

Enhanced Photocatalytic Remediation Using Graphene (G)-Titanium Oxide (TiO₂) Nanocomposite Material in Visible Light Radiation

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Abstract

The petroleum compounds were photocatalytically remediated from water using graphene (G)-titanium oxide (TiO₂) nanocomposite material in visible light radiation. The G-TiO₂ nanocomposite was synthesized using sol-gel technique, and its structural & morphological properties were studied using scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM), particle analyzer and UV-Visible spectroscopy (UV-Vis) measurement techniques. Various petroleum-based chemicals (toluene, naphthalene and diesel) were remediated, and samples were analyzed using optical and gas chromatography (GC) techniques. The mechanism of photocatalytic remediation of petroleum compounds using G-TiO₂ nanomaterials is understood and well compared with data available in literature.

Keywords

G-TiO₂, Photocatalyst, Decontamination, Toluene, Naphthalene, Petroleum

1. Introduction

The last decade has shown an increase in health problems due to enhanced organic pollutants in environment (air and water) [1]-[5]. So, chemical, physical and biological processes have been adopted to remediate organic pollutants from environment [6]-[13]. The petroleum is a major pollutant of water which consists of alkanes, unsaturated hydrocarbons, cycloalkanes and aromatic hydrocarbons, and it is being remediated through biore-

mediation, absorption, membrane and filtration techniques, respectively [2] [10] [14]-[17]. However, petroleum remediation recognized by each individual technique has advantages and disadvantages, and it leaves the trace above the threshold values set by Environmental Protection Agency (EPA) and World Health Organization (WHO), except for bio-remediation which runs with its peculiar drawbacks [18]-[20]. The photocatalysts have been employed to remediate even trace amount of organic pollutants in water [21]-[23]. The catalyst, “titanium dioxide (TiO₂)” has been extensively used for photocatalytic remediation of water [24] [25]. The band gap of TiO₂ is 3.2 eV, and has shorter wavelengths of light radiation (<415 nm, in UV light spectrum). TiO₂ being chemically inert has widely used as industrial photocatalyst due to high efficiency, photostability, and lower cost [24] [26] [27]. Recently, a survey of photocatalytic materials has been performed for environmental decontamination based on TiO₂ and TiO₂ composite with fullerene, graphite and carbon [28]. TiO₂ based photocatalyst faces two major drawbacks for decontamination of water; as it has faster electron hole recombination time [29], and its operating band gap energy is too high (3.2 eV) falling under the UV light spectrum [30]. The research has been directed on modifying TiO₂ by doping nitrogen, fluorine and metal ions (iron, silver, platinum etc.). The doping induces disorder in TiO₂ through hydrogenation which reduces recombination time but increases the quantum efficiencies and modifies band structure for efficiently working under wide spectrum of solar radiation [31]-[36]. The control of operational parameters to remediate completely the azo dyes in textile waste water using TiO₂ nanomaterials have been studied [37]. The structure modification of TiO₂ in nanotubes form has been studied for dye degradation [38].

Recently, optical absorption of TiO₂ has been shifted by making composite with graphene [39]. Graphene (G) “a 2D material” is a monolayer of graphite (3D) [40], has attracted attention due to its unique electrical [40], photonics and optoelectronics [41], energy storage [42], photovoltaics [43] and photo-electrochemical [44] properties. Graphene increases photocatalytic properties of TiO₂ due to its large surface area, absorbing, electronic and environmentally friendly characteristics [39] [45]. The photocatalytic activities of TiO₂ are greatly influenced due to particle size, dopant, surface area, structure and morphologies [46]. Based on our earlier studies of the use of silicon oxide-graphene composite as well as graphene-TiO₂ composite, it has been agreed that surface area of composite nanoparticles can be enhanced than pristine TiO₂ nanoparticles [47] [48]. G-TiO₂ can be synthesized by hydrothermal method, sol-gel, and colloidal blending methods [48]-[50]. The earlier study on G-TiO₂ nanomaterials has shown the complete remediation of methyl orange in water under visible light [48].

Under this manuscript, we optimized G-TiO₂ nanoparticles synthesis process for obtaining the large surface area and toluene, naphthalene and diesel based organics in water were remediated in visible light. The G-TiO₂ nanoparticles were synthesized using sol-gel technique, and studied. G-TiO₂ nanoparticles were characterized by XRD, SEM, TEM, UV-vis and particle analyzer based techniques. The quantitative and qualitative remediation of toluene, naphthalene and diesel were met. In an experimental setup, initially, a given organic concentration in DI water (mL) in closed glass container with fixed amount of photocatalyst was used. Simulating the solar intensity of 800 - 1000 W/m² using a soft light bulb illuminated in the visible light radiation, and samples were collected as a function of time (hours). The samples were centrifuged and gas chromatography (GC) was employed to measure the amount of organic pollutant in the water.

2. Experiment

2.1. Materials

Hydrochloric acid (HCl), propanol and titanium (IV) isopropoxide, methyl orange, toluene, diesel, naphthalene, and other reagents were purchased from Sigma-Aldrich (USA), and used without purification unless and until reported. Toluene, naphthalene and diesel solutions in water were prepared as per requirement of the experiment. The graphene platelets of size < 20 - 50 nm were obtained from a commercial company “Angstrom Materials’ (USA)”.

2.2. Synthesis of G-TiO₂ Nanocomposite

The synthesis of G-TiO₂ nanocomposite materials showed better yield through a sol-gel synthesis process [48]. The synthesis of nanocomposite G-TiO₂ was initiated by using a mixture of titanium (IV) isopropoxide in propanol solution. Initially, 1.93 gram (g) of graphene was mixed with 200 ml of propanol with an addition of 40 mL of titanium (IV) isopropoxide, and left on stirring for 30 minutes. HCl was added drop wise and the solution was left stirring for 24 hours at room temperature. The precipitate formed after 24 h of reaction under stirring

was washed in deionized water for removal of any unreacted organic residues by centrifugation process. The centrifuged G-TiO₂ nanoparticles were dried at 100°C for 24 h.

2.3. Sample Preparation and Decontamination Setup

The organic contaminants (toluene, naphthalene and diesel) at different concentrations were used to decontaminate using G-TiO₂ nanocomposite photocatalyst. A 100 W lamp was employed to simulate the solar light intensity of 800 - 1000 W/m². The contaminants solution of G-TiO₂ were stirred in closed glass container, and kept closed during the completion of the experiment. Samples were collected at regular intervals, and centrifuged to separate composite G-TiO₂ particles from measuring solution. The centrifuged sample of 1 μL solution was passed through a gas chromatography. Diesel, toluene and naphthalene containing water samples have been kept in the identical conditions, and decontaminated water samples have been collected as a function of time using G-TiO₂ photocatalyst. These petroleum molecules may get evaporated especially under stirring and light exposure conditions. It is useful to add a control experiment using the same equipment setup while changing the G-TiO₂ to pure TiO₂.

