxacin before exposure to UV radiation and SnO₂/PVC membrane.

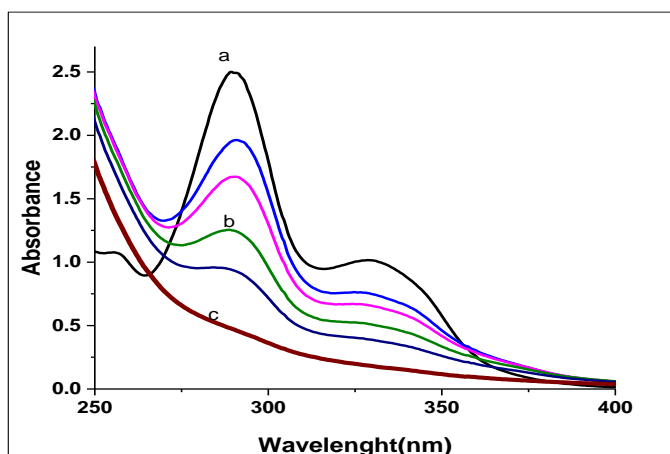


Figure (3.20): Gradual removal of 10×10^{-5} M Levofloxacin upon photocatalytic degradation process using SnO₂ membrane (after-a:0 min, b:60 min, c:180 min).

B.4.2 Effect of initial concentration of Levofloxacin:

The effect of initial concentration of Levofloxacin on the decomposition under UV radiation ($\lambda=254\text{nm}$) is investigated as a function of the time of illumination. The results indicates that the degradation rate is strongly dependent on the initial concentration. The efficiency of photodegradation of Levofloxacin decreases with increasing the initial concentration. As the initial concentration of the drug increases, more molecules, are adsorbed on the surface of photocatalyst, thus the generation of OH^\bullet is reduced and the active site will occupied by the molecules. An increase of the amount of Levofloxacin adsorbed on the catalyst surface decrease the catalytic activity of the photocatalyst. Although the decreasing in concentration have a negative effect on the efficiency of the degradation process, and it is attributed to the recombination of OH^\bullet and form a byproduct in the reaction. Figure (3.21) illustrates the remaining ratio of different concentrations of Levofloxacin along 180 minutes of photocatalytic degradation process. As a general trend, the remaining ratio of the

Levofloxacin under test increases as the concentration increases, also if the concentration is less than that, it will affect the efficiency of the process.

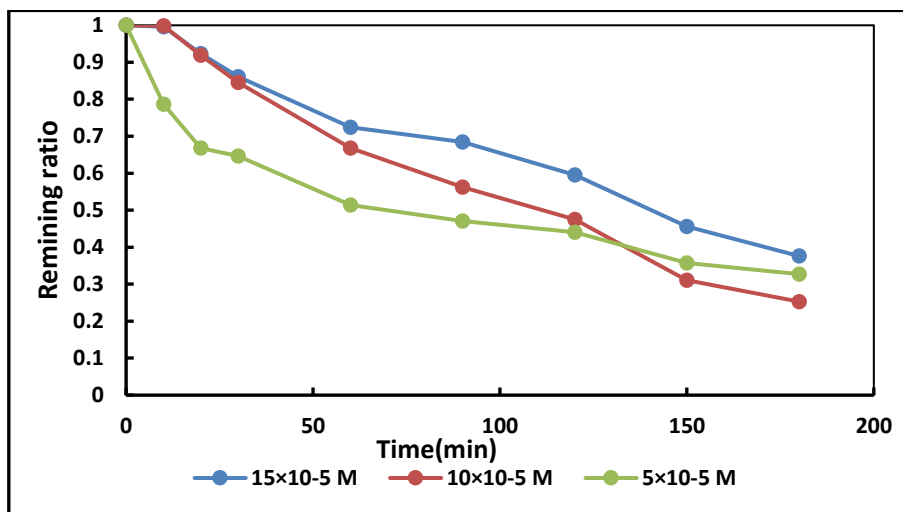


Figure (3.21): Effect of concentration of Levofloxacin on the removal efficiency upon photocatalytic degradation using SnO₂/PVC photocatalyst membrane.

Table (3.9) illustrates the % degradation of different concentrations of Levofloxacin after 180 minutes of exposure to UV radiation and SnO₂ photocatalyst membrane. The degradation decreased with increasing the concentration up to 10×10⁻⁵M . Using initial concentration of 5×10⁻⁵M results into a degradation of 68%, however by doubling the concentration, a degradation of 75% is obtained after 180 min of the reaction.

