Chapter 8
Optimizing Nanocatalyst's and Technological Factors Influencing on Photocatalytic Degradation of Organic and Inorganic Pollutants

Sushma Dave and Pratik Jagtap

Abstract In recent decades, water pollution with organic and inorganic contaminants is a chief environmental concern. Enormously increasing industrial sectors such as textile dyes, pigments, ink, polymers, plastics, medicine and cosmetics effluent discharges are the main contributors toward the depleting water reservoir qualities. Which potentially have toxic effect on the organism depending on it that also includes humans too. Many of them are destruction resistant by conventional degradation methods. Thus, optimization of photocatalytic degradation methods has proven a new era in global water pollution remediation and cleaning related fields. Photocatalysts are considered as a great potential, economical, eco-friendly, sustainable and show promising role in water remediation of wastewater without generating secondary waste. However, the development of such an advanced system in large scale is still in the optimization phase. The design and development of efficiency, photocatalyst with optimum operational parameters, configuration and integration of photocatalysis is still need to be provoked generously. This chapter will be emphasized on the mechanism and diversifying factors influencing on photocatalysis degradation that should be taken into consideration during optimization and development of the photocatalysis system depending upon the load of the organic and inorganic contaminants. Various electromagnetic spectrum-based excitable nanoparticles or nanomaterials have been studied as photocatalyst that potentially degrade the contaminants from water. TiO_2, Fe_2O_3, CuO, ZnO, CdS, SnO_2, ZnS, etc. were extensively studied for the efficiency controlled optimizing factors in the degradation of pollutants. Optimization of Influencing factors and their effect on photocatalytic degradation activity of the photocatalyst on organic and inorganic water pollutants will be the point of convergence of this chapter. Within this frame of reference surface area, morphology of photocatalyst, higher light intensity, presence of oxidant and doping agents were

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perceived to be effective toward photocatalytic activity. Moreover, the general mechanism of photocatalysis and recent development in nanoparticles/nanomaterials and composite material will be discussed here.

Keywords Photocatalysis · Photocatalyst · Nanoparticles · Nanomaterials · Pollutants · Factors influencing · Water treatment

8.1 Introduction

Population explosion and the rapidly increasing industrial development sectors nearly hit the highly complex and difficult to manageable water pollution that ultimately threatened the massive effect on the climate (Lai et al. 2014) changes in many regions of the world. Also draining the increase in water consumption throughout the globe. Thus, it becomes more challenging to figure out an eco-friendly and more sustainable approaches to remediate the water pollution. Treated waste water becomes a general necessity of the human needs these days. Although the sewer systems, collection of waste water systems and treatment were not much accommodated as per the generated ratio. In addition to this, the present infrastructure facing the increasing demands to produce safer quality of water utilizing less amount of energy inputs (Soutsas et al. 2010). According to the existing planning it is practically difficult to design and develop such a huge system in the rapidly developing regions of the world. These challenges acquired attention of the more advanced but effective system toward the sustainable applications.

In the current scenario of the safe water available for the consumption is continuously deteriorated due to the direct or indirect discharge of the effluents from the industries such as pharmaceutical, food processing, textile, dyes, ink, rubber, plastic, polymers, chemical batteries and domesticated sewers as well as agricultural fertilizers or pesticide. All these industrial sectors contribute the contaminants are containing organic (industrial or textile dyes, herbicides or pesticides, halogenated hydrocarbons, pharmaceuticals by-products, some aromatic compounds such as polycyclic aromatic hydrocarbons) and inorganic (heavy metal ions, free radicals, carcinogens) pollutant molecules which are usually difficult to degrade by traditional methods and can cause the nuisance to the natural water reservoirs (Cacho et al. 1999; Gupta et al. 2006). These pollutants can cause the severe health damages to vital organs like kidneys, reproductive system, nervous system, lungs, lever even at very minute quantities (at ppm and ppb levels).

Several methods (in Fig. 8.1) already been applied to the waste water treatment before discharging out of the mainstreams. Each of processes from the method manifests with advantages and disadvantages.

