Feasibility of Photocatalytic Degradation of an Organophosphorus Pesticide using Graphene Oxide-TiO₂ Nanocomposite

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Abstract— Contamination of water by pesticides is an alarming ecological problem. Pesticides are majorly used in agriculture for maximizing crop production and in public health for vector control. This has resulted in accumulation of these toxic substances in waterbodies. Such extensive use is highly detrimental to the aquatic and terrestrial ecosystem. Pesticide residues in drinking water have also become a major challenge over the last few years. Although, organophosphate pesticides have rapidly replaced more persistent organochlorines, yet the problem persists. Dichlorvos (2,2-dichlorovinyl dimethyl phosphate) is a widely used synthetic organophosphorus pesticide. It is used as a broad spectrum insecticide to control pests for public health and for product storage related applications. Heterogeneous photocatalysis is an economical process that degrades pollutants rapidly without the generation of sludge. The present study focuses on assessment of degradation efficiency of graphene oxide-TiO₂ nanocomposite under irradiation (UV and visible) with varying amount of the photocatalyst.

Keywords— Dichlorvos, Nanocomposite, Heterogeneous photocatalysis, Graphene oxide-TiO₂, Degradation

I. Introduction

Green revolution has resulted in improved varieties of crops, increased use of fertilizers and increased use of synthetic pesticides. Pesticides have greatly benefited developing nations located close to the equator where insect-borne and endemic diseases are more predominant under the hot and humid conditions [1]. Insecticides are extensively used worldwide for enhancing agricultural production and minimizing crop destruction by pests. The largest consumer of pesticides is the agricultural sector. It is also used for weed elimination in horticulture and to control vector-borne diseases. Pesticides restrict the growth of pests such as insects, algae, fungi and bacteria in food storage and packaging industry [2, 3]. Pesticides consist of an active component and a variety of additives which improve the effectiveness of their application. The universal utilization of pesticides has resulted in their presence in various compartments of the environment as persistent organic pollutants (POPs). Pesticides have the potential to leach into water bodies, volatilize and get sorbed onto soil particles. The risk of insecticide exposure to human health is a matter of concern. Users of pesticides are at a very high risk of bodily absorption of pesticides and their residues.

Dichlorvos is a widely used organophosphate insecticide. Being a volatile broad spectrum insecticide it is used against a wide range of pests that affect plants and farm animals. It is an officially registered pesticide and is approved for use all over the world. Metabolites of dichlorvos may easily get assimilated into natural enzymatic pathways. Its exposure results in neurotoxicity by disrupting the normal functioning of acetylcholinesterase and cholinesterase enzymes [4, 5]. World Health Organization (WHO) has classified dichlorvos as a highly hazardous pesticide.

Heterogeneous photocatalysis may have potential for degradation of such pesticides. The process involves use of a catalyst in the presence of an irradiation source to degrade the pollutants through a series of redox reactions [6]. Although, the semiconductor, TiO₂, is commonly used for degradation of pollutants, it has two major drawbacks. Firstly, it has a high bandgap energy of 3.2 eV for anatase which restricts its use in the visible range. Secondly, the high tendency for electron-hole recombination reduces the efficiency of the catalyst.
Graphene has a two-dimensional lattice comprising of sp² hybridized carbon atoms. It is a promising material as it has unique properties such as high thermal conductivity, specific surface area and charge carrier mobility [7, 8]. Hybrid materials such as graphene oxide (GO) bonded with titanium have been proposed to promote visible light activity. Under irradiation, TiO₂ nanocrystals with GO allows the excited electrons from the conduction band of TiO₂ to be transferred from the conduction band to GO sheets. Schottky barrier suppresses the recombination of excited electron-hole pairs, thus, enhancing photocatalytic efficacy of the nanocomposite. This can result in development of cost effective systems that may harness solar energy for degradation of pollutants. The present study focuses on assessment of degradation efficiency of graphene oxide-TiO₂ (GOT) nanocomposite with varying amount of the photocatalyst under both UV and visible irradiation.

II. Materials and Methods

A. Reagents

Graphite powder, titanium chloride and dichlorvos was purchased from Sigma-Aldrich. Hydrogen peroxide (30%), sulphuric acid (98%), sodium nitrate and potassium permanganate were purchased from Merck.

