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Study of the impact of some inorganic ions on the photocatalytic activity of TiO₂

Discussed on: 30/10/2020

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Dedications

“I don't know what your destiny will be, but one thing I know: the only ones among you who will be really happy are those who have sought and found how to serve.”

Albert Sweitzer

For those who answer the call from near and from far, for those who answer the call for help with no expectation of personal gain, My beloved parents: I am so proud and so delightful to dedicated this dissertation to you. My dear Mother: words cannot describe my gratitude and my love to you. My father: This modest work is dedicated to you as well, you've waited so long for this moment, thank you for all love and support. My brother the supporter in my worst times. To all my friends who helped me to reach this point.

OUSSAMA

Dedications

Greetings of grandeur and reverence to the best of people:

To the spring of tenderness to the one who stayed up for our comfort and spared no effort to please us, my dear mother.

Whoever spent his life for us and did his best to teach us and our success, my dear father.

To those who have supported us in this life and at all times, my dear brothers.

to the big family, to our friends, to our colleagues, to our teachers.

Passin

Thanks and gratitude

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List of Abbreviations

List of Abbreviation

Symbol	Meaning
R	molecule for state stable.
R*	electronically - excited molecule.
λ	wavelength.
ν	the frequency of oscillation.
$\bar{\nu}$	wave number.
N_A	Avogadro constant.
E	Molar absorption coefficient
S ₀	Ground state.
S ₁	Excited singlet state.
T ₁	Excited triplet state.
V _r	vibrational relaxation.
I _c	Internal conversion.
I _{sc}	Intersystem crossing.
IUPAC	International Union of Pure and Applied Chemistry.
VB	Valence band.
CB	Conduction band.
$h^{(+)}$	Positive gap.
UV	Ultraviolet.
RX	Organic contaminant.
OH*	Hydroxide radical.
BOD	Biological Oxygen Demand.
COD	Chemical Oxygen Demand.
AOP	Advanced Oxidation Processes.
CBZ	Carbamazepine.

General Introduction

General Introductions

Environmental pollution is one of the biggest problems facing the world, and has increased significantly due to industrial and non-convention of resources and divided into three types:

-air pollution: A large amount of gases and toxic substance in the air (carbon and sulfur oxides, auto exhausts,...) have a great risks to human respiratory system and other environmental problems.

-soil pollution: Because of fertilizers and agricultural pesticides to a large extent, we also do not forget industrial waste.

- Water pollution: It is any defect that affects the quality of water and makes it unexploitable due to industrial waste and sewage disposal, Oil and gas are polluted with sea water as a result of exploration operations and the sinking of giant oil tankers in the ocean. [1.2]

Dyes are among the most common organic pollutants of water due to their increasing use and ignorance of their health and environmental harms.

For example, the Crystal violet is used as an antiseptic and is also used for dyeing papers and printing, but it has great damage to the eyes and has a very toxic impact on environmental organisms. [2]

Therefore, there are several advanced methods to rid the environment and to save human health of these pollutants, among them are the advanced oxidation methods (AOPs) that depend mainly on photocatalysis in the presence of a photocatalyst..[3]

As water contain many of inorganic ions, many research have been conducted to study the impact of these ions on the efficiency of photocatalysis reaction, The effect varies with the type and concentration of ions and the method of affecting the reaction, “Xiaoya Gao and al” in their study of was signified that netrate ions reduce the photocatalytic activity of titanium dioxide TiO_2 , “Yan Xiaojua and al” in their study “Effect of Inorganic Ions on the Photocatalytic Degradation of Humic Acid1” was confirmed the inhibitor impact of some ions on the photocatalytic effeciency.[4.5]

Our research has been based on a group of studies conducted on anionic and cationic ions where we classified the memory to three chapters:

In the First chapter we dealt with photochemistry, generalities on the light, Direct Photodegradation, Photocatalysis (Homogeneous/ Heterogeneous) and properties photocatalyst Titanium dioxide.

The second chapter includes definition, classification, and effects of dyes on human health and environment, we also presented the properties and preparation methods of Violet crystal, Elimination Methods of dyes (biological, physical, chemical methods), The advanced oxidation processes (AOPs).

The third chapter contains a study of the effect of inorganic ions, The effect of inorganic anions (NO_3^- , Cl^- , HCO_3^-), and the effect of inorganic cations (Al^+ , Ca^{2+} , Mg^{2+}).

General Introduction

We concluded this research with a general summary in which we explained the most important theoretical results that we reached, as well as our future outlook regarding the research topic.

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Chapter I: photodegradation

I.1 photochemistry:

I. 1.1 Introduction:

Photochemistry is the branch of chemistry which is one of the methods of chemical reactions (named photochemical reactions) that depend on the emergence of molecules excited electronically, these molecules are produced by absorbing photon in the spectrum of ultraviolet rays and the visible light.[1,2]

The photochemical reaction are one of the simplest and most important ways in which an atom or free radical can be generated by exposing a particular molecule to radiation of a specific wavelength in accordance with the two laws in photochemistry.[3]

-The Grotthuss – Draper law: “The chemical must absorb light for a photochemical reaction to occur” or “Molecules that do not absorb light at a specific frequency for which it does not happen to any photochemical reaction”.[3]

-The Stark – Einstein law: “Each photon is absorbed by a chemical system that activates one molecule in a photochemical reaction”.[3]

I.1.2 generalities on the light:

The light is an electromagnetic radiation visible to the eye, its wavelength ranges from 400 (nm) to 800(nm) between infrared (longer waves) and ultraviolet (shorter waves).

Visible light is emitted and absorbed in the form of small "bundles" called photons that can be studied as particles or waves, this characteristic of light is called the duality of a particle wave.

The main characteristics of light are: intensity, direction of propagation, frequency or wavelength, spectrum, polarization, and velocity (speed of propagation).

The development of the quantum theory in the early twentieth century allowed predictions to be made relating to the properties and behavior of matter and light. The electrons in matter have both wavelike and particle-like properties, and quantum theory shows that the energy of matter is quantized. The quantized energy levels of matter have a separation that is of the same order as the energy of visible or ultraviolet light. Thus, the absorption of visible or ultraviolet light by matter can excite electrons to higher energy levels, producing electronically excited species.[1]

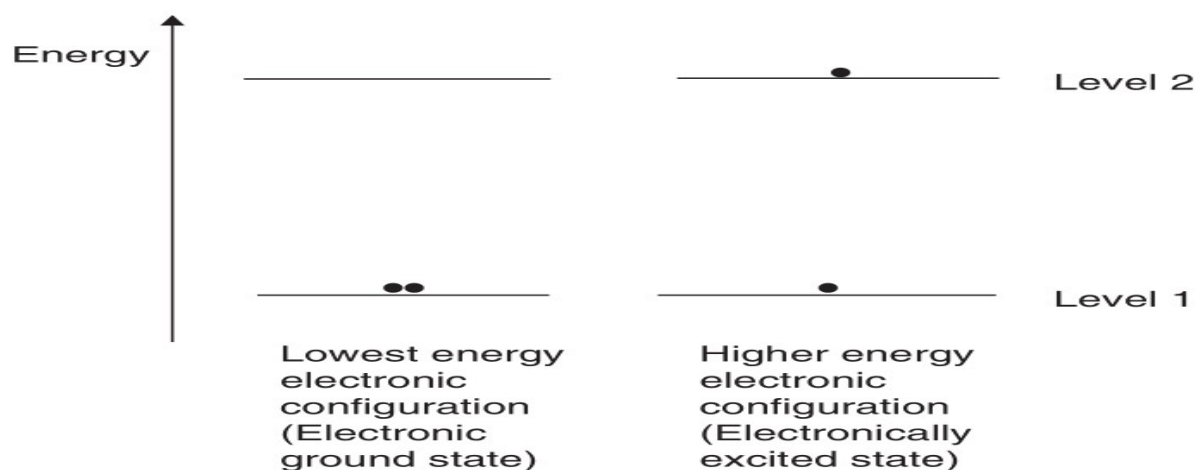


Figure (I-01): The transfer of electrons in the material from the state of stability to the state of excitation.[1]

According to the quantum theory, light is also quantised. The absorption or emission of light occurs by the transfer of energy as photons. These photons have both wavelike and particle-like properties and each photon has a specific energy which is given by this equation (named Planck's law).

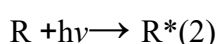
The Planck's law: $E = h\nu$ (1)

E: the energy (J).

h: Planck's constant (6.62×10^{-34} J.s).

ν : is the frequency of oscillation (s^{-1}) or Hertz(Hz).[1]

For example, for a molecule R in its stable state which absorbs a photon to produce an electronically - excited molecule, R*, we write the reaction as:



The rays can be described using the wavelength, which is the distance of one cycle or the distance between two consecutive peaks or bottoms. Also, the rays can be described by frequency, which is the number of turns that pass at a certain point during the unit of time.[4]

The relationship between wavelength and frequency is given by:

$$\lambda = c/\nu \quad (3)$$

λ : wavelength (m).

c: the speed of light (3×10^8 m/s).

ν : frequency (s^{-1}) or (Hz).

The units used for the wavelengths of different spectrum regions vary from (angstrom) unit of the X-ray region to the unit of meters of the radio area.

$$1.0 \text{ \AA} = 10^{-10} \text{ m} = 10^{-8} \text{ cm} = 10^{-4} \text{ \mu m} = 10^{-1} \text{ nm}$$

Another term is the wave number which is considered the reciprocal of the wavelength and its unit (cm^{-1}).

$$\bar{\nu} = 1/\lambda = \nu/c \quad (4)$$

So, we can express energy in another relationship, which is:[4]

$$E = hc/\lambda = hc\bar{\nu} \quad (5)$$

Table (I-01): Properties of visible and ultraviolet light.[1]

Colour	$\lambda(\text{nm})$	$\nu \cdot 10^{14}(\text{Hz})$	$\bar{\nu} \cdot 10^4(\text{cm}^{-1})$	$E(\text{Kj} \cdot \text{mol}^{-1})$
Red	700	4.3	1.4	170
Orange	620	4.8	1.6	193
Yellow	580	5.2	1.7	206
Green	530	5.7	1.9	226
Bleu	470	6.4	2.1	254
Violet	420	7.1	2.4	285
Ultraviolet	<300	>10.0	>3.3	>400

I.1.3 Light Absorption:

All photochemical and photophysical processes are initiated by the absorption of a photon of visible or ultraviolet radiation leading to the formation of an electronically - excited state.

For an effective interaction between the photon and the absorbing material:

- There should be a correspondence between the energy of the photon and the energy of a pair of electronic energy levels in the absorber.
- The strongest absorptions occur when the initial and final wave-functions (ψ and ψ^*) most closely resemble one another.[1]

When subjecting the material to photon, it results in an electron transfer from a lower energy level to a higher energy level, where absorption is achieved if the energy of the photon is equal to the energy difference between the two orbitals.[5]

-The energy is one mole of a quantum or photon (1 Einstein) given by the relationship:

$$E = N_A hc/\lambda \text{ (j/mol)} \quad (6)$$

N_A : the Avogadro constant (6.023×10^{23}).