Meanwhile, photocatalytic degradation treatment of pollutants is one of the best sustainable methods and proven a promising approach to clean the water sustainably using renewable sources and nanohybrid semiconductor materials. For efficient
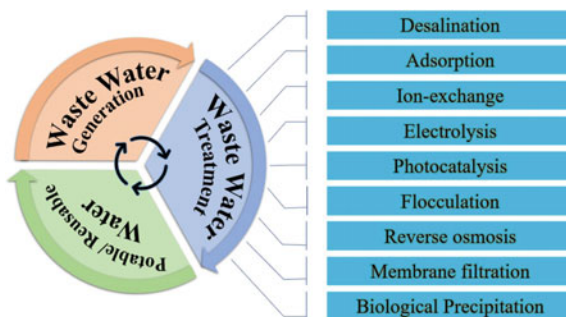
optimum photocatalytic degradation of waste water pollutants, influencing operational factors of the reaction should be taken into consideration. This chapter reviews the most important properties of the nanoparticles as photocatalysts and also focuses on the rigorous introduction of photocatalysis mechanism and factors that influencing the rate of photocatalytic degradation reaction of pollutants present in wastewater (Dahiya and Patel 2021) (Fig. 8.2).

In the context, Nanotechnology offers better opportunities that can develop hyphened techniques relay for the next generation water supply systems. This chapter reviews the promising role of the nanoparticles/nanomaterials and nanocomposites in the water treatment processes to transform or degrade the possible organic and inorganic pollutants from the wastewater (Dave et al. 2021a). The tremendous versatility of the nanoparticles harnesses the great abilities such as high surface area, photosensitivity, catalytic activity, electromagnetic properties, anti-microbial effects and the regulatory pore size capacities etc. are the aspects in the many applications. This application may include quality monitoring sensors, catalytic sites, disinfection agents and distinctive performing matrix/membrane (Gupta and Mondal 2021) s. The development of such a nanotechnological-based application in the waste water treatment processes must be conjointly soothe with the environmental health and safety
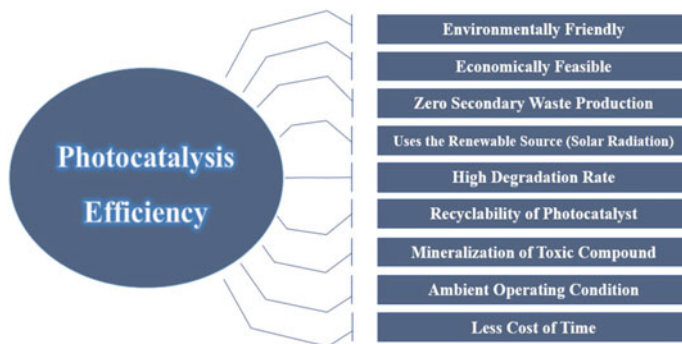

Fig. 8.2 Efficiency of photocatalysis reaction supporting in the sustainable development waste water treatment

research values that hand out the sustainable development. Highly expected prosecution of the nanotechnology in the water treatment may require the consideration of the expensive nanomaterials that might play vital role in obtaining reusable water to relieve the risks of the public and environmental health by potential minimizing the nanoparticles in the water and lift the safer ways of purification/decontaminations (Prajapati and Mondal 2021; Mallick et al. 2021).

