REVIEW ARTICLE

Photocatalytic Degradation of Textile Dyes from Aqueous Solutions in the Presence of Zinc Oxide Nanoparticle: A Review

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ABSTRACT

During the past years, dyes are considered one of the utmost important and most dangerous contaminants in water because of their toxicity and great stability in water and their presence in high concentrations in water. The dyes are widely used all over the world, so pollutants must be removed from the water. The traditional methods of removing organic and inorganic pollutants and dyes are useless from water and wastewater. To prevent further contamination, there are several techniques for removing contaminants and dyes, and their occurrence and decomposition and removal processes applied to a particular class of micropollutants. This study identified several treatment systems from the most important easy and simple imitation techniques (coagulation, filtration, flocculation, biological processes, and sedimentation), adsorption and advanced oxidation methods (AOPs), membrane processes, and compound roads. This study found that zoning, Fenton/photo-Fenton, and semiconductor photocatalysis are the utmost widely used methods. Combined methods seem to be the top way to treat liquid contaminants containing antibiotics, counting those utilizing renewable energy and secondary materials.

Keywords: Advanced oxidation processes, Nanomaterial, Zinc oxide (ZnO).

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INTRODUCTION

Unpolluted water is an important and basic source for all living organisms on the surface of the earth. Clean water is also an important resource in the main industries of the food beverage industry, the gas, oil, and petrochemical industries, and is also used in the pharmaceutical industries and in agriculture. The amount of clean water consumed annually in industries increases by 50% above the 1995 level by 2025.[1,2] One of the utmost significant challenges facing the world is to meet the many demands on the use of clean water, where a clear decrease has been observed in the recent period due to an increase in the population, expansion in the use of industries, climate change and other factors that lead to water pollution.[3,4] As the United Nations asserts, between 2 to 7 billion people will face water shortages in the middle of the twenty-first century. The lack of water can affect human health and the economic situation, the lack of industries, and the shortage in the production of drinks and foods, which leads to an increase in diseases such as diarrhea and other chronic diseases.[5]

Nanomaterial

Nanoscience is considered one of the most important phenomena that affect the systems with nanometer sizes. It is concerned with the unique parts, the nano parts exclusively with the small sizes of the systems. The term 'Nano' is a term for chemistry, materials science, and biology to some extent.[6] Nanotechnology is considered one of the most important and latest modern technologies, which causes important changes in physical systems when its dimensions approach a scale nanometre (10^{-9} m).[7]

It contains some differences in the physical nano properties when the material moves from microparticles to nanoparticles. There are several important properties in different properties, the most important of which is the increase in the surface size, and the particle size moves to dominance where quantum confinement prevails as the electronic energy levels become separate. One of the most important effects of quantum confinement is the exceptional optical properties that depend on the shape and size of the nanocrystal, so a different set of uses have been identified for optoelectronic devices in solar energy photocatalysis, etc.[8] (Table 1).

In terms of structures and shapes of commonly used nanoparticles, common examples are dots, columns, spirals, flowers, donuts, cups, and many more, where a small group has been shown in Figure 1.

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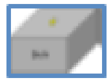
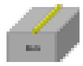
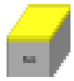
Table 1: The dimension nano-structures[9]

Dimension nanomaterial (Quantum confinement)		*Example*	*Shapes*
Dimension Three	<100 nm	Nanoparticles, quantum dots, Nanoshells, Nano rings	
Dimension Two	<100 nm	Nanotubes, fibers, nanowires	
Dimension One	<100 nm	Thin films, layers and coatings, Nano well	

Semiconductors

Semiconductors are generally a material or compound or a solid chemical element that has an electrical conductivity among conductors and insulators.[11] The important character to make the ZnO, TiO_2, and some semiconductors a good sensitivity for light in redox processes is the electronic structure of these semiconductors. Semiconductor materials are materials in that together of CB and VB are isolated via E_g.