Table (3.9): %Degradation of Levofloxacin of different concentrations after 180 min of photocatalytic degradation by SnO₂/PVC membrane.

Initial Concentration	Degradation %
5×10 ⁻⁵ M	68
10×10 ⁻⁵	75
15×10 ⁻⁵	63

In addition to the above mentioned discussion, another reason may be responsible for the reduction of SnO₂ photocatalytic activity which may be the increase in initial levofloxacin concentration is the generation of its intermediates which would be adsorbed on the surface of the catalyst and slow diffusion of the generated intermediates from the catalyst surface that can result in the deactivation of the active sites of SnO₂ photocatalyst (Rasul et al., 2011). Another possible factor is the competition between the adsorbed molecules and H₂O molecules for photogenerated h⁺ resulting in reduction in the generation of the most reactive oxidative species OH[•] radical and other reactive species (Abdollahi et al., 2012).

B.4.3 Effect of solution pH:

The pH of the solution affects the efficiency of photocatalytic degradation process, and it has been taken into consideration. The effect of pH on the degradation rate depends on the ionization state of the organic substance to be degraded, especially acids and amines, as well as acid-base properties of the photocatalyst and can be explained on the basis of zero point charge (Pzc). The effect of the solution pH was studied in the range pH of 3 to 11 and UV-irradiation time up to 180 min for Levofloxacin. Figure (3.22) shows that the photodegradation was higher in acidic medium at pH value of 3 with degradation of 82% and in neutral medium with degradation of 83% after 180 min from the reaction. The photodegradation was reduced up to 59%, whereas at basic medium pH=11. The degradation efficiency is the optimum at acidic medium (pH=3) because the pH at the point zero charge (PZC) is 4.8, the photo degradation increases by lowering the pH whereas increasing the pH up to 11 decreases the efficiency of decomposition to about 59%, and this can be explained by SnO₂ surface charge density, where the point of zero charge (Pzc) of SnO₂ is 4.8 and SnO₂ surface can become charged by reacting with H⁺ (acidic environment) or OH⁻ (basic

environment). In acidic medium ($\text{pH} < 4.8$) the SnO_2 surface is positively charged. Whereas in basic medium ($\text{pH} > 4.8$) it is negatively charged. Positive charge excess in the SnO_2 surface promotes a strong interaction with COOH group of the Levofloxacin. A negative charge excess in basic environment promotes the repulsion of the SnO_2 surface, decreasing the catalytic activity of the semiconductor.

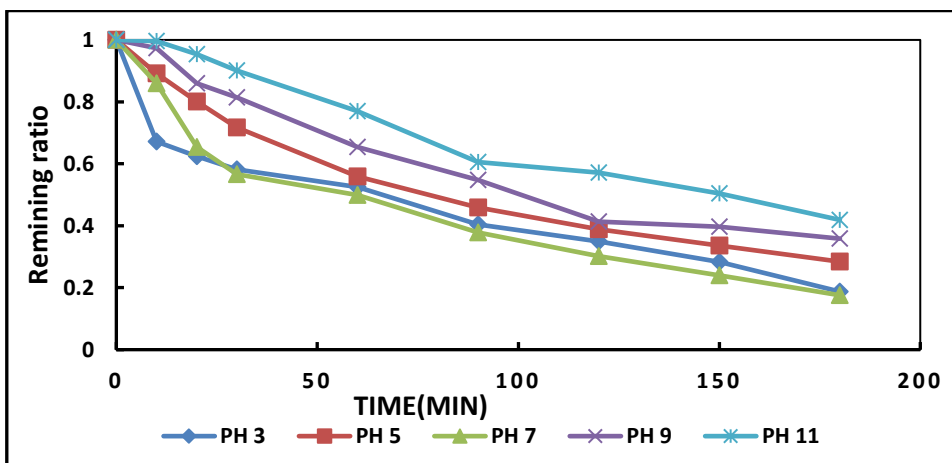


Figure (3.22): Effect of pH on removal of 10×10^{-5} M Levofloxacin by photocatalytic degradation using SnO_2/PVC membrane.

Percent remaining of 10×10^{-5} M Levofloxacin after 120 minutes of the photocatalytic degradation reaction was calculated and the values were plotted as a function of pH. The curve is shown in Figure (3.23). The degradation percentage after 120 minutes at different pH values (3, 5, 7, 9 and 11) were 65%, 61%, 70%, 59% and 43% respectively.