8.2 Significance of Photocatalysis in Water Treatment

Photocatalysis is mediated through the light irradiations on photocatalyst particles have vital significance that leads to degradation of toxic pollutants from waste water. Photons are absorbed to obtain the charge which takes place in the redox reaction of toxic pollutant oxidation. Surface area plays a vital role in the mechanism. Succession of the reaction ultimately gives rise to form a hydroxyl free radical and acts as a potent oxidant to degrade the toxicants (Sarangapany and Mohanty 2021; Díez et al. 2021; Merouani and Hamdaoui 2021) (Fig. 8.3).
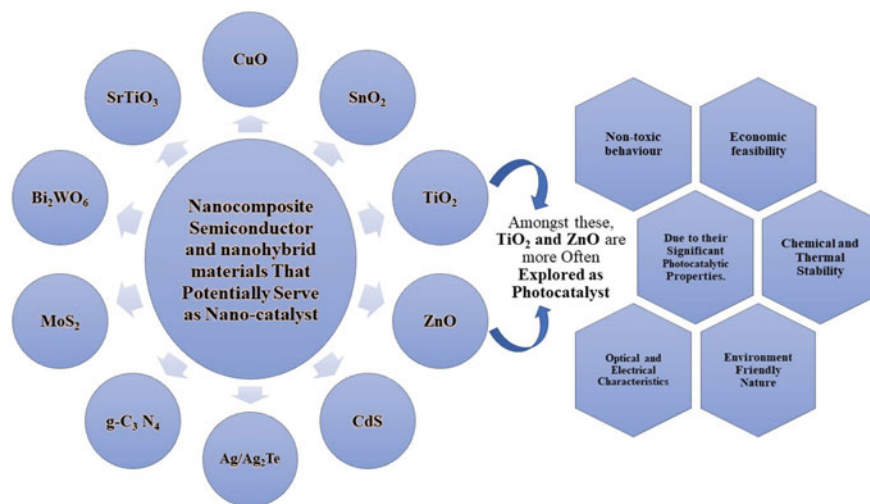

Fig. 8.3 Various photocatalyst semiconductors/ nanohybrid materials used in the photocatalysis reaction of pollutants in the water
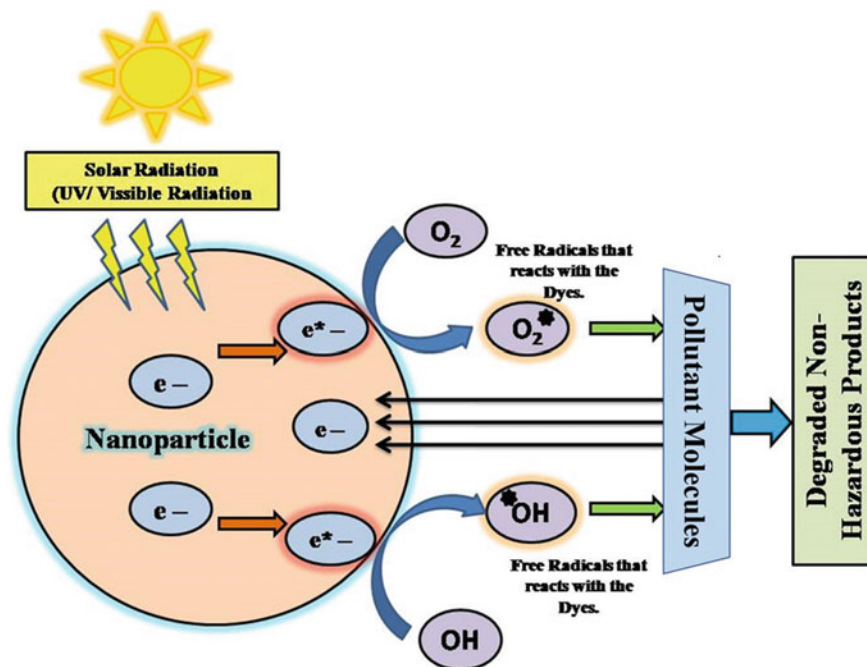
Fig. 8.4 Photochemical mechanism of nanoparticle for the formation and redox reaction causing waste water pollutant degradation

8.3 Mechanism of Nanoparticles (Photocatalyst) Involved in Photocatalysis of Wastewater Pollutants

A general mechanism of photocatalysis is driven by the photochemical transformation organic and inorganic pollutants from the waste water by absorbing the light radiation through the surface chemistry of the photocatalyst that leads to redox reaction. Nanocatalyst semiconductor material captures the energy released by the charge carriers which transfer the charge to the redox reaction of pollutants (Kumar et al. 2021). Apparently, photocatalyst can absorb the light radiation only on an appropriate illumination causing the excitation of charge carriers. Photochemical reaction mechanism produced light induced by the charge carriers and separated as Holes (H^+) and Electrons (e^-) which are responsible for oxidation of pollutants and degradation of pollutants from the waste water respectively (as shown in Fig. 8.4).

