Chapter – 1

INTRODUCTION
1.1. Water pollution

Water is an essential element for life. Fresh water comprises 3% of the total water on earth. Only a small percentage (0.01%) of this fresh water is available for human use. Unfortunately, even this small proportion of fresh water is under immense stress, due to the rapid population growth, urbanization and unsustainable consumption of water in industry and agriculture. According to a UNO report (2011), the world population is increasing exponentially, while the availability of freshwater is declining. Many countries in Africa, Middle East and South Asia will have serious threats of water pollution in the next two decades. In developing countries, the problem is further aggravated, due to the lack of proper management [1].

1.1.1. Water pollution in India

Geometric increase in population has resulted in high impact on quality and quantity of water in India. Water quality problems in India are due to partially treated and untreated wastewater from urban settlements, industrial establishments and poor management of municipal solid waste. It is estimated that about 38,000 million litres per day (mld) of wastewater are generated in the urban centres having population more than 50,000 in India. The municipal wastewater treatment capacity developed so far in India is about 11,000 mld accounting for 29% of wastewater generation in these two classes of urban centers. It is estimated that the projected wastewater from urban centres may cross 1,00,000 mld by 2050 and the rural India will also generate not less than 50,000 mld. Thus, the water quality management in India is accomplished under the provision of Water Act, 1974 (Prevention and Control of Pollution). The basic objective of this act is to maintain and restore the national aquatic resources by prevention and control of pollution. However, wastewater management is not addressed to that pace till now [2].
1.1.2. Water quality trend in India

The water quality monitoring results obtained during 1995 to 2010 indicate that the organic and bacterial contamination are continued to be critical in water bodies. This is mainly due to the discharge of domestic wastewater mostly in untreated form from the urban centres of the country. The water quality monitoring results were analysed with respect to the indicator of oxygen consuming substances (bio-chemical oxygen demand). The result of such analysis shows that there is a gradual degradation in water quality [2, 3]. The water quality status for the period 1995 to 2010 in terms of number of observations having values of parameters in different ranges is given in the Fig. 1.

1.1.3. Water pollution due to endocrine-disrupting chemicals (EDCs)

Endocrine disruptors enter waterways via wastewater effluent, urban and agricultural runoff. Pharmaceuticals and excreted drugs move through municipal sewage treatment plants and return to our waterways as endocrine disruptors. Spray-drift and runoff of pesticides from agriculture, livestock waste runoff from confined animal feeding operations, aquaculture, and leaching from municipal landfills and septic systems can also introduce endocrine disruptors into the environment. In recent decades, EDCs enter waterways as synthetic chemicals, such as solvents, plasticizers, insecticides, herbicides, and fungicides, into the environment through industrial, agricultural, medical, and domestic activities [3].

On this way, EDCs such as bisphenol A, resorcinol, nonylphenol 4-chlorophenol, and 2,4,6- trichlorophenol are of serious environmental concern, because of their widespread occurrence throughout the environment. They are found in wastewater, sludge products, surface waters, and groundwater.
Fig. 1. The water quality status for the period 1995 to 2010 in terms of the number of observations having the values of parameters in different ranges.
The impacts of trace concentrations of EDCs on wildlife naturally lead to concerns about their potential effects on humans. The sources and health effects of such EDCs are given in Table 1.

1.1.4. Hazardousness of certain EDCs in water pollution

They are known to mimic or block natural hormones in aquatics, animals and human beings. The U.S. Environmental Protection Agency (EPA) defines that EDCs interfere with the “synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior” [2-10]. It is therefore, pertinent to have an understanding of the water pollution, water management initiatives, and their impacts on water and the environment. Thus, wastewater-treatment technologies are crucial components of urban water systems to control the water pollution.

1.2. Wastewater treatment technologies: A Review

Wastewater treatment is becoming more critical, due to the diminishing water resources, increasing wastewater disposal costs, and stricter discharge regulations that have lowered permissible contaminant levels in waste streams. Untreated wastewater generally contains high levels of organic material, numerous pathogenic microorganisms, nutrients and toxic compounds leading to the environmental pollution and health hazards. Hence, the waste water must be treated appropriately before final disposal, which leads to the protection of the environment with public health and socio-economic concerns. Understanding the nature of wastewater is fundamental to design an appropriate wastewater treatment plant and technologies. The following points are to be considered for choosing a suitable treatment process [11].
Table 1. The sources and health effects of EDCs

<table>
<thead>
<tr>
<th>S.No</th>
<th>EDCs</th>
<th>Sources</th>
<th>Health effects</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bisphenol A</td>
<td>Plastics and epoxy resins</td>
<td>Hormonal imbalance, male infertility, breast cancers and reproductive damages</td>
<td>[6]</td>
</tr>
<tr>
<td>2</td>
<td>Resorcinol</td>
<td>Manufacture of adhesives, dyes and as an ingredient in pharmaceutical Preparations</td>
<td>Adverse endocrine effects on aquatic organisms and human beings</td>
<td>[7]</td>
</tr>
<tr>
<td>3</td>
<td>p-nonylphenol</td>
<td>Surfactants, detergents, cleaners, paints and pesticides</td>
<td>Cause significant ecological damages to living organisms by mutagenic condensation and estrogenic activity</td>
<td>[8]</td>
</tr>
<tr>
<td>4</td>
<td>4-chlorophenol</td>
<td>Dyes, drugs and fungicides</td>
<td>Cause endocrine effects to human and aquatic organisms</td>
<td>[9]</td>
</tr>
<tr>
<td>5</td>
<td>2, 4, 6-trichlorophenol</td>
<td>Petrochemicals, paper making, plastic, fungicide, herbicide, insecticide and antiseptic</td>
<td>Endocrine disruption, carcinogenic effects, causing lymphomas, leukemia, and liver cancer</td>
<td>[10]</td>
</tr>
</tbody>
</table>
The cleanliness of the final water effluent from the plant/industry

The quantities and nature of the influent to be treated

The physical and chemical properties of the pollutants

The cost of treating water, including the cost of treating process

Physical, chemical and biological methods are used to remove the contaminants from waste-water. In order to achieve different levels of contaminant removal, individual waste-water treatment procedures are combined into a variety of systems. Sludge resulting from waste-water treatment operations is treated by various methods in order to reduce its organic content and make it suitable for final disposal and reuse. Waste-water treatment methods are broadly classifiable into physical, chemical and biological processes. Figure 2 lists the unit operations included within each category.

