ABSTRACT

Design and development of an environmentally friendly and non-toxic photocatalysts system for the complete mineralization of persistent organic pollutants is an emerging and hottest challenge throughout the globe. However, poor visible light harvesting capacity, faster rate of recombination of photogenerated electron and hole pairs, low charge transfer and agglomeration of photocatalysts in aqueous medium are some of the major bottlenecks in this study area. This review paper presents the comprehensive details about the findings of the photocatalytic degradation of biological recalcitrant pollutants using non-metallic graphitic carbon nitride (g-C3N4) and ZnO photocatalysts system. The basic mechanism of photocatalysis and photocatalytic degradation of phenolic compounds has been presented. The structural manipulation, challenges and application of g-C3N4 photocatalysts by doping with non-metallic elements and molecules, formation of heterojunction photocatalytic system by g-C3N4 with carbon quantum dots (CQDs) and ZnO photocatalyst have been discussed. In addition, detailed information regarding important roles of CQDs, metalloporphyrins photosensitizer and supporting carrier materials like hydroxyapatite in enhancement of photocatalytic activity has been focused.

Keywords: Graphitic carbon nitride; carbon quantum dots; ZnO; metalloporphyrin photosensitizer; hydroxyapatite; phenol.

1. INTRODUCTION

The major sources of phenol introduced into the aquatic environment are due to the various anthropogenic activities. Currently, the worldwide rate of production of phenol has reached 6 million ton per year, with an increasing trend [1]. Various industries discharge phenol to the receiving environment, for instance, petroleum oil refineries (6–500 mg/l), manufacture of petrochemicals (2.8–1220 mg/l), coke oven wastewater (28–1200 mg/l), coal mining (9–6800 mg/l) [2,3]. Similarly effluents of pulp and paper, pharmaceutical, wood preservative, paint industries comprises phenolic pollutants in the ranges of 0.1–1600 mg/l [2]. Phenolic compounds are also produces during the gasification of coal and liquefaction processes. The phenolic compounds are the common water contaminants in environment owing to their higher solubility in water i.e. 82.8 g/l. It is also reported that phenolic wastewater sometimes leaches into the soil, pollutes the surrounding water resources and cropland, even rivers and lakes at low concentration. Further, due to the acute toxicity, carcinogenic and biological recalcitrant nature, these compounds cause significant environmental damage and human health hazard. These pollutants are also well-known as endocrine disrupting chemicals and genotoxicity compounds [4]. Therefore, these phenolic pollutants are listed as priority pollutant by US-EPA since 1976. Further, phenol has been listed as the top 20 hazardous and noxious substance by international maritime organization (IMO) [5]. The Environmental Protection Agency (EPA) has fixed the permissible limit of phenol at less than 1 ppb (parts per billion) in surface waters. Similarly, the European Union, set 0.5 ppb of phenol as the permissible limit in potable and mineral waters, whereas, it is fixed at 0.5 mg/l for surface waters and 1 mg/l for the sewerage system [2].

Several technologies are available in the literature for removal of phenolic compounds from the polluted environment such as bioremediation, thermal treatment (incineration, pyrolysis), chemical and biochemical treatments. Though bioremediation is an eco-friendly technique and inexpensive method, however, it is not feasible for biological recalcitrant compounds and takes a long hydraulic residence time. Sometimes viability of the biological system is doubtful under high toxic pollutant loading rate. Thermal treatments which include incineration and pyrolysis, possess many limitations, for instance, significant emission of secondary hazardous pollutants as well as not economically feasible. Chemical treatments such as precipitation, coagulation and flocculation, adsorption, ion exchange, reverse osmosis and air stripping, etc., do not completely degrade the toxic pollutants rather transfer from one phase to other and consequently accumulates these pollutants which necessitate a post-treatment additional steps and cost [6]. Further, adsorption generates huge quantity of toxic sludge and need further treatment and its safe disposal is not feasible. The advanced oxidation process (AOP) is one of the widely accepted techniques for degradation of phenolic pollutants from contaminated wastewater via generation of different free radicals such as hydroxyl and superoxide radicals. There are several advanced oxidation methods, for instance, UV-Vis, ozone, Fenton-based processes and photocatalytic processes. Electrochemical oxidation is an expensive process which is not viable towards commercialization. Similarly, chemical treatments produce different intermediate toxic waste and need post-treatment thus increases the cost of treatment. Fenton and ozone based techniques use potentially hazardous oxidants such as ozone, hydrogen peroxide etc.
2. CHEMICAL & PHYSICAL PROPERTIES OF PHENOL

Phenol was first extracted from coal tar in impure form in 1834 by the German analytical chemist Friedlieb Ferdinand Runge. It is a hygroscopic colorless to white crystalline solid at ambient temperature and pressure. Phenol is highly soluble in ether, ethyl alcohol, and in many polar solvents, even in benzene. It is detected by a typical medicinal pungent smell or tar odour. Phenol has a considerable aqueous solubility (83 g/l at 20 °C). The detail about the physicochemical properties of phenol is given in Table 1.

| Property               | Value       |
|------------------------|-------------|
| Molecular weight (g/mol) | C₇H₇O₇  |
| Color                  | Colorless to light pink |
| Physical state         | Deliquescent crystals (liquefies with 8% water) |
| Melting point          | 40.9 °C     |
| Boiling point          | 181.8 °C    |
| Odour                  | Distinct aromatic, acidic |
| Solubility in water    | 83 g/l, soluble in many organic solvents |
| pKa                    | 9.82-10.0   |

Aromatic hydrocarbons having - OH group can also be called phenol such as quinols, xylenols, cresol, catechol, guaiacol and resorcinol. The nature and position of the substituents determine the acidity and aqueous solubility of the substituted phenol. The effect of substituents on acidity and solubility are noticeable if the substituents are O- or P- positioned electron withdrawing groups. For example the pKa value for phenol and p-nitro phenol are 10.0 and 7.2 respectively.

2.1. Industrial uses of phenol.

35% of phenol is used for the preparation of phenol-formaldehyde resins which are used as adhesives, coatings and used for the production of moulded products. 28% of phenol is used to produce bisphenol A which is a monomer of epoxy resins. 16% of phenol is used for the production of cyclohexanone & cyclohexanone-cyclohexanol mixtures by the selective catalytic hydrogenation. Then cyclohexanone is transferred into its oxime and to caprolactam which is a monomer of nylon 6. Oxidation of cyclohexanone-cyclohexanol is carried out by nitric acid to produce adipic acid which is one of the monomer of nylon-6, 6. Polyphenoxy, polysulphone, polyester & polyester polyols are synthesized by the use of phenol. Phenol is a main constituent for the production of aspirin. For its antiseptic, germicidal and anaesthetic properties, phenol is used for the preparation of some shaving cream and soap, veterinary medicine. It is used as a peptizing agent in adhesives, as a solvent for the extraction of lubricants, as an isocyanate capping agents. Phenol is used in the preparation of fertilizers, surfactants, paints & paint removers, plasticizers, curing agents and antioxidants.

2.2. Toxicity of phenol.

Due to the industrial activities and environmental pollution, the worker and the common public are exposed to phenol through inhalation, eye or skin contact, intake by consumption of contaminated water and absorption through the skin. Upon contact with phenol, it absorbs through the skin very easily and is highly corrosive to the respiratory tract, eyes, and skin as a result can initiate skin and eye burns. Sometimes due to exposure of phenol causes serious convulsions and comas, which lead to death. Phenol also affects the normal function of major vital organ of human body such as liver, lungs, kidneys, as well as blood vascular system. Phenol also initiates denaturation of living cell protein components of living system. Phenol toxicity is related to the hydrophobicity of the individual compound and formation of free radicals [8]. For example, the increase of hydrophobicity of chlorophenols is related to the increasing number of chlorine atoms that enhances the toxicity of the individual compound [9]. After penetration of phenol into the living cell, it undergo biological active transformation, mediated by various enzymatic system particularly cytochrome oxidase P450 in the mitochondrial...
oxidative phosphorylation. The toxicity of substituted phenols to living cells is caused due to its uncoupling effects on mitochondrial oxidative phosphorylation, consequently increases the membrane permeability to proton and alteration of transmembrane pH gradients as well as electrical potentials [10]. The uncoupling activity of these substituted phenols causes fatal to microorganisms. In addition, formation of phenolic dimers further exaggerated the uncoupling activity. There are several literature reports on the toxicity of substituted phenol on microbial cell and offers resistance to enzymatic degradation due to its shared resonance electrons on its aromatic ring. Further, substitution of halogens on the aromatic ring enhances the stability of the structure due to its electron withdrawing effect as well as steric hindrance to enzymes [11,12]. Very often the biotransformation processes of phenol generate more toxic intermediate compounds as a result enhances the toxicity profile. These intermediate electrophilic metabolites some time bind and damage DNA or enzymes of living system and initiate health hazards. The noxious influence of phenols and metabolic intermediates causes acute toxicity as well as induces mutagenicity and carcinogenicity [13].

