Sustainable Synthesis and Enhanced Photocatalytic Activity of Titanium Oxide-Clay Nanocomposite Toward Persistent Polychlorinated Biphenyl Degradation in Real Samples

Jasem Chanani

Khorramshahr University of Marine Science and Technology

Foad Buazar (✉ fb@kmsu.ac.ir)

Khorramshahr University of Marine Science and Technology

Yadollah Nikpour

Khorramshahr University of Marine Science and Technology

Research Article

Keywords: Sustainable Synthesis, Enhanced Photocatalytic Activity, Titanium Oxide-Clay , Persistent Polychlorinated Biphenyl Degradation

Posted Date: August 13th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-789637/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.
[Read Full License](#)

Abstract

This study presents the green synthesis of TiO₂-clay nanocomposite using an eco-friendly method based on carbohydrates. Glucose and soluble starch function as the bioreductant and stabilizer agent during the reaction, respectively. The UV-vis analysis ascertained the formation of TiO₂-clay nanocomposite presenting a distinctive absorption peak at 360 nm and an optical band gap of 4.3 eV. TEM and XRD results indicated the anatase phase of spherical TiO₂-clay with a median crystallite size of 18.36 nm. EDX and XRF techniques revealed the presence of titanium, oxygen peaks, and TiO₂ compound (58 wt%) along with the elemental composition of clay. The BET values of specific surface area, average pore diameter, and pore volumes are 47.48 m²g⁻¹, 17.39 nm, 0.19 cm³g⁻¹, respectively. The benign TiO₂-clay nanocomposite demonstrated superior photocatalytic efficiency toward photodegradation of polychlorinated biphenyl pollutant in industrial wastewater with a removal rate of 98.32%, greater than untreated TiO₂ NPs.

Introduction

Aquatic pollution is a global issue that quite often occurs when hazardous substances such as microorganisms or inorganic and organic chemicals contaminate the water supplies, deteriorating freshwater quality and making it detrimental to the health of ecosystem¹. It is reported that exceeding 80 percent of the world's untreated effluent is ultimately returned to the environment, contaminating safe water bodies including lakes, rivers, oceans, and aquifers. It is estimated that more than 400 cubic kilometers of polluted water annually are drained into the world's surface waters. Whereas water shields 75% of the world's surface, the total volume of saltwater on the earth is 97.5%, and the residual 2.5% proportion of freshwater is most unattainable sources, storing as frozen or underground water. As a result, a quite less than one percent of the earth's fresh water quantity is readily available for drinkable purposes indicating that our water sources are utterly finite². Moreover, as populations rise, in many countries, the amount of water accessible to each individual is dropping in which in turn would emerge water-scarce regions in the world. Hence, pollution intensifies the problem and human activities are main source of ruined and polluted water. Water contamination leads to an algal bloom in freshwaters or marine water systems and advent waterborne pathogens such as cholera, giardia, and typhoid diseases are an account of unsafe water^{3,4}. Nowadays the major sources of water pollution are classified as agricultural, sewage and wastewater, oil, radioactive substances pollution which are a complex of heavy metals, poly aromatic hydrocarbons and other emerging impurities⁵.

Polychlorinated biphenyls (PCBs) are a broad group of synthetic halogenated organic compounds known as chlorinated hydrocarbons. Due to chemical stability, nonflammability and high boiling point, PCBs are widely utilized for various commercial and industrial applications such as heat transfer, plastics, dyes, insulating and cooling fluids, pigments^{6,7}, to name but few. Environmentally, disposal PCBs are notorious persistent contaminants in aquatic ecosystem and highly likely maintain tendency to accumulate in the organic entities of the environmental medium where they are ascertained^{8,9}. Although PCBs can be

found in water, soil, and air, they facilely accumulate in tissue and sediment, and are highly likely detected at the highest concentrations in seafood cycles^{10,11}. Therefore, the initial encounter of human to PCBs exposure in the environment was resulted from consumption of food products predominantly fish, and animal-derived foods such as meat, dairy and also to a lesser degree, vegetable crops. Studies show that discharge and exposure to a high level of inadvertent PCBs in water, may cause a variety of adverse health effects predominantly multiple types of cancer risk in humans^{12–16}, hence; USEPA has categorized PCBs as potential human carcinogens¹². Several procedures have been developed for PCB detection and remediation including biological, chemical, physical and thermal methods^{17–19}. Yet, the most conventional technologies used for PCBs removal are landfilling or incineration²⁰. In recent years, nanotechnology as emerging field, has demonstrated as a reliable alternative technique in effective and economical mineralization of organic contamination such PCBs and poly aromatic hydrocarbons (PAHs)²¹. In literature numerous reports have been addressed using a versatile nano-scale materials for wastewater treatment^{22,23}.