Treatment of wastewater in industry is carried out in four stages. They are preliminary, primary, secondary and tertiary treatment.

1.2.1. Preliminary treatment

Preliminary treatment prepares the waste-water influent for further treatment by reducing or eliminating the non-favourable waste-water characteristics. These characteristics include large solids and rags, abrasive grit, odours, and, in certain cases, unacceptably high peak hydraulic or organic loadings. Preliminary treatment processes consist of physical unit operations, namely screening and comminution for the removal of debris and rags, grit removal for the elimination of coarse suspended matter, and flotation for the removal of oil and grease. Other preliminary treatment operations include the flow equalization, septage handling, and odour control methods.
Fig. 2. Unit operations of waste-water treatment methods
1.2.2. Primary treatment

Primary treatment involves the partial removal of suspended solids and organic matter from the waste-water by means of physical operations, such as screening and sedimentation. Pre-aeration or mechanical flocculation with chemical additions can be used to enhance the primary treatment. Primary treatment acts as a precursor for the secondary treatment. It is aimed mainly at producing a liquid effluent suitable for downstream biological treatment and separating out the solids as a sludge that can be conveniently and economically treated before the ultimate disposal. The effluent from primary treatment contains a good deal of organic matter and is characterized by a relatively high BOD.

1.2.3. Secondary treatment

The purpose of secondary treatment is the removal of soluble and colloidal organics and suspended solids that have escaped the primary treatment. This is typically done through the biological processes, namely treatment by the activated sludge, fixed-film reactors, or lagoon systems and sedimentation.

1.2.4. Tertiary/advanced waste-water treatment

Tertiary treatment goes beyond the level of conventional secondary treatment to remove significant amounts of nitrogen, phosphorus, heavy metals, biodegradable organics, bacteria and viruses. In addition to biological nutrient removal processes, unit operations frequently used for this purpose include chemical coagulation, flocculation and sedimentation, followed by the filtration and the activated carbon. Less frequently used processes include the ion exchange and the reverse osmosis for the specific ion removal or for dissolved solids reduction [12].
1.3. Treatment technologies for endocrine disrupting compounds (EDCs) in wastewater

The adverse environmental impact of untreated wastewater bodies is as follows -

(i) The decomposition of the organic materials contained in wastewater can lead to the production of large quantities of malodorous gases.

(ii) Untreated wastewater (sewage) containing a large amount of organic matter, if discharged into a river/stream, will consume the dissolved oxygen for satisfying the biochemical oxygen demand (BOD) of wastewater and thus, deplete the dissolved oxygen of the stream; thereby, causing the death of fishes and other undesirable effects.

(iii) Untreated wastewater usually contains numerous organic compounds, especially EDCs. They would alter the normal functioning of the endocrine and reproductive systems by mimicking or inhibiting the endogenous hormone actions. Therefore, for the above-mentioned reasons, the treatment and disposal of wastewater, is not only desirable, but also necessary.

Endocrine disrupting compounds (EDCs) are the chemicals with the potential to elicit the negative effects on the endocrine systems of humans and wildlife. In the past few decades, research efforts to combat this problem have grown immensely. Key to the solution for this problem is the identification of EDCs, the accurate measurement of their presence in aquatic systems, and development of methods for their elimination from the environment. EDCs are a latent crisis to humans and the environment. Theoretically this crisis could be easily controlled, if EDCs can be completely removed from the sewage at sewage treatment plants before final release into the environment.
EDCs removal methods fall into three categories, such as, physical methods, biodegradation and chemical advanced oxidation (CAO) as discussed below.

1.3.1. Removal of EDCs by physical methods

(a) Using activated carbon

Use of activated carbon (AC) is a well-known process for removing the various organic contaminants. In the past few years, many researchers have demonstrated that AC also has a strong capability of removing a broad range of representative EDCs for artificial and real waste water in the laboratory and pilot and full-scale plants [13, 14]. Studies on EDCs removal by AC mainly focus on the removal efficiency of EDCs in different water systems and the influence factors of the physicochemical properties of the EDCs and the types of AC produced from different materials. In a study by Abe [15], absorbability of about 70 EDCs by AC was estimated from their chemical structures, and then their adsorption by AC was proven effective for their removal from wastewater. Results denoted that the adsorption capability increased with activation time. However, adsorption capacity decreased with the total years of operation.

(b) Using membranes

The membrane process is gaining wide use for the contaminant removal in advanced water and wastewater treatment. Compared to conventional processes, its remarkable advantage is the high quality of effluent, including extremely low organic concentration. In recent years, research on EDC removal by the membrane process has greatly increased. This research can be sorted to three categories:

(i) Physicochemical properties of EDCs on the effective rejection by membrane,

(ii) Influence of the membrane module on the rejection of EDCs, and
(iii) Other influence factors, such as the membrane fouling, or, the presence of organic solutes in removal water.

The rejection efficiency of EDCs by membranes strongly depend on EDCs physicochemical properties, such as molecular weight, water solubility, electrostatic property and so on. EDCs retention by the membrane processes is mainly, due to the size exclusion, charge repulsion and adsorption. In comparing the membrane types over most cases, EDCs rejection rate by reverse osmosis is the highest, followed by the nano-membrane types, then ultra-membranes, with the rejection of micro-membranes as the lowest [16]. Studies on the rejection of EDCs by the membrane process were based only on chemical analyses, and no bioassay methods were reported. Removal of EDCs by physical means is not like biodegradation or chemical oxidation, as no byproducts or metabolites are newly produced.

1.3.2. Removal of EDCs by biodegradation

Among the waste-water treatment systems, the activated sludge process is the most widely used one, and as the proportion of removal by primary settling, chemical precipitation, aerating volatilization and sludge absorption was small, the majority of EDCs in wastewater is regarded as removed by the biodegradation [17, 18].