-The energy equation becomes: $E \approx 1.2 \times 10^5 / \lambda_{(\text{nm})}$ (KJ/Einstein).

(1 Einstein = 1 mole of photon = N photon).

- The intensity of the falling photon (I_0) is determined according to the number of moles emitted (n) during the time of irradiation (t). [3,5]

$$I_0 = n / t \text{ (Einstein/s)} \quad (7)$$

-When the irradiation process occurs:

$$I_0 = I_a + I_r + I_t \quad (8)$$

I_a : Absorbed photon.

I_r : Reflected photon.

I_t : the transmitted photon.

-The absorption coefficient is given by: $\epsilon = I_a / I_0$ (9)

As well as the reflection coefficient is given by:

$$R' = I_r / I_0 \quad (10)$$

-And also the transmission is given:

$$T = I_t / I_0 \quad (11)$$

The extent of light absorption varies greatly from one substance to another, depending on the nature of the material, the wavelength and the intensity of the light.

a-The Beer's law: "When a single-wave light passes into a cell with a fixed width, the absorption is directly proportional to the concentration".[4]

$$T = I_t / I_0 = 10^{-kc} \quad (12)$$

$$\log T = \log I_t / I_0 = -kc \quad (13)$$

b-The Lambert's law: "If a single wave light passes through a constant concentration solution, the absorption is directly proportional to the width of the cell".[4]

$$T = I_t / I_0 = 10^{-kL} \quad (14)$$

$$\log T = \log I_t / I_0 = -kL \quad (15)$$

Through the previous two laws, "the Beer-Lambert Law" resulted in a logarithmic relationship between the light transmittance (T) and the product of the molar absorption coefficient ϵ (l/mol.cm), cell width L (cm) and solution concentration C (mol/l).[6]

$$T = I_t / I_0 = 10^{-\epsilon LC} = 10^{-A} \quad (16)$$

$$A = -\log T = \log I_0 / I_t = \epsilon LC \quad (17)$$

So the absorbance is: $A = \epsilon LC$ (18)

We use the wavelength (200-800 nm), which is the field for electronic transitions $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, and the energy of the photon is between (10^{-18} - 3×10^{-19} j/photon), so that the great value of energy is (600 kJ/mol), even though the particles need less energy than that to reach the state of electronic excitation.

The photochemistry reactions take place through a series of reactions and ultimately produce free radicals.[6]

I.1.4 Physical deactivation of excited states:

The Physical relaxation processes classified as follow:

a- Intramolecular processes:

- **Radiative transitions:** it is an emission of electromagnetic radiation from the excited molecule to return to a stable state and is occurs what known as luminescence.

- **Radiationless transitions:** where no emission of electromagnetic radiation accompanies the deactivation process.

b- Intermolecular processes:

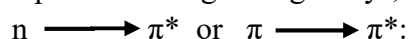
- **Vibrational relaxation:** when a rapid collision occurs between particles with excess vibrating energy with each other or with solvent particles to produce particles with lower vibrational energy.

- **Energy transfer:** where the electronically excited state of one molecule (the donor) is deactivated to a lower electronic state by transferring energy to another molecule (the acceptor), which is itself promoted to a higher electronic state.

- **Electron transfer:** considered as a photophysical process, involves a photoexcited donor molecule interacting with a ground-state acceptor molecule. An ion pair is formed, which may undergo back electron transfer, resulting in quenching of the excited donor.[1]

c-Jablonski diagram:

Upon absorbing the light rays, an electronic transmission is produced



Molecules in the stable state (the ground level) the spin of all its electrons is paired ($\uparrow\downarrow$).

This state is called the singlet state (S_0). In the excitation state, the electronic state is divided into two states:

$$M=2S+1 \quad (19)$$

1 - The spin of the electrons is paired, is called the singlet state (S_1, S_2, \dots) for a short period (10^{-9} - 10^{-6} sec), so that the electron returns to a stable state (S_0) in order to occur in what is known as Fluorescence.

2- The spin of the electrons is unpaired, this state is called a triplet state (T).

The level (T) is less energy than (S) the corresponding.

The photo excitation can only transfer the electron from S_0 to S_1, S_2, \dots, S_n

The levels (T) can be reached indirectly by the process of (Inter System Crossing), then the electron returns to the state of stability at a time of its capacity (10^{-3} -10sec) and this is known as Phosphorescence.[4]

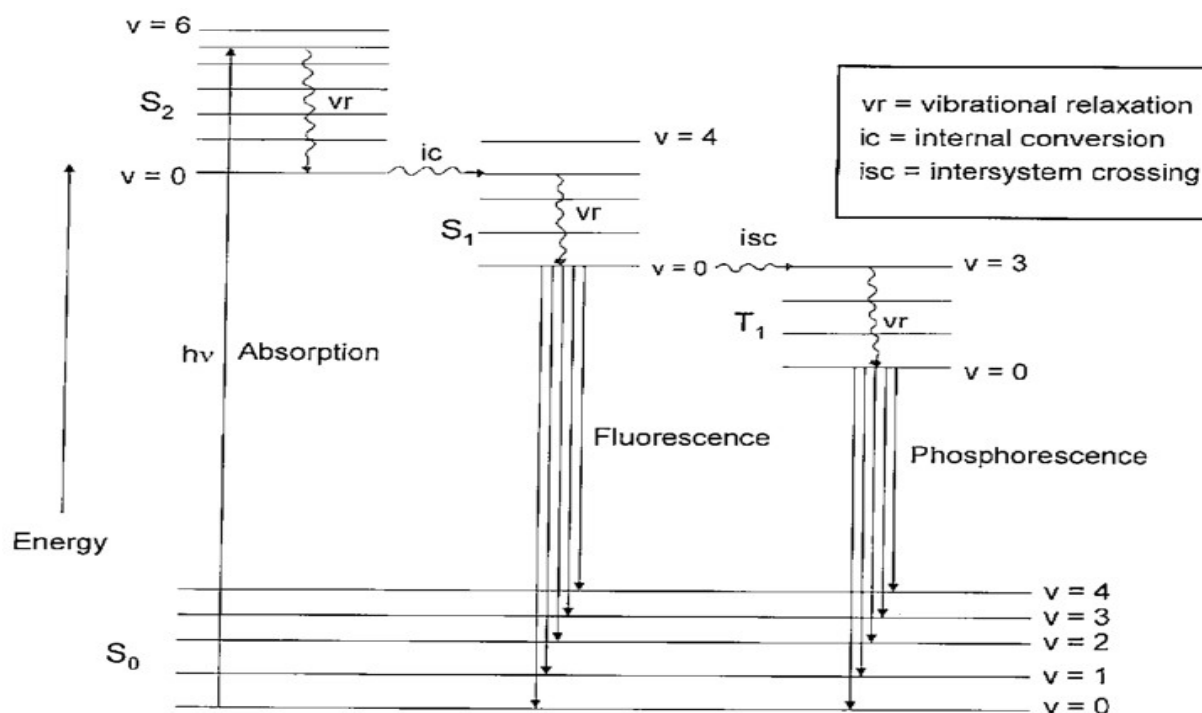


Figure (I-02): Jablonski diagram for an organic molecule, illustrating excited - states photophysical processes.[1]

-Vibrational relaxation: Involves transitions between a vibrationally - excited state and the $v = 0$ state within a given electronic state when excited molecules collide with other species such as solvent molecules in his time (10^{-13} - 10^{-9} sec), and excess vibrational energy is dissipated as heat.[1]

For example: $S_1(V=2) \longrightarrow S_1(V=0)$.

-Internal conversion: Involves radiationless transitions between vibronic states of the same total energy (isoenergetic states) and the same multiplicity, for a time between excited states (10^{-14} - 10^{-11} sec) and (10^{-9} - 10^{-7} sec) between S_1 and S_0 . [1]

For example: $S_3(V=0) \longrightarrow S_2(V=n)$ or $T_2(V=0) \longrightarrow T_1(V=n)$.

-Intersystem crossing: Intramolecular spin - forbidden radiationless transitions between isoenergetic states of different multiplicity, for a time (10^{-11} - 10^{-8} sec).[1]

For example: $S_1 \longrightarrow T_1$ or $S_3 \longrightarrow T_3$.

-Fluorescence: involves a radiative transition between states of the same multiplicity (spin allowed) and accompanied by a photon emission, usually from the lowest vibrational level of the lowest excited singlet state, S_1 . [1]

$S_1(V=0) \longrightarrow S_0+h\nu$. (20)

-Phosphorescence: involves a spin - forbidden radiative transition between states of different multiplicity and accompanied by a photon emission, usually from the lowest vibrational level of the lowest excited triplet state, T_1 . [1]

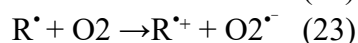


I.2 Photodegradation:

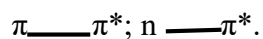
It is a chemical reaction in which a chemical compound is broken down by photons, it is defined as the interaction of one photon with one target molecule. Photodecomposition is not limited to visible light. Any photon with sufficient energy can affect the chemical bonds of a chemical compound, or simply it is a separation due the energy of light. [7]

I.2.1 Direct Photodegradation:

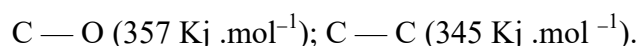
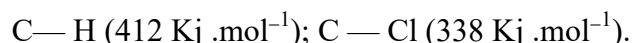
Pollutants can be separated by exciting them with direct light rays, to do this, pollutants must have a high absorption capacity of light to be excited and react with dissolved oxygen in water before they are converted into by-products. [5]



Molecular irradiation in the field of absorption spectrum is accompanied by various electronic transitions between bonding, non-bonding and anti-bonding molecular orbitals $\sigma \longrightarrow \sigma^*$;



The energies acquired by these transfers differ between 300 to more than 800 kilojoules, in order to have the ability to break bonds like:



The photodegradation rate of organic compounds depends mainly on the intensity of the absorbed light, the molar absorption coefficient at the wavelength of radiation, the quantitative yield of the reaction and the experimental practical conditions (pH, solvent,...). [8]

I.2.2 Photocatalysis:

Photocatalysis is a combination of two words: photo (“phos” means light) and catalysis (“katalyo” means to break apart, decompose).

Research began with photocatalysis in the early 1970's where the technique of using ultraviolet radiation with titanium dioxide (TiO_2) proposed to remove pollutants from water. Studies have proven the effectiveness of the method on a group of very different organic compounds such as hydrocarbons, pesticides, dyes, and greasy acids. This type of reaction is accelerated in the presence of a catalyst (semiconductor)

By (IUPAC) photocatalysis is a reaction carried out in the presence of a semiconductor and light. It only can be done by the presence of a catalyst and there are two types of these light reactions, homogeneous if the catalyst can dissolve in water and heterogeneous if the catalyst can't dissolve in water.[7]

Mostly, this photocatalyst is in the form of a semi-conductor that has an energy gap between the valence band and the conduction band, and the photocatalysis process can be summarized in the following steps:

- Exiting the photocatalyst.
- Transferring the pollutant particles to the surface of the photocatalyst.
- Photodegradation reactions.