B. Synthesis of graphene oxide-TiO₂

GO was synthesized using Improved Hummers’ Method [9]. In this method, 0.3 g of graphite flakes was taken to which 6.9 mL of H₂SO₄ and 0.15 g of NaNO₃ was added. The mixture was then cooled to 0 °C. To this mixture, 0.9 g of KMnO₄ was added. The reaction temperature was kept below 20°C. Subsequently, the mixture was heated to 35°C under continuously stirred for 7 hours at 85 rpm. Additional 0.9 g of KMnO₄ was added and stirred for 12 hours at 35°C at 85 rpm and cooled to room temperature. To this mixture, 40 mL of ice cold water was poured followed by 0.3 mL of 30% H₂O₂. The solution was centrifuged at 12000 rpm for 15 minutes and the solid was then washed with 100 mL of water and 100 mL of ethanol. The solid obtained was dried at room temperature.

Graphene oxide-titanium dioxide nanocomposite was synthesized using the dried product. To 40 mg of GO, 30 mL of distilled water was added. The suspension was sonicated for 15 minutes at room temperature. Self-assembly method was used for the synthesis of GOT nanocomposites as reported by Chen et al. (2010) [10] with minor modifications. To 10 mL of the solution, 0.5 mL of sodium dodecylsulfate (0.05 M) was added. Later 390 mL of distilled water was added to the mixture. Then 50 mL of TiCl₃ (0.12 M) was added to the solution and stirred for 1 hour. This was followed by addition of 10 mL of Na₂SO₄ (0.6 M) and 5 mL of 30% H₂O₂. The reaction mixture was stirred for 16 hours at 90 °C. The precipitate obtained was washed by centrifugation at 12000 rpm for 15 minutes. Subsequently, the solids were resuspended and washed with distilled water and ethanol. The pellet was air dried at 70°C. Calcination was carried out in the presence of air for 2 hours at 400°C. After synthesis, a 10 mg sample of GOT was acidified using 5 mL each of HNO₃ and HF and the sample was completely digested at 200°C for 15 min. After digestion, the residue was filtered and the volume was made up to 25 mL with deionized water and Ti was quantified using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP AES) analysis.

degrees for 15 minutes. The growth of nanocrystals of TiO₂ on GO sheets was achieved using a two-step method. Initially, TiO₂ nanoparticles were coated on GO sheets and subsequently, nanocrystals of anatase phase TiO₂ were formed on the sheet.

C. Characterization of graphene oxide-TiO₂

The nanocomposite was characterized using different techniques. UV-Diffuse Reflectance Spectroscopy (UV-DRS) DRS-3600, Shimadzu, Japan, was used to obtain the spectra of the GOT nanocomposite. The nanocomposite was mixed with KBr prior to characterization in Fourier Transform Infrared Spectroscopy (FTIR). The functional groups associated with GOT nanocomposite was assessed by 300 Hyeron Microscope with vertex 80 FTIR system Bruker, Germany.

X-Ray Diffraction (XRD) of the sample was analyzed using PANalytical Xpert Pro, X-Ray Diffractometer, Netherland. The surface morphologies of GOT nanocomposite was examined by Transmission Electron Microscope (TEM) PHILIPS CM200, Japan and Field Emission Gun-Scanning Electron Microscope (FEG-SEM) JSM-7600F. Surface area of the nanoparticles was analyzed using Surface Area Analyser, Smart Sorb 92/93, Smart Instruments.

D. Photocatalytic degradation

The photocatalytic activity of the nanocomposite was assessed by photodegradation of the organophosphorus pesticide, dichlorvos. Variation in photodegradation of dichlorvos (initial concentration 50 µg/L) was studied using 100 mg and 10 mg of the photocatalyst. The studies were conducted in a batch photoreactor equipped with 125 W low pressure UV lamp with a radiant flux of 42 W/m². Later studies were repeated using a 3 W LED light with a radiant flux of 1.2 W/m². The total reaction volume was 150 mL.

The suspension was initially stirred in the dark to achieve adsorption–desorption equilibrium over 1 h. The lamps (UV and visible) provided a full-spectrum emission with no filter. The experiments were carried out at pH 7.6-8 at room temperature. From the batch reactor, 10 mL of the mixed suspension was extracted at various irradiation time and the photocatalyst was removed by centrifugation at 12000 rpm for 10 min. The concentration of residual pesticide and pesticide residues was determined based on total organic carbon (TOC) analysis.
III. Results and Discussion