Phenol derivatives particularly pentachlorophenol, bisphenol A (BPA), and nitrophenol are also known to be carcinogenic and mutagenic agent. Exposure of BPA and chlorophenol from industrial effluents is a major concern to human health as it is a common endocrine disrupting chemical (EDC), which alters the hormones of living beings and causes serious health hazards. Chlorophenol, is an organochloride of phenol, usually comprises one or more covalently bonded chlorine atoms. Chlorophenol and nitrophenol are present in effluent of industrial wastewater such as pulp and paper, pesticides, herbicides, pharmaceutical and wood preservatives etc. Chlorophenol and nitrophenol are well known carcinogenic xenobiotics and listed as “Priority Pollutants” by both the European community and US Environmental Protection Agency, and their concentrations are restricted to below 10 mg/l in natural waters.

3. ADVANCED OXIDATION FOR REMOVAL OF PHENOL

3.1. Electrochemical Oxidation.

The application of electrochemical oxidation for removal of phenolic pollutants has been investigated extensively even in bench and pilot plant scale operation [14]. This process consists of generation of highly oxidant species by electrolysis. The major factors associated with the efficiency of electrochemical oxidation process are current density, pH, physicochemical properties of reacting solution, electrochemical cell design, type of electrolyte and concentration, concentration of pollutants and their properties, electrodes material and geometry. During electro-oxidation process at the surface of anode, water molecule oxidizes to generate hydroxyl radical (·OH) which oxidizes the pollutants into non-toxic innocuous end product. The presence of oxygen in the electrochemical process plays a vital role as it can be reduced to hydrogen peroxide or water at the cathode under acidic pH. Very often the hydrogen peroxide generates in the anode during the process interacts with the hydroxyl radicals to produce hydroperoxy radicals as shown in equation 1:

$$\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \quad (1)$$

All these free radicals such as hydroxyl radicals, hydroperoxy radicals and hydrogen peroxide generate during the electrochemical process strongly oxidize the organic and inorganic pollutants into non-toxic innocuous end product. These electrochemical oxidation processes are two types i.e., direct and indirect oxidation. The anodic oxidation (direct) process occurs through adsorption of the target pollutants onto the surface of the anode. However, the low efficiency of the anode stimulates to design and develop an extensive variety of electrode materials such as platinum, graphite, RuO\(_2\), IrO\(_2\), PbO\(_2\), SnO\(_2\) and boron-doped diamond (BDD). Among these electrode systems, boron-doped diamond and PbO\(_2\) are proving to be more efficient due to its high oxygen over potential. Electrochemical oxidation of phenol follows pseudo first-order kinetics. The efficiency of electrochemical oxidation process is evaluated by the instantaneous current efficiency or electrochemical oxidation index and apparent current efficiency. On the other hand, intermediary redox reagents in indirect oxidation process facilitates the electron transfer between electrode and pollutants, thus, it prevents fouling of electrode by the pollutants. The availability of chloride ions increases removal of phenolic contaminants via generation of Cl\(_2\) or ClO\(^-\) in the electrochemical oxidation process. However, BDD electrodes are highly expensive due to the substrate (Nb, W, Ta) used in the process onto which the BDD film is deposited. Therefore, it is very vital to reduce the treatment time without compromising its efficiency since most of the electrode system exhibits a comparatively short life span and high cost. It was very important to consider that the time of electrochemical process is directly proportional to that of energy consumption and consequently increases the treatment cost during the process. Nevertheless, application of electrochemical process is not yet commercialized due to its high operating cost as well as incurs equipment and energy costs. Further, addition of salt is highly essential for poor conducting effluent, which further increases the operating cost. Several authors also reported the use of electrochemical oxidation for the destruction of substituted phenols [15,14], but not yet commercially due to its high operating cost. The advantage of the electrochemical technique is that electrons are generated or assimilated by the electrodes. Thus it supplies a clean reactant and does not enhance the number of chemical associated in the process.

3.2. Advanced Oxidation Processes.

The advanced oxidation process (AOP) degrades organic pollutants via generation of various free radicals especially hydroxyl, superoxide radicals. AOPs usually refer to a specific subset of processes that involve O\(_3\), H\(_2\)O\(_2\), semiconductor catalysis, Fenton’s reaction and/or UV-visible light. All these methods generate different free radicals which can oxidize a wide range of organic and inorganic pollutants, including phenolic compounds.

3.3. Ozonation.

In general the wastewater containing various pollutants is saturated with ozone and UV irradiation at 253.7 nm. It is reported that extinction coefficient of O\(_3\) at 253.7 nm is found to be 3300 L.mole\(^{-1}\)cm\(^{-1}\), which is larger than that of H\(_2\)O\(_2\) (18.6 L.mole\(^{-1}\)).
The AOP process of ozone is initiated by the photolysis of ozone under UV irradiation which produces two hydroxyl radicals as shown below.

\[ H_2O_2 + O_3 + h\nu \rightarrow 2\cdot OH + O_2 \]  \hspace{1cm} (2) \]

\[ 2\cdot OH \rightarrow H_2O_2 \]  \hspace{1cm} (3) \]

Ozonation process associated with either direct reaction between target substrate with molecular ozone (O₃) or generation of free radicals such as hydroxyl radicals(OH), hydroperoxy radicals (HO₂⁻), superoxide radicals (O₂⁻), and species particularly, O₂^— and HO₂ which then oxidizes the target pollutants. Similar observations are also reported in literature that organic pollutants are degraded by direct oxidation with molecular ozone or mediated by indirect oxidation with formation of hydroxyl radicals ('OH) generated by the transformation of ozone under alkaline conditions [16, 17]. Ozone is a well-known environmental friendly strong oxidizing agent that can oxidize different inorganic and organic pollutants present in contaminated wastewaters. Further, the efficiency of ozone treatment for degradation of xenobiotic compounds drastically enhances in presence of catalysts or along with UV light or H₂O₂. In general, the ozone molecule interacts specifically with compounds having certain functional groups (e.g., OH, CHₓ, OCH₃, C=O bonds, and anions particularly N, P, O, S groups. Generally direct oxidation reaction of ozone occurs under acidic environment and in the presence of radical scavengers that inhibit the chain reaction responsible for ozone decomposition. On the other hand oxidizing action of 'OH is a non-selective process. Similarly, indirect reaction predominates under alkaline conditions or in the presence of solutes that support the formation of 'OH radicals due to the tremendously rapid and non-selective properties of 'OH radicals [18]. However, the presence of radical scavengers like carbonate and bicarbonate species in wastewater, oxidation of pollutants is primarily regulated by the presence of molecular ozone [19]. Ozonisation treatments have been investigated by many researchers on dye degradation. Fernando et al. [20] studied the degradation of phenolic compounds under ozone treatment and found a higher degradation rate constant compared with TiO₂ photocatalysis. Salokannel et al. [21] reported the application of ozonation and O₃/H₂O₂ process for the treatment of pulp and paper mill wastewater. However, low solubility in water, high generation cost and low oxidation rate towards stable organic compounds are some of the major bottleneck of the technique. In addition, the rate of pollutant degradation by ozone is a slower process, which necessitates higher O₃ dosages.

3.4. Ultrasonication

Ultrasonication causes fragmentation of water molecules consequently generates hydrogen and hydroxyl radicals. Very often these radicals combine together and produce other oxidative species like peroxy and super oxide radicals along with hydrogen peroxide. The amount of free radicals depends upon ambient conditions and the operating parameters. Therefore, these free radicals are used to oxidize the soluble organic and inorganic pollutants into innocuous end products. Several researchers investigated the application of ultrasonication techniques in degradation of phenolic pollutants from contaminated environment [22, 23, 24].

4. PHOTOCATALYSIS: A PROMISING ROUTE FOR ENERGY AND ENVIRONMENT

It is a catalytic process by semiconductor materials with exposure to photon energy from solar irradiation. In general, semiconducting nanomaterials are suitable for good photocatalyst owing to narrow gap energy between the valence and conduction bands. Photocatalytic degradation of organic and inorganic pollutants is based on the application of semiconductor under UV or visible solar light system. A good semiconductor photocatalyst needs to be visible light photocactive, chemically as well as biologically inert, photostable, non-toxic and inexpensive. Though many semiconductor materials have been investigated for their photocatalytic activities, among them carbon quantum dot, graphic carbon nitride, metalloporphyrins photosensitizer are found to be attractive catalysts for the oxidation of organic and inorganic pollutants under solar visible light irradiation due to its narrow band gap energy. In addition, due to their quantum confinement effect, the CQDs nanomaterials possess size-dependent photoluminescence (PL) emission, high surface to volume ratio, ultra-small particle size, large absorption coefficient and sharper spectrum.