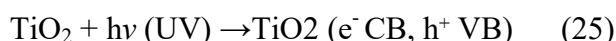
a)-Homogeneous photocatalysis :

When the reactant and photocatalyst such as *Zinc oxide* (ZnO) exist in the same phase, the reaction is called homogeneous photocatalysis. In general, these reactions are in two classes (reduction / oxidation) and (acid / base).

The speed of homogeneous photocatalysis reactions depends on many factors such as reactants, catalyst concentration, temperature and pressure.

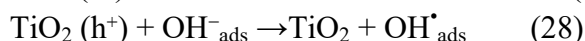
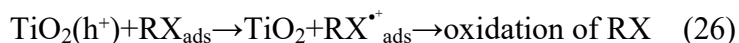
b)-Heterogeneous photocatalysis:

Here the reactant and photocatalyst exist in different phases. This technique occurs when the catalyst is a semiconductor such as titanium dioxide (TiO₂), when a light beam hits the TiO₂ catalyst with a wavelength less than 380nm, which means with energy greater than the energy gap of the catalyst in this case it must be greater than 3,2 eV, the electrons move from the valence band (VB) to the conduction band (CB) so there becomes e⁽⁻⁾ in the conduction band and a positive gap h⁽⁺⁾ in the valence band. [9],[10].



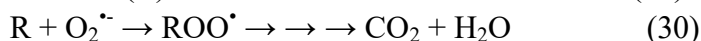
-At valence band (VB):

Oxidation reactions caused by electron transport from (organic contaminant RX), water molecules H₂O and hydroxyl ions OH⁻ adsorbed on the catalyst surface.



-At conduction band (CB):

Oxygen molecule participates with electron transfer reactions from the conduction band of the catalyst to the oxygen molecule according to the reaction:[7]



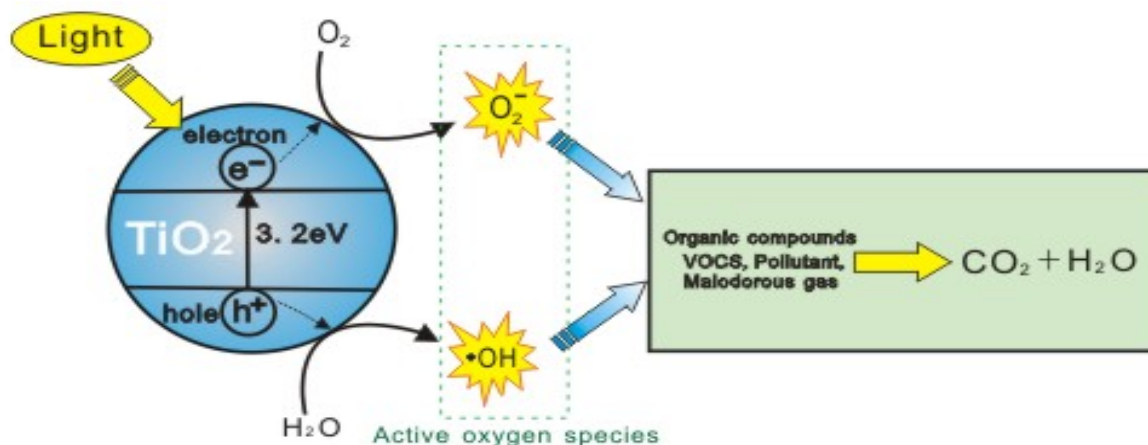
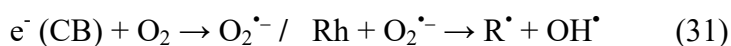


Figure (I-03): The mechanism of photocatalysis in the presence of TiO₂.

The presence of O₂ is an important factor in the occurrence of a photo oxidation reaction, it acts as a stabilizer for the photocatalytic electrons which is located in the conduction band, forming the radicals of super oxide ions (O₂⁻) that react with adsorbed particles on the surface of the catalyst, forming free radicals according to the interactions:



I-2-3 Titanium dioxide:

Titanium dioxide is a semiconductor found in the form of a white powder which is one of the materials of titanium metal, it is spread by 0.6% in the Earth, discovered by the German scientist “Klaproth” in the year 1870 and it was first produced commercially in 1923.

Titanium dioxide (TiO₂) has been widely used as a photocatalyst in many environmental and energy applications due to its efficient photoactivity, high stability, thermal stability, corrosion resistant, less treatment and preparation what makes it low cost, and safe to the environment and humans.

Table (I-02): Some physical and chemical properties of TiO₂.

Chemical formula	TiO ₂
Molecular mass	9,87g/mol
The appearance	White
Density	4,23 g/Cm ³
Melting point	1870 C°
boiling point	2972 C°
Specific heat	298,13 J/(mol .°C)
Solubility ₁₀	Insoluble in water
The energy gap	3.2 ev

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Chapter II:

Dyes and Pigment

II-1 Introduction:

Human use dyes and pigment since ancient cycle times, where colors were used in writing and archaeological drawings in caves and others (such as the red cinnabar) and were used in dyeing clothes (such as the indigo). The origin of these dyes was initially natural and extracted from plants and animals.[1]

The first discovery of industrial dyes was by the English chemical scientist “**William Henry Perkin**” in 1856. From that time, industrial dyes replaced natural dyes and invaded all domains such as paint, textiles, food matters, and others.[2]

These are some industrial dyes and their history of discovery: Mauveine 1856, maganta 1859, chrysoidine 1876, phenothiazine 1883, phtalocyanines 1928, triazinyl 1954, triazine 1954, diketopyrrolopyrrole (DPP) 1974.[3,4]

In 1876, the scientist, **Witt**, discovered that colored materials contain a groups called chromophores which has double bonds (π) and is responsible for absorbing light, and contains another groups called auxochromes which is responsible for fixing color and dye Where Table (II-01) represents some groups chromophores and auxochromes, while Table (II-02) represents the wavelengths and the observed color.[5]

Table (II-01): Some groups chromophores and auxochromes.[3.5]

Groups chromophores	Groups auxochromes
N=N: Azo group	NH ₂ : Amine
N=O: Nitroso group	NHR: Secondary amine
C=O: Ketone or carbonyl group	NR ₂ : Tertiary amine
C=C: Vinyl or ethenyl group	OH: Hydroxyl
C=S: Thio carbonyl group	OR: Alkoxy
CH=N: Azomethine group	OCH ₃ : Metoxy
N=N=O: Azoxy group	I: Iodine
-NO ₂ : Nitro group	Br: Brome
C=S: Sulfide group	Cl: Chlorine

Table (II-02): Absorbed wavelength and observed corresponding color.[5]

λ Absorbed wavelength (Å)	Observed color (transmitted)
4000 (violet)	Greenish-yellow
4250 (dark blue)	Yellow
4500 (blue)	Orange
4900 (blue-green)	Red
5100 (green)	Purple
5300 (yellow-green)	Violet
5500 (yellow)	dark blue
5900 (orange)	Blue
6400 (red)	Blue green
7300 (purple)	Green

Nearly 100,000 types of dyes are produced annually, which is equivalent to 700,000 tons. For example, China alone produced in 2010 about 224,000 tons of dyes. A large proportion of these dyes are lost in sewage and rivers.[4,6]

Most of these dyes are of diverse nature and are also potentially toxic and carcinogenic in nature and are classified as pollutants. And the treatment of these effluents is imperative for the protection of the environment.[7]

II-2 Definition of dyes:

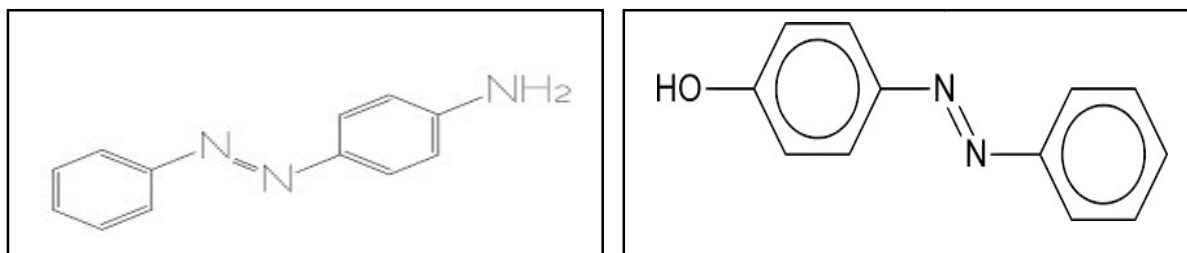
Dyes are the aromatic compounds that absorb the visible spectrum between (380-750 nm) and contain the groups of chromophores and auxochromes, which give their color to another substance and are usually used for coloring, painting, and dyeing the textile.[2]

The major difference between dyes and pigments is the particle size. Dyes are much finer than pigments. Therefore dyes are not UV stable whereas pigments are usually UV stable.[8]

II-3 Chemical classification of dyes:

II-3-1 Azo dyes:

These dyes are distinguished by the Azo functional group ($-N=N-$), which binds between two groups of alkyls or aryls and often have an aromatic nature and are most used for warm colors (yellow, orange, and red), It is used in dyeing fibers and cellulose.[2,7]



Figure(II-01): The chemical formula for azo dyes.

II-3-2 Anthraquinonique dyes:

They are anthracene compounds mediated by a cycle quinone (chromophore) to which the hydroxyl and amines groups may be attached. These dyes are important and contain a large range of colors but these are often used in cold colors (violet, green, blue), it used for dyeing, printing cotton, fibers and polyester with cellulosic fibers.[2,5,7]

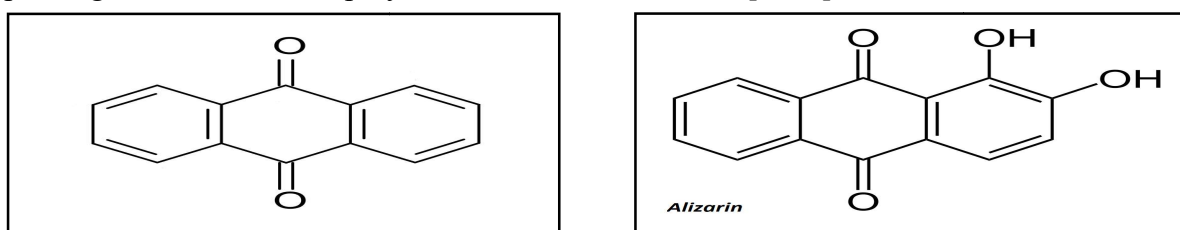


Figure (II-02): The chemical formula for anthraquinonique dyes.[9]

II-3-3 Indigo dyes:

It is a group of dyes bearing indigo color that are classified of type (Vat dyes or water-insoluble dyes) and can interact with compounds like sulphur or oxygen than result in a color offset (hypsochromes) from orange toward turquoise, it used to dye cellulose, cotton and denim fabric.[2,3,10]