8.4 Factors Influencing on the Photocatalysis Mechanism

(A) **Ultrastructure of Photocatalyst**:

a. **Effect of Size and Surface area**: Size and surface area of the photocatalyst are most crucial factor to affect the photocatalytic degradation as the adsorption is directly involved. As the smaller size corresponds to higher surface area available for direct toward number of active sites, adsorption of contaminants and absorption of photons in efficient mechanism that ultimately lead to oxidation and degradation of pollutants. Thus, Nanoparticles play a vital role in the photocatalytic degradation as it exhibits better optical activity and also possesses the electrical photochemical properties (Zulkifili et al. 2018; Leroy et al. 2020; Isac et al. 2019).

b. **Effect of Morphology(shape)**: Morphology is definitely controlling the efficiency of photocatalysis of pollutants as the active sites and photon capture are based on it. It has been tested that ZnO nanorods, ZnO spindles and ZnO Nanoflowers can degrade the several chemical dyes. In which, the ZnO Nanorods found to be the most effective against the photocatalytic degradation. This is due to the higher number of reactive species and active site interaction on the ZnO Nanorods (Haruna et al. 2020).

(B) **Photocatalyst Doping Element**

Some Impurities are artificially added to the photocatalyst during synthesis that can potentially increase the photochemical activities. Such impurities were called as Doping agent or dopants. It increases the photochemical activity by means of elevated energy levels of dopants, better trapping of electrons, efficiently generating the oxygen deficient sites, producing more active sites for the adsorption of pollutant molecules and most importantly altering the light capturing bandgaps for more reactivity. Doping photocatalyst can be broadly classified as follows (Song et al. 2021; Ojha et al. 2020; Wang et al. 2019; Nada et al. 2020; Li et al. 2020; Teh et al. 2020; Zhang et al. 2019):

a. **Noble Metal Doping**
b. **Metal Doping**
c. **Rare Earth Metal Doping**
d. **Non-Metallic Doping**
e. **Co-Doping**
f. **Self-Doping**

(C) **Reactant Accessibility**

a. **Amount of Catalyst**: Photocatalysis rate of reaction is directly proportional to the hydroxyl ion free radical and the positive holes under the radiation. These two primarily take a part in the photocatalytic reaction of the pollutants present in the water. Photocatalysis may increase with the amount of catalyst but exceeding to certain limit it inhibits the rate of

reaction. With the higher concentration of photocatalyst turbidity of the solution increases and prohibited the light entry in the water, also causes the scattering of UV–Vis radiation. Agglomeration is also a main cause of high concentration of nanocatalyst which ultimately blocks the active site and leads to lowering down the photocatalysis (Laurenti et al. 2020; Anju Chanu et al. 2019; Deveci and Mercimek 2019; Tichapondwa et al. 2020).

b. **Concentration of Pollutants**: Surface area is associated with the amount of pollutant where the photocatalysis depends upon pollutants adsorbs. This adsorption is also depending upon the initial concentration pollutants and gradually increases in the water. However, higher than a certain limit, here is significant decrease in the photocatalysis observed due to the higher initial concentration of pollutants adsorbed (Hu et al. 2016). As the photocatalyst's surface is totally covered with the adoption of pollutants, thus light photons were absorbed by the pollutant molecules instead of photocatalyst. Ultimately this reduces the production of hydroxyl ion free radicals and the positive hole. The occupied active sites of photocatalyst by pollutants show reduction in photochemical process (Zelekew et al. 2021).