1.3.3. Removal of EDCs by chemical advanced oxidation

Within the past few years, there have been numerous studies on the removal of EDCs through the use of different chemical oxidants, known as chemical advanced oxidation (CAO). The essential mechanisms of CAO are the mineralization of pollutants in wastewater to CO₂ or transference of pollutants to some other metabolite products by some strong oxidizers through oxidation–reduction reactions. Therefore, the key point for CAO is the choice of oxidizer. To increase the removal effect, some
combinations such as UV/O₃, UV/H₂O₂, UV/Fenton were widely applied to the removal of EDCs. These methods are characterized by the generation of the hydroxyl radical (OH), for which the redox potential is 2.80V, and the higher redox potential can give better results [19]. The removal of EDCs by CAO can be divided to three categories:

(i) Removal effectiveness and optimization of the operational conditions for CAO
(ii) Degradation dynamics research on EDCs removal by CAO
(iii) Degradation pathways of EDCs by CAO.

All of these are thrust intention of numerous ongoing studies. However, heterogeneous photocatalytic oxidation is an advanced oxidation process for removal of trace contaminants and EDCs.

1.4. Heterogeneous photocatalysis - Advanced oxidation process: Historical review

Heterogeneous photocatalysis has recently appeared as a new emerging “Advanced Oxidation Process” (AOP), with more than 2000 recent publications on the subject at the beginning of the 21st century. Photocatalysis has presently become a major discipline owing to two factors:

(i) The intuition of the pioneers of last 20th century and
(ii) The mutual enrichment of scientists arising from different fields as shown in Figure 3.

Initially, photocatalysis originated from the different catalysis laboratories in Europe, but, later received valuable contributions from other chemical sub-disciplines. In 1972, Fujishima and Honda reported, the photocatalytic splitting of water on TiO₂ electrodes, in the review “Nature” [20].
Fig. 3. Contributions to photocatalysis from various sub-disciplines
Unfortunately, recent scientists in the field of photocatalysis have poorly read this article and improperly cite it as the starting point of photocatalysis, which is obviously erroneous. Actually, the first reference including the term “photocatalysis” in its title has been published in 1964 by Doerfler et al [21] in the “Journal of Catalysis”. However, Fujishima and Honda work on the photocatalysis has marked the beginning of a new era in heterogeneous photocatalysis. Since then, research efforts in understanding the fundamental processes and in enhancing the photocatalysis have come from extensive research performed by chemists, physicists, and chemical engineers.

1.4.1.1. Heterogeneous semiconductor photocatalysis: Fundamentals and mechanism

Over the last 10 years the scientific and engineering interest in the application of semiconductor photocatalysis has grown exponentially. Semiconductor photocatalysis with a primary focus on semiconductor as a durable photocatalyst has been applied to a variety of problems of environmental interest in addition to the water and air purification. In a semiconductor photocatalysis system, photo-induced molecular transformations or reactions take place at the surface of a catalyst. Depending on where the initial excitation occurs, photocatalysis can be generally divided into two classes of processes. When the initial photoexcitation occurs in an adsorbate molecule, which then interacts with the ground state catalyst substrate, the process is referred to as a catalyzed photoreaction. When the initial photoexcitation takes place in the catalyst substrate, and the photoexcited catalyst then transfers an electron or energy into the ground state molecule, and the process is referred to as a sensitized photoreaction. The fundamental semiconductor photocatalysis follows the 5-step process of chemical engineering as shown in Fig. 4.
HETEROGENEOUS PHOTOCATALYSIS

1. Transfer of reactants in the fluid phase

2. Adsorption of the reactants at the surface of the catalyst

3. Reaction in the absorbed phase
   - Adsorption of photons by the solid
   - Creation of photo-induced electrons and holes
   - Electron Transfer Reactions

4. Desorption of the final products

5. Removal of the final products in the fluid phase

Fig. 4. The basic 5-step process common to the heterogeneous photocatalysis
Fig. 5. Energy band diagram for photocatalytic degradation mechanism
Semiconductors (e.g., TiO₂, ZnO, Fe₂O₃, CdS, ZnS, and etc) can act as sensitizers for the light-reduced redox processes, due to their electronic structure, which is characterized by a filled valence band and an empty conduction band. When a photon with energy of \( h\nu \) matches or exceeds the band gap energy (\( E_g \)) of the semiconductor (TiO₂ as an example), an electron, is promoted from the valence band (VB) into the conduction band (CB) leaving a hole, behind as shown in the Fig. 5. Excited-state conduction-band electrons and valence-band holes can recombine and dissipate the input energy as heat, get trapped in the metastable surface states, or react with the electron acceptors adsorbed on the semiconductor surface.

In the absence of suitable electron and hole scavengers, the stored energy is dissipated within few nanoseconds by a recombination. If a suitable scavenger or surface defect state is available to trap the electron or hole, recombination is prevented, and subsequent redox reactions may occur. The valence-band holes are powerful oxidants (+1.0 to +3.5 V vs NHE depending on the semiconductor and pH), while the conduction-band electrons are good reductants (+0.5 to -1.5 V vs NHE).

The conduction and valence band positions of selected metal oxide semiconductors at pH 10 are given in Fig. 6. Most organic photodegradation reactions utilize the oxidizing power of the holes either directly or indirectly; however, to prevent a buildup of charge one must also provide a reducible species to react with the electrons [22]. Upon excitation, the fate of the separated electron and hole can follow several pathways. The following chain reactions have been widely postulated. Both the oxidation and reduction can take place at the surface of the photo-excited semiconductor (SC) photocatalyst (Scheme 1). Recombination between electron and hole occurs unless oxygen is available to scavenge the electrons to form superoxides (\( O_2^- \)), its protonated form, the hydroperoxyl radical (\( HO_2^- \)) and subsequently H₂O₂.
Fig. 6. The conduction and valence band positions of selected metal oxide semiconductors
Scheme 1. Photo-excited semiconductor (SC) photocatalyst

SC + hv ⇌ e_{CB}^- + h_{VB}^+

H_2O + h_{VB}^+ ⇌ OH^- + H^+

O_{2(ads)} + e_{CB}^- ⇌ O_2^{2-}

OH^-_{(ads)} + h_{VB}^+ ⇌ OH^-_{(ads)}
1.4.2. Modification of semiconductor photocatalysts

The modification of semiconductor surface can be done in a number of ways to enhance the photosensitivity of semiconductor for successful applications as shown in Fig. 7. However, photocatalyst modification by architecture of desired size and morphology of semiconductor has received greatest attention as discussed below.