Nano-sized titanium oxide (TiO₂)-clay composite is n-type semiconductor that has hold promising potential due to photochemical stability, non-toxicity, and low cost photocatalysts for efficient treatment of domestic and industrial wastewaters^{24,25}. It is found that immobilization of optical TiO₂ nanoparticles (NPs) on clay mineral would improve recovery and photocatalytic activity of TiO₂ NPs through curbing the recombination of the photogenerated hole-electron pairs²⁶. Meanwhile, clay mineral due to safety, layered structure, mechanical stability, and cation exchange capacity is considered as significant support material comparing to other immobilizer substrates such as quartz and stainless steel²⁷. A variety of fabrication recipes including dip coating, boil deposition, sol–gel, hydrothermal, impregnation, and metal organic chemical vapor deposition have been addressed for clay-modified titania. One can be noted that most preparation methods contain unsafe chemicals in which may induce significant damage to aquatic systems increment toxicity and environmental risks²⁸. As result, in this attempt, we have presented a facial green synthesis for eco-friendly TiO₂-clay nanocomposite and explored for the photodecomposition of 2,2',5,5'- Tetrachlorobiphenyl (PCB-52) as a typical representative of PCBs congener pollutants under UV irradiation in real aquatic environment.

Result And Discussion

XRD analysis

The result of XRD pattern of green TiO₂-clay nanocomposite was illustrated in Fig. 1. The peaks highlighted at 2 θ degree of 25.371°, 37.875°, 48.080°, 53.970°, 55.095°, 62.812°, 68.878°, 70.303°, 75.100° relating to the (110), (111), (210), (211), (204), (116), (220), and (115) planes show tetragonal structure of TiO₂ NPs with anatase phase^{29,30}. Other peaks assigned with blue asterisk are probably attributed to the minerals associated with nanoclay supporter³¹. The obtained results are well matched with (JCPDS No. 00-003-0016) and (JCPDS No. 98-005-1528) of TiO₂ and Montmorillonite (Aluminum hydrosilicate) clay,

respectively. The determined crystallite size from the Scherrer equation at 25.371° , the most intense diffraction peak of TiO₂, was 18.36 nm.

FTIR analysis

FTIR is a powerful qualitative toll in which elucidate the surface chemistry of organic-decorated nanostructures presenting fingerprint regions of main functional groups in compounds and molecules as well. As it can be seen in Fig. 2, there are an array of 8 main peaks that appeared in FTIR spectrum of TiO₂-caly nanocomposite sample. the presence three stretching bands between 3800 and 3600 cm⁻¹ are likely assigned to OH groups of absorbed water molecules as well as water coordinated to magnesium or surface of clay structure ³². The fairly wide peak appread at 3419 cm⁻¹ is attributed to O–H stretching vibration, representing hydroxyl groups of glucose and starch hydrocarbons ³³. The vibrational motion of absorbed CO₂ was observed specifically around 2355 cm⁻¹ on a FTIR spectrum during the sample preparation process ³⁴. The peak at 1641 cm⁻¹ likely reflects the presence bending vibration of OH group of water molecules in interlayer of TiO₂-caly nanostructured. The vibration of Si-O-Si bonds at fingerprint region of 1036 and 1461 cm⁻¹ perhaps are representative of sheet-like silicates in clay mineral ³². Finally, Ti–O bonding of anatase type was appeared at 528 cm⁻¹ and 440 cm⁻¹ bands indicating immobilization of the titania NPs on clay structure ^{35,36}.