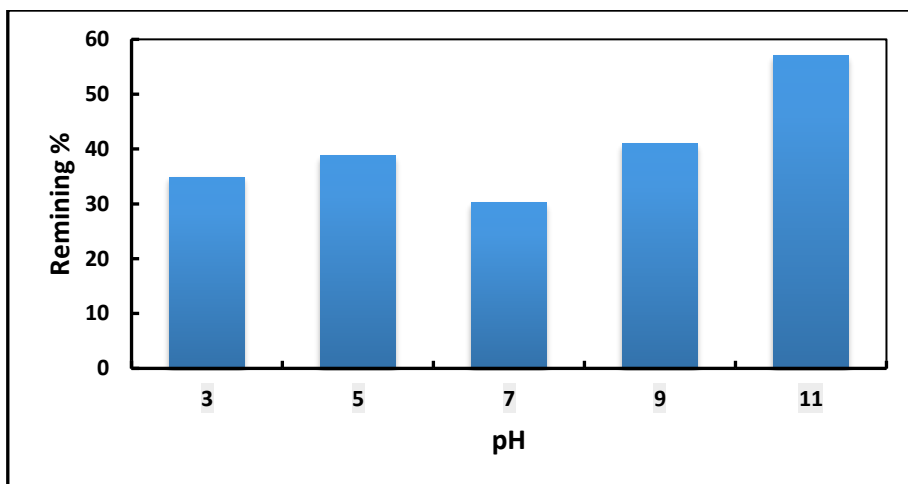


Figure (3.23): %Remaining of $10 \times 10^{-5} \text{M}$ Levofloxacin after 120 minutes of photocatalysis process utilizing SnO_2/PVC membrane.

B.4.4 Effect of H_2O_2 concentration

OH^\bullet radicals play an important role in the photocatalytic degradation, electron acceptor such as H_2O_2 were added to the solution. Hydrogen peroxide has been found to increase the degradation of compound due to more efficient generation of OH^\bullet radical and inhibition of electron/hole pair recombination. It was observed in figure (3.24) that the photodegradation was affected by adding H_2O_2 to the Levofloxacin solution. The maximum degradation was found at 0.05 M of H_2O_2 , however by using higher concentration of H_2O_2 , the degradation efficiency decreased. The electron hole recombination is a problem in photocatalytic degradation in the presence of the SnO_2 .

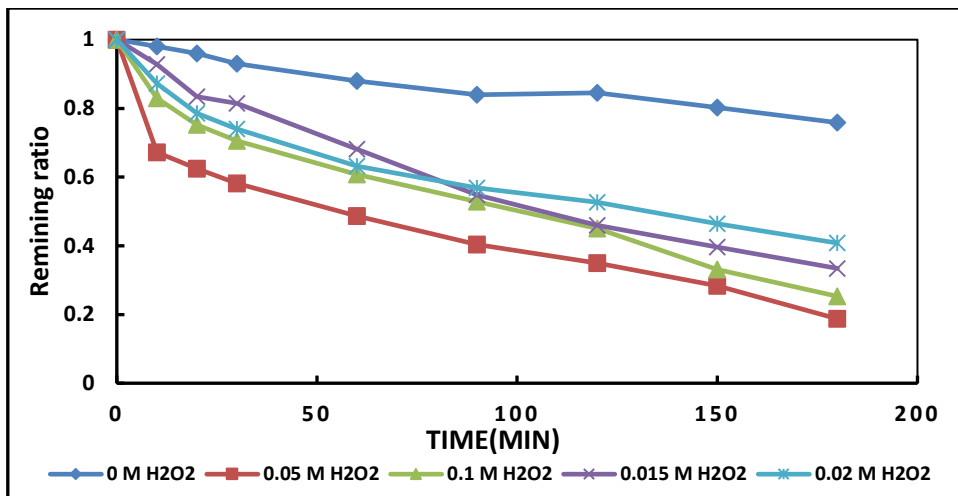


Figure (3.24): Effect of H₂O₂ concentration on removal efficiency of 10×10^{-5} M Levofloxacin by photocatalytic degradation process using SnO₂/PVC membrane.

It was observed that less than 25% of Levofloxacin was degraded after 180 minutes in the absence of H₂O₂ compared to 82% of Levofloxacin removal when H₂O₂ concentration was 0.05M. Figure (3.25) represents UV-Vis absorption spectra of 10×10^{-5} M Levofloxacin at specific point of time (after 90 minutes) of photocatalytic degradation reaction upon addition of different concentrations of H₂O₂. As this figure shows, absorption intensity of Levofloxacin increases as the concentration of the added H₂O₂ increases from 0.05 M to 0.2 M.