Fig. 7. Various modification methods of the photocatalysts

1.4.3. Modification by controlling the size and morphology

Generally, on bulk semiconductor electrodes only one species, either the hole or electron, is available for reaction due to the band bending [23]. However, in very small semiconductor particle suspensions, both the species are present on the surface. Therefore, the influence of size of semiconductor on redox properties has become an important topic of investigation. Moreover, the interest in nanoscale materials stems
from the fact that new properties are acquired at this length scale and, equally important, that these properties change with their size or shape. The change in the properties at this length scale is not a result of scaling factors. It results from different causes in different materials. In semiconductors, it results from further confinement of the electronic motion to a length scale that is comparable to or smaller than the length scale characterizing the electronic motion in bulk semiconducting material (called the electron Bohr radius, which is usually a few nanometers). The past couple of decades has witnessed an exponential growth of activities in this field, driven both by the excitement of understanding new science and by the potential hope for environmental applications and economic impacts. The largest activity in this field at this time is in the synthesis of new nanoparticles of different sizes and shapes for the enhanced optical and photosensitivity properties.

Quantum confinement is a widely used terminology in the study of semiconductor nanocrystals. In a bulk crystal, the properties of the material are independent of the size and are only chemical composition-dependent. As the size of a crystal decreases to the nanometer regime, the size of the particle begins to modify the properties of the crystal. The electronic structure is altered from the continuous electronic bands to discrete or quantized electronic levels. As a result, the continuous optical transitions between the electronic bands become discrete, and the properties of the nano-material become size-dependent [24]. Moreover, the size and shape control of semiconductor nanostructures has attracted considerable attention due to the fact that they have unique and size or shape dependent absorption, emission and photocatalytic properties.
1.4.3.1 Effect of size and morphology on absorption and emission properties

Optical absorption spectroscopy is the most commonly used technique in exploring the quantum effects in semiconductor nanoparticles. By using this method, one can observe the development of discrete features in the spectra and the enlargement of the energy gap in semiconductor quantum dots (QDs). However, many times, the discrete states are not readily visible in the absorption spectra, due to the homogeneous broadening, which can be traced to the size, shape, and surface defect distributions in the nano-particles. Absorption peak changes as the nanoparticle size changes for CdSe, CdS, and CdTe QDs. The absorption spectra show a consistent red shift as the size of the particle increases, and up to 10 discrete optical transitions can be resolved, which corresponds to the transitions between the discrete energy levels of the QDs [24, 25]. Moreover, as the size of semiconductor falls below the critical radius, the charge confinement leads to a series of discrete electronic states. As a result, there is an increase in the effective band gap and a shift in the band edges. Thus, by varying the size of the semiconductor particles, it is possible to enhance the redox potential of the valence-band holes, and the conduction-band electrons. With the decrease in the particle size, the diffusion of the photoinduced electrons or holes from bulk to surface becomes fast, which may lead to an enhancement of the photocatalytic activity.

It is well established that a broad emission can be observed, which blue shifts with decreasing the radius of the semiconductor. In addition, both the resonant and non-resonant Stokes shifts increase as the size of the semiconductor nanoparticles decreases [26]. The substantially increased surface to volume ratio in a nanostructure leads to the significant rearrangement of emission characteristics. Generally, smaller
sized semiconductor nanostructures might favor high-level surface defects, which account for the increase in the defect emission relative to the UV emission [24-26]. It has been reported that the photocatalytic activity is highly related to the concentration of defects on the surface of the nanomaterials [24-27]. Usually, higher photocatalytic activity of semiconductor nanostructures has been attributed to the high concentration of surface donor defects (oxygen vacancies and zinc interstitials). The higher activity in the presence of more surface defects (oxygen vacancies) was attributed to the lower recombination between photo-generated electrons and holes with oxygen vacancies serving as the electron traps [27].

1.4.3.2. Effect of size and morphology on photocatalysis

The absorption of light leads to the generation of electron-hole pairs in the semiconductor particle, which are oriented in a spatially random fashion along the optical path. These charge carriers subsequently recombine or diffuse to the surface, where they undergo chemical reactions with suitable solutes or catalysts deposited on the surface of the particles. Since in size quantized semiconductors, the diffusion of charge carriers from the interior to the particle surface can occur more rapidly than their recombination, it is feasible to obtain the enhanced quantum yields for photo redox processes. In addition, particle size of a photocatalyst decides the “quantum-size effect”. This frequently used term means that when the size (radius) of solid particles becomes smaller than their Bohr radius, the bottom of the conduction band and the top of the valence band shift in negative (high electronic energy) and positive (low electronic energy) directions, respectively, resulting in the expansion of the band gap. Nanostructures of semiconductors can adopt geometries, which are not seen in the bulk state. Consequently, there could be important variations in the oxygen/metal
ratio. Oxygen vacancies, not common in the bulk state could be present in the nanoparticles, thus enhancing its reactivity. Therefore, the structure of nanomaterial, including morphology, particle size, and two-dimensional and three-dimensional architectures, can play important roles in determining the photo catalytic properties. Some factors that influence the photocatalytic performance and stability of ZnO photocatalysts are

- Morphology
- Particle size/Surface area
- Crystal orientation
- Crystallinity
- Oxygen defects

The effect of crystallite size and particle size on the photocatalytic performance of semiconductor photocatalyst has been attributed to their influence on the charge carrier recombination rate and specific surface area. Therefore, synthesis methods need to be developed to fabricate the semiconductor nanostructures with various sizes and morphologies and clearly reveal the effect of particle size and morphology on the photocatalytic activity.