Two types of semiconductors named n and p-kind.[12] The energy possibility of an energy level being having via an electron is exactly 1/2 at 0 K is level Fermi. The level Fermi of the semiconductor movements in the region bandgap. The Fermi level of n-kind doping shifts toward the CB edge, and the doping of p-kind shifts toward the VB edge as shown in Figure 2.[13]

Band theory is important for elucidating the properties of semiconductors. At 0 K in this theory, an ideal semiconductor crystal has a set of very close and filled electronic states; this is called the valence band (VB). The empty and closed electronegativity is called the conduction band (CB), and Eg between them is called the energy gap. Table 2 summarizes the utmost common semiconductor utilized in photocatalysis, their gap band and respective sensitivity wavelength.[14]

A doped semiconductor has a large several in the concentration, of the two kind of carriers charge. When the semiconductor is edgy, holes and electrons are created via the absorption of light. The sensitivity of a semiconductor to the photon energy is indicated via the energy bandgap. A significant effect is the recombination of semiconductors. Direct recombination might happen when the returns electron from CB edge to VB edge. Indirect recombination occurs with an intermediate energy level. This way of recombination can be particularly effective because the intimidating energy level can capture the electron and hole.[15]

Heterogeneous Photocatalysis

The heterogeneous photocatalytic operations comprises of utilizing close ultraviolet (UV) radiation (λ<380nm).[16] That type of catalyst semiconductor for photoexcite in the found of O_2. Photocatalysis is a procedure in that substance (photocatalyst) absorbs radiation light and energy transfers to the reactant. To define photocatalysis is the science of activating the catalytic via the photons without utilizing heating(thermal energy).[17] The species oxidizing, either

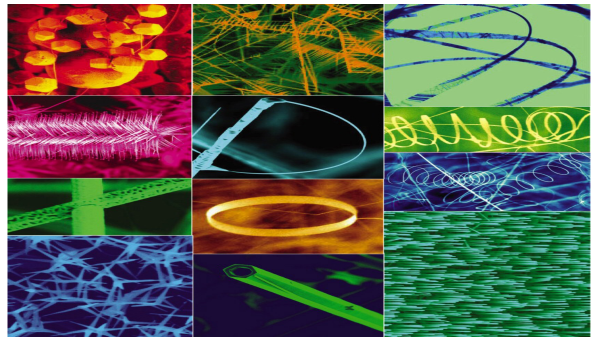


Figure 1: Several morphologies of semiconductor Nano structures.[10]

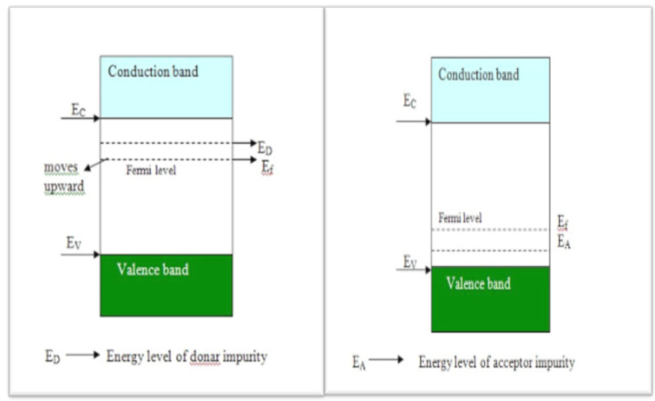


Figure 2: Energy level diagram of n and p-kind semiconductors.13

Table 2: Bandgap energy and sensitivity wavelength of several semiconductors.[14]

Semiconductor	*λ (nm)*	*Eg (eV)*
CdS	517	2.4
Fe_2O_3	539	2.3
MoS_2	709	1.75
$SrTiO_3$	388	3.2
TiO_2 (rutile)	413	3.0
TiO_2 (anatase)	388	3.2
WO_3	443	2.8
ZnO	378	3.2
ZnS	344	3.6

hole-free or bound radicals hydroxyl are formed. The significant condition to excite the electrons in VB to jump up to CB in a semiconductor particle must be absorbed hν $\geq E_g$, and in this manner, charged carry are formed, as appear in Figure 3.[18]

In photocatalysis, organic contaminants can be wholly mineralized reacting by the oxidizers to form, H2O and CO_2, dilute the conc, of simple acids mineral. This procedure is careful as response heterogeneous due to the multiple phases active, solid and liquid. The photocatalytic splitting discovery on electrodes titanium dioxide in 1972 via Fujishima and Honda,[19] novel method to purification the air and H2O have much attracted of attention it is heterogeneous photocatalysis.[20,21] They utilize successfully heterogeneous photocatalysis in the oxidation, mineralization of inorganic and organic pollutants, or decontamination in wastewater without generating harmful via products.[22]