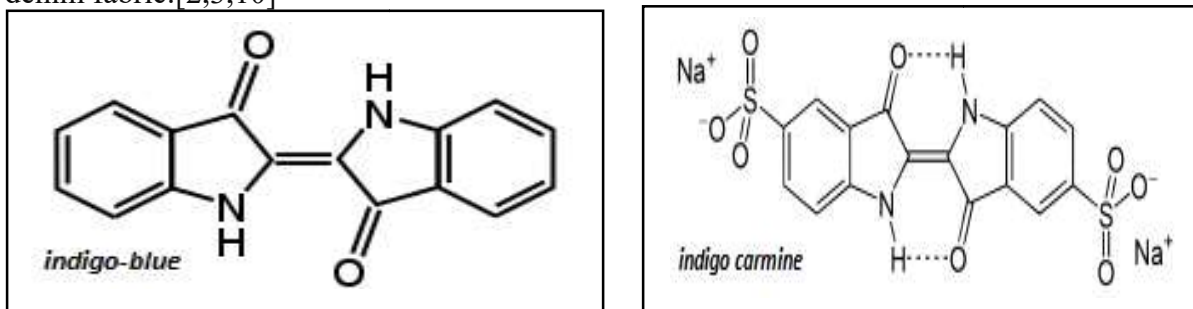


Figure (II-03):The chemical formula for indigos dyes.[11.12]

II-3-4 Phthalocyanines dyes:

These dyes are the result of a dicyanobenzene reaction with the presence of a mineral (Cu, Ti, Zn, Ba, Pb, Fe, Mo, Ca, Al,...) where it results a complex compound in center of an metallic atom usually is copper (Cu). It is distinguished by its dark blue color, and is used in colors of printing, solar cells and Pc-devices (sensors, transistors ...).[3,5,13]

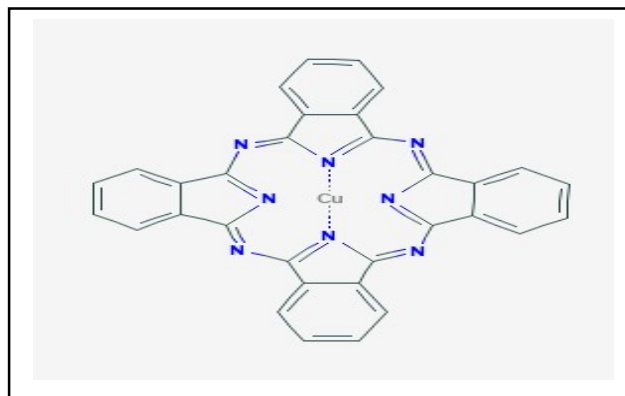


Figure (II-04): The chemical formula for phthalocyanines dyes.

II-3-5 Nitrate and nitroso dyes:

It is a group of limited and old dyes characterized by its appropriate price and simple structure, as it contains the nitrous group (NO_2) in the Ortho position in for is electro-donor function (hydroxyl or amines), used in paint and dye rubber, plastic.[14]

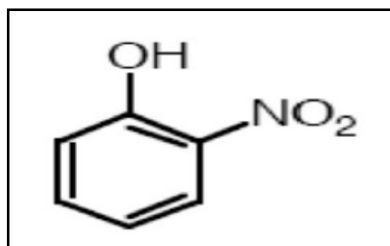


Figure (II-05):The chemical formula for nitrate and nitroso dyes.

II-3-6 Triphenylmethane dyes:

It is a derivative of methane, as it contains three substituted phenyl groups that are carriers of one oxygen atom or one nitrogen at the para position, and it is considered one of the oldest dyes. It is used in the paper industries and fabric, also for dyeing nylon, leather, wool, silk and cotton.[14]

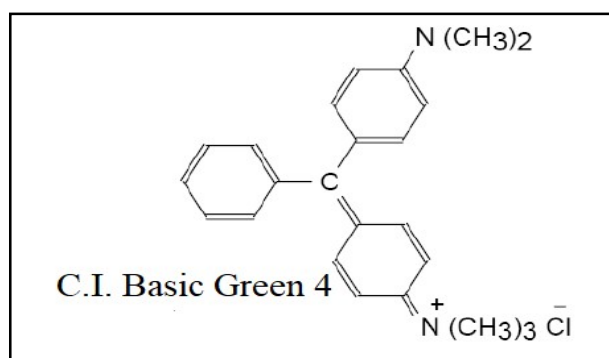


Figure (II-06) :The chemicals formula for triphenylmethane dyes.[2]

II-3-7 Xanthene dyes:

It is a derivative of fluorescein and is used as indicators in marine roads and rivers for the intense fluorescence. It is used in a little food colors, cosmetics, textile and printing.[14]

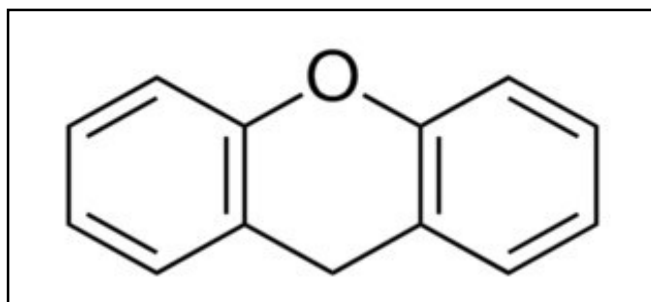


Figure (II-07): The chemical formula for xanthene dyes.

II-4 Classification of dyes according the application fields:**II-4-1 Acid or anionic dyes:**

They are water-soluble dyes that contain carboxyl and sulfonate groups and allow the dyeing of both silk, wool, nylon, polyamide. They are usually azo dyes.[3,14]

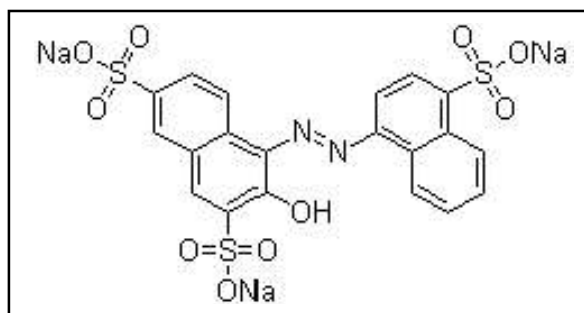


Figure (II-08): The chemical formula for Acid or anionic dyes.[14]

II-4-2 Basic or cationic dyes:

They are the dyes of organic amino salts, which makes them quickly dissolve in water. Also are used in dyeing the animal fibers and acrylic fibers. They are usually (azo, anthraquinonic, triphenylmethane) dyes. [3,14]

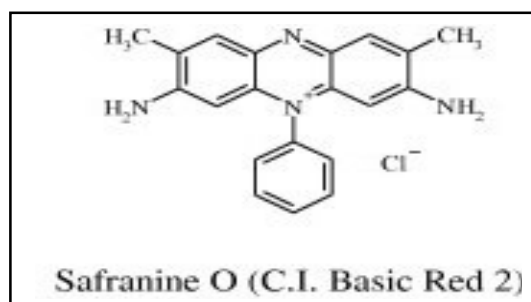


Figure (II-09): The chemical formula for basic or cationic dyes.

II-4-3 Direct dyes:

They are characterized by the presence of sulfonate groups (R-SO₃Na), they have great solubility, are considered available, low in price and easy to apply, they are used for dyeing lining fabrics, woolen threads, carpets and for many inexpensive items. They are usually (azo, phthalocyanines) dyes. [3,14]

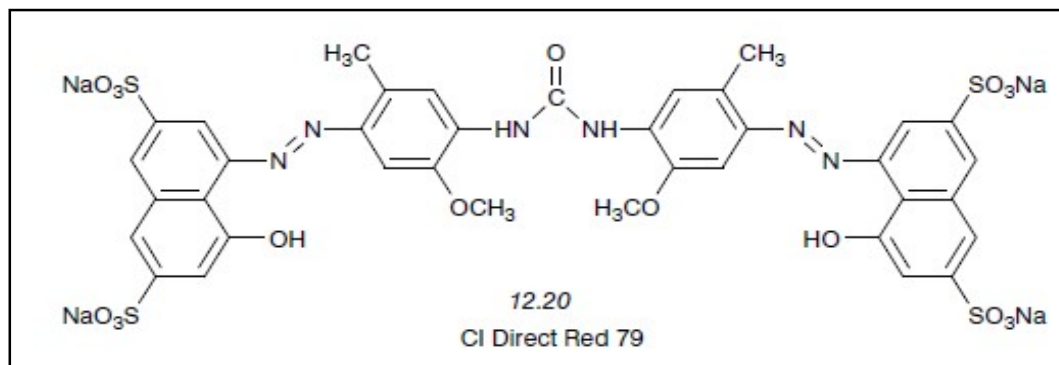


Figure (II-10): The chemical formula for direct dyes.[15]

II-4-4 Reactive dyes:

They are characterized by the presence of a group (chromophor) that is fixed on an electrophilic to form a stable, covalent and chemical bonding with the functions of hydroxyl cellulose and NH₂ or NH of polyamides, they are used in clothing and fabrics. They are often azo dyes or metalliferous and phthalocyanines, anthraquinonic dyes.[3,14]

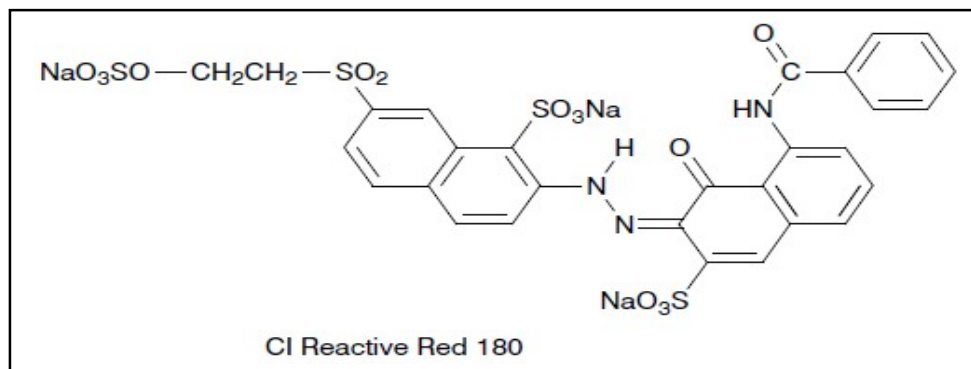


Figure (II-11): The chemical formula for reactive dyes.[15]

II-4-5 Disperse dyes:

They are characterized by their fastness color, insoluble in water, forms a suspension and are used in dyeing cellulose acetate and synthetic fibers, of from trade names or commerciale marque Artisil (SANDOZ), Celiton (BASF), Cibaset (CIBA), Duranol (ICI), Setacyl (GEIGY), Acetoquinone (FMC). Generally include (azo, metalliferous, anthraquinonic, nitroso) dyes.[3,14]

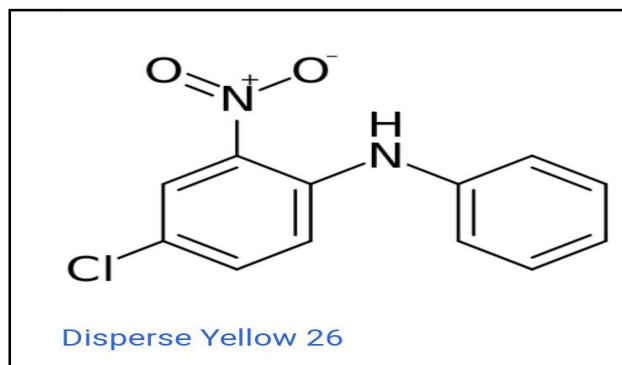


Figure (II-12): The chemical formula for disperse dyes.

