Water Pollution, Big Problem: A Research

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Abstract: ***In recent times, presence of persistent organic pollutants (POPs) in waste water and rapid depletion in conformist energy sources have ascended as a major problematic threat not only to aquatic organisms but also have harmful effect on human's sustainable development. Discharge of volatile organic pollutants (outdoor and indoor air) causes serious health problems. As contact to various VOPs (volatile organic pollutants) such as aromatic/aliphatic hydrocarbons, alcohols, aldehydes, amines, etc. lead to many health problems like headache, giddiness, illness, eye/throat irritation, nausea, liver and nervous system damage, cancers as well as many breathing diseases.***

Keywords: persistent organic pollutants, photocatalysis, nanocomposites, phosphorous doping, heterojunction formation

1. Objectives of research

To enhance the photocatalytic performance of g-C_3N_4 based nanocomposites, several pivotal requirements have been considered such as need of light harvesting photocatalyst having narrow band gap for maximum solar energy absorption, increase in surface area, superior photogenerated electron hole pairs (EHP) separation and facilitating transportation process of charge carriers. Therefore there are many techniques which we can use to upgrade photocatalytic efficacy of g-C_3N_4. Doping of phosphorous in g-C_3N_4 improves photocatalytic efficacy of g-C_3N_4 *via* increasing surface area, reducing band gap and minimizing photogenerated charge carrier recombination. Heterojunction formation includes integration of g-C_3N_4 (with increased internal surface area) with other photocatalyst where g-C_3N_4 acts as appropriate host for other semiconductor. Nanocomposite photocatalyst enclose several advantages such as more light absorption: Semiconductors with narrow band gap have greater visible light absorptability to utilize and functionalize semiconductor photocatalyst with large band gaps; effective photogenerated EHP separation and transference using p–n junction (semiconductor/ semiconductor heterostructure). In view of that aim and objectives of the present study are precisely listed below:

1) To fabricate g-C_3N_4 and phosphorous doped g-C_3N_4 *via* thermal polymerization of nitrogen-rich precursors such as melamine and BmimPF_6 precursors.
2) To synthesize phosphorous doped g-C_3N_4/fullerene (C_{60}), phosphorous doped g-C_3N_4/CNT, phosphorous doped g-C_3N_4/graphene and phosphorous doped g-C_3N_4/graphitic oxide heterojunctions.
3) To characterize the as-synthesized nanocomposites materials using various techniques such as scanning electron microscope (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), fourier-transform infrared spectroscopy (FTIR) and energy-dispersive X-ray spectroscopy (EDX) analysis. UV-DRS, photoluminescence (PL), electrochemical impedance spectroscopy (EIS), BET isotherm, XPS, Raman analysis etc.
4) To evaluate of antibacterial activity for the removal of *Escherichia coli (E.coli)* bacteria using synthesized nanocomposites.

To eradicate imidacloprid and malathion pesticides from water using as synthesized nanomaterials and exploration of different reaction parameters such as effect of catalyst dosage, pH under light/dark conditions and kinetics of pesticide removal.

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Release of many detrimental pollutants, microorganisms, from pharmaceuticals activities, different industries as well as accumulation of sewage wastes into water resources have adverse effect on living organism's life Discharges of herbicides and pesticides from agricultural practices have affected the ecosystem owing to their persistence in environment, biodegradation resistance, chemical stability and high water solubility that pierce deep into ground water Pesticides are posing an excessive intimidation to environment as well as living organisms due to their extensive use, toxic nature, highly persistence and bioaccumulation. The pesticides are very tough to degrade by microorganisms as many of them are biological refractories and have potential toxicity to humans and other species. It is one of the extremely utilized pesticides on sunflower, corn, cotton, potato, sugar beets, rice, soy, rapeseed, fruits and ornamental plants all over the world and is efficient to kill those insects which are highly resistant to carbamates, organophosphates and pyrethroids2.

IMI is creating danger to all living organisms as a result of its extensive use, comparatively high solubility (0.58 g dm-3) and high persistence in surface waters .A survey has been conducted across multiple countries and it has been reported that IMI level in surface waters is 0.001-320 mg/L 3.