1.5. Preparation of semiconductor nanostructures of different size and morphology

In the emerging field of nanotechnology, a goal is to make the nanostructures or the nanoarrays with special properties with respect to those of bulk or single particle species. Semiconductor oxide nanoparticles can exhibit unique chemical properties due to their limited size and a high density of corner or edge surface sites. In recent years, methods have been developed for the preparation of novel
nanostructures of oxides [28, 29]. They can be generated by a number of preparation methods that are typically described as

- Physical methods
- Chemical methods

Physical-like methods include gas/vapor condensation, thermochemical/flame methods, and spray pyrolysis. Gas condensation methods, which form a supersaturated vapor of metals in a first stage of condensation under (high pressure) inert gas with a subsequent stage of oxidation, are among the earlier preparative methods, due to their ease of performance and high purity of the resulting solids, although they have the drawbacks of high cost and low yield. Thermochemical methods are typically used to synthesize the ceramic precursor powders, and are customarily referred to as chemical vapor deposition. This method is industrially used due to its low cost, but control of particle size and morphology is somewhat difficult. Finally, spray pyrolysis involves the generation of aerosol droplets by nebulization of a starting solution, sol or suspension of a precursor, further evaporation of the solvent and thermolysis at high temperature to form microporous particles. A disadvantage of spray pyrolysis is the large amount of solvent required. On the other hand, current liquid-phase chemical methods are sol-gel, micellar, and chemical/mechanochemical precipitation method. Some of the chemical methods may offer potential routes to obtain better materials in terms of chemical homogeneity, particularly in case of mixed oxides, and morphological control (i.e., primary and secondary particle size) with respect to the above-mentioned physical methods.

Sol-gel is becoming a standard method in synthesizing the oxides and is based on the hydrolysis of the reactive metal precursors, resulting in a gel that is
subsequently thermally or hydrothermally treated to yield the nanostructured product. Advantages of this preparation are the production of ultrafine powders having high chemical homogeneity, but controlling the morphology and particle size is quite difficult. Mechanochemical synthesis involves the mechanical activation of solid reactions by the milling of precursor powders (usually a salt and a metal oxide) to form the desired nanoscale compound, which can be typically obtained after heating and purification. Other chemical methods currently used include the use of complexing agents (e.g., citrate). Finally, it can be mentioned that the need of a degree of control of size in the nanometer range has diminished its utility significantly [27-29]. Therefore, the development of a simple, environmentally friendly method to prepare the oxide nanostructures with controllable morphology is crucial to their practical applications, and has thus become an important topic of investigation. The precipitation approach compared with the other traditional methods provides a facile way for low cost and large-scale production, which does not need expensive raw materials and complicated equipment. The process involved the precipitation approach, which is discussed below.

1.5.1. Preparation of semiconductor nanostructures by precipitation method

The kinetics of nucleation and particle growth in homogeneous solutions can be adjusted by the controlled release of the anions and cations. Careful control of the kinetics of the precipitation can result in monodisperse nanoparticles. Once the solution reaches a critical supersaturation of the species forming particles, only one burst of nuclei occurs. The particle size is influenced by the reactant concentration, pH, and temperature. By engineering these factors, nanoparticles with narrow size distributions, such as Zr(OH)$_4$, Ba-TiO$_3$, YBa$_2$Cu$_3$O$_6$, CdS, HgTe, HgTe, and CdTe have been produced. Although, the method of using the precipitation to prepare
nanoparticles is very straightforward and simple, very complicated nanostructures can also be constructed using this method such as CdS/HgS/ CdS, CdS/(HgS)$_2$/CdS and HgTe/CdS quantum well systems and other core/shell structures [24]. Therefore, it is essential to control the factors that determine the precipitation process, such as the pH, temperature and the concentration of the reactants and ions. In this way, organic molecules (surfactants) are used to control the release of the reagents and ions in the solution, during the precipitation process to control the size and morphology of nanoparticles [30, 31].

1.5.2. Growth mechanism of nanostructures in the precipitation method

Growth mechanism of nanostructures in precipitation method involves two steps

- Nucleation and particle growth
- Micellar action

1.5.2.1. Nucleation and particle growth

The chemical growth of nanometer-sized materials inevitably involves the process of precipitation of a solid phase from solution. Thus, in the case of nanoparticle formation, for nucleation to occur, the solution must be supersaturated either by directly dissolving the solute at higher temperature, and then cooling to low temperatures, or, by adding the necessary reactants to produce a supersaturated solution during the reaction. After the nuclei are formed from the solution, they grow via molecular addition, which relives the supersaturated step.

When the concentration drops below the critical level, nucleation stops and the particles continue to grow by molecular addition, until the equilibrium concentration of the precipitated species is reached. On the other hand, when the reactants are depleted, due to the particle growth, Ostwald ripening or defocusing will occur, where
the larger particles continue to grow and the smaller ones get smaller and finally dissolve. If the reaction is quickly stopped at this stage, the particles will have a broad size distribution, which is featured by a distribution centering two size regimes, a bigger one and a smaller one, and the critical size at this saturation is in between. Once the reaction (mainly the growth of the particles) goes into this stage, it is difficult to get the monodisperse particles unless the reaction is extended to long enough times to completely deplete the supersaturation and the smaller nuclei. To finally produce the stable nanoparticles, these nanoparticles must be arrested during the reaction either by adding surface protecting reagents, such as organic ligands or inorganic capping materials.

