Journal of Nanopores Systems

Original Research Paper

Methyl orange dye pollutant photodegradation over visible light active titania extrudate mesoporous ordered material

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Article history
Received: 14 October 2024
Revised: 29 April 2025
Accepted: 2 May 2025

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Abstract: Titanium dioxide (TiO_2) represents a well-studied photocatalyst that has been widely considered in research activities and is also commercialized. Because of its appealing physical and chemical properties, it was found that it can be useful in a wide spectrum of applications. The present study provides a process for the production of a porous, extruded visible light active titania-based material comprising mesopores. Today It has been surprisingly found that using a cellulose porogen during the extrusion of a titania-based material enables the formation of the mesopores following removal of the porogen by thermal or oxidative decomposition. The second aspect of the present study provides the characterization results of the prepared mesopores based on the techniques with DRS, AFM, and TEM. Finally, the photodegradation of MO dye was examined with different operational parameters such as pH, concentration of nanophotocatalyst, reusability investigated. As an excellent result, the best photocatalytic activity was measured at pH=3 with catalyst concentration of 200 mg/L and the prepared nanophotocatalyst has good reusability up to 5 runs.

Keywords: Photocatalysis, Methyl orang dye, Mesopores, Titania, Photodegradation

Introduction

The use of photocatalysis for wastewater treatment is an important area of research, which is not yet fully exploited at an industrial level and has a significant potential in the disposal of many industrial effluents, particularly the effluents that are difficult to treat by conventional treatment processes [1-5]. Current challenges in this field aim to develop novel TiO_2-based photocatalysts that can operate under visible light radiation and exhibit extended charge separation. Narrowing the band gap and prolonged charge separation can be achieved via doping of TiO_2 with metallic and non-metallic species, co-doping with more than one element, and coupling TiO_2 with other semiconductors [6-8]. Mahu et al. [9] reported the synthesis of the porous titania by an ultrasound-assisted sol-gel route. The synthesis process was empirically modeled and optimized by using the response surface methodology (RSM). Regarding to the application it is necessary to say that the synthesized TiO_2 samples were tested for the photodegradation of two water-soluble organic pollutants under UV–Vis irradiation, and the maximal removal efficiencies of 98.4% and 46.3% for the photodegradation of CR dye and 2,4-D herbicide, was calculated, respectively. In addition, the photodegradation kinetics revealed the pseudo-first-order rate constants, showing the photodegradation of CR is about 1.3-fold faster than the photodegradation of 2,4-D pesticide.

The present study relates to a porous, extruded titania-based material comprising mesopores, extruded, titania-based material comprising mesopores suitable for use as a photocatalyst for photodegradation methyl orange (MO) dye. The first section of this work relates to a process of preparing the extruded titania-

based material comprising mesopores and as an application investigation of the methods for the photocatalysis removal of dye pollutants under visible light irradiation.

Experimental

Materials

Titanium oxide (Degussa p25 Titanium Dioxide (TiO_2), Rutile/Anatase: 85:15, 99.9%, 20nm quantity) and a cellulose (($C_6H_{10}O_5$)n), (Aldrich, Sigmacell Type 101) were purchased. Sodium poly aspartate was purchased from green-mountainchem.

Visible light active titania extrudate comprising mesopores synthesis

A porous, titania-based extrudate was prepared by mixing a predetermined amount of titanium oxide and cellulose in a mechanical mixer (Royaniran-250W-3000 rpm) and then formulated with an aqueous solution of sodium poly aspartate in a 360° rotating mixer (Rotating Mixer Shaker – RMO-80Pro-JOANLAB) to obtain a paste with a mass ratio of titania to cellulose and sodium poly aspartate of 1.0:0.5:2.0. The obtained paste was extruded using a mechanical extruder (Sanaf) through a die with 1/18 inch diameter holes to obtain extrudates with cylindrical rod geometry. The extrudate was dried at 110° C. overnight, followed by calcination at 500° C for four h (2° C/min).

Characterization

The BET (Brunauer-Emmett-Taller) specific surface area was obtained from N_2 adsorption-desorption isotherm measured at 77 K in an automated adsorption apparatus (Tristar II 3020 Operator's Manual v3.02, Micrometric). To obtain information about the surface morphology of the catalysts, images were taken at different magnifications on the BRISK atomic force microscopy (AFM). A UV-Vis spectrophotometer (Shimadzu UV-3600) was used for UV diffuse reflectance spectra (DRS) in the range of 200 to 700 nm to approve the visible light active nanophotocatalyst preparation.