The highest absorption intensity is observed in the absence of H₂O₂. In other words, the remaining of Levofloxacin, increased as H₂O₂ concentration increased from 0.05 M to 0.2 M, and the percent remaining was the maximum at 0 M of H₂O₂.

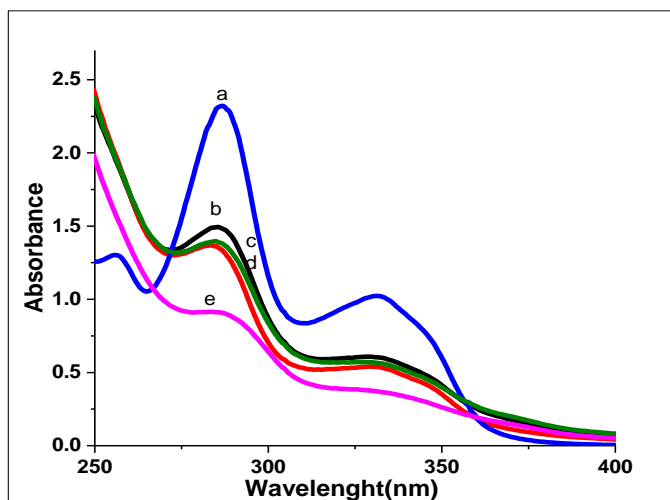


Figure (3.25): UV-Vis absorption spectra after 90 minutes of 10×10^{-5} M Levofloxacin removal by SnO₂/PVC membrane upon addition of different H₂O₂ concentrations (a:0 M, b:0.2M, c:0.15M, d:0.1M, e:0.05M).

The previous result is summarized in Figure (3.26).

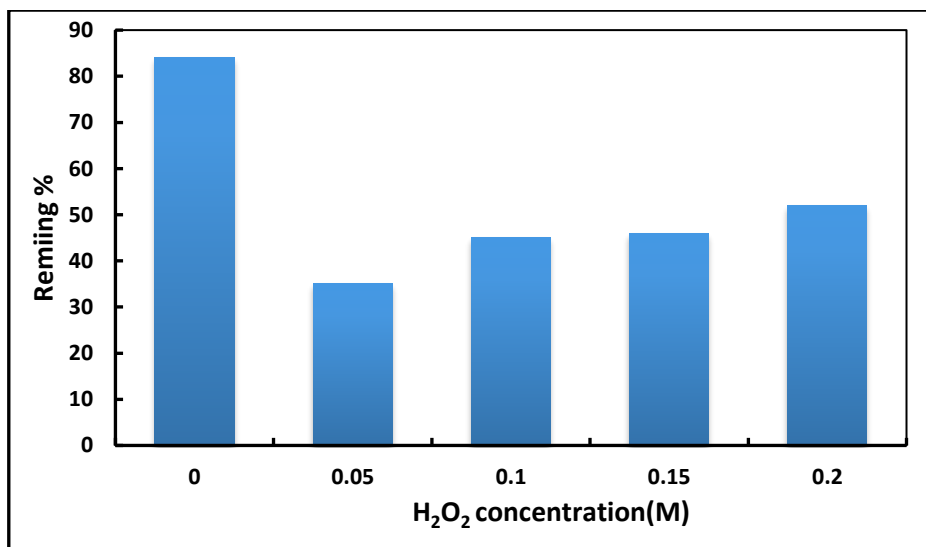


Figure (3.26): %Remaining of 10×10^{-5} M Levofloxacin after 120 minutes of photocatalytic reaction at different H₂O₂ concentrations.

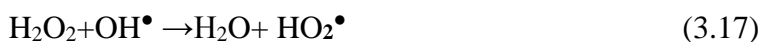
It is concluded that the effect of H₂O₂ concentration on enhancing photocatalytic degradation of 10×10⁻⁵ M Levofloxacin is as the following order:

$$0.05M > 0.1M > 0.15M > 0.2M > 0M.$$

As the previous order shows, the degradation efficiency of Levofloxacin decreases with increasing H₂O₂. An expected interpretation for these results is as the following:

In the absence of H₂O₂, very little OH[•] radicals would be formed, therefore the degradation process is strongly retarded since the oxidation of the Levofloxacin will not take place effectively.