4.1. Graphitic carbon nitride.

Graphitic carbon nitride (g-C₃N₄) is a yellow colored metal-free polymeric layered material and belongs to p-type semiconductor. g-C₃N₄ is a stacked 2D layered structure bound by Van der Waals forces, where the single layer nitrogen heteroatom is substituted in the nanosheets of graphite, by forming sp² hybridization between C and N atoms [25]. In addition, due to its enormous electronic and optical properties along with consistent thermal and chemical stability in aqueous suspension and narrow band gap energy of ~2.7 eV, it acts as a very potential material for harvesting solar energy [26, 27]. The optical absorption of g-C₃N₄ lies around 460 nm. It is also an eco-friendly, biocompatible and non-toxic material. Further, the CB position of g-C₃N₄ is much more negative than those of conventional inorganic semiconductor which facilitates its photocatalytic activity. However, pure g-C₃N₄ has many limitations such as fast electron-hole pair recombination, low carrier mobility, low visible light absorption capacity, small specific surface area. Therefore, recently many researchers have attempted to synthesize modified g-C₃N₄ to produce different extremely tailorable hybrid photocatalysts with convenient size, pore structures, size distributions, compositions and morphologies by changing synthesis technology, manipulation of electronic structure and design of nanostructure [28]. For instance, synthesis of mesoporous structures, incorporation of suitable functional groups on the surface (amine-functionalized g-C₃N₄), metal (Au, Ag, Fe, Pd) and nonmetal (S, P, O, B, I, F,) species resulted in the production of potential photocatalyst system. Metal and non-metal doping as well as defects formation, promote narrowing of the band gap energy, minimization of the electron and hole pair recombination and creation of more active sites for target compounds. Recently, many novel nano structured g-C₃N₄ based photocatalysts, have been synthesized such as 1D nanorods, 2D nanosheets and 3D hierarchical structures [29].
4.1.1. Basic mechanism of heterogeneous photocatalyst.

The basic mechanism of heterogeneous photocatalysis involves seven key stages as shown in Figure 1. Photocatalysis reaction of semiconductor materials associated with seven important steps, which can be categorized into seven main classes: harvesting of light (stage 1); proper excitation of charge (stage 2); efficient charge separation and transfer, bulk charge recombination, surface charge recombination (stages 3, 4 and 5); surface reduction reactions and surface oxidation reactions (stages 6 and 7). Firstly, harvesting of light (stage 1) is governed by the structure and surface morphology of photocatalysts.

![Figure 1. Photocatalytic reactions on a semiconductor surface typical stages: (1) harvesting of light; (2) proper excitation of charge by photon energy; (3) separation of charge and its transfer; (4) bulk charge recombination; (5) charge recombination in surface; (6) occurance of reduction reactions at surface; (7) oxidation reactions at surface.](image)

The light harvesting capacity of a photocatalytic system can be improved by formation of the hierarchical macroporous or mesoporous architectures, owing to its multiple reflections and scattering effects. Therefore, the light harvesting capacity of g-C$_3$N$_4$ with flat and smooth surface of 2D structure is very poor. Secondly, proper charge excitation of the electron from valence band to conduction band of the heterogeneous semiconductor photocatalyst it ought to absorb photon energy in the visible/ultra violet wavelength range of solar light. The proper charge excitation is strongly correlated to the electronic structures of the semiconductor materials. In general, the electron in the VB jumps to its CB when photon energy of the incident light is higher than or equal to the band gap energy (E$_g$) of the semiconductor, creating a vacant (positive hole) in the VB. Therefore, in order to improve visible light harvesting capacity, the band gap of g-C$_3$N$_4$ ought to be further narrowed by metal and nonmetal doping, creating a defect in the structure as well as other possible sensitization strategies. i) Heterogeneous semiconductor photocatalyst with high absorption of visible light is having the foremost emphasis in research as 42 to 43% of sun light is under the visible light region (400-700 nm). Thirdly, recombination of photogenerated electron and hole pair in the bulk (stage 4) and on the surface (stage 5) of a photocatalytic materials is unfavorable to the separation and transfer of charge (stage 3) to surface/interface active sites, is considered as the crucial factor for evaluating the photocatalytic quantum efficiency of a semiconductor. The electron of the conduction band and the hole of the valence band of the photocatalytic system must diffuse from bulk of the semiconductor to its surface for effective degradation of contaminants present in wastewater. Generally rate of recombination can efficiently be reduced by constructing interfacial electric fields or minimizing the diffusion length of photogenerated charge carriers, as a result, the photocatalytic activity can be improved significantly [30,31,32]. In order to minimize the electron hole recombination, the electron needs to transfer from surface of the photocatalyst to desired reactants. Very often a co-catalyst and/or metal/non-metal doping is essential to facilitate surface charge transfer. Finally, the electrons and holes that transfer to the surface of the photocatalyst consequently entrapped by the surface active sites or co-catalysts, which facilitates the electro-catalytic reduction (stage 6) and oxidation (stage 7) of the reactants/pollutants adsorbed on the surface of the semiconductor. The photocatalytic redox reactions occur only when the oxidation and reduction potentials are more negative and positive than VB and CB levels, respectively [29]. For a good semiconductor catalyst, the redox potential of the photogenerated valence band hole should be adequately positive to produce 'OH radicals for degradation of toxic organic and inorganic pollutants. Similarly, the redox potential of the photo generated electron in the conductance band of the catalyst should be adequately negative which facilitates reduction of soluble oxygen to form superoxide radicals.

4.1.2. Design principle of g-C$_3$N$_4$.

Various techniques such as changing the structural dimension of g-C$_3$N$_4$ as well as by loading co-catalysts and nano carbons can enhance the pollutant photocatalytic degradation of the g-C$_3$N$_4$ photocatalyst. Defect control and band gap engineering is a promising tool to improve photocatalytic activity. Similarly, design of heterojunction photocatalyst creating Z-scheme, doping of metal and non-metal, application of photosensitizers have been extensively studied to enhance the photocatalytic degradation of organic pollutants. The g-C$_3$N$_4$ based photocatalytic degradation of various organic pollutants has also been extensively studied in degradation of various organic pollutants present in water and wastewater.

In pure g-C$_3$N$_4$ based metal-free photocatalyst material systems, the major active species associated with photodegradation of various pollutants are superoxide and hydroxyl radicals [29]. Zhang et al. [33] synthesized g-C$_3$N$_4$ nanosheets using hydrothermal method. They achieved enhanced degradation of nitrophenol compared to pristine g-C$_3$N$_4$ under illumination of visible light. Hu et al. [34] synthesized an oxygen functionalized g-C$_3$N$_4$ followed by doping with S and P by hydrothermal method. They achieved very high phenol degradation efficiency in anoxic conditions under visible light irradiation. The three-dimensional g-C$_3$N$_4$ composite material offers high specific surface area, porosity, facilitates adsorption of target pollutants; as a result improve the rate of pollutant photocatalytic degradation. Similarly Yu et al. [35] synthesized a direct TiO$_2$/g-C$_3$N$_4$ Z-scheme photocatalyst system without an
electron mediator. They reported a high photocatalytic decomposition of formaldehyde. Katsumata et al. [36] prepared WO\textsubscript{3}/g-C\textsubscript{3}N\textsubscript{4} heterojunction photocatalyst systems. They achieved 1.4 times higher photo degradation of acetaldehyde compared to pristine g-C\textsubscript{3}N\textsubscript{4}[36].

4.2. ZnO as a photocatalyst.

Among the various visible light active photocatalyst, ZnO is believed to be promising photocatalyst for degradation of various pollutants under solar visible light illumination condition. Zinc oxide is II – VI group photocatalytic semiconductors. Due to the presence of an oxygen vacancy defect, ZnO behaves as an n-type semiconductor. It has an alternating arrangement of zinc and oxygen atoms in the crystalline planes. In all crystalline structure of ZnO such as cubic zinc blende, hexagonal wurzite and rocksalt crystalline structure, the zinc and oxide centres are tetrahedral [37]. ZnO semiconductor exhibits extraordinary photochemical and physical behavior. It has a wide direct band gap of 3.2–3.37 eV and hence it exhibits near UV emission. It has a large exciton binding energy of 60 meV at room temperature. Moreover, electron in valence band of ZnO can be excited at room temperature under low excitation energy. Due to these unique properties, along with high quantum efficiency, affordable cost, non-toxicity, bio-safe and biocompatible nature, ZnO has been widely applied in the field of photocatalysis either alone or in the form of nanocomposite. ZnO can be used for the removal of various biological recalcitrant pollutants by heterogenous photocatalysis. ZnO possesses optical, electrical and piezoelectric properties.