Structures Crystal of ZnO

Zinc oxide (ZnO) is a II-VI semiconductor by a wide direct gap band of 3.37 eV (i.e. in the range near-UV) and a great exciton binding energy of near 60 meV at 300 K.[23] It was significant to note that the values of Zinc oxide energy of gap band reported in literatures are no necessarily the same. Due to the existence of several levels of O2 vacancies in samples, the Zinc oxide crystallized of the Zinc oxide have three forms under several conditions: cubic zinc blende, hexagonal wurtzite, and structure rock-salt. The rock-salt structure crystal (Figure 4a), alike the structure crystal NaCl, is only stable under comparatively great pressures of 10-GPa. In contrast, the structure cubic zinc blende-kind (Figure 4b) can only be stabilized via epitaxial growth of zinc oxid on substrates by structure cubic lattice. In the structures zinc blend (like ZnS), the several type of ions to form two interpenetrating lattices fcc, alike structure rock-salt, but it varies in terms of the positions of the two lattices. As illustrated in Figure 4 (b), the ions Zn and O2 have coordination tetrahedral, i.e., each ion zinc is surrounded tetrahedrally via four ions O_2 and vice versa.[24]

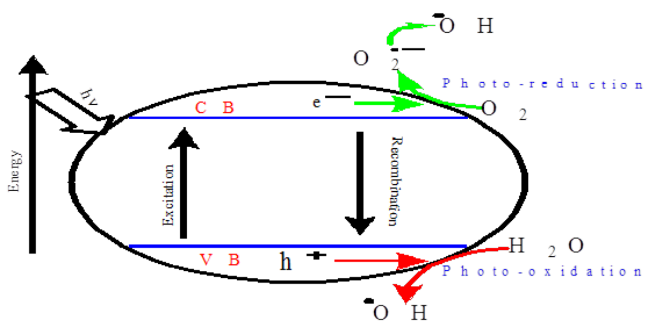


Figure 3: General significant events that take place on an ir-radiated semiconductor particle.[18]

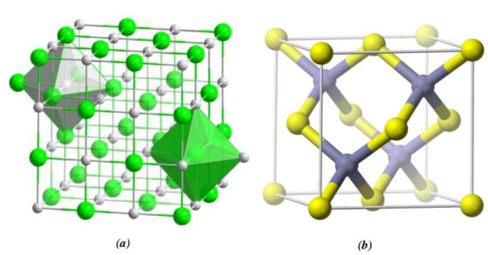


Figure 4: Ball and Stick representation of structures crystal zinc oxide: (a) structure rock-salt; (b) zinc cubic blende unit cell.

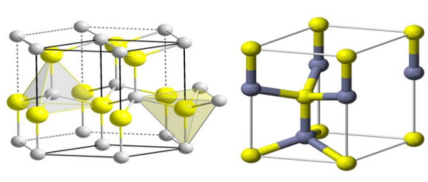


Figure 5: Ball and Stick representation of Zinc oxide structures crystal : (a) structure quartzite; (b) structure quartzite unit cell.

From a thermodynamic point of view, the most stable zinc oxide structure is hexagonal quartzite, so it is the most widely used of the three structures. In terms of optimal conditions, zinc oxide crystallizes in the quartz composition with great favorites. As in the zinc blende structure, the ions present in the quartzite structure often have a tetrahedral coordinate (Figure 5b). Each class of ions often represents a separate hexagonal bundle of the closed class (hcp), different from the fcc class for the zinc blende structure, as appears in Figure 5a.[25]

Catalyst Properties

The catalyst depends on the difference in the rate of a chemical reaction and also on the rate reaction, depending on the addition of a basic substance in the reaction called a catalyst, as this substance is not consumed during the chemical reaction, as the action of this catalyst depends on the combination of one or more reactants. Hence, the reaction remains Without any change to the end of the response. This catalyst is constantly reused as the reaction continues, as when two or more chemical reactions occur in parallel or in sequence, the role of the catalyst can also be essential in accelerating the reaction depending on the second reaction. The catalyst in the nanoworld depends on two main parts: (1) the catalyst depends on the nanomaterial preparation methods, quantum dots, and a variety of different nanostructures; (2) The role of the catalyst is the chemical response to some nanostructures.[25]

Properties of ZnO

One of the utmost significant properties of zinc oxide, such as reflection, optical absorption, transmission, photoluminescence, and others (Table 3). Where the role of optical properties is the semiconductors with internal and external effects. Where it depends on the movement between J electrons in CB and holes in VB as intrinsic optical transitions, Coulomb. It also depends on external influences of electronic states that occur