Malathion (S-1, 2-bis (ethoxicarbonyl) ethyl 0, 0-dimethylphosphorodithioate), a widely expended organophosphorus pesticide (OPP), is repeatedly squirted on citrus fruits (a vital agricultural product) to control mosquitoes, Mediterranean fruit flies Generally, nanograms (ng) to several micrograms (mg) per litre of malathion pesticide have been identified in polluted water)4, but 507 $\mu g\ L^{-1}$ is the supreme levels of malathion detected in the Babolrood River in Iran 5. The pesticide as a nerve poison, has caused serious neurological disease and has threatened wildlife animals and public health due to suppression of acetylcholinesterase (AChE) enzyme which is essential for nerve function in both insects and humans .Toxicological studies have stated cytotoxic and genotoxic effects of malathion on mammals and can cause DNA and chromosomal damage in human beings .The studies also stated that high chemical stability and high toxicity of malathion resists its biodegradation.

The human body is a household to a number of microbes. Many microorganisms are beneficial to living organisms and ecosystems however, some have hazardous effect resulting in several diseases. The category „microorganisms" contains a huge number of organisms comprising bacteria, viruses, protozoa, fungi, algae, archaea, etc. Extreme levels of *E. coli* in drinking water resources can cause severe disease (inflammation) and finally death. *Escherichia coli* as a waterborne pathogenic microorganism causes approx. 73,480 illnesses, 2,168 hospitalizations and 61 deaths every year in United States which have been reported previously .Adsorption is also considered as a facile approach for wastewater treatment but used absorbents are tough to be recycled for further reuse. 6 Another method i.e. chemical oxidation is capable to totally degrade organic pollutants into small molecules i.e. CO_2 and H_2O but in addition it may lead to production of secondary pollutants.7. Though pre-chlorination or disinfection methods have been described as an effective process for oxidizing pollutants but caused generation of secondary pollutants. For example, many reports stated that malathion during chlorination process was not completely mineralized or removed but was simply converted to malaoxon, more toxic molecular form, *via* replacement of sulphur atom with an oxygen atom in P=S bond in parent molecule and creating a P=O double bond in transformation product.8. Malaoxon is highly obstinate in chlorinated water and is 100 times more poisonous than malathion as well as it is more threatening to human health.

Since above-mentioned traditional drinking water treatment processes are ineffective to eliminate toxic pollutants from waste water as they are small in size and possess high water solubility. Therefore, several advanced treatment technologies have been considered in recent years. These remediation technologies include advanced oxidation processes (AOPs) Accordingly, production of natural photosynthesis systems to generate host materials for energy storage is a crucial goalmouth of present Chemistry. As a result, scientists have reached a consensus, in which the use of solar energy is one of the sustainable/green ways to address the above issues. In this perspective, advanced oxidation processes (AOP"s), a photocatalytic technique for eradication of harmful contaminants, has emerged rapidly and widely as an economic, efficient and environmental friendly technique.

AOP"s are classified into two main processes *i.e.* homogeneous and heterogeneous processes. The mostly used AOP"s are classified as:

Fenton reactions (Fenton (Fe^{2+}/H_2O_2), (v) photo-Fenton ($Fe^{2+}/H_2O_2/UV$), (ii) ozone and ozone-hybrid mechanism (O_3, O_3/UV, O_3/H_2O_2 and $O_3/H_2O_2/UV$), (iii) photocatalysis (TiO_2/UV and $TiO_2/H_2O_2/UV$) (iv) H_2O_2 with UV radiation (H_2O_2/UV) and (vi) sono-Fenton ($Fe^{2+}/H_2O_2/US$) (Mamba and Mishra, 2016; Abdollahi *et al.*, 2011). However these methods are highly effective in wastewater treatment but some of techniques possess drawbacks like need of sophisticated apparatus, ozone"s short half-life time, UV light absorption, partial removal of pollutants and these procedures requires high costs.). The photoexcited electrons are transmitted from photocatalysts to oxidants to produce reactive species (•OH, $•O_2^-$, $SO_4•^-$) which enhanced speedy immigration of electrons and thereby augmented photocatalytic removal of pollutants from waste water.