4.2.1. Basic mechanism of ZnO photocatalyst.

Upon irradiation of solar light on the ZnO photocatalyst and when the photon energy (h\textnu) is equal to or greater than the excitation band gap energy (Eg), then the electron jumps (e\textsuperscript{-}) from the valence band (VB) to the conduction band (CB). Therefore, it generates a hole pair or vacancy in the valence band, consequently generates electron-hole (e\textsuperscript{-}/h\textsuperscript{+}) pairs. Then migration of electron-hole pairs to the ZnO surface occurs where they engaged in redox reactions. The h\textsuperscript{+} generated in the process interact with water molecule and hydroxide ions in the aqueous medium to generate hydroxyl radicals. Similarly, in the conduction band the e\textsuperscript{-} interacts with the dissolved oxygen present in the aqueous medium to make superoxide radical anions and finally generates hydrogen peroxide (Eq. (5)). Hydrogen peroxide produced in the photocatalytic process then react with superoxide radicals to produce hydroxyl radicals (Eqs. (7)–(9)). Therefore, in the photocatalytic process generation of strong oxidising agents such as hydroxyl radicals, superoxide radicals and hydrogen peroxide oxidizes the biological recalcitrant pollutants such as phenol adsorbed on the surface of ZnO to innocuous end product and finally CO\textsubscript{2}, H\textsubscript{2}O and mineral acids as given in (Eq. 11). Figure 2 demonstrates the redox reaction occurs in photocatalysis process for degradation of various organic pollutants. The detailed mechanism of photo degradation of organic pollutants such as phenol is given as follows:

\[
\text{ZnO} + h\nu \rightarrow \text{ZnO}(e\textsuperscript{-}(\text{CB})) + (h\textsuperscript{+}(\text{VB})) \tag{4}
\]

\[
\text{ZnO}(h\textsuperscript{+}(\text{VB})) + H_{2}O \rightarrow \text{ZnO} + H^{+} + \cdot OH \tag{5}
\]

\[
\text{ZnO}(h\textsuperscript{+}(\text{VB})) + OH^{-} \rightarrow \text{ZnO} + \cdot OH \tag{6}
\]

Further, the surface properties and photocatalytic activity can be enhanced by the immobilization of the catalyst onto supporting materials with a larger surface area. Since HAP offers a larger surface area, thus it facilitates more substrate involvement in photocatalytic reactions and consequently improves the mass transfer coefficient. In addition, the supporting material i.e., HAP prevents aggregation of photocatalyst in the aqueous medium. The supporting material should have a strong affinity, easy recognition and trapping of pollutants for its degradation. In addition, the supporting material should be transparent or semi-transparent for better penetration of UV and visible radiation through it. Hydroxyapatite (HAP) possesses most of the above mentioned properties and found to be a good supporting material for the catalyst, owing to its transparency and excellent adsorption properties for various pollutants in aqueous system [38, 39, 40]. Thus HAP has been employed as a potential and non-toxic electron donor for scavenging photogenerated holes. It also exhibits photocatalytic activity due to generation of superoxide radicals (O\textsuperscript{2-}) by changing the electronic state of the surface PO\textsubscript{4}\textsuperscript{3-} group under UV irradiation [41]. The hydroxyl groups of HAP plays a vital role in scavenging the photogenerated holes and consequently produces strong oxidizing hydroxyl radicals, thus the

\[
\text{ZnO}(e\textsuperscript{-}(\text{CB})) + O_{2} \rightarrow \text{ZnO} + O_{2}\textsuperscript{2-} \tag{7}
\]

\[
O_{2}\textsuperscript{2-} + H^{+} \rightarrow \text{HO}_{2}\textsuperscript{•} \tag{8}
\]

\[
2\text{HO}_{2}\textsuperscript{•} \rightarrow H_{2}O_{2} + O_{2} \tag{9}
\]

\[
\text{ZnO}(e\textsuperscript{-}(\text{CB})) + H_{2}O_{2} \rightarrow \cdot OH + \cdot OH \tag{10}
\]

\[
\text{H}_{2}O_{2} + O_{2}\textsuperscript{•} \rightarrow \cdot OH + \cdot OH + O_{2} \tag{11}
\]

\[
\text{H}_{2}O_{2} + h\nu \rightarrow 2\cdot OH \tag{12}
\]

\[
\text{Organic pollutants} + \cdot OH \rightarrow \text{Intermediates} \tag{13}
\]

\[
\text{Intermediates} \rightarrow \text{CO}_{2} + H_{2}O \tag{14}
\]

In order to reduce the rate of recombination of photoexcited electron-hole pairs, doping of metal and non-metals is highly essential. The transition metal doping (M\textsuperscript{2+}) helps to trap the photoinduced electrons and consequently inhibits the rate of recombination of electron-hole pairs in the photocatalytic system, and largely improves the photocatalytic activity and its stability. Further, in order to check the recombination of electron-hole pairs, application of hydroxyapatite (HAP) with the ZnO photocatalyst is very essential. Application of photosensitizer in photocatalytic system improves the visible light harvesting capacity as well as enhances the rate of formation of electron-hole pairs consequently drastically increases the rate of pollutant degradation.

4.3. Hydroxyapatite [Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}(OH)\textsubscript{2}].

In order to check the recombination of electron-hole pairs, application of hydroxyapatite (HAP) with the photocatalyst is an essential tool. The hydroxyl groups of HAP plays a vital role in scavenging the photogenerated holes and consequently produces hydroxyl radicals as follows:

\[
\cdot OH \text{(from HAP)} + h^{+} \rightarrow \cdot OH \text{(hydroxyl radical)} \tag{15}
\]
rate of photocatalytic degradation process or biological recalcitrant pollutant increases drastically. In addition, it prevents the anodic photocorrosion, which enhances the oxidation of different pollutants present in wastewater [42, 43, 44].

4.4. Metalloporphyrins as sensitiser.

4.4.1. Metal-tetracarboxyphenyl porphyrin (M-TCPP).

Application of photosensitizer in photocatalytic system improves the visible light harvesting capacity as well as enhances the rate of formation of electron-hole pairs as well as generating singlet oxygen consequently drastically increases the rate of pollutant degradation. Among the photosensitizer system, metalloporphyrins found to be the most superior photosensitizers owing to the presence of large π-electron systems, larger visible light absorption coefficient as well as excellent chemical stability in comparison with other dye sensitizers. The general chemical structure of metalloporphyrins is shown in Figure 2. In addition, application of metalloporphyrin system enhances the interfacial charge transfer as well as minimizes the recombination rate of the electron-hole pairs [45]. A details mechanism of metalloporphyrins photosensitiser (M-TCPP) based on Jablonski diagram is shown in Figure 3 given below.

![Figure 2. Structure of metal-tetracarboxyphenyl porphyrin (M-TCPP).](Image)

![Figure 3. Mechanism of metalloporphyrins photosensitiser (M-TCPP) based on Jablonski diagram.](Image)

A metalloporphyrin complex produces singlet oxygen or various superoxide radicals. Metalloporphyrin photosensitizers have high triplet state quantum yield as well as long triplet lifetimes, therefore, M-TCPP is known for degradation of pollutants as well as transformation of alkanes and alklenes. The efficiency of metalloporphyrins can be improved by changes in the central metal or axial ligands and change of the porphyrin ring. Upon exposure to solar radiation, the photosensitiser (PS) molecule is excited to the singlet state (\(^{1}\text{PS}^{*}\)) and then transforms to the triplet state (\(^{3}\text{PS}^{*}\)) through intersystem crossing (ISC). The triplet state (\(^{3}\text{PS}^{*}\)) transfers its energy to ground state oxygen (\(^{1}\text{O}_2\)) and finally produces excited singlet state oxygen (\(^{1}\text{O}_2^{*}\)), via type II mechanism. In the type II mechanism, the singlet oxygen generated.

\[
\text{PS} + h\nu \rightarrow ^{1}\text{PS}^{*} \rightarrow ^{3}\text{PS}^{*} \quad (16)
\]

\[
^3\text{PS}^{*} + ^3\text{O}_2 \rightarrow ^1\text{PS}^* + ^1\text{O}_2 \quad (17)
\]

\[
^1\text{O}_2 + \text{substrate} \rightarrow \text{Oxidation of substrate} \quad (18)
\]

Sometimes the interaction between substrate molecules or ground-state molecular oxygen with the excited triplet state (\(^{3}\text{PS}^{*}\)) generates few strong oxidising agents such as: superoxide and hydroperoxyl radicals, which consequently oxidizes target pollutants into innocuous end products by type I mechanism.

\[
^3\text{PS}^{*} + ^3\text{O}_2 \rightarrow ^{3}\text{PS}^{*} + ^3\text{O}_2 \quad (19)
\]

\[
^3\text{PS}^{*} + \text{substrate} \rightarrow ^{3}\text{PS}^{*} + \text{substrate}^{*+} \quad (20)
\]

\[
^3\text{PS}^{*} + ^3\text{O}_2 \rightarrow ^3\text{PS}^{*} + ^1\text{O}_2 \quad (21)
\]

\[
O^{*+} + H_2O \rightarrow \text{OH} + \text{HO}_2 \quad (22)
\]

\[
\text{ZHO}^{*} \rightarrow ^1\text{O}_2 + H_2O_2 \quad (23)
\]

\[
H_2O_2+^1\text{O}_2 \rightarrow \cdot \text{OH} + \cdot \text{OH} + O_2 \quad (24)
\]

Both type I and type II oxidation processes may occur concurrently. Though type I and type II oxidation processes occurs simultaneously, but type II mechanism is more ubiquitous in photosensitized reactions.