Table 3: Several properties of Zinc oxide[28]

No	*Values*	*Parameters*
Stable phase at 300 K		*Quartzite*
1	a = o32495 nm, c = 0.52069 nm	Lattice constants at 300 K
2	5.67526 g/cm^3	density
3	2250 K	point Melting
4	81.389 g/mL	Molecular mass
5	0.28 m°	
6	0.59 m°	
7	8.656	dielectric constant of Static
8	2.008, 2.029	n
9	0.6–1.16 W/Km	Thermal conductivity
10	0.125 cal/g^°C	Specific heat
11	1200 mV/K	Thermal constant at 573
12	~210 cm^2/V.s	Electron mobility

in the band gap via doping/impurities or collectors and point defects, that affect emission and optical absorption. Zinc oxide is pure, colorless, transparent, has many advantages in having a large bandgap, has less electronic noise, high activation energy, higher voltage, high temperature, and the ability to maintain high electric fields. In addition, the bandgap of zinc oxide can be improved from ~3–4 V depending on the alloying of cadmium oxide and magnesium oxide (Table 4).[26]

Physical Factor for Zinc Oxide

There are some essential physical factors for the zinc oxide at RT listed; therefore, stable and reproducible p-kind doping of zinc oxide residue is unreachable and can be challenging. The data connected to the values related to the movement of the hole Another figure that is still in doubt is the efficient mass.[27,28]

Applications of Zinc Oxide[29]

Rubber Industry

The ratio of utilizes zinc oxide about in the rubber industry, produced in levels of 10^5 tons per year.

Medical Application

Calamine is a mixture of Zinc oxide by iron (III) oxide (Fe2O3) at 0.5% and is widely used in calamine lotion. Zinc oxide is characterized by its ability to inhibit the properties of bacteria. It has an essential role in body cream/antiseptic creams that help heal and reduce pain and redness of the skin.It also has wide uses in medicine and industries and is included in the installation of toothpaste. Depending on its ability to absorb ultraviolet light, zinc oxide acts as a sunscreen that reduces sunburn. Others utilized zinc oxide to protect the skin from the harms of light UV.[30]

Catalysis Application

Safe, stimulating properties of zinc oxide. It is based on studies that recent literature reveals that zinc oxide nanoparticles have a clear interest as a heterogeneous catalyst because it is considered a low-cost, cheap, non-toxic material and has many beneficial properties for the environment.[29]

The Textile Industry

Most researchers adopt industries with water-resistant, anti-ultraviolet, self-cleaning, and industrial applications, not only with biological zinc oxide, or nano-zinc oxide, which is more air permeable and UV-effective compare to its bulk counterparts. Industrial textiles that have marketing for nano products play an important role in protecting the body from harmful UV rays.[30]

The pH Effect on ZnO

The influence of pH is very important on the properties/composition of zinc oxide and is considered to have a significant part in estimating the quality of a substance. The pH solution has a key role in estimation structure and the particle size during the solution method. The precipitation/solution morphology must depend on the prepared metal oxides' H^+ or OH^- ions.[31]

Oxidation Processes

Chlorination

Depending on the low cost, the use of chlorine gas or hypochlorite has been widely used in the treatment and disinfection of water and where it is used automatically in many treatments and disinfection and sterilization of drinking water distribution stations. The use of this way was adopted in the treatment of water drinking that contains pharmaceutical pollutants. Biological treatments were also used to oxidize these pollutants into compounds that can be degraded and easily disposed of and become less dangerous and toxic. Of the chlorinated varieties, hypochlorite has a standard high oxidation capacity.[32]

Advanced Oxidation Processes

The nature of liquid pollutants that contain medicines and antibiotics eliminate these very dangerous pollutants using traditional biological treatments. The most important of these methods are advanced oxidation processes (AOPs). AOPs is an important oxidizing technology that works to provide intermediate radicals, hydroxyl radicals (OH–), and this process is highly reactive and has low selectivity compared to other oxidants, for example (ozone, chlorine.). The standard oxidation potential (E0 ¼ 2.8 V) is better than conventional oxidants, which can be highly effective in oxidizing a wide variety of organic compounds. These radicals are provided by agents oxidizing like (ozon) or (peroxide hydrogen), and are usually mixed with semiconductors and/or UV rays or with metallic catalysts. In these methods, organic compounds are oxidized to a less heat-resistant medium.[33]