Photocatalytic test

The photodegradation of MO dye under visible light irradiation was used to investigate the photocatalytic activities of the synthesized nanophotocatalysts. The photocatalytic experiments were carried out using a glass beaker as a temperature-controlled reactor system. The used light source was a 250 W halogen lamp [10,11]. In a typical run, 25 ml of MO at 12 mg/L concentration was prepared [12-15]. A known amount of catalyst was then added to the solution. To obtain the adsorption-desorption equilibrium, the reaction mixture was magnetically stirred in the dark for 15 min before exposure to visible light. The catalyst was removed by centrifuging at 13000 rpm for 20 min at given intervals of 15 min [16-20]. The concentration of the samples was determined using the UV-Vis spectrophotometer (SHIMADZU UV-2600 UV Spectrophotometer device). The photodegradation of the MO solution was followed by a decrease in the intensity of the absorption band of the MO spectra. The absorption band is typically located at 507 nm. The MO degradation efficiency was calculated using the following eq. (1) [21]:
MO photodecoloration (%) =C0-C/C0×100

Results and Discussion

DRS

DRS analysis of synthesized photocatalysts was performed and shown in Fig. 1. Diffuse reflectance spectroscopy is a scientific technique used to probe the optical band gap energy of nanomaterials. The Kubelka-Munk function along with the Tauc plot method can be used to determine the optical band gap energy of visible light active titania extrudate comprising mesopores. The band gap indicates the difference in amount of the energy between the top of the valence band filled with electrons and the bottom of the conduction band devoid of electrons. It was observed that the nanophotocatalyst sample has an absorption band at wavelengths from 250 to 450 nm, and the wavelength of cut-off absorption is around 430 nm, which confirms the sensitization of titania extrudate comprising mesopores with a low band gap compared to the absorption on the bandgap of anatase titania extrudate comprising mesopores. Quantization effects that improve the photocatalytic properties are indicated by the increase in band gap energy of visible light-activated TiO_2 [18, 21].

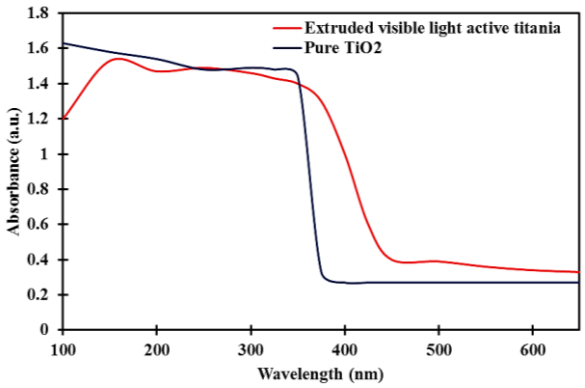

Fig. 1. DRS analysis of the resulted extruded visible light active titania-based material comprising mesopores nanophotocatalyst and pure TiO_2

AFM

The surface topography of the extruded visible light active titania-based material comprising mesopores nanophotocatalyst was scanned by AFM (Fig. 2). The

extruded visible light active titania consisted of spherical and regularly shaped particles with a narrow size range (50-80 nm). The extruded visible light active titania nanophotocatalyst formed relatively uniform particle sizes with no agglomeration and had a grape cluster-type structure as shown in Fig. 2.

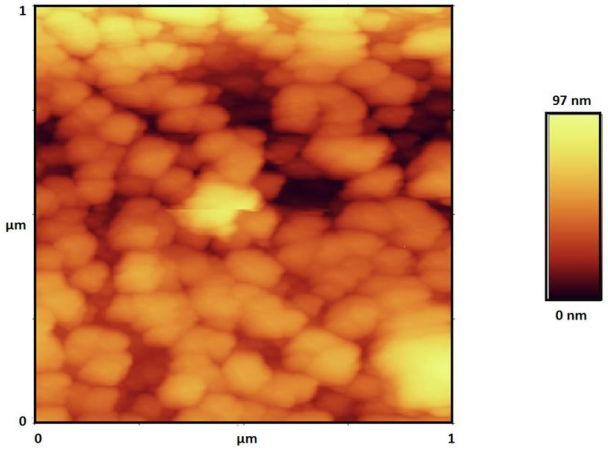

Fig. 2. AFM image of the resulted extruded visible light active titania-based material comprising mesopores nanophotocatalyst

Brunauer-Emmett-Teller (BET) analysis

Fig. 3 represents the nitrogen adsorption-desorption isotherms of the results extruded visible light to active titania-based material that comprised mesoporous nanophotocatalyst. The isotherms of the extruded visible light active titania-based material comprising mesopores nanophotocatalyst sample could be attributed to type IV, and the curves exhibited hysteresis loops at high relative pressures, indicated a mesoporous structure. Furthermore, the specific surface areas and average pore sizes of these samples as calculated by the BET method extruded visible light active titania-based material comprising mesopores nanophotocatalyst resulted in BET surface areas of (59.04 m^2/g) and the average pore sizes of (19.8940 nm). This result is obtained may be because the average pore size is related to the crystallite size of a TiO_2 nanophotocatalyst sample. Due to the presence of sodium poly aspartate as a surfactant, the nanospheres of TiO_2 dispersed with high monodispersity and no growth and agglomeration, which cause the high surface area of TiO_2 nanoparticles and create meso size and uniform voids.