The retention time (in min) vs. area under curve was plotted to understand each organic contaminant in the water sample. The ratio of concentrations as C₀ (initial concentration) and C_n (concentration of solution at different timed samples with % of sample remained in the solution) were used to understand the change in percentage of concentration with the use of G-TiO₂ nanocomposite photocatalyst [48].

3. Characterization

3.1. TEM Study

Figures 1(a)-(d) exhibits TEM picture of the G-TiO₂ nanocomposite at different magnifications. The Figure 1(a) observed the particle size of 20 - 50 nm for G-TiO₂ nanoparticle. Further, magnification in Figure 1(b) and Figure 1(c) reveals well-defined graphene coated TiO₂ nanoparticles.

Figure 2 reveals the d-spacing with inter-planar structure of G-TiO₂ nanocomposite. The Y-axis shows the d-spacing of different crystalline planes present in the G-TiO₂ nanocomposite material. The x-axis in Figure 2

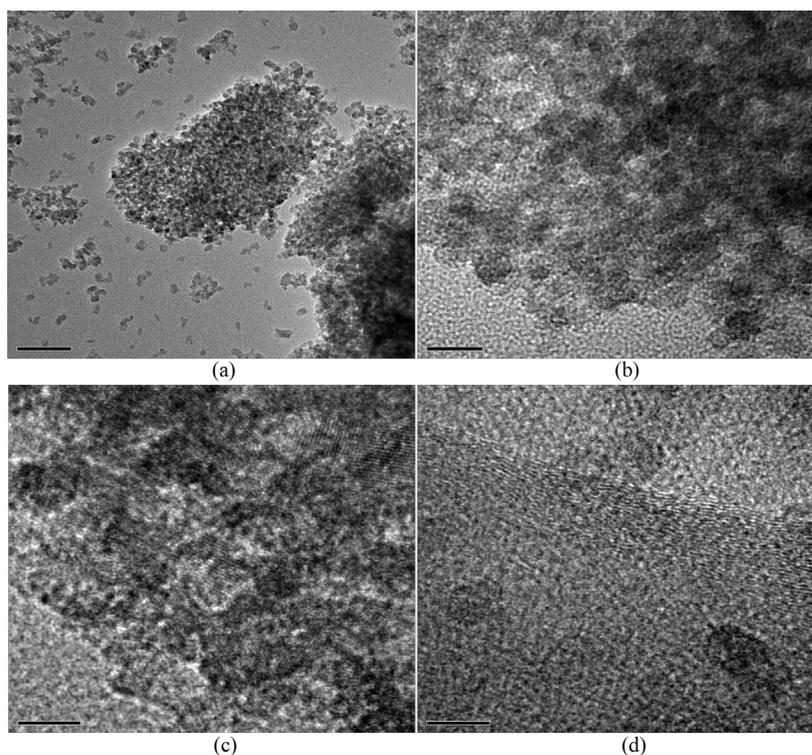


Figure 1. TEM pictures of G-TiO₂ nanocomposite at different magnification (a)-(d).

is the characteristics ring used for calculation of inter-planar place of G-TiO₂ based polycrystalline nanocomposite. The error bar is calculated using 10 different measurements per crystalline structure. It reveals polycrystalline structure in G-TiO₂ nanocomposite.

3.2. SEM Study

The surface morphology of G-TiO₂ nanocomposite have been studied using SEM as shown in **Figures 3(a)-(d)**.

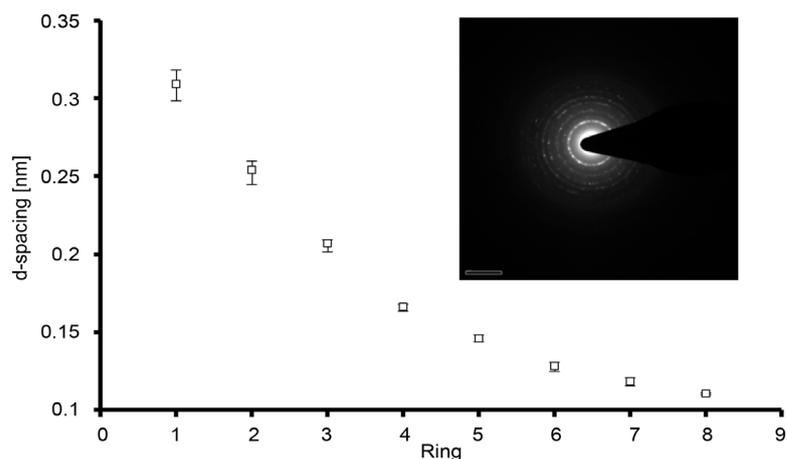


Figure 2. Cross sectional TEM image where Y-axis shows the d-spacing of the different crystalline planes and X-axis represents the ring used for calculation of interplanar place of the polycrystalline nanocomposite.