BET characterization

The textural properties including the surface area, average pore volume, and average pore size of nanopowder were obtained using BET analytical method through the adsorption of nitrogen molecules on the solid surface. In comparison to raw clay, incorporating TiO₂ NPs in plate-like clay would remarkably enhance the values for BET surface area (S_{BET}), pore size and pore volume as twice time as raw clay (Table 1) ³⁷. These experimental results impart higher capability of TiO₂-clay nanocomposite in environmental remediation through increment the site numbers for pollutants adsorption ³⁸

Table 1			
Texture properties of pristine clay and green TiO ₂ -caly nanocomposite calcinated at 500 °C			
Sample	Specific surface area, S _{BET} (m ² g ⁻¹)	Pore diameter (nm)	Total pore volume (cm ³ g ⁻¹)
TiO ₂ -caly	47.48	17.39	0.19
Pristine clay	22.26	8.15	0.09

TEM investigation

The images results of TEM analysis illustrated in Fig. 3a-c. It is clearly indicated the distribution of TiO₂ NPs on the layer surface of montmorillonite clay. The produced green nanoscale TiO₂-clay powder hold spherical shape with median particle size of 50.84 nm obtained via TEM-histogram of 203 particles (Fig. 3d), confirming immobilization of TiO₂ NPs on clay structure.

SEM and EDX observations

The SEM micrographs of green TiO₂-Clay nanocomposite are depicted in Fig. 4a-c. the results indicated that montmorillonite possess a stacked plate-like sheets in which substantially decorated by round form titania particles. In addition, the roughly homogeneous distribution of TiO₂ NPs on the surface of the clay is clearly observed indicating an average particle size value of 68 nm (Fig. 4c). The elemental composition of the surface in TiO₂-Clay nanocomposite was further examined using SEM-EDX analysis. The results revealed the detection of the main constituent elements of clay minerals such as oxygen, silicon, magnesium, aluminum, iron, small proportion of Na, K, Ca along with titanium showing proper incorporation of TiO₂ NPs as it can be seen in Fig. 4d and Table 1S (see supplementary) as well.

XRF analysis

chemical composition of green synthesized TiO₂-clay is presented in Table 2. One can noted the different loading of various oxides such as CaO, Fe₂O₃, K₂O, Al₂O₃, and SiO₂, which mainly associated with clay structure³⁹. The XRF result exhibits that advent of TiO₂ with approximately large proportion (58%) in nanocomposite structure indicating an effective incorporation of titania into clay mineral³⁸.

Table 2 Composition (wt.%) of TiO ₂ -clay nanocomposite obtained by XRF analyzer							
SiO ₂	CaO	Al ₂ O ₃	K ₂ O	Fe ₂ O ₃	Na ₂ O	TiO ₂	MgO
27.08	0.98	6.65	0.55	3.99	0.57	58.34	1.38

Photocatalytic activity of green TiO₂-clay nanocomposite

The photocatalytic ability of TiO₂ impregnated montmorillonite nanocomposite was explored toward the PCB-52 contaminant in real sample provided from local petrochemical wastewater. In order to compare the removal efficiency, two other types of nanosorbents including TiO₂ NPs and clay nanoparticles were also investigated under identical conditions. The degradation process of PCB-52 organic pollutant was performed in dark as well as UV light condition that optimized at pH=7, contact time 120 min, 100 mg

adsorbent, the temperature of 35°C, and 35 mL of contaminant solution with a concentration of 8 mg/mL (Figs. 1-4S). As it is observed in Table 3, all applied nanoabsorbents reveal higher removal efficiency in the presence of UV light than in the dark regime. The UV-light triggered photocatalytic activity of aforementioned absorbents trend is in a sequence: TiO₂-clay > TiO₂ NPs > clay NPs (Fig. 5). Discernibly, TiO₂-clay nanocomposite with an adsorption capacity of 37.65 mg/g demonstrates superior photocatalytic degradation against of persistent organic PCB-52 pollutant with a removal rate higher than 97%. It is presumed that loading nanosized titania on the surface of montmorillonite clay afford additional active surface sites, and therefore increase the photodegradation rate of targeted substance through the production of highly reactive intermediates such as the photogenerated holes, superoxide ions, hydroxyl radical, peroxide radicals⁴⁰⁻⁴². On the other hand, the presence of clay as a immobilizer significantly enhances the decomposition process of selected environmentally detrimental material, curbing the agglomeration, and aggregation of clay-anchored TiO₂ NPs^{38,43}