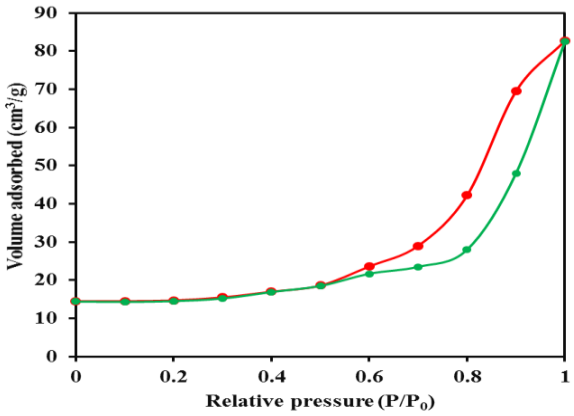

Fig. 3. Nitrogen adsorption-desorption isotherms of the resulted extruded visible light active titania-based material comprising mesopores nanophotocatalyst

Photocatalytic results

The effect of extruded mesopores nanophotocatalyst

The results of photocatalyst efficiencies of extruded visible light active titania-based material comprising mesopores nanophotocatalyst are given in Fig. 4 and compared with pure titania and MO blank sample without catalyst. Photocatalytic activity of extruded visible light active titania-based material comprising mesopore nanophotocatalyst by photo decoloration of MO under visible light illumination was tested and all results are shown in Fig. 4. The amount of all samples and conditions were constant and the same, in a way that 2 mg of samples was employed. As seen in Fig. 4, the first blank tests as MO self-photocatalysis were made in the absence of a nanophotocatalyst, and no MO photodegradation was observed. The second control test was carried out in the presence of TiO_2 nanopowder. TiO_2 nanopowder has low photocatalytic activity in the UV region due to the high band-gap energy of TiO_2 and the low UV part of the applied lamp in this test [18, 21]. Another reason is the poor dispersion of active phases. As seen in Fig. 4, MO degradation was increased for extruded visible light active titania-based material comprising mesopores nanophotocatalyst. Its photocatalytic efficiency is increased as a result of the high porosity of TiO_2.

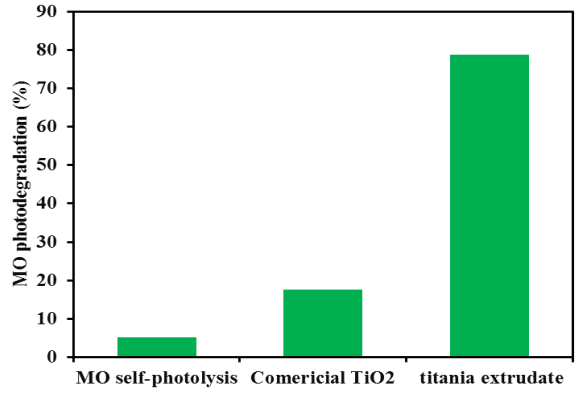

Fig. 4. Results of MO photodegradation over extruded visible light active titania-based material comprising mesopores nanophotocatalyst and control samples

The effect of pH

Results of photocatalyst efficiencies at different pH over extruded visible light active titania-based material comprising mesopores nanophotocatalyst are presented in Fig. 5. The amount of nanophotocatalyst for each pH test was constant and the same, in a way that 2 mg of sample nanophotocatalyst was employed. As seen in Fig. 5. It is obvious that at the pH=3 photocatalytic efficiency is increased. Thus, the best pH value for MO photodegradation is obtained at 3. As can be seen from these results, either increasing or decreasing the pH value from 3, the photocatalytic efficiencies will decrease significantly [22]. The change in pH plays a critical role in the adsorption of dye molecules on the surface of the photocatalyst and then the photodegradation reaction. In other words, changing the pH can change the surface charge of the photocatalyst or change the charge of the dye molecules and then affect the interaction between the dye molecules and the nanocomposite surface [15, 21]. By photodegradation of anionic MO dye, which has negatively charged groups due to the presence of sulphuric group in its structure, better attraction of MO molecules to the extruded visible light active titania-based material comprising mesopores nanophotocatalyst surface will occur at pH = 3. (Fig. 6)

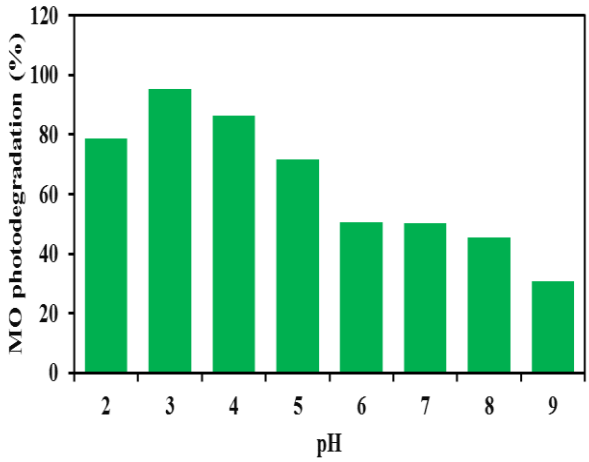

Fig. 5. Results of MO photodegradation over extruded visible light active titania-based material comprising mesopores nanophotocatalyst at different pH.