4.5.1. Carbon quantum dots (CQDs).

Carbon quantum dots (CQDs) are distinct quasi-spherical and discrete amorphous nanoparticle with a size less than 10 nm and made of carbonic materials. In general, CQDs comprises a graphitic sp\(^2\) core hybridized with sp\(^3\) carbons atoms and demonstrate excellent electron transfer and reservoir properties [46]. Further, as a conjugated π materials, the CQDs can stimulate faster separation and transfer of photogenerated electron and hole pairs leading to significantly improved photocatalytic activities [47]. CQDs possess different functional groups such as C-O-C, C=O, C=O, O=C-OH, etc. [48]. Due to the existence of these functional groups, particularly carboxyl moiety, the aqueous solubility of the CQD is very high. Furthermore, the presence of hydroxyl, carbonyl, epoxy and amino functional groups on the surface of CQDs facilitates the quantum dot to interact with several inorganic, organic, polymeric or biological materials leading to enhanced adsorption, surface passivation and facile surface modification of CQD. Moreover, due to the quantum confinement effect with high facile surface modification ability, the CQDs exhibit tremendous tunable electrical and photoluminescence (PL) properties [49,50,51]. Further, the presence of higher visible light harvesting ability and resistance to photobleaching properties, the CQDs are highly popular in photocatalysis, photoluminescence and electrocatalysis applications. In addition, CQDs possess several unique properties such as fine particle size, abundant surface functional groups, chemical stability, tunable photoluminescence behaviour, excellent electron-reservoir and electron-transfer properties, upconversion ability,
low cost, low toxicity and biocompatibility, CQDs believed to be the potential candidate in the field of green photocatalytic activities [52,53]. In general CQDs are synthesized employing electrochemical, microwave, hydrothermal, carbonization and oxidation methods. The synthesis process of CQDs uses the eco-friendly and cost-effective precursors such as candle soot, lamblack, citric acid, glucose, starch, papaya, grass, watermelon peels, chitosan, chitin, cashew gum, potato, dextrin, rice flour, etc. [54, 55]. These green synthesis processes are extremely suitable as compared to toxic chemical methods.

4.5.2. Major roles of carbon quantum dots (CQDs) in photocatalytic degradation of biological recalcitrant pollutants.

4.5.2.1. Electron mediator: CQDs possess an immense electron storage capacity [56]. Upon irradiation of UV light CQDs work as an electron reservoir by capturing electrons released from the conduction band of the narrow band gap photocatalyst, therefore, it prevents recombination of electron and hole pairs. Further, doping of heteroatoms like sulfur in CQDs, improves its electron transfer capability. Similarly, doping of nitrogen in CQDs stimulates delocalization of photogenerated charge carrier and decreases the work function of carbon, consequently improving photoluminescence properties. In addition, the recombination of charge carriers slows down due to the shuttle and displacement of the photo-excited electrons in the CQD network. Therefore, photocatalyst and CQDs heterojunction nanocomposite prove to be a potential candidate for degradation of organic pollutant from contaminated wastewater.

4.5.2.2. Photosensitizer: CQDs exhibits excellent optical absorption capacity both in the visible as well as ultraviolet region. In order to enhance the photocatalytic degradation activity of the wide-bandgap semiconductors under visible light, CQDs can work as a photosensitizer [57]. Also, CQDs harness photon energy from visible light sources which form the charge carriers on their surface and assist the photocatalytic process. Therefore, CQDs is found to be a suitable alternative and can substitute toxic conventional photosensitizers such as organic dyes, noble metals and metal sulphides [58].

4.5.2.3. Spectral converter: In CQD-based hybrid photocatalysts system, CQDs act as spectral converter owing to its up-conversion photoluminescence properties, which absorbs lower energetic infrared or visible light and releases shorter wavelength or higher energy light via up-conversion photoluminescence phenomenon (UCPL), consequently, drastically promote the photocatalyst activities to generates electron and hole pairs and utilizes the full spectrum of sunlight [59,57]. Miao et al. [60] investigated the coupling of CQDs with semiconductors such as g-C3N4, TiO2 and ZnO as a light absorber. They reported that hybrid photocatalytic system can absorb longer-wavelength and multi-photon visible light efficiently and eventually discharges shorter wavelength high energetic ultraviolet light [61,62]. This phenomenon happens due to the quantum confinement effect of different sizes of CQD or/and different states of emissive trap on the CQD surface [63]. This phenomenon facilitates the excitation of more charge carriers and improves the efficiency of the photocatalytic process [64, 65].

4.5.2.4. Sole photocatalyst: There are several reported literature that, CQDs also acts as direct photocatalyst for photocatalytic degradation and hydrogen evolution [66,67]. Further, the presence of CQDs increases the pollutants sorption capacity onto the surface of photocatalyst.

4.5.3. CQDs modified wide band gap photocatalysts.

The modification of wide band gap photocatalysts like ZnO, TiO2, BiOBr with CQDs significantly increases the photocatalytic activity due to several reasons i.e., i) minimizes electron and hole pairs recombination, ii) exhibits up-conversion photoluminescence activities iii) acts as photosensitiser for the wide band semiconductor materials [68]. Further, doping of sulfur and nitrogen into CQDs, improves the electron transfer capability of CQDs. Presence of different functional group on the surface of the CQDs facilitates facile tuning of CQDs and thus, greatly influences its photocatalytic performance. For instance, the band-bending effect of CQDs increases by the formation of intramolecular hydrogen bonds between oxygen-containing groups on the CQDs, therefore, it improves the separation of photoinduced charge carriers as well as its stability. Ali et al. [69] investigated the photocatalytic degradation of 4-chlorophenol using P25/CQDs photocatalyst system under visible light irradiation. They achieved superior 4-chlorophenol degradation efficiency by the P25/CQDs nano-composite as compared to that of bare P25 photocatalyst. They also reported that ‘OH radical are the predominant species associated in degradation of phenolic compounds. Ji et al. [70] synthesized a CQDs modified BiOBr nanocomposite photocatalyst system by hydrothermal method for degradation of tetracycline (TC) and Bisphenol A (BPA). They obtained 73% of BPA degradation in 150 min under irradiation of visible light, which is better than that of bare BiOBr. The improved photocatalytic activities are due to the synergetic effect between BiOBr and CQDs. Di and co-workers, [71] prepared CQDs modified Bi2WO6 nano composites by the hydrothermal method for degradation of tetracycline hydrochloride (TC), bisphenol A (BPA) and ciprofloxacin (CIP). In this study, a superior photocatalytic degradation activity was obtained by the CQDs/Bi2WO6 nanocomposite compared to that of bare Bi2WO6 photocatalyst for degradation of TC and BPA. The higher degradation activities obtained by CQDs/Bi2WO6 nanocomposite might be due to the faster transfer of the photogenerated electrons from conduction band of the Bi2WO6 catalyst to CQDs as well as its electron reservoir properties. Similarly, incorporation of CQDs into the photocatalyst enhances separation of e−–h+ pairs and its up-conversion properties improve the efficiency of BPA degradation. Shen et al. [72] synthesized CQDs modified TiO2 nanocomposite by hydrothermal methods, they employed glucose (G) and citric acid (CA) as the precursors for CQDs. They observed CQDs modified G/TiO2 photocatalyst system showed superior phenol degradation efficiency under UV light irradiation as compared to CQDs modified CA/TiO2 photocatalytic system. They also reported that, the absorption of phenol on the surface of CQDs/TiO2 photocatalyst is mediated by the existence of the π-π interaction of CQDs and phenol. Further, the superior phenol degradation efficiency is due to the application of CQDs which act as reservoirs of electron as well as entrap the photogenerated electrons from the conduction band of TiO2. Therefore, application of CQDs enhances photogenerated electrons and hole pairs’ separation, as a result, photocatalytic activity is found to be accelerated [72].
4.5.4. CQDs modified heterojunction photocatalysts.

A CQD modified BiOCl/BiOBr heterojunction was synthesized by Solvothermal method [73]. The results revealed that degradation efficiency of tetracycline hydrochloride, ciprofloxacin (CIP) and bisphenol A (BPA) were 2.1, 2.8 and 3.0 times higher than that of bare BiOCl/BiOBr, BiOBr, BiOCl photocatalyst respectively under irradiation of visible light. A Z-scheme N-CQDs modified Bi2O3 heterojunction was prepared and its phenol degradation ability has been evaluated [74]. They achieved 96.8% phenol degradation within 120 min by the nanocomposite under visible light illumination. The superior photocatalytic activity of the nanocomposite is attributed due to the improved light harvesting capacity and formation of Z-scheme heterojunction between Bi2O3 and CQDs. Zhang et al. [75] synthesized a CQDs/Ag/Bi2O3CO3 heterojunction and its Bisphenol A (BPA) degradation ability was evaluated. They reported 54.88% of BPA degradation using the CQDs/Ag/Bi2O3CO3 nanocomposite under illumination of visible light. A CQDs modified Bi/BiOCl/TiO2 heterojunction was prepared using solvothermal process, afterwards a hydrothermal method and its p-nitrophenol degradation efficiency were evaluated [76]. About 82% of PNP degradation was obtained within 240 min by CQDs/Bi/BiOCl/TiO2 nanocomposite, which is 10.3 times higher as compared to bare BiOCl/TiO2. The improved photocatalytic activities are ascribed due to the fact that Bi co-catalyst and CQDs act as electron donors, on the other hand BiOCl and TiO2 serve as electron trappers, consequently enhances the separation of photogenerated electron and hole pairs. In addition, the electron reservoir and up-conversion nature of CQDs along with surface plasmon resonance effect of Bi co-catalyst serve a vital role in the improvement of photocatalytic activities of hetero-junction nanocomposite.