TiO₂-caly nanophotocatalyst recyclability

The steadiness of nanocatalyst was examined by the catalytic cycle test. At the end of each cycle, the solution was filtered and the green TiO₂-caly was assessed in the next cycle. In this study the produced green clay-incorporated titania semiconductor was subjected to six successive run and degradation rate of polychlorinated biphenyl was calculated as seen in Fig. 6. it is found that TiO₂-clay nanocomposite remained its remarkable photocatalytic efficiency without significant change in its removal percentage. The effective immobilization of nano-sized titania possibly would improve its surface area, chemical stability and photocatalytic performance during photodegradation reaction in UV region supporting the previous findings²⁸ and current results (see table 3).

Table 3 Comparative catalytic efficiency of different type of nanoabsorbents		
Absorbent	UV irradiation	absence of UV light
Clay NPs	72.6	38.36
TiO ₂ NPs	80.8	55.63
TiO ₂ -clay nanocomposite	98.32	65.25

Conclusion

We successfully developed a facile ecofriendly approach for synthesis of green and economical TiO₂-caly nanocomposite using carbohydrate as reducing and stabilizer agent. The biofabricated clay-supported titania were systematically studied using an array of characterization tools and its efficiency was explored toward persistent an environmental PCB-52 pollutant. XRD, EDX and XRF indicated that TiO₂-caly exhibit crystal structure with pure anatase phase and possess appropriate elemental composition with an average crystallite size of 18.36 nm. The TEM, SEM results demonstrate that produced clay-incorporated TiO₂ NPs show round-like shape in which distributed on the surface of plate layers of clay with a median particle size of 50.84 nm. BET surface area of nanocomposite was estimated to be around 47.48 m²g⁻¹. In comparison with other absorbents, the highly reusable TiO₂-caly nanocomposite confirmed superior photocatalytic efficiency with removal rate of 97.45% toward environmental PCB-52 contaminate from aqueous solution due to more active sites and ample reactive oxygen species. Owing to the global concern of hazardous chemical impact, we believe that the photocatalytic process based on biogenic approaches paves the way for a safe aquatic environment, yet, quite a lot of attempts are demanding in improving the performance of environmental photocatalysis pathways.

Material And Method

Raw Materials and reagents

All chemical materials were purchased from Sigma-Aldrich company. Glucose and soluble starch reagents were utilized as green template. Titanium butoxide (Ti(OBu)₄, purity 97%) was used as precursor for preparation of titanium dioxide nanoparticles. Montmorillonite nanoclay consists of ~ 1 nm thick aluminosilicate layers surface substituted with metal cations and stacked in ~ 10 µm-sized multilayer stacks and was served as immobilizer and supporter of TiO₂ NPs. Polychlorinated biphenyl (PCBs-52) persistent environmental pollutant was collected from industrial waste water of local petrochemical manufacturing industry, Mahshahr, Iran. It was employed without any purification and stored in a glass bottle and kept in the refrigerator for further experiments. All standard solutions were made up by double distilled water.

Green synthesis of TiO₂-Clay nanocomposite

In a typical preparation, a 100 mL of a 0.001 M of titanium butoxide solution was added to 10 mL of a 0.2% (wt) aqueous solution of soluble starch and stirred until homogeneous solution obtained. Afterword, a 5 mL of a 0.10 M aqueous solution of glucose, bioreductant, was steadily added under a constant stirring. Separately, in 150 mL conical flask, 1 mg of nanoclay was well dispersed in 70 mL of ethanol under 2000 rpm stirring. Subsequently, the resultant is gradually impregnated with milky titanium solution and magnetically stirred for 1h to achieve a complete dissolution. In order to attain an effective reaction between the reactants, the obtained suspension was further sonicated for 120 mins. After centrifuging at 10,000 rpm for 10 min, the TiO₂ – clay sample was filtered and then wet powder heated at 120°C for 2h to

remove absorbed water and other impurities to a large extent. Lastly, the product was heated to 500°C for 2h in air at a rate of 5°C/min.