(D) **Heterogeneity of Oxidants**

Effect of H_2O_2, $KBrO_3$, $(NH_4)_2S_2O_8/K_2S_2O_8$, HNO_3 was seen while photocatlytic dye degradation (Sadik et al. 2004; Sadik et al. 2004; Ovhal et al. 2021). The study on the effect of oxidants such as $(NH_4)_2S_2O_8$, $KBrO_3$ and H_2O_2 on the photooxidation of AR18 reveals that the addition of $(NH_4)_2S_2O_8$ and $KBrO_3$ increases the dye removal whereas the addition of H_2O_2 decreases the photocatalytic degradation. The unusual decrease by the addition of H_2O_2 is due to its low adsorption on the ZnO surface (Sobana and Swaminathan 2007)

(E) **Miscellany Factors**

a. **Effect of pH**: One of the preliminary factors in the photocatalysis is pH. At higher pH (alkaline) free radicals are the predominantly active, while at lower pH (acidic) oxidation of pollutants and positives holes with high oxidation potential are the key factors for photocatalysis of contaminants in the wastewater (Yeganeh et al. 2020; Vijay et al. 2019; Deshmukh et al. 2020; Laishram et al. 2018). As the pH value increases in the solution hydroxyl ion was generated in between the reaction of positive holes and hydroxyl free radicals which cause increase in the degradation rate. If the pH reaches too high (pH > 11/12) the excessively formed hydroxyl ions it starts competing with the pollutants and get absorbed on the photocatalyst, as a result the active site for acidic pollutants gets blocked. Vice-versa, when pH lowers, surface of the photocatalyst gets protonated causing the reduction in the cationic pollutants adsorption which end up with significant decrease in the photodegradation (Suthar et al. 2021; Dave et al. 2021b; Purohit et al. 2021).

b. **Effect of Temperature**: Photocatalysis can even occur at room temperature. However, degradation and recombination of electrons and positive hole pairs, releases energy, thus the temperature of the reaction medium gradually increases. Artificially increase in the temperature can gradually increase the rate of photocatalytic degradation reaction. But higher than 80 °C temperature can reduce the lifespan of the charge carriers through recombination with each other. Also, in temperature lower than 20 °C the reaction medium causes increase in the apparent activation of energy. Therefore, 20–80 °C is considered optimum temperature range for the photocatalysis which shows minimum apparent activation energy and low dependency of the rate of degradation (Dahiya and Patel 2021; Gupta and Mondal 2021; Prajapati and Mondal 2021; Mallick et al. 2021; Dave et al. 2021c; Satapathy et al. 2021).

c. **Effect of Light Intensity available**: The photocatalytic dye degradation in presence of sunlight when conducted in between 10 a.m. to 4 p.m. has resulted in the inference that when the maximum quantity of sunlight is available with high intensity and energy then the catalytic activity is more. The reports demonstrate that sunlight has capability to degrade the dye in presence of these photo catalyst which clearly indicates its energy economy approach thus making it more economic and green method for the industries (Mehta et al. 2016; Ali and Ameta 2013; Borhade et al. 2020; Adhikari et al. 2020).

d. **Effect of Inorganic Ions**: Waste water significantly consists of various inorganic, anionic and cationic pollutants. Presence of such dissolved inorganic ions are large enough to affect the photocatalysis efficiency. These inorganic ions may compete with the pollutant molecules and adsorbed on the surface of the photocatalyst ultimately reduced the active site for photochemical reaction. Inorganic ions affect the photocatalysis particularly by precipitation on the surface, blocking active sites, reacting with catalyst and scavenging radical and positive holes. Also, the Cl^-, SO_4^{2-}, HCO_3^- and PO_4^{3-} inorganic anions were revealed as holes and radical scavengers and reduce the rate of photocatalysis, along with inorganic cations such as Mg^{2+}, Zn^{2+}, Fe^{3+}, Cu^{2+} etc., in wastewater can also significantly affect the photodegradation activity.

8.5 Conclusion

As a future perspective there will be emphasis on the mechanism and diversify factors influencing on photocatalytic degradation that should be taken into consideration during optimization and development of the photocatalysis system depends upon the load of the organic and inorganic contaminants. Various electromagnetic spectrum-based excitable nanoparticles or nanomaterials are been studied as photocatalyst that potentially degrade the contaminants from water.

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