4.5.5. Doping in quantum dots.

Band gap and the $e^-h^+$ recombination is widely known as a major short coming, which draws mounting attention. The narrowing of band gap and slowdown of $e^-h^+$ recombination rates can be improved by metal or non-metal doping which serve as electron sink thereby producing a reducing site on the photocatalyst to diminish electron-hole recombination [77]. The transition metal doping (M2+) helps to trap the photoinduced electrons and consequently inhibits the rate of recombination of electron–hole pairs in the photocatalytic system, and largely improves the photocatalytic activity and its stability. Doping in Qdots plays a pivotal role when CQDs are employed in different technological applications. These impurities are known as activators which perturb the band structures by generating a local quantum state that lies within the band gaps of the semiconductor. Due to quantum confinement, the dopants used in CQDs are auto-ionized without thermal activation. Auto ionization occurs when the band-gap energy increases with the decreasing size of Qdots (quantum confinement energy surpass Columbic interaction between hole or electron of the carrier (impurity p-type and n-type)). Numerous transition elements such as Cr, Fe, Mn, Co, and Ag, Cu and other elements like P, S, B, N, Li and Na have been doped in Qdots for application in different fields. The optical and electrical properties of Qdots can be improved by changing the quantity as well as positions of the dopants in the Qdots.

4.6. General proposed mechanism of phenol degradation.

The •OH radical generated during the photocatalytic reaction attacks and oxidizes the phenyl ring of the phenol, as a result, the phenol is converted to catechol and hydroquinone followed by disintegration of the phenyl rings which produces p-benzoquinone. A schematic representation of photocatalytic degradation of phenol is shown in Figure 4.

Due to the sequential oxidation reaction by the free radicals generated during the photocatalytic process, different short-chain organic acids are generated, for instance, fumaric, maleic, succinic and oxalic acids and consequently converted to CO2 and H2O. H+ generated during the free radical attack of H bonds of phenyl ring by •OH is considered as a vital active free radical in the photo degradation process. During this process, oxygen scavenges the H+ or H+ to form HO2• radicals, which finally transfer to ‘OH radicals. Thus, •OH radicals play a vital role in degradation of organic pollutants from contaminated environment.

4.7. Phenolic compounds in photocatalytic medium.

Phenolic derivatives such as cresol, chlorophenol, bromophenol and nitrophenol are highly soluble in water. The solubility of the phenolic compounds is shown in Table 2 below. During the photocatalytic degradation of phenolic compounds, the hydroxyl radicals attack the carbon of the aromatic ring which generates different oxidative intermediates products such as hydroquinone, catechol, and p-benzoquinone and so on.

| Compound | Solubility(gml⁻¹) |
|-----------|-----------------|
| Phenol    | 94.8            |
| m-chlorophenol | 22.5          |
| o-chlorophenol | 20.4          |
| p-chlorophenol | 27.7          |
| m-nitrophenol | 21.9          |
| o- nitrophenol | 21.0          |
| p- nitrophenol | 13.4          |

The secondary intermediate products generate during the photocatalytic degradation of phenolic compounds particularly
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chboro-hydroquinone, resorcinol and 4-chlorocatechol are ultimately converted to maleic acid, oxalic acid, carbon dioxide and water.

4.8. Recovery and recycling of the photocatalysts.

It is very difficult to recover and recycle powder homogeneous photocatalyst system after treatment of the wastewater in large scale applications. This is a very time consuming and expensive process. Further, it decreases the penetration of solar light in the aqueous system with depth. Thus, it is very essential to immobilize the catalyst system with a highly porous transparent and inert supporting material [78]. In literature, several carriers for immobilization of photocatalyst system have been reported for example: silicon, titanium sheets, glass, ceramics, porous adsorbent, clay and different polymer. Immobilization of nanocomposite onto the polyurethane foam (PUF) is found to be a suitable highly efficient carrier material owing to its high stability, porous structure and low cost. Very less work has been done by employing polyurethane foam (PUF) sponge as carrier material for photocatalytic system. Zhang et al., [79] reported a very good tetracycline hydrochloride degradation performance by immobilizing Bi$_2$WO$_6$ photocatalyst on to PUF.

5. FUTURE PROSPECTS

In order to improve the photocatalytic activity of the non-metal carbon based photocatalytic system further, investigations should be carried out on these strategies such as dimensionality tuning, construction of Z-scheme and texture tailoring. The surface of the CQDs needs to suitable modified with different functional groups, which may form covalent bond with different surfaces of filters or membranes and hence facilitates for its easy separation and recycle. Further design and development of magnetic nanocomposites photocatalysts can be an alternate solution.

6. CONCLUSIONS

The eco-friendly metal-free carbon-based g-C$_3$N$_4$ photocatalyst system reveals promising results for its versatile applications. The efficiency of g-C$_3$N$_4$ photocatalytic system can be further improved by implementing different design strategies, like; dimensionality tuning, pore texture tailoring, Z-scheme construction, co-catalyst, carbon quantum dot loading, incorporation of photosensitizer and carrier supporting material. Designing and development of environmentally friendly non-toxic heterojunctions photocatalytic system by using g-C$_3$N$_4$ with CQDs and ZnO, particularly in Z-scheme format are known to be a promising alternative to enhance its photocatalytic activities. The major motivations for enhancement of CQDs coupled g-C$_3$N$_4$ photocatalytic activities are due to facilitate modification capacity, up-conversion ability, high resistance to photo-bleaching, electron reservoir ability of the CQDs. In addition, presence of the conjugated π structure in CQDs enables the adsorption of pollutants on its surface. The electron transfer ability of CQDs can be further enhanced by doping with sulfur. Similarly, doping of nitrogen on to CQDs stimulates delocalization of charge as well as decreases the work function of carbon consequently improves the photoluminescence properties. Similarly, incorporation of photosensitiser into the wide band photocatalysts such as ZnO enhances visible light harvesting capacity. By immobilizing the photocatalytic system with supporting carrier materials like HAP overcomes severe shortcomings like aggregation of nanomaterials in aqueous medium, hole scavenging and photobleaching. Since g-C$_3$N$_4$- CQDs photocatalytic systems are non-toxic, eco-friendly in nature and cost effective with tunable physicochemical characteristics, they are known to be a promising candidate and a very good alternative to address several environmental pollution issues.

5. REFERENCES

1. Jordan, W.; van Barneveld, H.; Gerlich, O.; Kleine-Boymann, M.; Ullrich, J. Phenol. In:Ullmann’s Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag. 2002.
2. Busca, G.; Berardinelli, S.; Resini, C.; Arrighi, L. Review-Technologies for the removal of phenol from fluid streams: A short review of recent developments. J. Hazard. Mater. 2008, 160, 265–288, https://doi.org/10.1016/j.jhazmat.2008.03.045.
3. Pal, P.; Kumar, R. Treatment of coke wastewater: A critical review for developing sustainable management strategies. Sep. Purif. Rev. 2014, 43, 89–123, https://doi.org/10.1080/15422119.2012.717161.
4. Arques, A.; Amat, A. M.; Garcia-Ripoll, A.; Vicente, R. Detoxification and/or increase of the biodegradability of aqueous solutions of dimethoate by means of solar photocatalysis. Journal of Hazardous Materials, 2007, 146, 447-452, https://doi.org/10.1016/j.jhazmat.2007.04.046.
5. ITOPF. Technical Information Paper (TIP 17): Response to marine chemical incidents. The international tanker owner’s pollution federation, available from: http://www.itopf.com/knowledge-resources/documents-guides/document/tip-17-response-to-marine-chemical-incidents 2011.
6. Ahmed, S.; Rasul, M. G.; Martens, W. N.; Brown, R.; Hashib, M. A. Heterogeneous photocatalytic degradation of phenols in wastewater: A review on current status and developments Desalination 2010, 261, 3–18, https://doi.org/10.1016/j.desal.2010.04.062.
7. Zangeneh, H.; Zinatizadeh, A. A. L.; Habibi, M.; Akia, M.; Hasnain Isa, M. Photocatalytic oxidation of organic dyes and pollutants in wastewater using different modified titanium oxides: A comparative review. J. Ind. Eng. Chem. 2015, 26, 1–36, https://doi.org/10.1016/j.jiec.2014.10.043.
8. Hansch, C.; Mccarns, S.; Smith, C.; Dodittle, D.; Comparative QSAR evidence for a free-radical mechanism of phenol-induced toxicity. Chem. Biol. Interact. 2000, 127, 61-72, https://doi.org/10.1016/S0009-2797(00)00171-X.
9. Boyd, E.; Killham, K.; Metharg, A. Toxicity of mono-, di- and tri-chlorophenols to lux marked terrestrial bacteria Burkholderia species Rasc C2 and Pseudomonas fluorescens. Chemosphere 2001, 43, 157-66, https://doi.org/10.1016/S0045-6535(00)00266-6.
10. Escher, B. T.; Snozzi, M.; Schwarzenbach, R. P. Uptake, speciation, and uncoupling activity of substituted phenols in...
energy transducing membranes. *Environ. Sci. Technol.* 1996, 30, 3071-3079, https://doi.org/10.1021/es960153f.