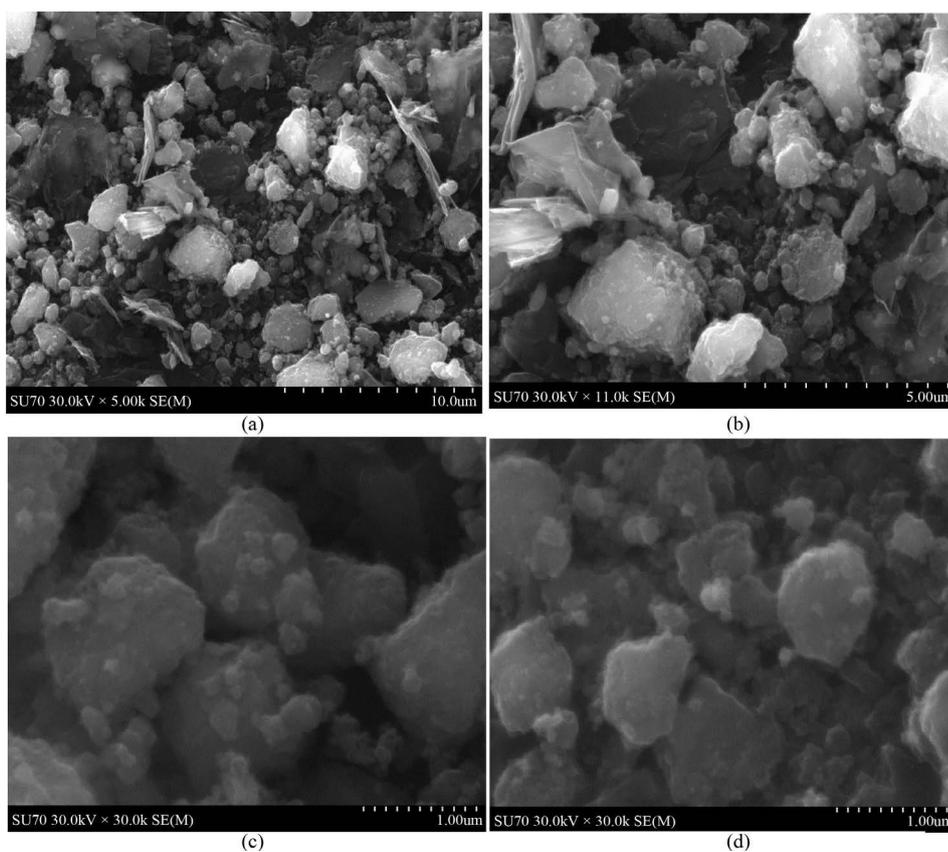


Figure 3. SEM images of G-TiO₂ nanocomposite at different magnifications (a)-(d).

The sol-gel synthesis of G-TiO₂ provides varying particle size from 20 - 50 nm as observed earlier in TEM measurement. The compact bundles of the nanomaterials have been observed in SEM studies. The compact particle distribution of G-TiO₂ is observed in **Figure 3(a)** and **Figure 3(b)** which attributes the dispersion of TiO₂ nanoparticles with graphene. The particle size varying from 20 - 50 nm for G-TiO₂ nanoparticles in **Figure 3(c)** and **Figure 3(d)**. We have not detected the size of nanoparticles in SEM studies due to aggregation of small particles in G-TiO₂ composite structure. There is always aggregation of nanoparticles so care is taken to disperse well in the G-TiO₂ composite material.

3.3. X-Ray Diffraction (XRD)

XRD analysis on G-TiO₂ is as shown in **Figure 4**. The strong diffraction peak at 26.51 is indicative of presence of graphene in G-TiO₂ structure. The presence of peaks at 25.27, 37.85, 47.83, 54.55, 63.59, 70.15, 83.1 degrees are due to TiO₂ anatase phase present in G-TiO₂ nanocomposite [47] [48]. The structure indicates the forms of crystallinity in G-TiO₂ nanomaterials.

3.4. Particle Analyzer

It is important to understand G-TiO₂ particle distribution in water. To realize such behavior, G-TiO₂ particles were dispersed in water. **Figure 5** displays the agglomeration of nanocomposite in water solution, indicating the distribution of particles in contaminated water. The nanocomposite particles in water form aggregation, and it shows agglomeration up-to μm in size. The small aggregation of 100 nm is also observed in **Figure 5**. **Figure 5** shows prominent 100 nm to 1 μm particle size distribution of G-TiO₂ in water samples.

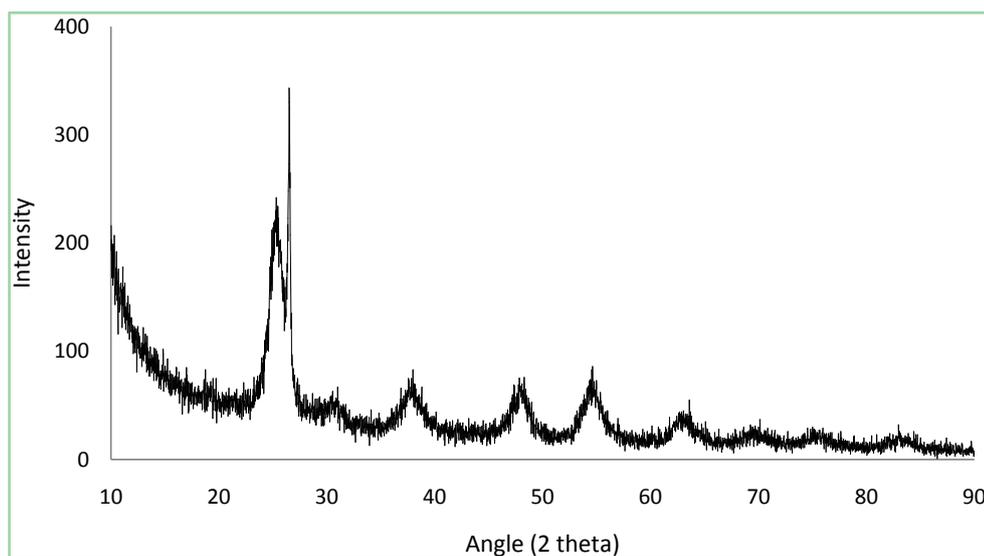


Figure 4. XRD image of G-TiO₂ nanocomposite.

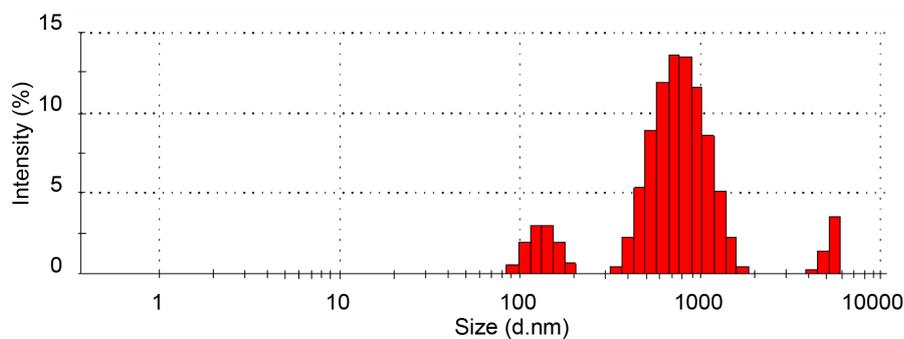


Figure 5. The particle distribution of G-TiO₂ nanocomposite in water.

3.5. UV-Visible Spectroscopy

Figure 6 displays UV-visible absorption spectrum of G-TiO₂ nanocomposite material. It has strong absorption band from 250 to 400 nm due to doping of graphene onto TiO₂, the absorption spectra strongly continues till 620 nm, suggesting that G-TiO₂ nanocomposite functions effectively in both UV and visible spectrum of light. The band gap of TiO₂ nanoparticles are estimated to be 3.2 eV. It can be stated that there is a red shift of band edge and reduction of band gap to 2.7 eV is due to graphene doping.

4. Decontamination Study

Figure 7 shows step-by-step procedure for pollutant decontamination using G-TiO₂ nanomaterials. It also shows sample collection, decontamination and sample analysis using gas chromatograph.