Photocatalytic degradation experiment

The photocatalytic performance of the TiO₂-clay nanocomposite against polychlorinated biphenyl was investigated at optimized conditions. All photodegradation experiments were conducted in a batch reactor. In a typical process, 100 mg of green nanocomposite was dispersed in 35 mL of 8 mg/L polychlorinated biphenyl solution. The suspension was constantly stirred in the dark for 20 min to acquire the adsorption-desorption equilibrium. Afterward, the mixture was subjected to ultraviolet light irradiation employing three 6-watt low-pressure UV lamps (Philips, $\lambda = 365$ nm) under vigorous stirring (500 rpm) at temperature 25°C. In all tests, UV lamps were maintained 10 cm above a Pyrex photoreactor containing the polluted water. After illumination at different time, the suspension is sampled and the photodegradation process of PCB-52 was monitored by UV/Vis absorption spectra at 208 nm. To ensure the repeatability, three trials of degradation of PCB-52 were carried out for each experiment. The removal percentage (%R) of PCB-52 as function of time is presented as Eq. 1:

$$\%R = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

Where C_0 is the initial concentration of PCB-52, C_t is the concentration of PCB-52 at certain reaction time t (min).

2.4. Physicochemical characterization of clay-supported TiO₂ nanocomposite

To determine the properties of green synthesized TiO₂-clay nanocomposite, XRD (X'Pert PRO MPD, Panalytical Co., Netherlands), UV-Vis (Analytik-Jena AG, Germany), TGA (PerkinElmer, Pyris 1, USA), FTIR (BRUKER Alpha-Germany), and TEM (LEO912-AB, Omega) techniques were operated. The average crystallite size of nanocomposite was estimated using the Debye-Scherrer equation (Eq. 1), where d is the diameter of crystallite size, k is the shape factor with the value 0.9, λ is the wavelength of X-ray radiation (0.154 nm), β is the full width at half the maximum intensity (FWHM), and θ is the Bragg angle.

Declarations

Author contributions

F. Buazar designed, supervised, and Writing - the original draft of this study. The synthetic experiments of nanoparticles and the relevant photocatalytic tests were accomplished by J. Chanani. Data analyses and

related results of experiments were investigated with the aid of Y. Nikpour. All authors contributed to the writing and editing of the paper.

Conflict of interest

The authors declare no competing interests.

References

1. Laws, E. A. *Aquatic pollution: an introductory text* (John Wiley & Sons, 2017).
2. Agnew, C. & Woodhouse, P. *Water resources and development* (Routledge, 2010).
3. Nichols, G., Lake, I. & Heaviside, C. Climate change and water-related infectious diseases. *Atmosphere*, **9**, 385 (2018).
4. Chowdhary, P., Bharagava, R. N., Mishra, S. & Khan, N. in *Environmental Concerns and Sustainable Development* 235–256 (Springer, 2020).
5. Madhav, S. *et al.* in *Sensors in Water Pollutants Monitoring: Role of Material* 43–62 (Springer, 2020).
6. Bani-Hani, E. & El Haj Assad, M. Halogenated Wastes Safe Disposal: Polychlorinated biphenyls. *International Journal of Petrochemistry and Research*, **1**, 76–78 (2017).
7. Anh, H. Q., Watanabe, I., Minh, T. B. & Takahashi, S. Unintentionally produced polychlorinated biphenyls in pigments: An updated review on their formation, emission sources, contamination status, and toxic effects. *Science of The Total Environment*, 142504 (2020).
8. Reddy, A. V. B., Moniruzzaman, M. & Aminabhavi, T. M. Polychlorinated biphenyls (PCBs) in the environment: Recent updates on sampling, pretreatment, cleanup technologies and their analysis. *Chem. Eng. J.*, **358**, 1186–1207 (2019).
9. Liu, J., Tan, Y., Song, E. & Song, Y. A. Critical Review of Polychlorinated Biphenyls Metabolism, Metabolites, and Their Correlation with Oxidative Stress. *Chemical Research in Toxicology*, **33**, 2022–2042 (2020).
10. Jing, R., Fusi, S. & Kjellerup, B. V. Remediation of polychlorinated biphenyls (PCBs) in contaminated soils and sediment: state of knowledge and perspectives. *Frontiers in Environmental Science*, **6**, 79 (2018).
11. González, N., Marquès, M., Nadal, M. & Domingo, J. L. Occurrence of environmental pollutants in foodstuffs: A review of organic vs. conventional food. *Food and Chemical Toxicology*, **125**, 370–375 (2019).
12. Alsen, M. *et al.* Endocrine disrupting chemicals and thyroid cancer: an overview. *Toxics*, **9**, 14 (2021).
13. Calaf, G. M., Ponce-Cusi, R., Aguayo, F., Muñoz, J. P. & Bleak, T. C. Endocrine disruptors from the environment affecting breast cancer. *Oncology letters*, **20**, 19–32 (2020).
14. Heiger-Bernays, W. J. *et al.* Human health risks due to airborne polychlorinated biphenyls are highest in New Bedford Harbor communities living closest to the harbor. *Science of The Total Environment*,