11. Copley, S. Diverse mechanistic approaches to difficult chemical transformations: microbial dehalogenation of chlorinated aromatic compounds. *Chem. Biol.* 1997, 4, 169-174, https://doi.org/10.1016/S1074-5521(97)90285-4.

12. Ubersoi, V.; Bhattacharya, S. K. Toxicity and degradability of nitrophenols in anaerobic systems. *Water Environ. Res.* 1997, 69, 146–54, https://doi.org/10.2175/10643097X125290.

13. Michalowicz, J.; Duda, W. Phenols Sources and Toxicity. *J. Environ. Stud.* 2007, 16, 347-362.

14. Wang, Y. H.; Chan, K. Y.; Li, X. Y.; So, S. K. Electrochemical degradation of 4-chlorophenol at nickel–antimony doped tin oxide electrode. *Chemosphere* 2006, 65, 1087–1093, https://doi.org/10.1016/j.chemosphere.2006.04.061.

15. Barros, L. M.; Macedo, G. R.; Duarte, M. M. L.; Silva, E. P.; Lobato, A. K. C. L. Biosorption of cadmium using the fungus *Aspergillus niger*. *Brazilian Journal of Chemical Engineering* 2003, 20, 229-239, http://dx.doi.org/10.1590/S0104-66322003000300003.

16. Rokhina, E. V.; Virkutyte, J. Advanced catalytic oxidation of emerging micropolutants. In: Treatment of Micropollutants in Water and Wastewater. *Integrated Environmental Technology Series*. Virkutyte, J., Varma, R.S., Jagatheesan, V. (Eds.), IWA Publishing, London, 2010; pp. 360–424.

17. Brosseus, R.; Vincent, S.; Aboulfaïl, K.; Daneshvar, A.; Sauve, S.; Barbeau, B.; Prevost, M. Oxide oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment. *Water Research* 2009, 43, 4707–4717, https://doi.org/10.1016/j.watres.2009.07.031.

18. Ning, B.; Graham, N.; Zhang, Y.; Nakonechny, M.; El-Din, M. G. Degradation of endocrine disrupting chemicals by ozone/AlOxPs. *Ozone Sci. Eng.* 2007, 29, 153–176, https://doi.org/10.1080/19319560701200012.

19. Nakada, N.; Shinohara, H.; Murata, A.; Kiri, K.; Managaki, S.; Sato, N.; Takada, H. Removal of selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant. *Water Res.* 2007, 41, 4373–4382, https://doi.org/10.1016/j.watres.2007.06.038.

20. Fernando, J.; Beltrán, F.; Rivas, J.; Gimeno, O. Comparison between photocatalytic ozonation and other oxidation processes for the removal of phenols from water. *J. Chem. Technol. Biotechnol.* 2005, 80, 973–984, https://doi.org/10.1002/jctb.1272.

21. Salokannel, A.; Heikkinen, J.; Kumpulainen, M.; Sillanpä, M.; Turunen, J. Tertiary treatment of pulp and paper mill wastewaters by ozonation and O3/H2O2. *Paper Timber* 2007, 89, 348–351.

22. Hamdaoui, Q.; Naffrechoux, E. Sonochemical and photosonochemical degradation of 4-chlorophenol in aqueous media. *Ultrasound. Sonochem.* 2008, 15, 981–987, https://doi.org/10.1016/j.ulsonch.2008.03.011.

23. Kwon, S. H.; Kim, J. H.; Cho, D. An analysis method for degradation kinetics of lowly concentrated PAH solutions under UV light and ultrasonication. *J. Ind. Eng. Chem.* 2009, 15, 157–162, https://doi.org/10.1016/j.jiec.2008.09.018.

24. Mohapatra, D. P.; Brar, S. K.; Tyagi, R. D.; Surampalli, R. Y. Concomitant degradation of bisphenol A during ultrasonication and Fenton oxidation and production of biofertilizer from wastewater sludge. *Ultrasound. sonochem.* 2011, 18, 1018–1027, https://doi.org/10.1016/j.ulsonch.2011.03.013.

25. Gong, Y.; Li, M.; Wang, Y. Carbon nitride in energy conversion and storage: recent advances and future prospects. *Chem. Sustain. Chem.* 2015, 8, 931–946, https://doi.org/10.1002/cssc.201403287.
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42. Nishikawa, H. A high active type of hydroxyapatite for photocatalytic decomposition of dimethyl sulfide under UV irradiation. J. Mol. Catal. A: Chem. 2004, 207, 149–153, https://doi.org/10.1016/S1381-1169(03)00472-2.

43. Anmin, H. L.; Tong, L.; Ming, C.; Chengkang, L.; Huiqin, L.; Dali. M. Preparation of Nanocrystals Hydroxyapatite/TiO2 Compound by Hydrothermal Treatment. Applied Catalysis B: Environmental 2006, 63, 41-44, https://doi.org/10.1016/j.apcata.2005.08.003.

44. Reddy, M.; Venugopal, A.; Subrahmanyam, M. Hydroxyapatite photocatalytic degradation of calmagite (an azo dye) in aqueous suspension. Appl. Catal. B: Environ. 2007, 69, 164–170, https://doi.org/10.1016/j.apcatb.2006.07.003.

45. Yao, B.; Peng, C.; He, Y.; Zhang, W.; Zhang, Q.; Zhang, T. Conjugated microspheres FeTcCPP–TDI–TiO2 with enhanced photocatalytic performance for antibiotics degradation under visible light irradiation. Catal. Lett. 2016, 146, 2553–2554, https://doi.org/10.1007/s10562-016-1888-1.

46. Di, J.; Xia, J.; Ji, M.; Wang, B.; Li, X.; Zhang, Q.; Chen, Z.; Li, H. Nitrogen-doped carbon quantum dots/BiOBr ultrathin nanosheets: In Situ strong coupling and improved molecular oxygen activation ability under visible light irradiation. ACS Sustain. Chem. Eng. 2015, 3, 136–146, https://doi.org/10.1021/acssuschemeng.5b00862.

47. Wang, Y.; Shi, R.; Lin, J.; Zhu, Y. Enhancement of photocurrent and photocatalytic activity of ZnO hybridized with graphite-like C3N4. Energy Environ. Sci. 2011, 4, 2922–2929, https://doi.org/10.1039/C0EE00825G.

48. Zuo, P.; Lu, X.; Sun, Z.; Guo, Y.; He, H. A review on syntheses, properties, characterization and bioanalytical applications of fluorescent carbon dots. Microchimica Acta, 2016, 183, 519-542, https://doi.org/10.1007/s00604-015-1705-3.

49. Barman, M.K.; Patra, A. Current status and prospects on chemical structure driven photoluminescence behaviour of carbon dots. Journal of Photochemistry and Photobiology C 2018, 37, 1-22, https://doi.org/10.1016/j.jphotochemrev.2018.08.001.

50. Lim, S. Y.; Shen, W.; Gao, Z. Carbon quantum dots and their applications. Chem. Society Review 2015, 44, 362–381, https://doi.org/10.1039/C4CS00269E.

51. Namdari, P.; Negahdari, B.; Eatemadi, A. Synthesis, properties and biomedical applications of carbon-based quantum dots: an updated review. Biomedical. Pharmacoche. 2017, 87, 209-222, https://doi.org/10.1016/j.biopha.2016.12.108.

52. Guo, Y.; Zhang, J.; Zhou, D.; Dong, S. Fabrication of Ag/CDots/BiOBr ternary photocatalyst with enhanced visible-light driven photocatalytic activity for 4-chlorophenol degradation. J. mol. liq. 2018, 262, 194-203, https://doi.org/10.1016/j.molliq.2018.04.091.