II-4-6 Sulfur dyes:

These dyes are insoluble in water and result from the dissolution of amine derivatives or phenols in the presence of sulfur, they are used in paints, available and easy to apply and has faded colors such as black and brown.[3,16]

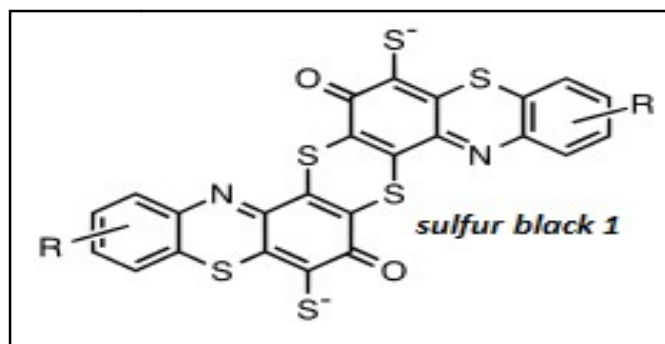


Figure (II-13): The chemical formula for sulfur dyes.

II-4-7 Mordant dyes:

These dyes contain a complex ligand that reacts with mineral salts (Al, Fe, Zn, Sn, Cr, Co, Ni, Cu) to give compounds of different colors with textile, they are considered insoluble compounds.[17]

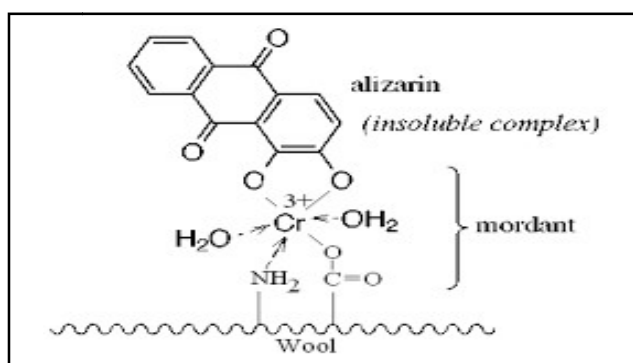


Figure (II-14): The chemical formula for mordant dyes.

II-4-8 Vat dyes:

These dyes do not dissolve in water but with the addition of the reducing agent sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_8$) they give a colorless or white Leuco derivative (A *leuco* dye is a dye which can switch between two chemical forms; one of which is colorless. Reversible transformations can be caused by heat, light or pH) that is soluble in water and has an affinity with some of the textile fibers by means of oxidation or oxidizing agent.

It is considered one of the most important group of dyes, they are widely used in food, cosmetic, pharmaceutical products, and paints. They are usually (anthraquinonic, indigos) dyes.[17]

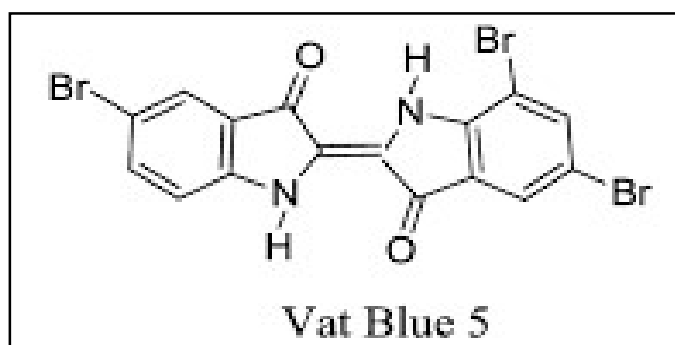


Figure (II-15): The chemical formula for Vat dyes.

II-5 Crystal violet dye study:

Crystal violet (also known as methyl violet 10B or hexamethyl pararosaniline chloride) is a triphenylmethane dye used as a histological stain and in **Gram's** method of classifying bacteria, it has antibacterial, antifungal, and antiemetic properties and was formerly important as a topical antiseptic. It is one of the components of methyl violet, a dye synthesized first time by “**Charles Lauth**” in 1861.[18]

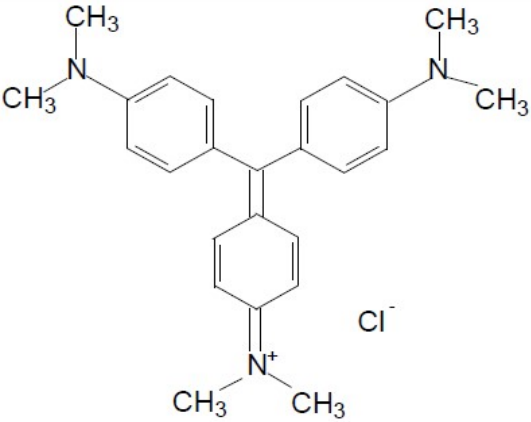
II-5-1 Methods of preparation:

- Manufactured with a mixture of (tetra-, penta-, and hexamethylated pararosanilines).
- Reaction of dimethylaniline with phosgene to give “4,4’bis(dimethylamino) benzophenone (Michler's ketone)” as an intermediate then reacted with additional dimethylaniline in the presence of phosphorus oxychloride and hydrochloric acid.[4,18,19].
- Can also be prepared by the condensation of formaldehyde and dimethylaniline to give a leuco dye.[18]

II-5-2 Physico-chemical characteristics of crystal violet:

The **Table(II-03)** represents the physico-chemical properties of the crystal violet dye.[18,19,20]

Table (II-03): the physico-chemical properties of the crystal violet.

Usual name.	Crystal violet
Molecular structure.	
Molecular formula.	$C_{25}H_{30}ClN_3$
Molar mass.	407.99 g.mol ⁻¹
Solubility in water.	High
Vapor pressure.	Low
Melting point.	205 C°, 401 F°, 478 K°.
use.	Chemical reagent. textile. dye in bacteriology.

II-5-3 Spectral properties: figure (II-16) shows the uv/visible absorption spectra of crystal violet (CV) in water.[21]

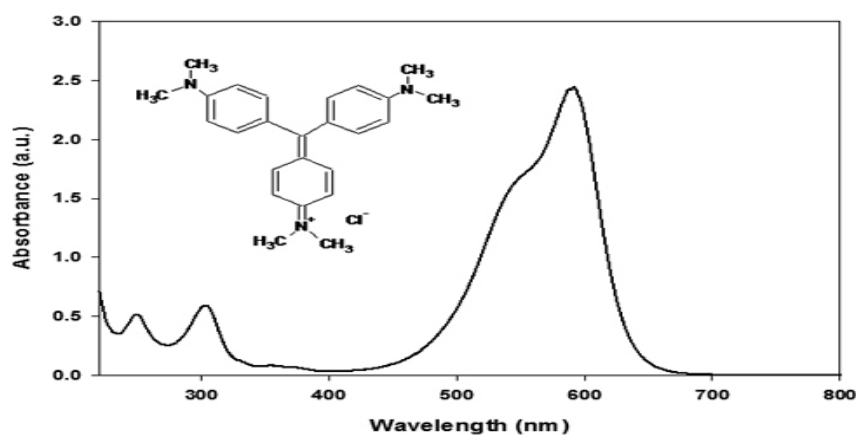


Figure (II-16): The UV/VIS absorption spectra of the violet crystal in water.

II-6 Effects of dyes on human health and environment:

The development in the manufacture of dyes are increasing their irrational use, as they propagate in all domains such as cosmetics, decorations, pharmaceuticals, paints and even of the foods.

While people ignore the risks, resulting from them and their impact on the environment and the health problems it causes to humans.

II-6-1 Impact on the environment:

-The discharge of dye industry residues in rivers and flats of water result to great damage to living organisms in the environment due to its complex chemical composition, where it is difficult to disintegrate, in addition to increasing the turbidity of water and distorting the natural views.[20]

-The presence of dyes in the water causes the occurrence of biological degradation processes, which result to the risk of the death of the aquatic organisms due to decreasing of dissolved oxygen in the water.[3,20]

-The dyes enter animal tissues either through exposure or swallowing, and their quantities increase from lowest the food chain which consisting of plankton and phytoplankton to reach The highest pyramid of the food chain animals and possibly humans, where the concentrations of the pollutant are at the lowest of the nanogram (ng/kg) chain to reach the gram (g/kg) level for the organisms in the highest chain. This is known as bioaccumulation.[2,3]

II-6-2 Impact on the human health:

-The dyes are toxic and cancirogenic, due to the functional groups they contain (aromatics, phthalogens, cyanides, barium salt and lead) that attack the pyrimidine bases of DNA and RNA and which cause mutations.[17]

-Decomposition of (-N = N-) bonds in the azo dyes results to the formation of primary amines that cause the methemoglobinemia which inhibit the transport of oxygen in the blood. the azo dyes are also responsible for the development of bladder cancer in humans.[2,17,22]

-As for the reactive dyes, they cause respiratory allergies, asthma, and rhinitis.[17]

-Triphenylmethane derivatives and also the amino dyes cause eczema,dermatitis and stomach pain (diarrhea).[18,21]

-The anthraquinonic and disperse dyes cause allergic and eczematic dermatitis.[2,22]

II-6-3 Some toxic and banned globally dyes:

The following Table (II-04) represents groups of toxic dyes that are harmful to humans and environment:[2,3,20,22]

Table (II-04): toxic and harmful dyes.

1-Uxanthol black G.	20-Erythrosine.	39-Citrus red.
2-Fuchsin.	21-Yellow AB.	40-Aniline.
3-Methylene blue.	22-Yellow OB.	41-Solid green.
4-Victoria blue.	23-Scarlet red.	42-Guinea green.
5-Methyl violet.	24-The sudan III.	43-Patent blue (V)
6-Anthracite black BT.	25-Orange SS (bold orange TX)	44-The light green SF.
7-Diamond green.	26-Amaranth.	45-Auramine
8-Orange sandocryl.	27-The culvert red.	46-Eosin.
9- Lanasyn Black.	28-The sudan I.	47-Fluorescein.
10-Tartrazine.	29- Rhodamine B.	48-Red chelate.
11-Crystallized violet.	30-Scheele green (copper arsenite).	49-Schweinfurt green (copper acetoarsenite).
12-1,4phenylenediamie.	31-1-amino 2-naphtol.	50-benzidine.
13- O-toluidine.	32- 2-naphtylamine.	51- 1-naphtylamine.
14- 4-aminodiphenyl.	33- 4-chloro-o-toluidine	52- 2-naphthalamine.
15- O-aminoazotoluol.	34- 2-amino-4-nitrotoluol.	53- P-chloraniline.
16- 2-4-diaminoanisol.	35- 4,4'-diaminodi phenylmethane.	54- 3,3'-dichloro-benzidine.
17- 3,3'-dimethoxyd-benzidine.	36- 3,3'-dimethylbenzidine.	55- 3,3'-dimethyl-4,4 Diamondi- phenylmethane.
18- P-kresdine.	37- 4,4'-oxydianiline.	56- 4,4'-thiodianiline.
19- 4,4'-methylene-to-(2-chloraniline).	38- 2,4-toluyendiamine	57- 2,5,5-trimethyl-aniline.