1 g of G-TiO₂ nanocomposite have been used with toluene at 100 ppm (250 ml) under 100 W visible light bulb. **Figure 8** shows ~90% of toluene decontamination in water for exposure of only an hour of visible light. Further, light exposure results in similar values indicating that toluene on surface of water mostly evaporated or there could be continual evaporation of toluene from water surface. We have earlier observed that without

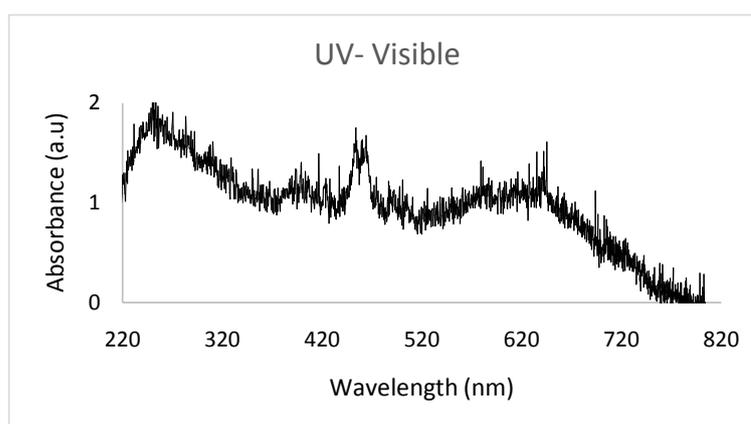


Figure 6. UV-visible spectrum of G-TiO₂ nanocomposite.

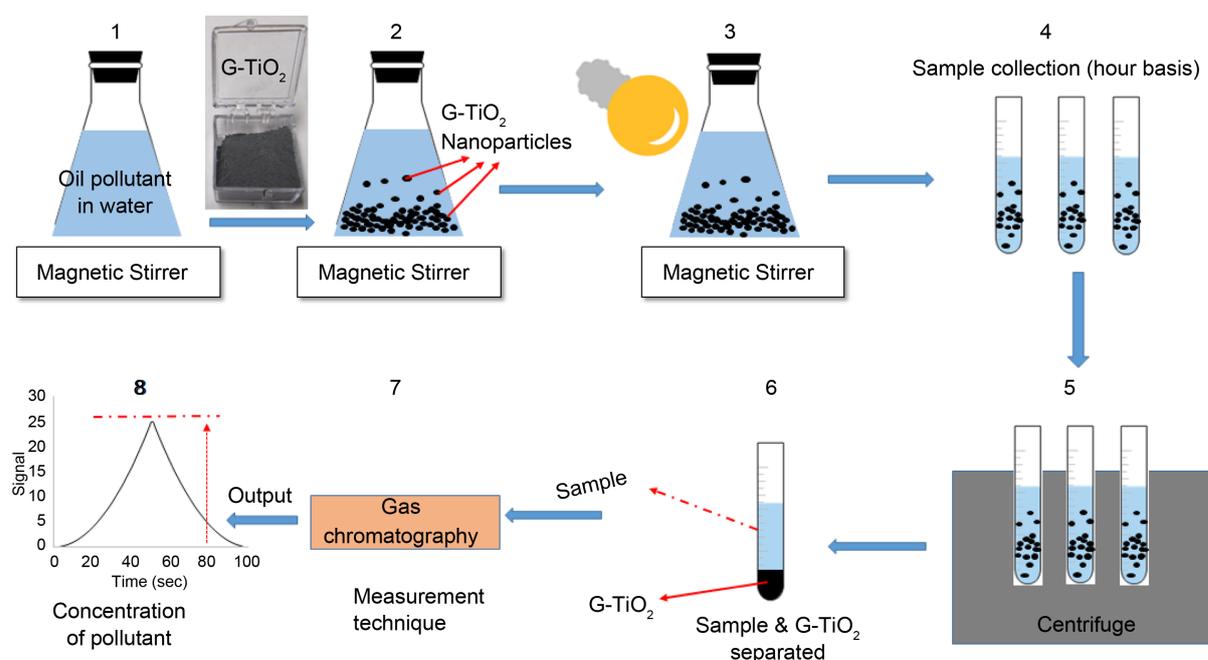


Figure 7. Schematic of sample collection and analysis shown in step in step process.

use of graphene in TiO_2 , remediation of organic in visible light excitation is poor.

The initial solution of naphthalene solution was $5000 \mu\text{g/mL}$ in methanol, analytical standard as obtained from Sigma Aldrich. $25 \mu\text{g/mL}$ naphthalene in DI water (250 mL) was prepared to recognize the effect of decontamination using G- TiO_2 (1 g sample) composite material under visible light. Naphthalene is sparingly soluble in water so we used methanol naphthalene solution. $25 \mu\text{g/mL}$ of solution was prepared and decontaminated. **Figure 9** shows decontamination of naphthalene under visible light in presence of G- TiO_2 nano-composite particles.

There was only 50% reduction of naphthalene under visible light over a period of 48 h, measured using GC which is shown in **Figure 9**. The composition of diesel in water obtained from Sigma Aldrich contains acetone, methanol and mineral oil type. $25 \mu\text{g/mL}$ of diesel in DI water (250 mL) was used with 1 g of G- TiO_2 . The methanol is soluble in water whereas acetone and oil are sparingly soluble in water. It is clear that without organic molecules much in contact with G- TiO_2 nanoparticle, it is difficult to decontaminate under visible light. **Figure 10** shows the change area of diesel measured as a function of time (in hours) under 100 W of visible light lamp. So, organic molecules present in diesel are not in contact with G- TiO_2 nanocomposite displaying ~40% reduction of diesel after 48 h of visible light irradiation.

90% of toluene, 50% of naphthalene and 40% of diesel have been remediated using G- TiO_2 nanomaterial under visible light as shown in **Figures 8-10**. **Figure 11** shows the pictorial representation for decontamination mechanism G- TiO_2 with petroleum pollutants. The insolubility of petroleum pollutants in water brings contaminant to the surface of water thereby inhibiting photocatalytic effect with G- TiO_2 . The contaminants soluble in water remain in contact with G- TiO_2 particles and are completely remediated. Surfactant (dodecyl sulphate),

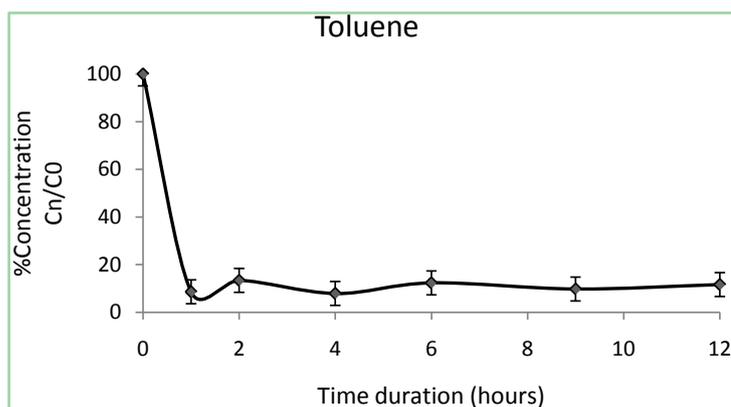


Figure 8. The change in the area in toluene measurement as function of hour for toluene decontaminated water in 100 W visible light.