As H₂O₂ concentration increases, OH[•] formation extent increases, thus enhancing photooxidation of the Levofloxacin molecules which means better mineralization rate. However, too much addition of H₂O₂ may inhibit the oxidation process strongly. This is attributed to adsorption of H₂O₂ molecules themselves onto the catalyst surface that would modify the catalyst surface subsequently decreases its photocatalytic activity. Moreover, H₂O₂ can be a scavenger of valence band holes and OH[•], which is the main oxidative species, when present at too high concentrations, forming HO₂[•] which is less reactive than OH[•] (Konstantinou and Albanis, 2004).



B.4.5 Effect of energy of radiation

Figure (3.27) show the effect of solar and UV irradiation with different wavelengths on the degradation efficiency of 5×10⁻⁵ M Levofloxacin by

using SnO₂ membrane for exposure time up to 120 minutes of photocatalytic degradation.

As it can be seen, the characteristic absorption peak was the lowest when the degradation carried out using UV irradiation with wavelength of 254nm, which means that, the higher degradation efficiency was obtained, while the efficiency dramatically decreased as longer wavelength of 365nm was applied. It is expected that UV with $\lambda=365\text{nm}$ was not energetic enough to achieve significant photodegradation. Solar radiation was found to give good efficiency, which is close to that obtained by application of UV ($\lambda=254\text{nm}$) radiation. This is attributed to the UV spectrum that already exists in the solar spectrum. Poor degradation is obvious under dark catalysis, which means that UV of shorter wavelength ($\lambda=254\text{nm}$) radiation has an essential influence on Levofloxacin degradation, which is the most energetic to achieve maximum degradation.

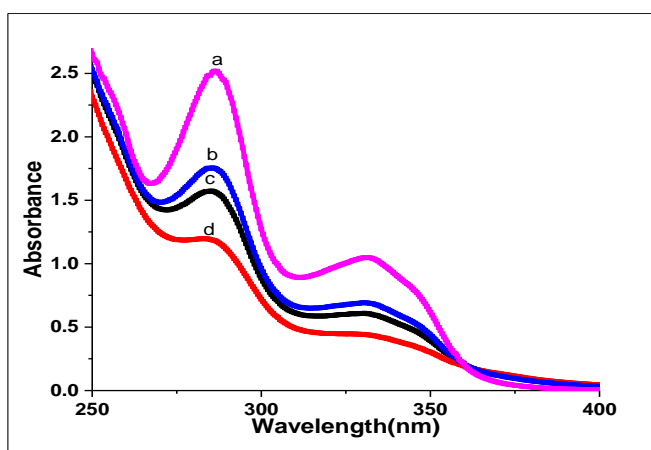


Figure (3.27): Absorption spectra of $10 \times 10^{-5}\text{M}$ Levofloxacin after 120 minutes of photocatalytic degradation using SnO₂/PVC membrane under different radiation wavelengths (a: dark, b:UV365 nm, c:solar, d:UV 254 nm).

B.4.6 Effect of co-occurring ions

Co-occurring substances such as sulphate, nitrate, bicarbonate, fluoride and other dissolved organic matter can significantly influence the photocatalytic degradation rate of organic pollutants. The effect of some ions such as NaNO_3 , NaHCO_3 , Na_2SO_4 and NaF on degradation efficiency of Levofloxacin using SnO_2 membrane under UV radiation was studied in this work. Percent degradation of 10×10^{-5} M Levofloxacin after 120 minutes of photodegradation were calculated and the obtained values were; shown in table (3.10). Percent degradation of Levofloxacin decreased in the presence of the previous mentioned salts .According to the obtained result, these inorganic ions have been found to be inhibitors for photocatalytic degradation of Levofloxacin.

Table (3.10): %Degradation of 10×10^{-5} M Levofloxacin after 120 minutes of photocatalytic reaction under UV254 nm in the presence of 120 ppm of NaF , NaNO_3 , NaHCO_3 , Na_2SO_4 using SnO_2/PVC membrane at pH 7.5.

Co-occurring ion	%Degradation(after 120 min)
Pure Levofloxacin	62
Tap water as a real sample	47
NaF	56
NaNO_3	55
NaHCO_3	57
Na_2SO_4	55

The Co-occurring ions act onto the catalyst surface as competitive species , semiconductor metal surface can adsorbed the ions instead of pollutant molecules to be degraded, It should be considered that constant HO^- ions

displacement from the surface of the catalyst would be taken place due to competitive adsorption process, thus reduces the generation of reactive radicals. Tap water as a real sample that contain ions such as F^- , NO_3^- , HCO_3^- , and SO_4^{2-} could be radical scavengers and react with OH^\bullet radicals, which were supposed to be attacked by dye molecules to oxidize it and then be degraded into simpler fragments or molecules, subsequently retarding degradation efficiency of the organic pollutants. Formation of inorganic radicals and radical anions under these circumstances is possible to occur (Yin,2012).