A. Characterization of graphene oxide-TiO$_2$

This synthesis protocol followed resulted in 3 g of GOT nanocomposite. If all the Ti in this formulation was converted to TiO$_2$ and the total mass was only due to GO and TiO$_2$ the mass of GOT expected would be 0.52 g. The significantly higher yield may be due to water of hydration associated with the product. Digestion of GOT and subsequent analysis revealed that 67% of the Ti used during synthesis was incorporated in GOT. The UV-DRS spectra of GOT was recorded as depicted in Figure 1(a). The spectra shows significant absorption in the UV region. This is attributed to the electron shift that occurs to the conduction band from valence band of TiO$_2$. The presence of GO in the nanocomposite influences the optical properties in the visible region significantly [11]. The optical bandgap of the nanocomposite was determined using Tauc plot where $F(R)\cdot hv$ versus photon energy was plotted [12]. The function $F(R)$ varies with %Reflectance (R) and is commonly referred as the Kubelka-Munk (KM) function. The corresponding bandgap energy was estimated to be 3.0 eV as depicted in Figure 1(b). By comparing this bandgap energy with that of anatase phase TiO$_2$ (3.2 eV), it is apparent that the GOT nanocomposite shows reduction in bandgap. Similar results have also been reported by Chen et al., (2010) [10].

XRD analysis was used to determine the phase purity and the crystalline properties of GOT nanocomposites. The XRD profile shows that the synthesized nanocomposite is crystalline in nature as depicted in Figure 2. The degree of oxidation of the material is proportional to the presence of oxygenated functional groups which relates to the interplanar spacing of the composite [9, 13]. From the XRD pattern of GO the interlayer distance for the characteristic peak for the (001) plane at 20 $= 10^o$ was obtained as 0.93 nm (XRD spectra not shown). This value is comparable to values reported in the literature [12, 14]. Presence of oxygen-containing functionalities results in large interlayer distance in GO. High d-spacing value indicates the oxidation of graphite into GO. From the XRD pattern of GOT it is evident that GO was exfoliated as the d-spacing was reduced to 0.35 nm and it was then used as an intercalation matrix. The peaks at 25.3°, 37.8°, 48.2°, 54.7°, 62.7°, 70.3°, and 75.0° can be indexed to the (101), (004), (200), (211), (204), (220), and (215) crystal planes of tetrahedral anatase phase TiO$_2$ respectively. Comparable results have been reported previously [15, 16]. These results indicate that the layered GO was initially exfoliated after which the titanium precursor in solution was adsorbed on the surface of GO before nucleation and growth of TiO$_2$ nanocrystals on GO.

FTIR spectroscopy was used to characterize the interaction between GO sheets and the attached TiO$_2$ nanoparticles. In the FTIR spectrum of the nanocomposite a distinct peak at $\sim 500$–700 cm$^{-1}$ was observed due to Ti–O–Ti vibration. A peak at $\sim 1210$ cm$^{-1}$ was observed in the spectrum for TiO$_2$. This can be assigned to Ti–O–C vibrations. Peaks were also observed at $\sim 1580$ cm$^{-1}$ due to the vibrations of GO. The IR absorption peak at 1720 cm$^{-1}$ can be attributed to the C=O stretching vibration [17].
The presence of both these peaks confirm the presence of GO and TiO$_2$ in the synthesized nanocomposite as illustrated in Figure 3. The spectrum shows a broad peak at \( \sim 3400 \text{ cm}^{-1} \) which indicates the presence of surface-adsorbed water. This peak is attributed to the presence of −OH groups on the surface of titanium. This has also been reported by Basheer, (2012) [18]. It has been reported in literature that hydrogen bonds are formed when the oxygen containing functionalities on GO interact with TiO$_2$ nanoparticles [7]. The degree of oxidation of GO can be determined by the colour of the product as reported by Hummer et al., (1958) [19]. Bright yellow colour indicates high degree of oxidation of GO, whereas green to brown colour indicates poor oxidation. GO synthesized was observed to be bright yellow indicating a high degree of oxidation.

The FEG-SEM micrograph of GOT showed TiO$_2$ nanospheres decorated uniformly over the surface of GO (Figure 4a). The average diameter of the nanoparticles was 14 nm. Energy Dispersive Spectroscopy (EDS) indicated the presence of C, O and Ti. The signal for C and Ti can be attributed to GO and TiO$_2$ nanoparticles, respectively. The signal for O may have originated partly from the TiO$_2$ nanoparticles and partly from the oxygen-containing groups on GO [20]. These results confirm successful formation of GOT nanocomposite. The weight percent of titanium on the surface was 57.07% while that of carbon and oxygen were 1.40% and 41.53%, respectively.