53. Yang, Z. C.; Wang, M.; Yong, A. M.; Wong, S. Y.; Zhang, X. H.; Tan, H.; Chang, A. Y.; Li, X.; Wang, J. Intrinsically fluorescent carbon dots with tunable emission derived from hydrothermal treatment of glucose in the presence of monopotassium phosphate. Chem. Comm. 2011, 47, 11615–11617, https://doi.org/10.1039/C1CC14860E.

54. Liu, R.; Huang, H.; Li, H.; Liu, Y.; Zhong, J.; Li, Y.; Zhang, S.; Kang, Z. Metal nanoparticle/carbon quantum dot composite as a photocatalyst for high-efficiency cyclohexane oxidation. ACS Catal. 2013a, 4, 328-336, https://doi.org/10.1021/cs400913h.

55. Chen, B.; Li, F.; Li, S.; Weng, W.; Guo, H.; Guo, T.; Zhang, X.; Chen, Y.; Huang, T.; Hong, X.; You, S. Large scale synthesis of photoluminescent carbon nanodots and their application for bioimaging. Nanoscale 2013, 5, 1967-1971, https://doi.org/10.1039/C2NR32675B.

56. Zhang, L. W.; Fu, H. B.; Zhu, Y. F. Efficient TiO2 photocatalysts from surface hybridization of TiO2 particles with graphite like carbon. Adv. Funct. Mater. 2008, 18, 2180–2189, https://doi.org/10.1002/adfm.200701478.

57. Yu, X.; Liu, J.; Yu, Y.; Zuo, S.; Li, B. Preparation and visible light photocatalytic activity of carbon quantum dots/TiO2 nanosheet composites. Carbon 2014, 68, 718–724, https://doi.org/10.1016/j.carbon.2013.11.053.

58. Deifallah, M.; McMillan, P. F.; Furio, C. Electronic and Structural Properties of Two-Dimensional Carbon Nitride Graphenes, TheJ. Phys. Chem. C. 2008,112, 5447-5453, https://doi.org/10.1021/jp711483t.

59. Ming, H.; Ma, Z.; Liu, Y.; Pan, K.; Yu, H.; Wang, F.; Kang, Z. Large scale electrochemical synthesis of high quality carbon nanodots and their photocatalytic property. Dalton Transaction 2012, 41, 9526–9531, https://doi.org/10.1039/C2DT30985H.

60. Miao, X.; Ji, Z.; Wu, J.; Shen, X.; Wang, J.; Kong, L.; Liu, M.; Song, C. gCiNs/AgBr nanocomposite decorated with carbon dots as a highly efficient visible-light-driven photocatalyst. J. Col. Inter. Sci. 2017, 502, 24–32, https://doi.org/10.1016/j.jcis.2017.04.087.

61. Cao, L.; Wang, X.; Meziani, M. J.; Lu, F.; Wang, H.; Luo, P. G. Y.; Lin, B. A.; Harruff, L. M.; Veca, D.; Murra, S. Y. et al. Carbon dots for multiphoton bioimaging. J. A. C. S. 2007, 129, 11318–11319, https://doi.org/10.1021/ja073527i.

62. Jia, X.; Li, J.; Wang, E. One-pot green synthesis of optically pH-sensitive carbon dots with upconversion luminescence. Nanoscale 2012, 4, 5572–5575, https://doi.org/10.1039/C2NR31319G.

63. Wang, Y.; Hu, A. Carbon quantum dots: synthesis, properties and applications. J. Mater. Chem. C. 2014, 2, 6921–6939, https://doi.org/10.1039/C4TC00988E.

64. Zhu, S.; Meng, Q.; Wang, L.; Zhang, J.; Song, Y.; Jin, H.; Zhang, K.; Sun, H.; Wang, H.; Yang, B. Highly photoluminescent carbon dots for multicolor patterning, sensors, and bioimaging. Angew. Chem. 2013, 125, 4045-4049, https://doi.org/10.1002/anie.201300519.

65. Bajorowicz, B.; Kobyląski, M. P.; Goląbiewska, A.; Nadolna, J.; Zaleska-Medynska, A.; Malankowska, A. Quantum dot-decorated semiconductor micro-and nanoparticles: A review of their synthesis, characterization and application in photocatalysis. Adv. Colloid Interface Sci. 2018, 256, 352-372, https://doi.org/10.1016/j.cis.2018.02.003.

66. Yang, P.; Zhao, J.; Wang, J.; Cui, H.; Li, L.; Zhu, Z. Pure carbon nanodots for excellent photocatalytic hydrogen generation. RSC Adv. 2015, 5, 21332–21335, https://doi.org/10.1039/C5RA01924A.

67. Ma, Z.; Ming, H.; Huang, H.; Liu, Y.; Kang, Z. One-step ultrasonic synthesis of fluorescent N-doped carbon dots from glucose and their visible-light sensitive photocatalytic ability. New J. Chem. 2012, 36, 861–864, https://doi.org/10.1039/C2NJ0042J.

68. Wang, P.; Li, X.; Fang, J.; Li, D.; Chen, J.; Zhang, X.; Shao, Y.; He, Y. A facile synthesis of CdSe quantum dots-decorated anatase TiO2 with exposed {0 0 1} facets and its superior photocatalytic activity. Appl. Catal. B. 2016, 181, 838-847, https://doi.org/10.1016/j.apcatb.2015.08.046.

69. Ali, M. M.; Nair, J. A.; Sandhya, K. Y. Role of reactive oxygen species in the visible light photocatalytic mineralization of rhodamine B dye by P25–carbon dot photocatalyst. Dyes and Pigments 2019, 163, 274-284, https://doi.org/10.1016/j.dyepig.2018.11.057.
investigation. Chin. Chem. Let. 2018, 29, 805-810, https://doi.org/10.1016/j.cclet.2018.05.002.

71. Di, J.; Xia, J.; Ge, Y.; Li, H.; Ji, H.; Xu, H.; Zhang, Q.; Li, H.; Li, M. Novel visible-lightdriven CQDs/Bi₂WO₆ hybrid materials with enhanced photocatalytic activity toward organic pollutants degradation and mechanism insight. Appl. Catal. B, 2015, 168, 51-61, https://doi.org/10.1016/j.apcatb.2014.11.057.

72. Shen, T.; Wang, Q.; Guo, Z.; Kuang, J.; Cao, W. Hydrothermal synthesis of carbon quantum dots using different precursors and their combination with TiO₂ for enhanced photocatalytic activity. Ceramic Int. 2018, 44, 11828-11834, https://doi.org/10.1016/j.ceramint.2018.03.271.

73. Hu, Q.; Ji, M.; Di, J.; Wang, B.; Xia, J.; Zhao, Y.; Li, H. Ionic liquid-induced double regulation of carbon quantum dots modified bismuth oxychloride/bismuth oxybromide nanosheets with enhanced visible-light photocatalytic activity. J. Colloid. Interface Sci. 2018, 519, 263-272, https://doi.org/10.1016/j.jcis.2018.02.057.

74. Yue, X.; Miao, X.; Ji, Z.; Shen, X.; Zhou, H.; Kong, L.; Zhu, G.; Li, X.; Shah, S. A. Nitrogen doped carbon dots modified dibismuthtetraoxide microrods: A direct Z-scheme photocatalyst with excellent visible-light photocatalytic performance. J. Col. Interface Sci. 2018, 531, 473-482, https://doi.org/10.1016/j.jcis.2018.07.086.

75. Zhang, Z.; Liu, S.; Cui, W.; Li, X.; Li, H. Enhanced photocatalytic activity of Ag/CQDs/Bi₂O₂CO₃ composite photocatalyst under full-spectrum light. Mater. Let. 2019, 234, 264-268, https://doi.org/10.1016/j.matlet.2018.09.115.

76. Li, W.; Zhao, C.; Zhang, Q. Synthesis of Bi/BiOCl-TiO₂-CQDs quaternary photocatalyst with enhanced visible-light photoactivity and fast charge migration. Catal. Comm. 2018, 107, 74-77, https://doi.org/10.1016/j.catcom.2017.11.011.

77. Mishra, J.; Pattanayak, D. S.; Das, A. A.; Mishra, D. K.; Rath, D.; Sahoo, N. K. Enhanced photocatalytic degradation of cyanide employing Fe-porphyrin sensitizer with hydroxyapatite palladium doped TiO₂-nano-composite system. J. Mol. Liq. 2019, 287, 110821, https://doi.org/10.1016/j.molliq.2019.04.098.

78. Mahmoodi, M. N.; Mokhtari, A. Bulk phase degradation of Acid Red 14 by nanophotocatalysis using immobilized titanium (IV) oxide nanoparticle J. Photochem. Photobiol. A: Chem. 2006, 182, 60–66, https://doi.org/10.1016/j.jphotochem.2006.01.014.

79. Zhang, F.; Zhang, S.; Zou, S.; Zhong, S. Facile synthesis of sponge-loaded Bi₂WO₆ photocatalyst and degradation of tetracycline hydrochloride under visible light. J. Mater. Sci.: Electron 2016, 27, 12141–12147, https://doi.org/10.1007/s10854-016-5367-7.

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