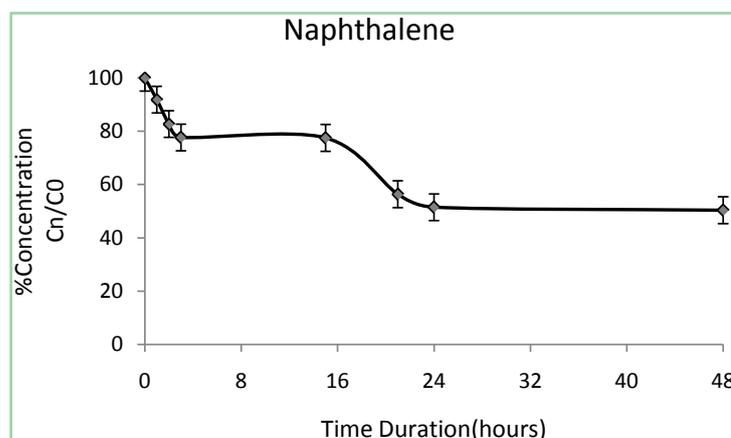


Figure 9. The change in the area in naphthalene measurement as function of hour for naphthalene decontaminated water in 100 W visible light.

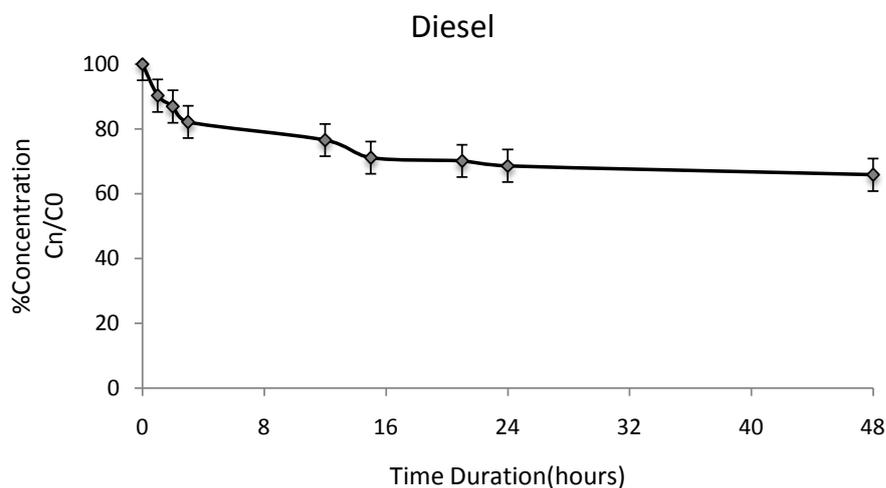


Figure 10. The change in the area in diesel measurement as function of hour for diesel decontaminated water in 100 W visible light.

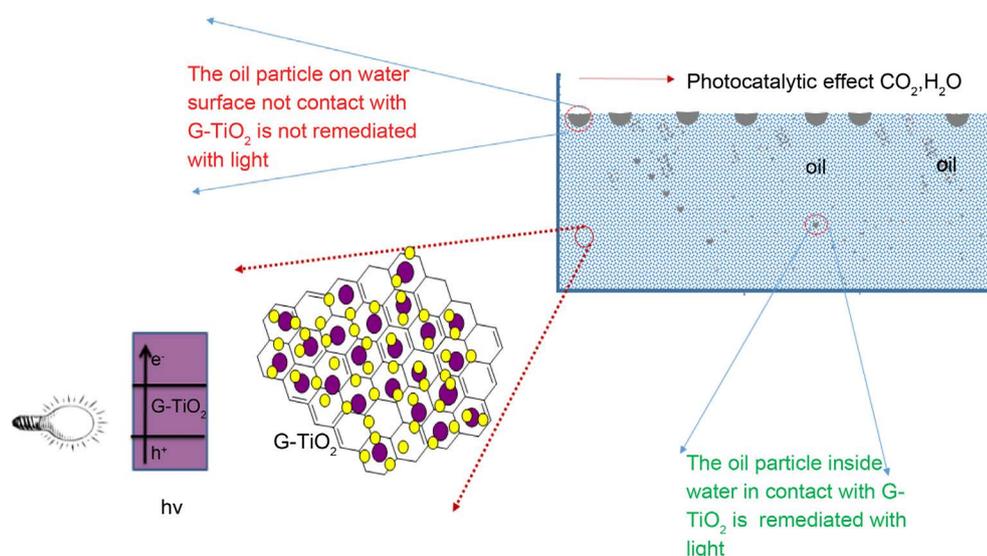


Figure 11. Pictorial presentation of soluble and insoluble organic compound decontamination using G-TiO₂ nanocomposite material.

polystyrene sulfonate) or biosurfactant (rhamnolipid) have been employed for increasing the solubility of petroleum contaminants, which helps contaminant to remain in contact with the photocatalyst. **Table 1** shows the results produced from our group for naphthalene decontamination with surfactant with G-TiO₂, suggesting importance of oil pollutant to come in contact with photocatalyst for complete remediation [48].

5. Conclusion

The G-TiO₂ nanocomposites have been synthesized using sol-gel synthesis process and characterized for mass production. The particle distribution has been studied in water, which shows the agglomeration from 100 nm to 1 μm size particle. G-TiO₂ was able to decontaminate 90% of toluene whereas with naphthalene shows only 50% of reduction and diesel reveals only 40% of reduction from water solution. Naphthalene and diesel insolubility is reason behind the ineffective photocatalytic effect using G-TiO₂ nanomaterial. The mechanism of petroleum based contaminant has been understood using G-TiO₂ nanocomposite material. We have also compared toluene and naphthalene remediation using different types of TiO₂ synthesized photocatalyst material with G-TiO₂ nanocomposite material. However, we have obtained interesting results from toluene, naphthalene and diesel as

Table 1. The compared remediation of G-TiO₂ with surfactant and without surfactant.

Material/Method	Pollutant/light source	Results	References
G-TiO ₂ /sol-gel with surfactant	Naphthalene (30 µg/mL) with Sodium dodecyl sulfonate as surfactant (aqueous media)/UV light	98.62% remediation after 48 h	[48]
G-TiO ₂ /sol-gel without surfactant	Toluene (aqueous media)/only Visible light	90% in one h	(Present manuscript)
	Naphthalene/(aqueous media)/only Visible light	50% in 48 h	(Present manuscript)
	Diesel/(aqueous media)/only Visible light	40% in 48 h	(Present manuscript)

Table 2. Comparative study of petroleum production remediation.