710, 135576 (2020).

15. Zani, C., Ceretti, E., Covolo, L. & Donato, F. Do polychlorinated biphenyls cause cancer? A systematic review and meta-analysis of epidemiological studies on risk of cutaneous melanoma and non-Hodgkin lymphoma., **183**, 97–106 (2017).
16. Yao, M. *et al.* Polychlorinated biphenyls and its potential role in endometriosis. *Environ. Pollut*, **229**, 837–845 (2017).
17. Khalid, F., Hashmi, M. Z., Jamil, N., Qadir, A. & Ali, M. I. Microbial and enzymatic degradation of PCBs from e-waste-contaminated sites: A review. *Environmental Science and Pollution Research*, 1–14(2021).
18. Munawar, A., Akram, M. S., Javed, M. T. & Shahid, M. *in Handbook of Bioremediation* 677–687(Elsevier, 2021).
19. Fan, G., Cang, L., Fang, G. & Zhou, D. Surfactant and oxidant enhanced electrokinetic remediation of a PCBs polluted soil. *Separation and Purification Technology*, **123**, 106–113 (2014).
20. Qi, Z. *et al.* Some technical issues in managing PCBs. *Environmental Science and Pollution Research*, **21**, 6448–6462 (2014).
21. Borji, H., Ayoub, G. M., Al-Hindi, M., Malaeb, L. & Hamdan, H. Z. Nanotechnology to remove polychlorinated biphenyls and polycyclic aromatic hydrocarbons from water: a review. *Environ. Chem. Lett*, **18**, 729–746 (2020).
22. Gautam, P. K., Singh, A., Misra, K., Sahoo, A. K. & Samanta, S. K. Synthesis and applications of biogenic nanomaterials in drinking and wastewater treatment. *Journal of environmental management*, **231**, 734–748 (2019).
23. Lu, F. & Astruc, D. Nanocatalysts and other nanomaterials for water remediation from organic pollutants. *Coord. Chem. Rev*, **408**, 213180 (2020).
24. Mishra, A. & Basu, S. Clay Supported TiO₂ Nanocomposites for Photocatalytic Degradation of Volatile Organic Compounds (VOCs) and Dyes(2019).
25. Chkirida, S. *et al.* Highly synergic adsorption/photocatalytic efficiency of Alginate/Bentonite impregnated TiO₂ beads for wastewater treatment. *Journal of Photochemistry and Photobiology A: Chemistry*, **412**, 113215 (2021).
26. Gombos, E. D. *et al.* Laponite immobilized TiO₂ catalysts for photocatalytic degradation of phenols. *Journal of Photochemistry and Photobiology A: Chemistry*, **387**, 112045 (2020).
27. Moma, J. & Baloyi, J. Modified titanium dioxide for photocatalytic applications. *Photocatalysts-Applications and Attributes* **18** (2019).
28. Onwuka, K., Achilike, K. & Eze, K. Montmorillonite Clay Enhanced TiO₂ Nanoparticle for Photocatalytic Degradation of Organic Pollutants: Mini Review. *Int J Pharma Sci*, **1**, 33–38 (2021).
29. Balaji, S. *et al.* Green synthesis of nano-titania (TiO₂ NPs) utilizing aqueous Eucalyptus globulus leaf extract: applications in the synthesis of 4 H-pyran derivatives. *Research on Chemical Intermediates*, 1–13(2019).