II-7 Methods for elimination dyes:

It is known that the dyes contain several harmful, pathogenic, and even carcinogenic compounds, humans must interfere in order to prevent the flow of these dyes into the environment. Therefore, several methods are used to treat dye wastes according to the type of dye. Among these methods used are (biological, physical, and chemical).

II-7-1 Biological methods:

This method depends on the microorganisms in the aerobic and anaerobic media, where the process leads to a biological decomposition to form (CO_2 and H_2O) if the decomposition is complete, and is often characterized by measurements (BOD, COD, and suspended matter). Some dyes were completely decomposed by bacteria "Aeromonas hydrophila Var.24B", and activated sludge was also used in the decomposition of red, blue, and yellow synthetic dyes.[2,20]

II-7-2 Physical methods:

II-7-2-1 Adsorption by activate carbon:

With the presence of many adsorbents, activated carbon is considered one of the most important adsorbents used in the treatment of dyes in the water, due to the presence of several factors, such as ease of re-use several times, availability and high efficiency.

Adsorption dye removal is affected by some physical and chemical factors such as dye-adsorbent reactions, adsorbed surface area, particle size, temperature, pH, and contact time. Activated carbon is very effective in adsorbing cationic, mordant, acid disperse, direct, vat, and reactive dyes. [2,7]

II-7-2-2 Membrane filtration:

Filtration methods such as ultrafiltration, nanofiltration and reverse osmosis can be used for filter and recycling controlled by hydraulic pressure.

Nanofiltration and reverse osmosis are best suited for partial reduction of colors and small organic molecules, nanofiltration is applied to the treatment of reactive dyes while microfiltration is applied to colloids (dispersed or Vat dyes), and for ultrafiltration it reduces COD and suspended solids matter. [2,7]

II-7-2-3 Coagulation-flocculation:

Coagulation / flocculation is often applied in wastewater treatment to remove color from sulfur and dispersed dyes, this process is based on the addition of a coagulant, which will form flocs with organic pollutants. These flocs are then removed by decantation and filtration.

Coagulation agents used are:

- Aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$); Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).
- Ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$); Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$).
- Calcium chloride ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$); Copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$).
- Pentaethylene ($\text{C}_{22}\text{H}_{46}\text{O}_6$); Hexamine ($\text{C}_6\text{H}_{12}\text{N}_4$).
- Ethylene dichloride ($\text{C}_2\text{H}_4\text{Cl}_2$).[2,7]

II-7-3 Chemical methods:**II-7-3-1 The ionic exchange method:**

It is a process for removing pollutants of the organic and inorganic type present in an aqueous medium, it depends on the presence of two compounds of different phase solid (resin) and liquid (solution). The principle of exchange is mainly relate to electrostatic interactions (attraction) and the forces of Van der Waals (affinity). The ionic exchange method proved to be effective in treating the (red, yellow, blue) dyes using resin (Amberlite IR 120).

There are several types of exchanges:

- The strong cations exchanges where the position is sulfonate groups (R-SO₃).
- The weak cations exchangers where the position is carboxylic groups (COOH).
- Anion exchangers where the sites are amino groups (NH₃).
- The inert exchangers with the ability to install compound to be eliminate.

Applications this method:

- Retention of toxic heavy metals (Cd²⁺, Pb²⁺, Ni²⁺, Zn²⁺, ...).
- Retention of anionic species such as nitrates (NO₃⁻), sulfates (SO₃⁻²), chloride (Cl⁻).
- Elimination of cationic and anionic dyes.
- Water softening (elimination of Ca²⁺ and Mg²⁺).[20]

II-7-3-2 Classic chemical oxidation processes:

It is applied to treat wastewater that contains non-degradable or toxic pollutants at high concentrations that other processes cannot treat it using the following oxidants (O₂, Cl⁻, H₂O₂, O₃,...).[2]

II-7-3-3 Advanced oxidation processes (AOPs):

They are processes during which chemical reactions occur that are able of producing agents with high oxidation activity, and are very effective for the disposal of organic pollutants and toxic dyes as they are partially or completely mineralized and result in them (CO₂ and H₂O). Table (II-05) represents some oxidizers used in water purification.[2,3]

Table (II-05): Oxidation potential of common oxidizing agents.[5,7]

Oxidizing agents	Redox equation	Oxidation potential (V/ESH) 25 c°
Xenon fluoride (XeF)	$\text{XeF} + e \rightleftharpoons \text{Xe} + \text{F}^-$	3.40
Fluorine (F ₂)	$2\text{OF}_2 (\text{g}) + 4\text{H}^+ + 4e \rightleftharpoons \text{O}_2(\text{g}) + 4\text{HF}$	3.06
Hydroxyl radical (OH•)	$\text{OH} + \text{H}^+ + e \rightleftharpoons \text{H}_2\text{O}$	2.80
Ozone (O ₃)	$\text{O}_3 + 2\text{H}^+ + 2e \rightleftharpoons \text{O}_2 + \text{H}_2\text{O}$	2.07
Hydrogenperoxide (H ₂ O ₂)	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e \rightleftharpoons \text{H}_3\text{O}_2^+$	1.78
Potassium permanganate(KMnO ₄)	$\text{MnO}_4^- + 8\text{H}^+ + 5e \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.67
Hypochlorousacid (HClO)	$\text{HClO}_2 + 3 \text{H}^+ + 4e \rightleftharpoons \text{Cl}^- + \text{H}_2\text{O}$	1.49
Chlorine (Cl ₂)	$\text{Cl}_2 + 2e \rightleftharpoons 2 \text{Cl}^-$	1.36
Molecularoxygen (O ₂)	$\text{O}_2 + 4\text{H}^+ + 4e \rightleftharpoons 2\text{H}_2\text{O}$	1.23

II-7-3-3-1 Advanced oxidation processes types:

a/ Photo-chemical oxidation processes: it generally depends on the use of light rays, especially ultraviolet rays (UV) in the presence of the oxidant.[3]

b/ Non-photo chemical oxidation processes: hydroxyl radicals are produced in the absence of light, usually by ozone in the presence of (Fe³⁺) as a catalyst.[3]

The following Table (II-06) summarizes the types of systems in advanced oxidation processes

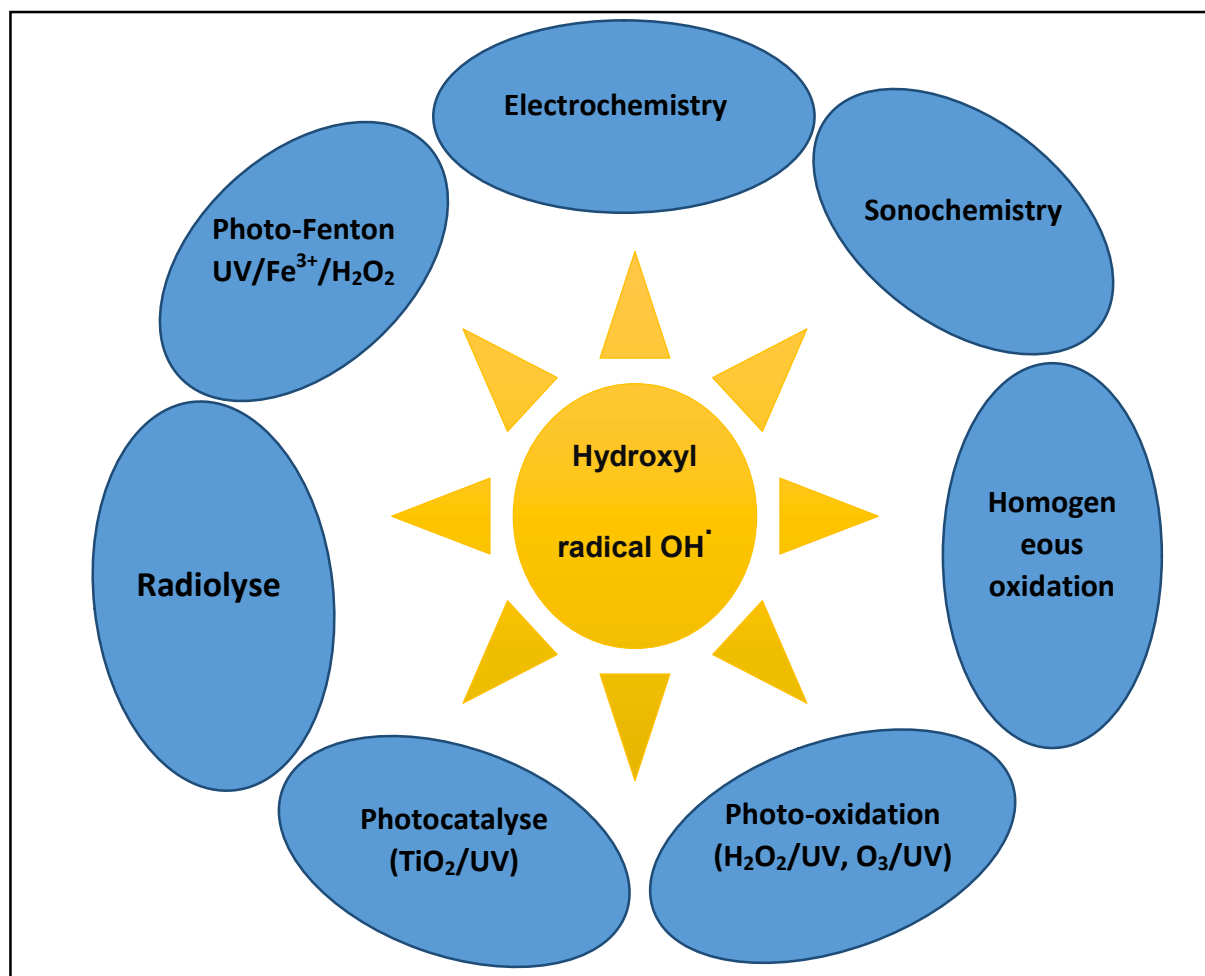
Table (II-06): The advanced oxidation processes (AOPs).[21]

Photo-chemical processes	Non-photo processes
-UV/H ₂ O ₂ .	-Peroxonation (O ₃ /H ₂ O ₂).
- UV/H ₂ O ₂ /O ₃ .	-Fenton (Fe ²⁺ /H ₂ O ₂).
-Photo Fenton.	-Sono chemistry.
-Heterogeneous photo catalysis.	- Radiolyse.
-Sono –photo –catalyse.	-Electro-Fenton.
- Water photolysis (UV/H ₂ O).	-Electrochemicaloxidation.

II-7-3-3-2 Hydroxyl radical properties:

The target of advanced oxidation processes is to produce hydroxyl radicals, which are considered one of the strongest oxidants ($E^\circ = 2.80 \text{ V/ESH}$, 25C°) for several reasons:

- React quickly with most organic compounds.
- Do not corrode equipment.
- Non-toxic.
- Do not cause secondary pollution.
- Simple to handle and inexpensive.[2,5,]



FigureII-17:The main advanced oxidation processes (AOP) to form hydroxyl radicals (OH^\cdot).