B.5 Reusability of SnO₂/PVC photocatalyst membrane:

In order to obtain good results by using photocatalyst membrane, photocatalyst performance should be stable for long time after consecutive usage cycles. SnO₂ catalyst was used and recycled for consecutive reuse on the Levofloxacin degradation; the process was repeated up to four times. While studying reuse of photocatalyst; all parameters including irradiation time, Levofloxacin concentration, pH of the medium, and H₂O₂ concentration keep constant. The SnO₂ recycling studies performed and the efficiency of the photodegradation process was evaluated and compared between the reuse cycles. The recovered catalyst was reused for four consecutive runs. Figure (3.28) and Figure (3.29) indicate the activity of SnO₂ photocatalyst is the same or slight decrease after four consecutive uses after the same irradiation time.

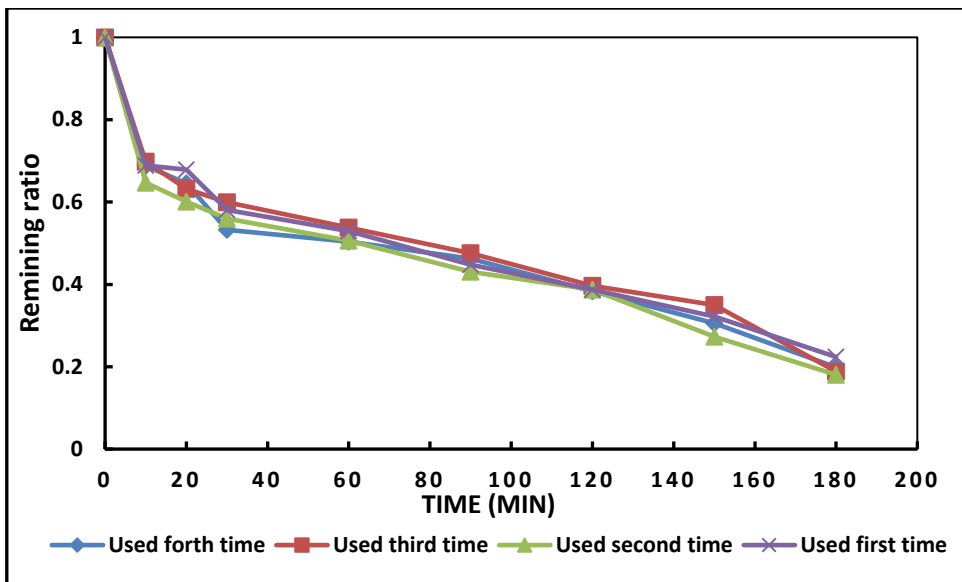


Figure (3.28): Effect of reusability of SnO₂/PVC membrane as photocatalyst for four consecutive times on removal efficiency of 10×10^{-5} M Levofloxacin.