H_2O_2 is a green oxidant and a promising high-energy product which has been extensively used in numerous fields (Campos-Martin *et al.*, 2007; Kim e*t al.*, 2008). As an oxidizing agent it has notable applications in the area of organic synthesis, waste water treatment and photocatalytic processes etc. It can be employed for disinfecting injuries and surgical tools in biomedical area.9 (Wernimont *et al.*, 1999; Fukuzumi *et al.*, 2012). Additionally, it has been used as a rocket fuel, in fuel cells to produce electricity by forming H_2O and O_2 byproducts, in environmental remediation, chemical industry, paper bleaching, textile bleaching as well as detergents production

Since past few decades, multi-walled carbon nanotubes (MWCNTs) and single walled carbon nanotubes (SWCNTs) with π-conjugated structure have captivated attention of researchers owing to their amazing mechanical strength, electrical and optical properties, high specific surface area, outstanding chemical inertness and water transport property. CNTs can be used as bolstering for nanocomposite preparation, as constituents in nanoscale integrated circuits and as a support in photocatalytic processes (Eshkalak *et al.*, 2017). One dimensional cylindrical shape of CNTs exhibits some novel possessions which do not exist in bulk graphite like capability to act as a metal or semiconductor on the basis of tube chirality and diameter.

This section comprises fabrication of GCN, PCN and CNT/PCN nanocomposites (different ratio of CNT *i.e.* 0.01, 0.02, 0.03 wt %) and exploration of their photocatalytic activity against IMI pesticide degradation and *E.Coli* disinfection.PCN possessed enhanced photocatalytic activity for IMI degradation than GCN due to auspicious texture and optical properties. In CNT/PCN nanocomposites, CNT acted asa support material and sink to capture electrons from PCN. H_2O_2 was added in photodegradation processes to improved charge carriers separation and to enhance degradation. XRD, FT-IR, XPS and EDAX analysis confirmed structural and chemical composition of synthesized photocatalysts while FE-SEM, HR-TEM analysis confirms the deposition of CNT nanoparticles on PCN surface. UV–Vis diffuse reflectance spectra, photoluminescence (PL) and EIS explored optical properties, photoinduced charge separation and transmission properties of the catalysts. Different catalysts dose, H_2O_2 concentration, pH experiments were performed to get optimal results. It was confirmed from the results that photocatalysts with H_2O_2 displayed superior photodegradation ability than photocatalysts without H_2O_2. 0.02 wt% CNT/PCN/H_2O_2 nanocomposite had 97 % IMI removal while 0.02 wt% CNT/PCN had 93 % IMI eradication at pH 4. The photocatalytic removal efficiency under visible light illumination without or with H_2O_2 follows the order as:

0.02 wt% CNT/PCN > 0.03 wt% CNT/PCN > 0.01 wt% CNT/PCN > PCN > GCN for photocatalysts without H_2O_2

and 0.02 wt% $CNT/PCN/H_2O_2$ > 0.03 wt% $CNT/PCN/H_2O_2$ > 0.01 wt% $CNT/PCN/H_2O_2$ > PCN/H_2O_2 > GCN/H_2O_2 for photocatalysts with H_2O_2. Scavenging results inferred that h^+, $•O_2^-$ and •OH radicals were principal reactive species in photodegradation processes. HPLC analysis was carried out to validate the degradation of pesticide compounds into simpler molecules.Recyclability test of 0.02 wt% $CNT/PCN/H_2O_2$ nanocomposite was also accomplished which unveiled no loss of catalysts for consecutive 10 cycles.

2. Conclusion

The main objective of current research work was to explore the capability of graphitic carbon nitride (GCN), phosphorous doped graphitic carbon nitride (PCN) and phosphorous doped graphitic carbon nitride based metal free nanocomposites *i.e.* PCN/CNT, PCN/C_{60}, PCN/GO and PCN/G, as a photocatalyst for the eradication of pesticides (Imidacloprid and Malathion) and bacterial (*E.Coli*) disinfection. The outcomes of research as well as new findings have been summarized accordingly in consecutive section of this chapter.

References

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