Material/Method	Pollutant/light source	Results	References
TiO ₂ (6 nm)/Sol-gel	Toluene (aqueous media)/UV light	Conversion of toluene to CO ₂ was achieved up to 55%	[51]
TiO ₂ -ZnO/Sol gel Annealed at 380 C		45.7% after 2 hrs. of light irradiation	
TiO ₂ -ZnO/Sol gel Annealed at 500		39.5% after 2 hrs. of light irradiation	
N doped TiO ₂ -ZnO/Sol-gel Annealed at 380 C	Toluene (aqueous media)/Visible light	28.6% after 2 hrs. of light irradiation	[52]
N-TiO ₂ /ZnO/Sol gel Annealed at 500 C		12.9% after 2 hrs. of light irradiation	
Without catalyst		73.2 % after 2 hrs. of visible light irradiation	
TiO ₂ -commercial P25	Toluene (aqueous media)/UV light	60 hours to completely remove toluene from water	[53]
TiO ₂ dip coated on Autoclaved aerated white concrete	Toluene (11 µg g ⁻¹) (air purification)/UV light	86% remediated after 20 hours	[54]
Rutile and anatase TiO ₂ /commercial products	Naphthalene (Acetonitrile/wate)/Visible light	Higher efficiency than anatase TiO ₂ particles for converting naphthalene to 2-formylcinnamaldehyde (is about only conversion)	[55]
TiO ₂ dispersions-commercial P25	Naphthalene (aqueous media)/Visible light	Feasible and fast within 30 min but for when naphthalene is less than 4 ppm (no details are given)	[56]
TiO ₂ -NiO/ <i>in situ</i> -modified sol-gel	Naphthalene (aqueous media)/Visible light & UV light	1.5 to 2.5 faster than TiO ₂ (sol-gel) material for less than 20 ppm of naphthalene for time of more than 100 hours	[57]
G-TiO ₂ /sol-gel	Toluene (aqueous media)/only Visible light	90% in one h	(Present manuscript)
G-TiO ₂ /sol-gel	Naphthalene/(aqueous media)/only Visible light	50% in 48 h	(Present manuscript)
G-TiO ₂ /sol-gel	Diesel/(aqueous media)/only Visible light	40% in 48 h	(Present manuscript)

shown in **Table 2**. The results shown in **Table 2** reveal that it is easy to remediate toluene than naphthalene or diesel from water. The decontamination depends upon solubility of organics in water or the layer of organics to remain in contact with photocatalysts. Naphthalene as well as diesel are sparingly soluble in water and do not remain in contact with the G-TiO₂ nanomaterials whereas toluene remains in contact with photocatalyst. Due to lower density than water both naphthalene and diesel molecules stay on the surface of water. The insolubility in water as well as no contact with G-TiO₂ makes diesel and naphthalene to remediate partially up-to 50% and 40% than their initial values. Based on our understanding, we are using various surfactant (dodecyl sulphonate, polystyrene sulfonate) and biosurfactant (rhamnolipid) with G-TiO₂ to effectively remediate various chemicals of petroleum including mineral oil A and B for future work as shown in **Figure 11**.

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References

- [1] Shannon, M.A., Bohn, P.W., Elimelech, M., Georgiadis, J.G., Mariñas, B.J. and Mayes, A.M. (2008) Science and Technology for Water Purification in the Coming Decades. *Nature*, **452**, 301-310. <http://dx.doi.org/10.1038/nature06599>
- [2] Broussard Sr, P.C. (1992) Water Clarification Method and Apparatus. US Patent 5277803A.
- [3] (1991) Toxics in the Community, National and Local Perspectives. In: U.S. EPA, Ed., *The 1989 Toxics Release Inventory National Report*, US Government Printing Office, Washington DC.
- [4] Pimentel, D., McLaughlin, L., Zepp, A., Lakitan, B., Kraus, T., Kleinman, P., Vancini, F., Roach, W.J., Graap, E., Keeton, W.S. and Selig, G. (1991) Environmental and Economic Effects of Reducing Pesticide Use. *BioScience*, **41**, 402-409. <http://dx.doi.org/10.2307/1311747>
- [5] Wania, F. and MacKay, D. (1996) Peer Reviewed: Tracking the Distribution of Persistent Organic Pollutants. *Environmental Science & Technology*, **30**, 390A-396A. <http://dx.doi.org/10.1021/es962399q>
- [6] Froehner, S., Martins, R.F., Furukawa, W. and Errera, M.R. (2009) Water Remediation by Adsorption of Phenol onto Hydrophobic Modified Clay. *Water, Air, and Soil Pollution*, **199**, 107-113. <http://dx.doi.org/10.1007/s11270-008-9863-0>
- [7] Mondal, P., Majumder, C. and Mohanty, B. (2006) Laboratory Based Approaches for Arsenic Remediation from Contaminated Water: Recent Developments. *Journal of Hazardous Materials*, **137**, 464-479. <http://dx.doi.org/10.1016/j.jhazmat.2006.02.023>
- [8] Nawar, S.S. and Doma, H.S. (1989) Removal of Dyes from Effluents Using Low-Cost Agricultural By-Products. *Science of the Total Environment*, **79**, 271-279. [http://dx.doi.org/10.1016/0048-9697\(89\)90342-2](http://dx.doi.org/10.1016/0048-9697(89)90342-2)
- [9] Megharaj, M., Ramakrishnan, B., Venkateswarlu, K., Sethunathan, N. and Naidu, R. (2011) Bioremediation Approaches for Organic Pollutants: A Critical Perspective. *Environment International*, **37**, 1362-1375. <http://dx.doi.org/10.1016/j.envint.2011.06.003>
- [10] Hicks, B. and Caplan, J.A. (1993) Bioremediation: A Natural Solution. [Decontamination of Soils and Groundwater]. *Pollution Engineering; (United States)*, **25**.
- [11] Head, I.M. (1998) Bioremediation: Towards a Credible Technology. *Microbiology*, **144**, 599-608. <http://dx.doi.org/10.1099/00221287-144-3-599>
- [12] Cunningham, S.D. and Berti, W.R. (1993) Remediation of Contaminated Soils with Green Plants—An Overview. *In Vitro Cellular & Developmental Biology-Plant*, **29**, 207-212. <http://dx.doi.org/10.1007/BF02632036>
- [13] Perelo, L.W. (2010) Review: *In Situ* and Bioremediation of Organic Pollutants in Aquatic Sediments. *Journal of Hazardous Materials*, **177**, 81-89. <http://dx.doi.org/10.1016/j.jhazmat.2009.12.090>
- [14] Krempen, J.P. and Medbury III, C.S. (1995) Process for the Decontamination of Soils Contaminated by Petroleum Products. US Patents US5415777 A.
- [15] Stein, C. and Duouenne, D. (1994) Process for Absorbing Organic Polluting Products. US Patent US5360548 A.
- [16] Kopylova, L., Kashirin, A. and Svitsov, A. (2013) Hybrid Technology for Separation of Oil-in-Water Emulsions Combining Coalescing Filtration and Microfiltration. *Petroleum Chemistry*, **53**, 585-589. <http://dx.doi.org/10.1134/S0965544113080082>
- [17] Boopathy, R. (2000) Factors Limiting Bioremediation Technologies. *Bioresource Technology*, **74**, 63-67. [http://dx.doi.org/10.1016/S0960-8524\(99\)00144-3](http://dx.doi.org/10.1016/S0960-8524(99)00144-3)
- [18] Kadlec, R.H. and Wallace, S. (2008) *Treatment Wetlands*. CRC Press, Boca Raton. <http://dx.doi.org/10.1201/9781420012514>
- [19] WHO (2004) *Guidelines for Drinking-Water Quality: Recommendations*. Vol. 1, World Health Organization.
- [20] WHO (2011) *Guidelines for Drinking-Water Quality*. Vol. 216, World Health Organization, 303-304.
- [21] Wist, J., Sanabria, J., Dierolf, C., Torres, W. and Pulgarin, C. (2002) Evaluation of Photocatalytic Disinfection of Crude Water for Drinking-Water Production. *Journal of Photochemistry and Photobiology A: Chemistry*, **147**, 241-246. [http://dx.doi.org/10.1016/S1010-6030\(01\)00615-3](http://dx.doi.org/10.1016/S1010-6030(01)00615-3)
- [22] Udom, I., Ram, M.K., Stefanakos, E.K., Hepp, A.F. and Goswami, D.Y. (2013) One Dimensional-ZnO Nanostructures:

- Synthesis, Properties and Environmental Applications. *Materials Science in Semiconductor Processing*, **16**, 2070-2083. <http://dx.doi.org/10.1016/j.mssp.2013.06.017>
- [23] Zhang, Y., Ram, M.K., Stefanakos, E.K. and Goswami, D.Y. (2012) Synthesis, Characterization, and Applications of ZnO Nanowires. *Journal of Nanomaterials*, **2012**, Article ID: 624520. <http://dx.doi.org/10.1155/2012/624520>
- [24] Fujishima, A. (1972) Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*, **238**, 37-38. <http://dx.doi.org/10.1038/238037a0>
- [25] Fujishima, A., Honda, K.-I. and Kikuchi, S.-I. (1969) Photosensitized Electrolytic Oxidation on Semiconducting n-Type TiO₂ Electrode. *The Journal of the Society of Chemical Industry, Japan*, **72**, 108-113. <http://dx.doi.org/10.1246/nikkashi1898.72.108>
- [26] Hoffmann, M.R., Martin, S.T., Choi, W. and Bahnemann, D.W. (1995) Environmental Applications of Semiconductor Photocatalysis. *Chemical Reviews*, **95**, 69-96. <http://dx.doi.org/10.1021/cr00033a004>
- [27] Fujishima, A., Rao, T.N. and Tryk, D.A. (2000) Titanium Dioxide Photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, **1**, 1-21. [http://dx.doi.org/10.1016/S1389-5567\(00\)00002-2](http://dx.doi.org/10.1016/S1389-5567(00)00002-2)
- [28] Di Paola, A., García-López, E., Marci, G. and Palmisano, L. (2012) A Survey of Photocatalytic Materials for Environmental Remediation. *Journal of Hazardous Materials*, **211-212**, 3-29. <http://dx.doi.org/10.1016/j.jhazmat.2011.11.050>
- [29] Carp, O., Huisman, C.L. and Reller, A. (2004) Photoinduced Reactivity of Titanium Dioxide. *Progress in Solid State Chemistry*, **32**, 33-177. <http://dx.doi.org/10.1016/j.progsolidstchem.2004.08.001>
- [30] Wold, A. (1993) Photocatalytic Properties of Titanium Dioxide (TiO₂). *Chemistry of Materials*, **5**, 280-283. <http://dx.doi.org/10.1021/cm00027a008>
- [31] Dvoranova, D., Brezova, V., Mazúr, M. and Malati, M.A. (2002) Investigations of Metal-Doped Titanium Dioxide Photocatalysts. *Applied Catalysis B: Environmental*, **37**, 91-105. [http://dx.doi.org/10.1016/S0926-3373\(01\)00335-6](http://dx.doi.org/10.1016/S0926-3373(01)00335-6)
- [32] Asahi, R., Morikawa, T., Ohwaki, T., Aoki, K. and Taga, Y. (2001) Visible-Light Photocatalysis in Nitrogen-Doped Titanium Oxides. *Science*, **293**, 269-271.
- [33] Anpo, M. and Takeuchi, M. (2003) The Design and Development of Highly Reactive Titanium Oxide Photocatalysts Operating under Visible Light Irradiation. *Journal of Catalysis*, **216**, 505-516. [http://dx.doi.org/10.1016/S0021-9517\(02\)00104-5](http://dx.doi.org/10.1016/S0021-9517(02)00104-5)
- [34] Chen, X., Liu, L., Peter, Y.Y. and Mao, S.S. (2011) Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals. *Science*, **331**, 746-750.
- [35] Seery, M.K., George, R., Floris, P. and Pillai, S.C. (2007) Silver Doped Titanium Dioxide Nanomaterials for Enhanced Visible Light Photocatalysis. *Journal of Photochemistry and Photobiology A: Chemistry*, **189**, 258-263. <http://dx.doi.org/10.1016/j.jphotochem.2007.02.010>
- [36] Yang, P., Lu, C., Hua, N. and Du, Y. (2002) Titanium Dioxide Nanoparticles Co-Doped with Fe³⁺ and Eu³⁺ Ions for Photocatalysis. *Materials Letters*, **57**, 794-801. [http://dx.doi.org/10.1016/S0167-577X\(02\)00875-3](http://dx.doi.org/10.1016/S0167-577X(02)00875-3)
- [37] Saggioro, E.M., Oliveira, A.S., Pavesi, T., Maia, C.G., Ferreira, L.F.V. and Moreira, J.C. (2011) Use of Titanium Dioxide Photocatalysis on the Remediation of Model Textile Wastewaters Containing Azo Dyes. *Molecules*, **16**, 10370-10386. <http://dx.doi.org/10.3390/molecules161210370>
- [38] Lai, C.W., Juan, J.C., Ko, W.B. and Bee Abd Hamid, S. (2014) An Overview: Recent Development of Titanium Oxide Nanotubes as Photocatalyst for Dye Degradation. *International Journal of Photoenergy*, **2014**, Article ID: 524135. <http://dx.doi.org/10.1155/2014/524135>
- [39] Khalid, N., Ahmed, E., Hong, Z., Sana, L. and Ahmed, M. (2013) Enhanced Photocatalytic Activity of Graphene-TiO₂ Composite under Visible Light Irradiation. *Current Applied Physics*, **13**, 659-663. <http://dx.doi.org/10.1016/j.cap.2012.11.003>
- [40] Geim, A.K. and Novoselov, K.S. (2007) The Rise of Graphene. *Nature Materials*, **6**, 183-191. <http://dx.doi.org/10.1038/nmat1849>
- [41] Bonaccorso, F., Sun, Z., Hasan, T. and Ferrari, A.C. (2010) Graphene Photonics and Optoelectronics. *Nature Photonics*, **4**, 611-622. <http://dx.doi.org/10.1038/nphoton.2010.186>
- [42] Stoller, M.D., Park, S., Zhu, Y., An, J. and Ruoff, R.S. (2008) Graphene-Based Supercapacitors. *Nano Letters*, **8**, 3498-3502. <http://dx.doi.org/10.1021/nl802558y>
- [43] Messina, R. and Ben-Abdallah, P. (2013) Graphene-Based Photovoltaic Cells for Near-Field Thermal Energy Conversion. *Scientific Reports*, **3**, Article No. 1383. <http://dx.doi.org/10.1038/srep01383>
- [44] Chang, H., Lv, X., Zhang, H. and Li, J. (2010) Quantum Dots Sensitized Graphene: *In Situ* Growth and Application in Photoelectrochemical Cells. *Electrochemistry Communications*, **12**, 483-487. <http://dx.doi.org/10.1016/j.elecom.2010.01.025>