Ozonation

The ozone is an oxidant strong (E0 ¼2.07 V) incapable of job indirect or direct. For oxidation direct by ozone molecular (in this case, this is not an AOP way), it is necessary that the study compound have (C-C) aromatic bonds, double bonds, or nitrogen, oxygen or phosphorous sulfur atoms since it only selectively reacts via molecules nucleophile. Then, the decomposition of O_3 in H_2O to form (OH.).[34]

Photolysis

The process of photolysis depends on the dissociation or decomposition of chemical compounds resulting from the process of artificial light, or natural light depends on the application of two widely photo-stimulated processes: it depends on indirect photolysis and direct photolysis. It depends on absorption, a UV light for organic compounds.[35] Photolysis Indirectly includes the photodegradation via photosensitizers for example peroxyl radicals, hydroxyl, oxygen. Though together indirect and direct methods can happen simultaneously, photolysis indirect shows the utmost significant kind in the half-life of the pollutants. The photolysis performance depended on the absorption spectrum of the target complex, intensity radiation and frequency, concentration of peroxide hydrogen and ozone (if utilized), and kind of matrix.[36]

Electrochemical Processes

The treatments of electrochemical are interesting methods to eliminate toxic compounds organic, applying an effective,

Table 4: Reviewing studies for photocatalytic degradation of different compounds by using different structures of ZnO.

S/N	*Catalyst*	*Dye*	*Catalyst load/conditions*	*Dye conce(mg/L)*	*Time (min)*	*Ref.*
1	Graphene/ZnO(1:5)	Methyl orange	50 mg, (8w UV Light)	0.02 mM	360	[42]
2	GO/ZnO	Methyl orange	0.01 mg, (UV light, PH=7)	10	120	[43]
3	ZnO/Fe3O4/g-C3N4-50%	Methyl orange	10 mg, (500w visible Light)	30	_	[44]
4	ZnO/Fe3O4/g-C3N4-50%	Alizarin Yellow R	10 mg, (500w visible Light)	30	_	[44]
5	2% ZnO/WO3	Methyl orange	0.1 g (1 kw halogen lamp)	10	180	[45]
6	3%Mn/ZnO	Orange II	0.06 g (sunlight ,PH=9)	10	210	[46]
7	Zinc oxide /PPY (Polypyrrole)	violet acid 7	0.05 g (15w UV light)	5	360	[47]
8	Kaolinite/Tio2/ZnO (50%:45%:5%)	Remazol red	_ , (sunlight, PH =2.5)	100	120	[48]
9	2% rGO / ZnO	Acid red 249	0.05 g, (15w UV light)	50	120	[49]
10	TiO2/Zn2TiO4/ZnO/C	Orange G	0.05 g, (sunlight)	20	50	[49]
11	Zinc oxide/ZrO_2/NiO (1: 2: 0.3)	Reactive blue 81	15 mg, (15w UVC light, PH=3)	5	180	[50]
12	Zinc oxide	Cibacron brilliant yellow 3G-p	400 mg, PH = 5.1	50	60	[51]
13	Ag/ZnO	Direct blue 71	2000 mg (UV light ,PH= 3)	100	210	[52]
14	Cu/ZnO	Direct blue 71	2000 mg (visible light ,PH=3)	100	210	[52]
15	ZnO/MWCNT	Reactive blue 203	5 mg, (PH =10)	20	20	[53]

charge-affective, versatile, ease and technology clean.[37] In the electrochemical method, the oxidation occurs over anodes (GO, titanium dioxide , Ti-based alloys, Ir or Ru oxides, boron-doped diamond) in the presence of an electrolyte. Contaminants can be destroyed electro-chemically via a direct oxidation anodic, that contaminants are first adsorbed on the surface anode and then destroyed by the electron anodic ex-change. Then again, if the molecules are tainted in the bulk liquid by the mediation of electro active species (like redox metallic couples e Ce (IV), Fe(III), Ag(II), Mn (III) or oxidants strong as O_3, H_2O_2, persulfate, per phosphate, percarbonate, and chlorinated species).[38-41]

CONCLUSION

Over the past years, pigments in abundance and their fate in environmental matrices have been noted and received special attention worldwide. These pollutants are stable and have high concentrations in the water and are resistant to decomposition, and accumulate in very large quantities in the aquatic environment. However, even in the case of their presence in low concentrations, they are discovered and cause many problems and damage to the water environment. They found it dangerous in the water.

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