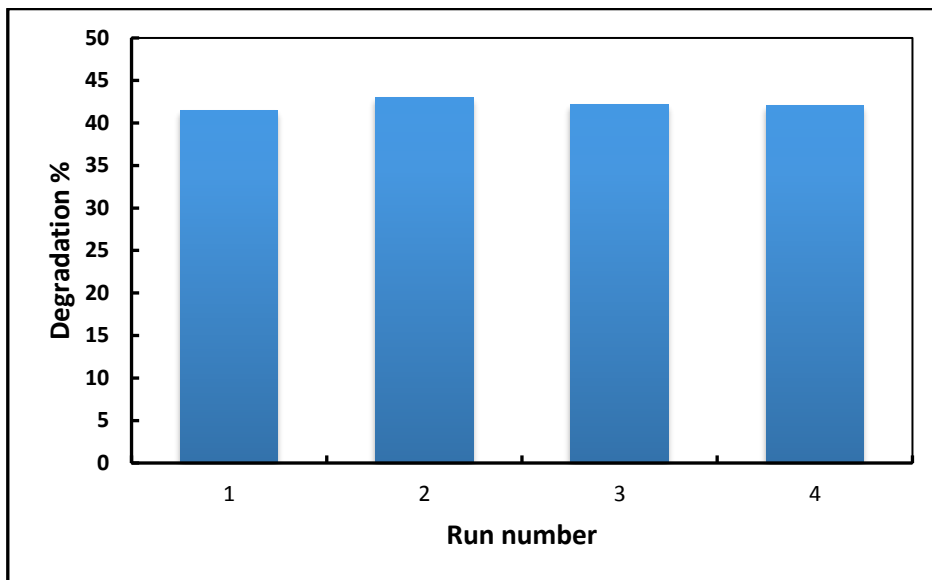


Figure (3.29): Catalytic efficiency of SnO₂/PVC membrane in degradation of 10×10^{-5} M Levofloxacin after 120 minutes of four consecutive usage times.

C: Effect of a sensitizer

The used photosensitizer has a small band gap and absorbs light wavelengths in the visible region, which leads to electron-hole generation in the dye molecule, by exciting the electrons from dye HOMO to LUMO. The generated electrons transported from the LUMO to the semiconductor conduction band, and then generation of hydroxyl is occurred followed by the oxidation of organic pollutant. The dye has a small band gap close to the visible range and can't itself oxidize the organic pollutant.

Eosin Y (EY), a xanthene dye, is a very good sensitizer(Xuet al.,2013; Liu et al.,2013) and it is used as a photosensitizer in the photocatalyst membrane in this study. Table (3.11) shows a remarkable enhancement of the photodegradation upon the exposure of Levofloxacin to the sun up to 89 % by loading EY on the surface of the SnO₂ nanoparticles. This result is very good and interesting comparing with a 70 % of photodegradation under the illumination of UV at wavelength of 254 nm within exposure time up to 120 minutes. On the other side the degradation efficiency reached to 85% using SnO₂ under the optimum condition without photosensitizer. This can be attributed to the large visible light harvesting by its conjugated xanthenes structure and the strong recombination of photo-excited electron-hole pairs (Zhang et al.,2014). The addition of the photosensitizer improves the degradation process under solar energy conditions and outperforms the photodegradation using UV irradiation. It is anticipated that supporting Eosin Y onto SnO₂ surface would sensitize it to visible light in the photodegradation process. The existence of a photosensitizer onto the surface of the semiconducting photocatalyst reduce the cost of the photodegradation using UV light and keep the harmful of using UV away.

C.1 Dye sensitizers of SnO₂ in Tartrazine degradation

Tartrazine undergo degradation under different condition, Table (3.11) represent the Percent of photodegradation activity of Tartrazine using SnO₂ sensitized with Eosin Y under different radiation after 120 minutes all after exposure to UV at 254nm, and as it show the best degradation performed. Degradation percent using SnO₂ sensitized with Eosin show the best Tartrazine degradation under the sun light 89% comparative of 70% degradation under UV at $\lambda=254$ nm. The sun light is a major resource for energy, while we can exploit that, it will save money and improve efficiency of degradation process. This result reflects the impact of using the photosensitizer which reduce the cost of the photodegradation process, in addition to the easy use of sun light instead of UV irradiation.

Table(3.11): Percent of photodegradation activity of Tartrazine using SnO₂ sensitized with Eosin under different radiation after 120 minutes all after exposure to UV at 254nm

Radiation type	Degradation percent Using SnO ₂ sensitized with Eosin	Degradation percent Using SnO ₂ only
Sun light	89	66
UV at $\lambda=254$ nm	70	85

C.2 Dye sensitizers of SnO₂ in levofloxacin degradation :

Levofloxacin degradation using SnO₂ sensitized with Eosin , it show its efficiency if it promote under the sun light , as Fig(3.30) show absorption spectra of 10×10^{-5} M Levofloxacin after 180 minutes of photocatalytic degradation using SnO₂/Eosin membrane under (a: $\lambda=254$ nm, b: sun light). The degradation under sun light more preferal sa it is more efficient in Levofloxacin degradation, at $\lambda=254$ nm the energy is specific and may

destroy some of the sensitizer molecules before the degradation process begin.