- [45] Xiang, Q., Yu, J. and Jaroniec, M. (2012) Graphene-Based Semiconductor Photocatalysts. *Chemical Society Reviews*, **41**, 782-796. <http://dx.doi.org/10.1039/C1CS15172J>
- [46] Zhou, K., Zhu, Y., Yang, X., Jiang, X. and Li, C. (2011) Preparation of Grapheme-TiO₂ Composites with Enhanced Photocatalytic Activity. *New Journal of Chemistry*, **35**, 353-359. <http://dx.doi.org/10.1039/C0NJ00623H>
- [47] Alam, T.E., Ram, M.K., Ladanov, M., Alvi, F., Mujumdar, A. and Kumar, A. (2012) Synthesis and Characterization of Novel Graphene Silicon Oxide Nanocomposite Material. *MRS Proceedings*, **1400**.
- [48] Gunti, S., Kumar, A. and Ram, M.K. (2015) Comparative Organics Remediation Properties of Nanostructured Graphene Doped Titanium Oxide and Graphene Doped Zinc Oxide Photocatalysts. *American Journal of Analytical Chemistry*, **6**, 708-717. <http://dx.doi.org/10.4236/ajac.2015.68068>
- [49] Williams, G., Seger, B. and Kamat, P.V. (2008) TiO₂-Graphene Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene Oxide. *ACS Nano*, **2**, 1487-1491. <http://dx.doi.org/10.1021/nn800251f>
- [50] Štengl, V., Bakardjieva, S., Grygar, T.M., Bludská, J. and Kormunda, M. (2013) TiO₂-Graphene Oxide Nanocomposite as Advanced Photocatalytic Materials. *Chemistry Central Journal*, **7**, 41. <http://dx.doi.org/10.1186/1752-153X-7-41>
- [51] Maira, A., Yeung, K.L., Soria, J., Coronado, J., Belver, C., Lee, C. and Augugliaro, V. (2001) Gas-Phase Photo-Oxidation of Toluene Using Nanometer-Size TiO₂ Catalysts. *Applied Catalysis B: Environmental*, **29**, 327-336. [http://dx.doi.org/10.1016/S0926-3373\(00\)00211-3](http://dx.doi.org/10.1016/S0926-3373(00)00211-3)
- [52] Ferrari-Lima, A.M., de Souza, R.P., Mendes, S.S., Marques, R.G., Gimenes, M.L. and Fernandes-Machado, N.R.C. (2015) Photodegradation of Benzene, Toluene and Xylenes under Visible Light Applying N-Doped Mixed TiO₂ and ZnO Catalysts. *Catalysis Today*, **241**, 40-46. <http://dx.doi.org/10.1016/j.cattod.2014.03.042>
- [53] Lannoy, A., Kania, N., Bleta, R., Fourmentin, S., Machut-Binkowski, C., Monflier, E. and Ponchel, A. (2016) Photocatalysis of Volatile Organic Compounds in Water: Towards a Deeper Understanding of the Role of Cyclodextrins in the Photodegradation of Toluene over Titanium Dioxide. *Journal of Colloid and Interface Science*, **461**, 317-325. <http://dx.doi.org/10.1016/j.jcis.2015.09.022>
- [54] Ramirez, A.M., Demeestere, K., De Belie, N., Mäntylä, T. and Levänen, E. (2010) Titanium Dioxide Coated Cementitious Materials for Air Purifying Purposes: Preparation, Characterization and Toluene Removal Potential. *Building and Environment*, **45**, 832-838. <http://dx.doi.org/10.1016/j.buildenv.2009.09.003>
- [55] Ohno, T., Tokieda, K., Higashida, S. and Matsumura, M. (2003) Synergism between Rutile and Anatase TiO₂ Particles in Photocatalytic Oxidation of Naphthalene. *Applied Catalysis A: General*, **244**, 383-391. [http://dx.doi.org/10.1016/S0926-860X\(02\)00610-5](http://dx.doi.org/10.1016/S0926-860X(02)00610-5)
- [56] Pramauro, E., Prevot, A.B., Vincenti, M. and Gamberini, R. (1998) Photocatalytic Degradation of Naphthalene in Aqueous TiO₂ Dispersions: Effect of Nonionic Surfactants. *Chemosphere*, **36**, 1523-1542. [http://dx.doi.org/10.1016/S0045-6535\(97\)10051-0](http://dx.doi.org/10.1016/S0045-6535(97)10051-0)
- [57] Sharma, A. and Lee, B.-K. (2015) Adsorptive/Photo-Catalytic Process for Naphthalene Removal from Aqueous Media Using *In-Situ* Nickel Doped Titanium Nanocomposite. *Journal of Environmental Management*, **155**, 114-122. <http://dx.doi.org/10.1016/j.jenvman.2015.03.008>



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