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**Chapter III:
Effect of inorganic
ions on photocatalysis**

III.1 Introduction:

As we know the water has a lot of inorganic ions and it plays a big role in the photocatalysis reactions and ether in other reactions. We can classified these inorganic ions into two classes cations (positive ions) and anions (negative ions), they can slightly decrease the photocatalysis reactions yield, and they affect exactly the photocatalyst activity, we can follow their effect on the photocatalytic efficiency using this formula:

$$\text{Photocatalytic efficiency \%} = ((C_0 - C)/C_0) \times 100 \dots \dots \dots (1) [1]$$

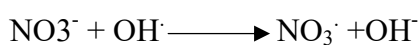
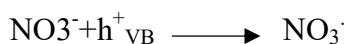
And also by the photocatalytic kinetic by using the equation:

$$\ln (1/C - 1/C_0) = kt + \ln (1/C_1 - 1/C_0) \dots \dots \dots (2) [1]$$

Carbamazepine (CBZ) is mainly used to treat epilepsy, anti-central neuralgia, and prevent or treat manic depression. The presence of CBZ not only causes environmental pollution but also poses a serious threat to human health. To make it clear we give this example of the photodegradation of CBZ as a pollutant to show the effect of the inorganic ions on the photocatalysis reactions. By tracking changes of photocatalytic efficiency and kinetic to all the inorganic ions that we put under study.

III.2 Effect of inorganic anions on photocatalysis:**a)- Effect of nitrate (NO₃⁻):**

NO₃⁻ inhibit the photocatalytic efficiency, the studies explain that the NO₃⁻ ions may play a role of radical scavenger which react with the positive holes h⁺ of the photocatalyst and the hydroxyl radicals OH[·], so it will form a new radicals in the reaction and its activity is lower than h⁺ and the OH[·]. They notice generally in all the experiences the photocatalytic degradation follow the pseudo-second order kinetic so automatically the degradation will be inhibited in the presence of nitrate ions (NO₃⁻). Also they notice that the half-time of the photocatalysis processes in the presence of (NO₃⁻) will increase. [1, 3]



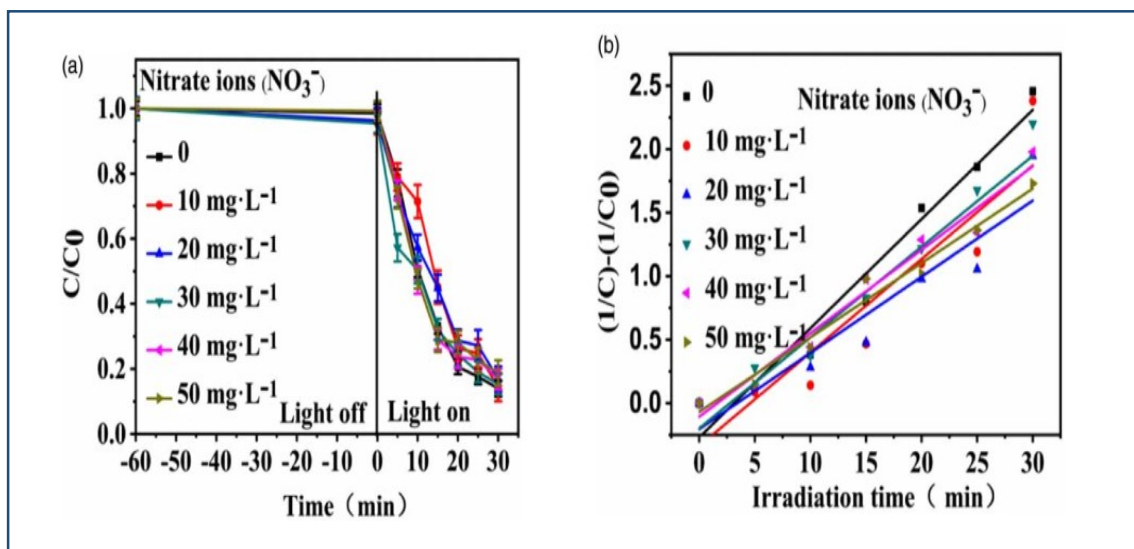
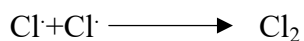
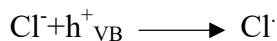


Figure (III-01): (a) shows the effect of NO_3^- on the photocatalytic efficiency and (b) shows its effect on photocatalytic kinetic.

b)- Effect of chloride (Cl^-):

As the nitrate ions (NO_3^-) the chloride ions (Cl^-) decreases the photocatalytic efficiency too by reacting with h^+ holes in the photocatalyst and with the hydroxyl radicals OH^\cdot to form chlorine radicals Cl^\cdot . As a fact Cl^- can decrease the solubility of the pollutants in which indicates that Cl^- enhance the adsorption of pollutant on photocatalyst. And then promote the photocatalytic degradation. This promotion can be related with the initial pH of the pollutant and the characteristics of the contaminants, when the pH is higher than the isoelectric point of the photocatalyst in which its surface is negative here the effect of the Cl^- on the photocatalyst can be ignored, but when the pH is lower than the isoelectric point of the photocatalyst the adsorption decreases when we increase the concentration of Cl^- . Moreover in acid condition Cl^- cannot make the adsorption weak but enhance the adsorption, so we can say that the effect of Cl^- on the photocatalytic degradation of the pollutant is related with the adsorption of the pollutant on the photocatalyst, so the adsorption can be promoted and also the photocatalytic degradation process and it can be inhibited when the change of Cl^- concentration is over large. [1,2,3]



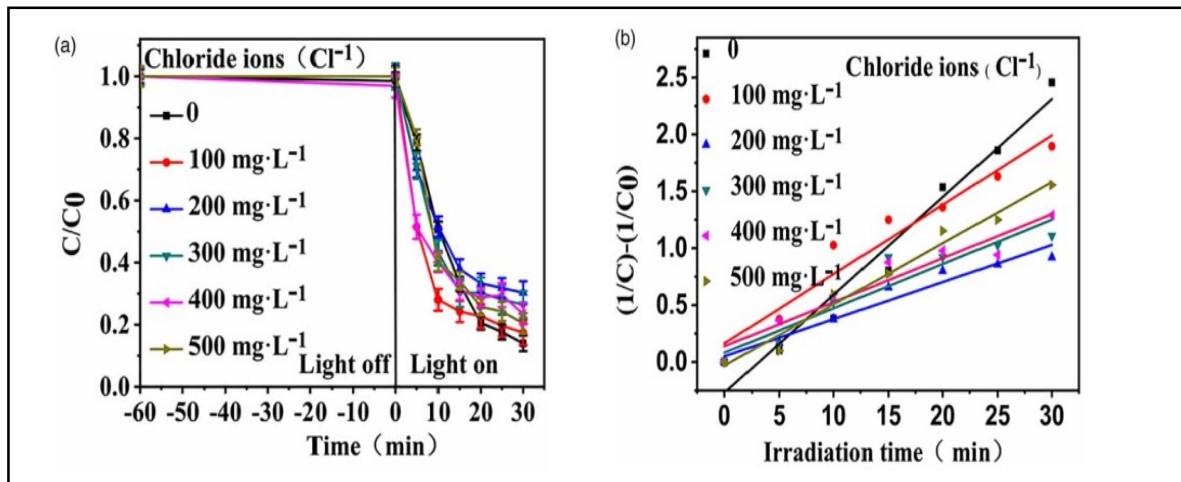


Figure (III-02): (a) shows the effect of Cl^- on the photocatalytic efficiency and (b) shows its effect on photocatalytic kinetic.

c)- The effect of bicarbonate (HCO_3^-):

The bicarbonate (HCO_3^-) is important ion in water and as the other anions in water it could make some problems in photocatalytic degradation process. And as the nitrate (NO_3^-) ions the bicarbonate (HCO_3^-) ions act as a scavenger for hydroxyl radicals OH^\cdot so as a result the degradation of contaminants will be decreased. In other hand bicarbonate (HCO_3^-) ions react with hydroxyl radicals OH^\cdot and it will be consumed and form the carbonate radicals ion ($\text{CO}_3^{\cdot-}$) which has weaker oxidative ability than the hydroxyl radicals, so it is hard to make it react with any organic substances that causes a big decrease for the photocatalytic degradation yield. So the effect of the bicarbonate ions on photocatalytic degradation is generally related to some specific conditions such as the reaction system, the type of the pollutants, the type of photocatalyst. [1,2]

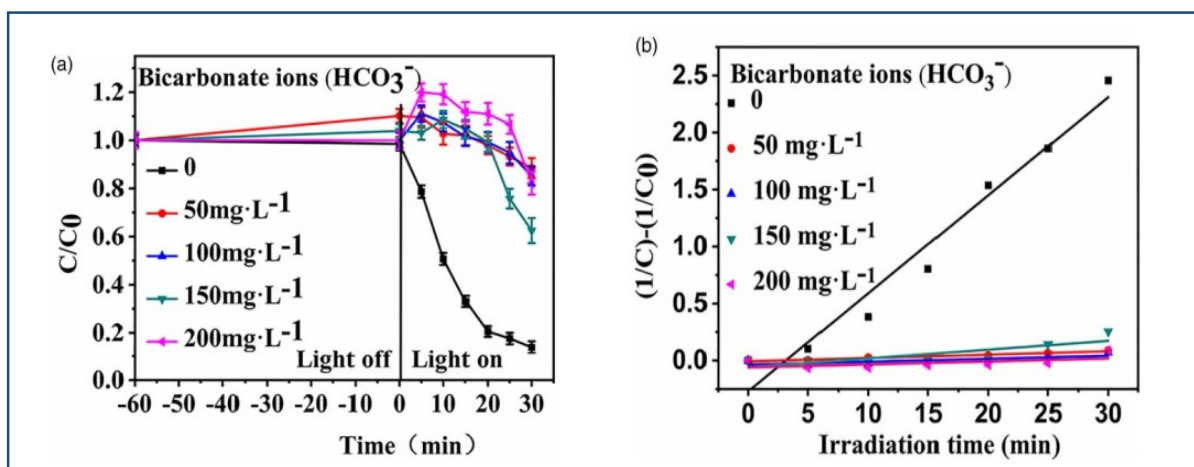
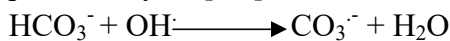


Figure (III-03): (a) shows the effect of HCO_3^- on the photocatalytic efficiency and (b) shows its effect on photocatalytic kinetic.

In the end and according to the previous remarks and studies we can say that the three anions have harmful effect on photocatalytic degradation by increasing the solubility of the contaminants so they will be adsorbed on the surface of photocatalyst which cause unwanted reaction between the anions and positive holes h^+ of the photocatalyst and the hydroxyl radicals $\cdot OH$.