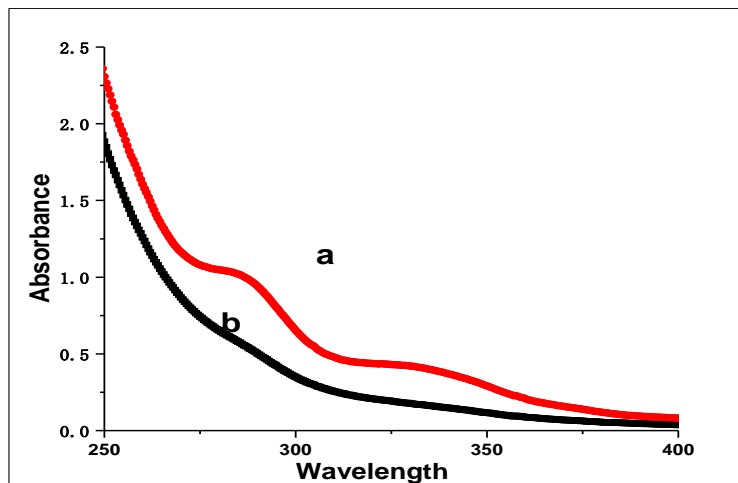


Figure (3.30): Absorption spectra of 10×10^{-5} M Levofloxacin after 180 minutes of photocatalytic degradation using $\text{SnO}_2/\text{Eosin}$ membrane under (a: $\lambda=254$ nm, b: sun light).

Figure (3.31) shows the effect of the addition of Eosin Y as sensitizer in levofloxacin photodegradation under different treatments. The best degradation efficiency observed using SnO_2 membrane that sensitized with Eosin Y under sun light, followed by SnO_2 membrane under UV at $\lambda=254\text{nm}$, then the SnO_2 sensitized with Eosin Y under UV at $\lambda=365\text{nm}$, and the minimum degradation occurs when SnO_2 sensitized with Eosin under UV at $\lambda=254\text{nm}$ used and finally SnO_2 membrane used under UV at $\lambda=365\text{nm}$.

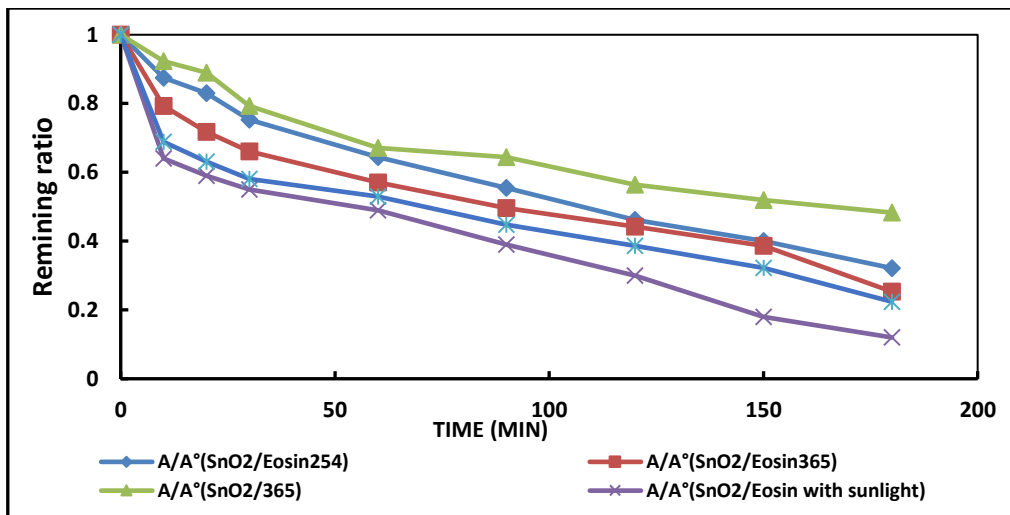


Figure (3.31): Effect of Eosin Y as sensitizer in levofloxacin photodegradation .

In conclusion, the efficiency of photocatalytic degradation of levofloxacin dependent on the membrane condition, the addition of the sensitizer improve the degradation process under solar energy conditions , it is anticipated that supporting Eosin Y onto SnO₂ would sensitize it to visible light in the photodegradation process. In real water purification projects, this is a viable economic solution, especially with the availability of the sun light, especially in region like Gaza, where the sun shines 360 days each year .

Table (3.12): Degradation percent of Levofloxacin after 120 minutes by using different catalysts membrane under the same condition of radiation(UV of 254 nm) .

Catalyst membrane	Degradation percent after 120 min
SnO ₂	62%
Fe ₂ O ₃	49%
SnO ₂ sensitized by Eosin	54%

As reported in the results chapter, Tartrazine Degradation percent using SnO₂ sensitized with Eosin is approximately 89%, some of the above methods have reached higher values but the distinctive of this method remains that they have used less potential as they are economical and suitable for the climate of our country. The membrane can be used many times with the same efficiency.

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