30. Muniandy, S. S., Kaus, N. H. M., Jiang, Z. T., Altarawneh, M. & Lee, H. L. Green synthesis of mesoporous anatase TiO₂ nanoparticles and their photocatalytic activities. *RSC advances*, **7**, 48083–48094 (2017).
31. Hadjltaief, H. B., Gálvez, M. E. & Zina, M. B. & Da Costa, P. TiO₂/clay as a heterogeneous catalyst in photocatalytic/photochemical oxidation of anionic reactive blue 19. *Arabian Journal of Chemistry*, **12**, 1454–1462 (2019).
32. Oliveira, W. V. *et al.* d. TiO₂ immobilized on fibrous clay as strategies to photocatalytic activity. *Materials Research* **23**(2020).
33. Moavi, J., Buazar, F. & Sayahi, M. H. Algal magnetic nickel oxide nanocatalyst in accelerated synthesis of pyridopyrimidine derivatives. *Scientific reports*, **11**, 1–14 (2021).
34. Schädle, T., Pejčić, B. & Mizaikoff, B. Monitoring dissolved carbon dioxide and methane in brine environments at high pressure using IR-ATR spectroscopy. *Anal. Methods*, **8**, 756–762 (2016).
35. Bagheri, S., Shameli, K. & Abd Hamid, S. B. Synthesis and characterization of anatase titanium dioxide nanoparticles using egg white solution via sol-gel method. *Journal of Chemistry* **2013** (2013).
36. Cheira, M. F., Kouraim, M. N., Zidan, I. H., Mohamed, W. S. & Hassanein, T. F. Adsorption of U (VI) from sulfate solution using montmorillonite/polyamide and nano-titanium oxide/polyamide nanocomposites. *Journal of Environmental Chemical Engineering*, **8**, 104427 (2020).
37. Yuan, L., Huang, D., Guo, W., Yang, Q. & Yu, J. TiO₂/montmorillonite nanocomposite for removal of organic pollutant. *Applied clay science*, **53**, 272–278 (2011).
38. Szczepanik, B. Photocatalytic degradation of organic contaminants over clay-TiO₂ nanocomposites: A review. *Appl. Clay Sci*, **141**, 227–239 (2017).
39. Li, X., Peng, K., Chen, H. & Wang, Z. TiO₂ nanoparticles assembled on kaolinites with different morphologies for efficient photocatalytic performance. *Scientific reports*, **8**, 1–11 (2018).
40. Papoulis, D. Halloysite based nanocomposites and photocatalysis: a review. *Appl. Clay Sci*, **168**, 164–174 (2019).
41. Chen, D. *et al.* Photocatalytic degradation of organic pollutants using TiO₂-based photocatalysts: A review. *Journal of Cleaner Production*, **121**, 125 (2020).
42. Kibanova, D., Cervini-Silva, J. & Destailats, H. Efficiency of clay – TiO₂ nanocomposites on the photocatalytic elimination of a model hydrophobic air pollutant. *Environmental science & technology*, **43**, 1500–1506 (2009).
43. Mishra, A., Mehta, A. & Basu, S. Clay supported TiO₂ nanoparticles for photocatalytic degradation of environmental pollutants: A review. *Journal of environmental chemical engineering*, **6**, 6088–6107 (2018).

Figures

Figure 1

XRD pattern of green TiO₂-caly nanocomposite calcinated at 500°C

Figure 2

FTIR spectrum of green TiO₂-caly nanocomposite calcinated at 500°C

Figure 3

TEM images (a-c), and histogram of size distribution of clay immobilized TiO_2 nanoparticle calcinated at 500°C

Figure 4

SEM images (a-c) and EDX spectrum (d) of green TiO₂-Clay nanocomposite calcinated at 500°C

Figure 5

Bar graph of selected absorbents toward elimination of PCB-52 pollutant in the presence of UV light radiation and dark condition

Figure 6

Recyclability of TiO₂-clay nanocomposite in photocatalytic degradation of organic PCB-52 substance under UV illumination.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [supplementary.docx](#)