1.5.2.2. Micellar action

When the surfactant concentration exceeds the critical micelle concentration (cmc) in water, micelles are formed as the aggregates of surfactant molecules. In normal micelles, the hydrophobic hydrocarbon chains of the surfactants are oriented toward the interior of the micelle, and the hydrophilic groups of the surfactants are in contact with the surrounding aqueous medium. Above the cmc, the physical state of the surfactant molecules changes dramatically, and the additional surfactant exists as aggregates or micelles. On the other hand, reverse micelles are formed in nonaqueous medium, where the hydrophilic head-groups are directed toward the core of the micelles and the hydrophobic groups are directed outward as shown in Figure 8. Reverse micelles can be formed by the ionic surfactants with double-long alkyl chains alone, such as diethyl sulfosuccinate (DES), sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), and Triton-X. Therefore, during the particle formation, the micelles are adsorbed onto the preferred planes and alter the
growth kinetics, thus resulting in the controlled size and desired morphology. Metal oxide nanoparticles can be prepared inside reverse micelles by the hydrolysis procedure, where the metal alkoxide is dissolved in oil, which reacts with water inside the droplets. ZnO, ZrO\textsubscript{2}, TiO\textsubscript{2}, SiO\textsubscript{2}, and Fe\textsubscript{2}O\textsubscript{3} nanoparticles have been prepared in this fashion. Metal sulfate, metal carbonates, metal oxides, and silver halides can also be produced by the precipitation reaction between reactants in reverse micelles. AgX, AgS, BaCO\textsubscript{3}, CaCO\textsubscript{3}, SrCO\textsubscript{3}, and BaSO\textsubscript{4} nanoparticles have also been prepared by using this method [24, 30, 31].

Fig. 8. Reverse and normal micelle structures

1.6. Recent developments in the photocatalytic degradation of EDCs

Currently available water treatment technologies such as adsorption or coagulation merely concentrate on the pollutants present by transferring them to other phases, but still remain and not being completely eliminated. Other conventional water treatment methods such as sedimentation, filtration, chemical and membrane technologies involve high operating costs and could generate toxic secondary
pollutants into the ecosystem. Therefore, in recent years, semiconductor photocatalytic process has shown a great potential as a low-cost, environmental friendly and sustainable treatment technology to align with the “zero” waste scheme in the water/wastewater industry. The ability of this advanced oxidation technology has been widely demonstrated to remove the persistent organic compounds and microorganisms in water. Among these AOPs, heterogeneous photocatalysis employing semi-conductor catalysts (TiO$_2$, ZnO, Fe$_2$O$_3$, CdS, GaP and ZnS) has demonstrated its efficiency in degrading a wide range of ambiguous refractory organics into readily biodegradable compounds, and eventually mineralized them to innocuous carbon dioxide and water [32]. Among the semiconductor catalysts, titanium dioxide (TiO$_2$) and zinc oxide (ZnO) has received the greatest attention in photocatalysis technology.

1.6.1.1. Photocatalytic degradation of organic contaminants (EDCs) over TiO$_2$: a review of modification, progress and problems

Photodegradation of EDCs has recently been the most widely investigated research topic. By far, TiO$_2$ has played a much larger role in this scenario, when compared to other semiconductor photocatalysts, due to its cost effectiveness, inert nature and photostability. Extensive literature analysis has shown many possibilities of improving the efficiency of photodecomposition over TiO$_2$ by combining the photoprocess with either physical or chemical operations. The recombination of photogenerated electrons and holes is the reason behind the low photoactivity of TiO$_2$. In order to enhance the efficiency of TiO$_2$ photocatalysis as well as the response into the visible spectrum of solar light, TiO$_2$ has been modified in different manner as shown in Figure 8.
However, the modification of TiO\textsubscript{2} by doping have been constantly explored to suppress the electron–hole recombination and to enhance the photosensitivity of TiO\textsubscript{2} for successful application [33].

1.6.1.1. Modification of TiO\textsubscript{2} by doping

Due to the constraints involved in ensuring the effective photoactivation, there has been a growing quest to go beyond the threshold wavelength of 388 nm which corresponds to the band gap of titania. The major practices involve the catalyst modification by doping, metal coating, surface sensitization, increase in surface area or by design and development of secondary titania photocatalyst. Since 1980s, TiO\textsubscript{2} has been modified mainly by metal loading or platinization to achieve a better photocatalytic activity [34, 35]. Successful doping can be achieved with either transition metal ion or with non-metal resulting in enhancing the efficacy of the photocatalyst system. Metal ion implantation with ions such as V, Cr, Mn, Fe and Ni, was found to cause large shift in the absorption band of titanium dioxide towards the visible region, and thereby increased the photocatalytic activity [34, 35]. Photocatalytic degradation of certain organic contaminants (EDCs) over pure and doped TiO\textsubscript{2} is given in Table 2.

However, there are two main disadvantages in the application of TiO\textsubscript{2}. One limitation is the rapid recombination of photogenerated electron–hole pairs. The other disadvantage is the limitation of utilizing the visible light, because, TiO\textsubscript{2} is only sensitive to UV light, due to its large bandgap (3.2 eV for the anatase phase and 3.0 eV for the rutile phase) [48]. Therefore, the suitable alternative to TiO\textsubscript{2} is ZnO, as discussed in the following section.
Fig. 9. Modification of TiO$_2$ in different manner (a) Steps of excitation with a sensitizer in the presence of an adsorbed organic electron acceptor (EA), (b) Scheme of TiO$_2$ band structures, chemically ion-doped TiO$_2$ and physically ion-implanted TiO$_2$ (c) Electron capture by a metal in contact with the semiconductor surface
### Table 2. Photocatalytic degradation of certain organic contaminants (EDCs) over pure and doped TiO$_2$

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Phenolic pollutant (EDCs)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>Phenol and 4-chlorophenols</td>
<td>[36, 37]</td>
</tr>
<tr>
<td></td>
<td>2,4,6-trichlorophenol</td>
<td></td>
</tr>
<tr>
<td>Co–TiO$_2$</td>
<td>Phenol, 2-chlorophenol</td>
<td>[35]</td>
</tr>
<tr>
<td>Pr–TiO$_2$</td>
<td>Phenol</td>
<td>[39]</td>
</tr>
<tr>
<td>N–TiO$_2$</td>
<td>4-Chlorophenol</td>
<td>[40]</td>
</tr>
<tr>
<td>La–TiO$_2$</td>
<td>Phenol, 4-chlorophenol</td>
<td>[41]</td>
</tr>
<tr>
<td>Au–TiO$_2$</td>
<td>Phenol</td>
<td>[42]</td>
</tr>
<tr>
<td>Zr–TiO$_2$</td>
<td>4-Chlorophenol</td>
<td>[43]</td>
</tr>
<tr>
<td>Ag–TiO$_2$</td>
<td>2,4,6-Trichlorophenol</td>
<td>[44]</td>
</tr>
<tr>
<td>Fe–Er codoped TiO$_2$</td>
<td>Bisphenol A</td>
<td>[45]</td>
</tr>
<tr>
<td>Ag/TiO$_2$ and Pt/TiO$_2$</td>
<td>Resorcinol, bisphenol A, 2,4-dichlorophenol</td>
<td>[46]</td>
</tr>
<tr>
<td>Au–TiO$_2$</td>
<td>Nonylphenol</td>
<td>[47]</td>
</tr>
</tbody>
</table>
1.6.2. Photocatalytic degradation of organic contaminants (EDCs) over ZnO: modification and progress