The morphology of GOT nanocomposites as revealed by TEM showed that the GO sheets were entirely covered by TiO$_2$ nanoparticles. Similar morphology was observed in FEG-SEM as well. Micrographs of the nanocomposites showed homogenous distribution over the sheets with aggregation at some places as depicted in Figure 4(b). Both the edge of graphene and the nanostructure of the TiO$_2$ nanoparticles could be clearly observed in the higher magnification image. The clear lattice of TiO$_2$ nanoparticles was measured as 0.35 nm. The diffraction pattern established high crystallinity of TiO$_2$ and confirmed that primarily anatase phase TiO$_2$ was formed as also shown by XRD [10]. Thus, successful self-assembly of TiO$_2$ on the GO sheets was confirmed. The diffraction pattern of the nanocomposite showed the formation of multiple crystalline layers. Similar results have been reported by Liang et al. (2010) [21].

It was observed that GOT had high Brunauer-Emmett-Teller (BET) surface area (147.2 m$^2$/g) as compared to the commercially available photocatalyst P25 (58 m$^2$/g). When more number of atoms reside on the surface, it enhances the ability of the photocatalyst to interact with organic pollutants. Photocatalysis is related with the density of electrons and holes on the surface of the nanoparticles. When the particles have a diameter in the nano range, the charge carriers readily move from the inside to the surface. Higher surface to volume ratio and smaller particle diameter reduces the time required for charge carriers to diffuse to the surface from the interior. This can reduce the probability of electron-hole recombination such that higher photocatalytic activity can be achieved.

![FTIR spectra of GOT](image)

**Fig. 3:** FTIR spectra of GOT

The photocatalytic efficiency of the synthesized catalyst was assessed by degradation of the pesticide dichlorvos under UV and visible light (LED) irradiation. Control experiments were conducted in the absence of catalyst (NC). Dark controls were maintained to check for adsorption on the surface of the nanocomposite wherein experiments in presence of the nanocomposite were carried out in the absence of light as depicted in Fig. 5. Dichlorvos does not absorb in the spectral range 300–400 nm [22] therefore its concentration was

![FEG-SEM micrograph and TEM micrograph of GOT](image)

**Fig. 4:** (a) FEG-SEM micrograph of GOT (b) TEM micrograph with diffraction pattern of GOT

**B. Photocatalytic degradation study**

The photocatalytic efficiency of the synthesized catalyst was assessed by degradation of the pesticide dichlorvos under UV and visible light (LED) irradiation. Control experiments were conducted in the absence of catalyst (NC). Dark controls were maintained to check for adsorption on the surface of the nanocomposite wherein experiments in presence of the nanocomposite were carried out in the absence of light as depicted in Fig. 5. Dichlorvos does not absorb in the spectral range 300–400 nm [22] therefore its concentration was
practically unchanged when irradiated in the absence of photocatalyst. Photocatalysis of dichlorvos in aqueous solution essentially involves two steps, i.e., adsorption of dichlorvos onto the nanocomposite followed by its degradation brought about by the nanocomposite in the presence of an irradiation source. Thus, removal of dichlorvos from the aqueous solution was due to both adsorption and degradation. Various researches have reported presence of intermediates during the degradation of dichlorvos i.e., dichlorvinylmethyl phosphoric acid (DVMP), dimethyl phosphoric acid (DMP), dichloracetaldehyde (DCA), formaldehyde and formic acid [22]. However, decrease in TOC indicates loss of both dichlorvos and its intermediates through adsorption and photocatalysis.

Removal of dichlorvos due to adsorption was 20% and 10% with 100 mg and 10 mg of the photocatalyst, respectively. Irrespective of the irradiation source (UV/Vis), comparable and significant removal was obtained after 90 min of photocatalysis. Under both UV and visible irradiation, 100 mg and 10 mg of the photocatalyst showed 75% and 66% additional removal of dichlorvos, respectively, beyond adsorption. The results confirm significant mineralization of dichlorvos under both UV and visible irradiation.

The light (UV/Vis) was irradiated after 60 min to ensure attainment of adsorption-desorption equilibrium of pesticide.

IV. Conclusion

Highly crystalline anatase phase TiO₂ nanospheres were observed on the surface of GOT. The results confirmed the feasibility of dichlorvos mineralization using GOT in the presence of both UV and visible light. Good photocatalytic property of the nanocomposite can be attributed to strong GO and TiO₂ interactions. The visible light activity can be attributed to reduction in bandgap in the nanocomposite.

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References