III.3 Effect of inorganic cations on photocatalysis:

a- The effect on aluminum ions (Al^{3+}):

Al^{3+} has a negative effect on photocatalytic degradation of pollutants it inhibits the reaction as it can react with hydroxyl groups which are the most active groups in the photocatalytic degradation to decrease the reaction activity and also according to the kinetics the photocatalytic degradation efficiency was reduced in the presence of (Al^{3+}). Also the half-life of the degradation was increased.[1]

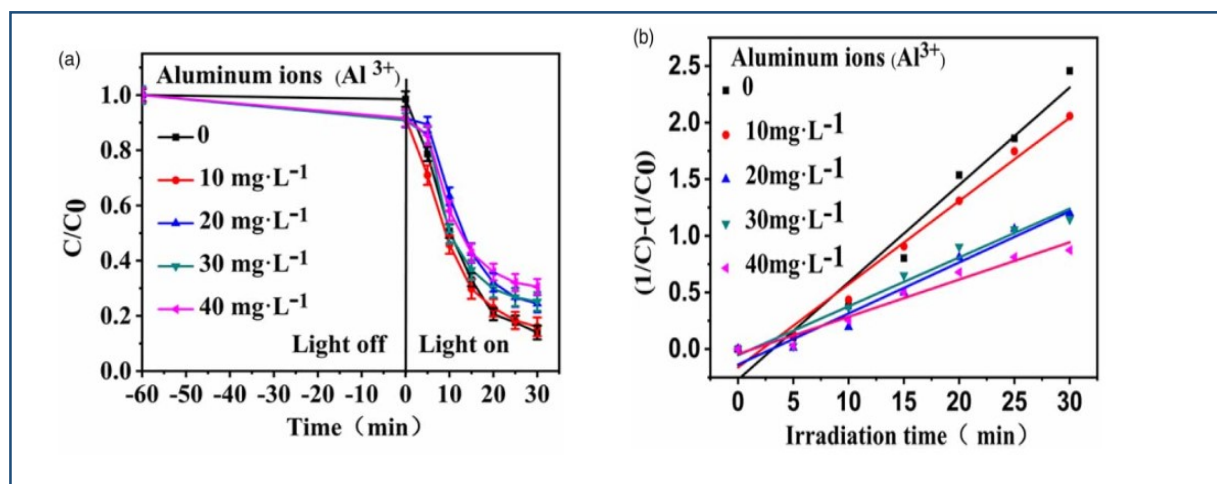


Figure (III-04): (a) shows the effect of Al^{3+} on the photocatalytic efficiency and (b) shows its effect on photocatalytic kinetic.

b- The effect on calcium ions (Ca^{2+}):

The presence of the calcium ions (Ca^{2+}) is totally different as a fact it can promote the photocatalytic degradation of pollutants in particular cases, but it can also increase the yield of photocatalytic degradation when the concentration of calcium ions (Ca^{2+}) is low,. The most interesting thing is that the kinetics change from pseudo-second order model to pseudo-first order model. We notice that in the low concentration of calcium ions (Ca^{2+}) the half-life of photocatalytic degradation of contaminants is reduced. The main cause of this large increasing of the yield of degradation is the photo-induced holes and the electrons transfer to the adsorbed pollutants (acceptor) on the surface of the photocatalysts. In thermodynamics it is required that the redox potential of the acceptor is more negative than the valence band potential (oxidation reaction) or more positive than the conduction band potential (reduction reaction). The valence band potential of TiO_2 is about 2.70 V and for the conduction band is about -0.50 V and the standard redox potential for ($E^0 Ca^{2+}/Ca$) is 2.87 V. according to

these potentials the calcium ions (Ca^{2+}) cannot react with the active positive holes or the electrons of the photocatalyst. The adsorption is important for a photocatalytic degradation reaction to succeed. In fact, the adsorption is humble without the (Ca^{2+}) presence because of the negative charge on the pollutants and the photocatalyst. As a result (Ca^{2+}) work as a bridge between the contaminants and the photocatalyst to increase the photocatalytic degradation yield.[1, 2]

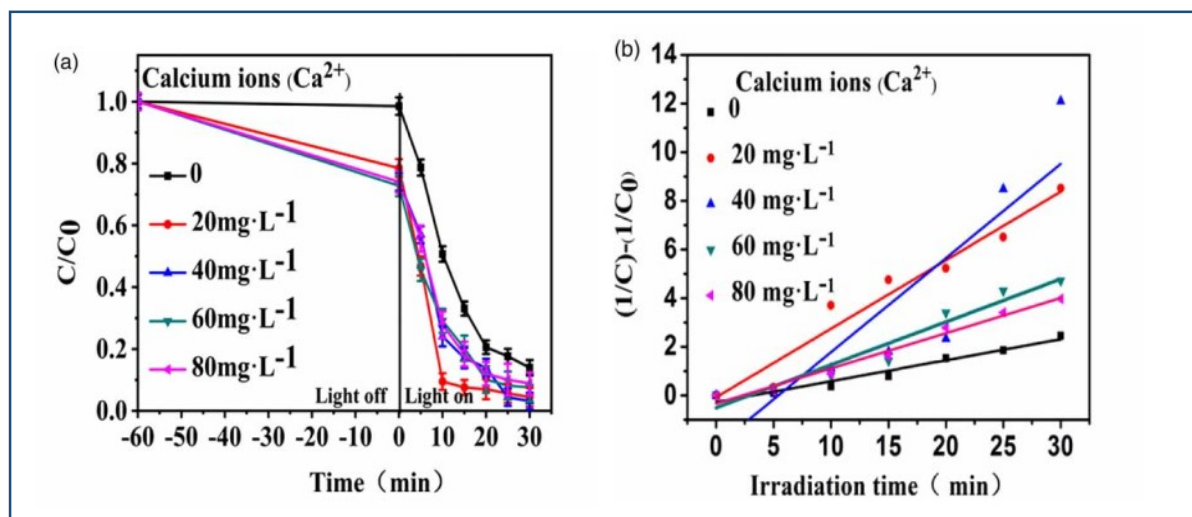


Figure (III-05): (a) shows the effect of Ca^{2+} on the photocatalytic efficiency and (b) shows its effect on photocatalytic kinetic.

c- Effect on magnesium ions (Mg^{2+}):

the presence of magnesium (Mg^{2+}) on photocatalytic degradation of pollutants can eventually causes inhibition in the degradation yield because of the adsorption of contaminants on photocatalyst. In general the kinetics of the degradation process of the pollutants in the presence of magnesium ions (Mg^{2+}) is abided pseudo-second order model at all concentrations of (Mg^{2+}) and this is due to the of valence band potential of $\text{TiO}_2 + 2.70 \text{ V}$ is more positive then the (Mg^{2+}) potential -2.38 V this causes adsorption on the surface of the photocatalyst and eventually reduce the reduction reaction on the valence band of TiO_2 and this lead us to say this reduce will directly decrease the photocatalytic reaction in general. Also we can notice that the half-life of the photocatalytic degradation is increase in the presence of the (Mg^{2+}) concentrations. [1, 2]

As conclusion the three inorganic cations impact the photocatalytic degradation according to different ways these cations could adsorb on the surface of the photocatalyst in that way affecting the photocatalytic degradation of pollutants by different impacts.

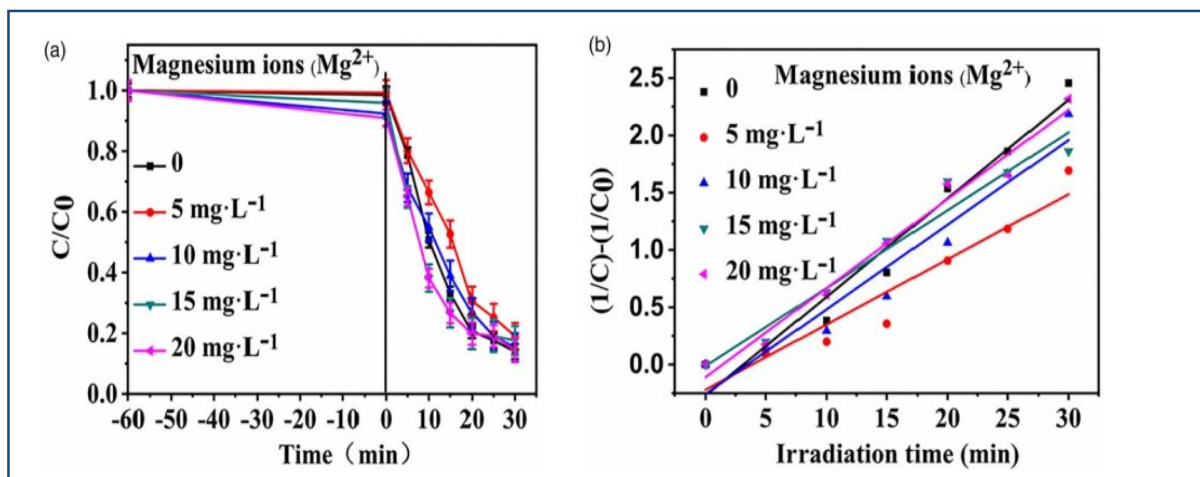


Figure (III-06): (a) shows the effect of Mg^{2+} on the photocatalytic efficiency and (b) shows its effect on photocatalytic kinetic.

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General conclusion

General conclusion

General conclusion

In this work, we focused on studying the effect of some inorganic ions on the effectiveness of photocatalysis in dissolving organic pollutants, and many studies were conducted on a group of organic pollutants where the following results were obtained:

- The advanced oxidation technology is effective in removing organic pollutants.
- Anions generally have an inhibitory effect on photolysis.
- Cations reduce the efficiency of photolysis.
- Calcium ions (Ca^{2+}) increase the speed of the photolysis reaction.

The effect of ions on the photolysis reaction, varies according to their type, which affects the positive holes (h^+) of the photocatalyst that interact with the free hydroxyl radical ($\text{OH}\cdot$).

We were relying on our work on the results of the practical part, but the epidemiological situation that Algeria and the rest of the world are going through prevented us from that, so we only studied the theoretical part of the topic of research, for whom we still hope to complete our work, especially in its practical part, such as:

- Application of the experimentally for study.
- Study the effect of the largest number of ions.
- Search for other methods increases the efficiency of photodegradation, and suitable for environment.

المخلص:

الهدف من هذا العمل هو دراسة تأثير بعض الشوارد اللاعضوية على الفعالية الضوئية للمحفز الضوئي ثاني أوكسيد التيتانيوم (TiO₂).

حيث أثبتت نتائج الدراسات التي أجريت على عدة ملوثات عضوية مختلفة أن للشوارد (أنيونات وكاتيونات) التي شملتها الدراسات لها تأثير تثبيطي حيث قللت من كفاءة التفكك الضوئي المحفز.

الكلمات المفتاحية: الفعالية الضوئية، المحفز الضوئي، التفكك الضوئي المحفز.

Abstract:

The target of this work is to study the effect of some inorganic ions on the photocatalytic activity of the photocatalyst titanium dioxide (TiO₂).

The results of studies conducted on several different organic pollutants have shown that ions (anions and cations) included in these studies have an inhibitory effect as they reduce the efficiency of photolysis..

Key words: photocatalytic activity, the photocatalyst, photocatalytic degradatio

Résumé:

L'objectif de ce travail est d'étudier l'effet de certains ions sur l'activité photocatalytique du photocatalyseur dioxyde titanium (TiO₂).

Les résultats d'études menées sur plusieurs polluants organiques différents ont montré que les ions (anions et cations) inclus dans ces études ont un effet inhibiteur car ils réduisent l'efficacité de photocatalyse.

Mots clés : l'activité photocatalytique, photocatalyseur, dégradation photocatalytique.