Although TiO$_2$ is universally recognized as the most photoactive catalyst, ZnO is a suitable alternative to TiO$_2$, as it has similar band gap energy (3.2 eV), and absorption over a larger fraction of the solar spectrum than TiO$_2$ [49]. Due to the position of the valence band of ZnO, the photogenerated holes have strong enough oxidizing power to decompose most of the organic compounds. Moreover, it is well known that ZnO exhibits the richest range of morphologies among the wide band gap semiconductors. Therefore, over the past few years, tremendous effort has been made to control the shape of ZnO nanomaterials in order to investigate the effect of morphology on the photocatalytic activities [50-54]. In addition, a number of efforts on the surface modification of ZnO have been made to improve the photocatalytic activities, since the simple modification can readily alter the mechanism, and accelerate the kinetics of photocatalysis. The most frequently employed modification method is doping the metals at ZnO surface. The principal of doping activities include the following,

- Incorporation of energy levels into the band gap of the ZnO,
- Changing the life time of charge carriers
- Substitution of the Zn$^{2+}$ with the cation of the same size
- Shifting the conduction band and/or valence band so as to enable the photoexcitation at the lower energies

ZnO has been doped with certain transition metals, non-metals and ionic components. Doped ions can also act as charge trapping sites, and thus reduce the electron–hole recombination. The effect of doping on photocatalytic activity is governed by several factors, e.g.
The type and concentration of dopant
Preparation method
The structure and morphology of photocatalyst
Physico-chemical properties of the catalyst

Both positive and negative results have been reported from doping with metal ions. The increase in charge separation efficiency will enhance the formation of both free hydroxyl radicals and active oxygen species [55]. Generally, the transition metal ions have been used to prepare the doped ZnO semiconductors [56]. Most of the studies attempted to describe the photoluminescence, optical activity, and magnetic properties of the doped ZnO semiconductor metal oxide. Only a few has conducted the photocatalytic studies to evaluate the effect of doping on ZnO. In this way, photocatalytic degradation of certain organic contaminants (EDCs) over pure and doped ZnO is given in Table 3.

<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>Phenolic pollutant (EDCs)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>4-chlorophenol</td>
<td>[56, 57]</td>
</tr>
<tr>
<td></td>
<td>2,4,6-trichlorophenol</td>
<td></td>
</tr>
<tr>
<td>Sm-ZnO</td>
<td>2,4-dichlorophenol</td>
<td>[59]</td>
</tr>
<tr>
<td>Fe-ZnO</td>
<td>2-chlorophenol</td>
<td>[60]</td>
</tr>
<tr>
<td>N-ZnO</td>
<td>Bisphenol A</td>
<td>[61]</td>
</tr>
<tr>
<td>S-ZnO</td>
<td>Resorcinol</td>
<td>[62]</td>
</tr>
<tr>
<td>ZnO</td>
<td>p-nonylphenol</td>
<td>[63]</td>
</tr>
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</table>
However, the studies concerning the effect of ZnO morphology and M doping on its photocatalytic activity are still of great importance and challenge to explore, as it plays an important role in determining the absorption, emission, and photocatalytic activity. Therefore, we have investigated the relationship between photo-catalytic activity, crystallinity, particle size, defects, surface area, and morphology of ZnO particles in detail. In addition, the influence of M (M= Zr, La, Ce, Mg and Ba) contents on the structure, morphology, absorption, emission, and photocatalytic activity of ZnO has been investigated systematically in the present study. In addition, studies on photocatalytic degradation of certain endocrine disruptors (Bisphenol-A, p-nonylphenol, 4-chlorophenol, resorcinol and 2,4,6 trichlorophenol) using pure and M-doped (M= Zr, La, Ce, Mg and Ba) ZnO has been carried out. In addition, in photocatalytic degradation of EDCs, the followings are operating parameters, which affect the photocatalytic process.

1.7. Operating parameters in photocatalytic processes

1.7.1. Catalyst loading, pollutant concentration, and monochromatic light

The influence of the physical parameters which govern the photocatalytic activity represented by the reaction rate is illustrated by Figure 10. In Fig. 10a, one can observe that the reaction rate ‘r’ is proportional to the mass ‘m’ of catalyst, before reaching a plateau, due to the full absorption of photons by the photocatalytic bed. Generally, in any given photocatalytic application, the optimum catalyst concentration must be determined, in order to avoid the excess catalyst and ensure the total absorption of efficient photons. This is because of the unfavourable light scattering and reduction of light penetration into the solution, which is observed with excess photocatalyst loading.
Fig. 10b represents the rate of photocatalytic oxidation with respect to the substrate concentration. During photocatalytic oxidation the concentration of the organic substrate over time depends upon photonic efficiency. At high-substrate concentrations, however, the photonic efficiency diminishes, and the catalysis surface becomes saturated leading to the catalyst deactivation. Figure 10c represents \( r = f(\lambda) \). Such a curve has to be established with monochromatic light and requires a rapid reaction to have an accurate measurement of ‘r’. It can be observed that this curve parallels the light absorption by the solid, and enables one to determine the energy band gap \( E_g \) by catalytic measurements. Moreover, increase in the degradation rate with increase in light intensity during the photocatalytic degradation is common.

Fig. 10. Influence of the physical parameters on the photocatalytic activity
1.7.2. pH of the solution

At a pH below its pKa value, an organic compound exists as a neutral species. Above this pKa value, an organic compound attains a negative charge. Some compounds can exist in positive, neutral, as well as negative forms in aqueous solution. This variation can also significantly influence their photocatalytic degradation behavior. The surface charge of a photocatalyst, and ionization of an organic pollutant can be profoundly affected by the solution pH. In addition, protonation and deprotonation of the organic pollutants can take place depending on the solution pH. Therefore, the pH of the solution can play a key role in the adsorption and photocatalytic oxidation of pollutants.

1.7.3. Doping

In order to enhance the photocatalysis as well as the response into the visible spectrum of solar light, photocatalyst has been doped with certain transition metals, non-metals and ionic components. Doped ions can also act as charge trapping sites and thus reduce electron–hole recombination. On the other hand, metal doping is always advantageous to the photocatalytic degradation, but the optimum dopant, either mol% or wt% may vary from a catalyst to catalyst. However, any further increase in the dopant content, exert negative effect on the activity of the photocatalyst. Therefore, effect of different reaction parameters has been investigated systematically in the present study to optimize the reaction conditions.

1.8. Overview and definition of the research problem

The increasing demands for the new products with complex chemical structures may be useful in many ways to mankind, but on the other side, they may create problems when not properly disposed after use, thus posing serious
environmental issues of public concern. The wastewater generated from these manufacturing industries will also be associated with many environmental problems in several ways. The environmental contaminants would alter the normal functioning of the endocrine and reproductive systems by mimicking or inhibiting endogenous hormone actions, or modulating the synthesis of hormones [64]. Such kinds of chemicals are termed to be “endocrine disrupting chemicals” (EDCs). The EDCs are composed of various types of chemicals used in a wide variety of herbicides, fungicides, insecticides, detergents, material of plastic and various industrial effluents contaminants. More importantly EDCs like bisphenol-A, p-nonyl phenol, 4-chloro phenol, resorcinol and 2,4,6 trichloro phenol may often act silently with severe latent adverse effects [65-67].

In addition, the wastewater / effluent containing EDCs discharged from various industries like coal tar, plastics, leather, paints, pharmaceuticals, steel, textile, paper pulp, insecticides, pesticides and oil refineries poses serious risk to the aquatic organisms and human beings. A series of diseases such as liver damage, diarrhea, mouth ulcers, dark urine and hemolytic anemia could be caused by the repeated exposure to the lower levels of EDCs in water.

The methods for the treatment of water containing EDCs include microbial degradation, chemical oxidation, photocatalytic degradation, ultrasonic degradation, enzymatic polymerization, adsorption etc. However, the conventional methods like chemical precipitation, activated carbon adsorption and ion exchange etc. usually transfer the contaminants from one medium to another and hence further treatment is required. Furthermore, biodegradation of EDCs is not only slow and incomplete, but also the by-products are more toxic than the contaminants. Therefore,
photocatalysis seems to be an economic one with respect to the energy aspects [68]. Semiconductor (metal oxides)-photocatalysis is of interest due to its potential to utilize solar radiation. TiO$_2$ is a well known effective photocatalyst, and the most extensively studied one for this purpose. However, different metal oxides like ZrO$_2$, MoO$_3$, Fe$_2$O$_3$, Co$_3$O$_4$, CuO, ZnO, CdO, HgO, Al$_2$O$_3$, PbO, PbO$_2$, SnO$_2$, Bi$_2$O$_3$, La$_2$O$_3$, CeO$_2$, Sm$_2$O$_3$, Eu$_2$O$_3$ and doped metal oxides were used for the degradation of dyes, organic pollutants, phenols and EDCs [68, 69]. Although, TiO$_2$ is widely and universally considered as the most photoactive catalyst, ZnO is a suitable alternative to TiO$_2$, as it has similar band gap energy, lower cost and better performance when compared to TiO$_2$ in both acidic and basic medium. This stimulated many researchers to further explore the properties of ZnO in many photocatalytic reactions. However, the pure metal oxides has some drawbacks, including the fast recombination rate of photogenerated electron hole pair, and a low quantum yield in the photocatalytic reactions in aqueous solutions, which obstruct the commercialization of photocatalytic degradation process. Therefore various methods have been developed to reduce the electron- hole recombination rate of ZnO. One of the interesting approaches is doping the metal atoms on the semiconductors, which have been shown to reduce the band gap energy, and improve the charge separation between photogenerated electrons and holes [70].

Though the different materials are used for the degradation / removal of few EDCs, there is scarce literature found regarding the usage of nano metal oxide semiconductors as photocatalysts for the degradation / removal of EDCs. It is well established that the shape control of semiconductor nanostructures has attracted considerable attention, due to the fact that they play very important roles in determining their physical and chemical properties [71]. Nanostructured zinc oxide
(ZnO) is a versatile and interesting semiconductor material to study because, it possesses very attractive physical properties such as a wide direct band gap (3.37 eV), a large exciton binding energy of 60 meV at room temperature, and unique electronic, catalytic, optoelectronic, and photocatalytic properties [72 -75]. A wide variety of synthetic routes have thus been proposed to prepare specific nanostructures of ZnO, including nanorods, nanowires, nanobelts, tetrapods and many other anisotropic prototypes in order to further the development of ZnO nanostructures. Among the many synthetic approaches, wet chemistry is an effective way for the production of ZnO nanostructures. In wet-chemistry processes, capping reagents are often required to control the crystal growth of the materials to enable the formation of nanostructures [75-78]. Most of the preparation methods, however, involve the complicated synthetic procedures, which may hinder the applicability of the products. Therefore, development of a simple, environmentally friendly method to prepare ZnO nanostructures with controllable morphology is crucial to their practical applications, and has thus become an important topic of investigation. Precipitation approach compared with other traditional methods provides a facile way for low cost and large-scale production, which does not need expensive raw materials and complicated equipments. Therefore, in this work, a series of ZnO nano particles with different morphologies were prepared via a simple precipitation route at low temperature and investigated the relationship between the photocatalytic activity, morphology, crystallinity and surface area of ZnO particles in detail.
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