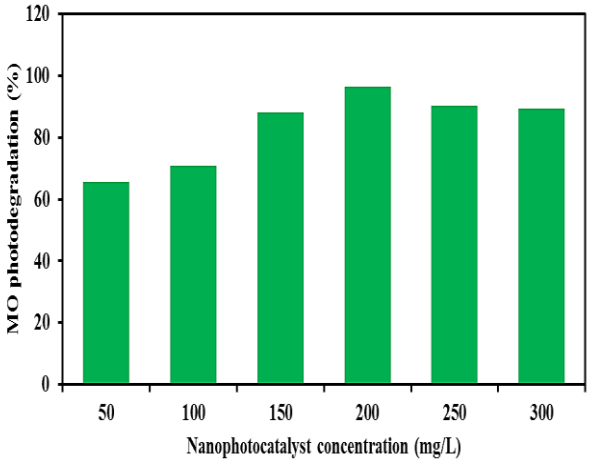

Fig. 6. Results of MO photodegradation over extruded visible light active titania-based material comprising mesopores nanophotocatalyst at different concentration at pH=3.

The effect of catalyst concentration

As it would be expected, an increase of the amount of catalyst leads to the higher photodegradation efficiencies and increased reaction rates as more active sites are provided for the adsorption of dye molecules. The initial reaction rates were found to increase proportionally with the amount of the catalyst up to 200 mg/L and then the rate of photodegradation and photocatalytic activity were decreased due to the low dispersity of nanophotocatalyst in the reaction solution [18, 22]. The obtained experimental results showed that the catalyst amount has both positive and negative impacts on the photodecomposition rate. The catalysts amounting to 200 mg/L demonstrated an increased photodegradation rate of MO from 96.3 to 89.4 %, which could be explained by a

decreased number of active sites from the nanophotocatalyst.

Stability of nanophotocatalyst study

In this part, the reusability of the prepared nanophotocatalyst for MO degradation has been investigated. For this purpose, the recycling and stability of the extruded visible light active titania-based material comprising mesopores nanophotocatalyst sample was tested under similar circumstances and optimal, concentration of nanophotocatalyst, pH, through successive 6 runs of photocatalyst experiment [22]. After each run nanophotocatalyst was separated, it was used immediately for further run without any treatment. The obtained results approved that the nanophotocatalyst stability slightly dropped in runs 2 to 6, producing about 92% photodegradation. Thus, the prepared nanophotocatalyst is stable for more than 6 cycles when used as a visible light active heterogeneous photocatalyst and can be employed for degradation purposes for industrial applications.

Conclusion

Photocatalysis processes especially visible light active heterogeneous photocatalytic degradation can be utilized as an appropriate remediation strategy. Heterogeneous nanophotocatalysts have many advantages over homogeneous catalysts, such as easy separation from the reaction mixture and their reusability. Extruded visible light active titania-based material comprising mesopores nanophotocatalyst proved to be highly efficient for photodegradation of these contaminants. The present study provides a process of the production of a porous, extruded visible light active titania-based material comprising mesopores and characterization results of the prepared mesopores based on the techniques with DRS, AFM, and TEM. Finally, the photodegradation of MO dye was examined and different operational parameters such as pH, concentration of nanophotocatalyst, and reusability were investigated. As an excellent result, the best photocatalytic activity was measured at pH=3 with a catalyst concentration of 200 mg/L and the prepared nanophotocatalyst has good reusability for up to 5 runs.

References

[1]. Nakata, K.F., ujishima, A., TiO_2 photocatalysis: Design and applications. ***Journal of Photochemistry and Photobiology C***, **2012**, 13, 169–189.

[2]. Coromelci-Pastravanu, C., Ignat, M., Popovici, E., Harabagiu, V., TiO_2-coated mesoporous carbon: Conventional vs. microwave-annealing process. ***Journal of Hazardous Materials*, 2014**, 278, 382–390.

[3]. Mirhoseini, F., Mirhoseini, B.S., Noor Mohammad Beigi, M., Understanding the photodegradation of amoxicillin antibiotic using visible light sensitized poly(methyl methacrylate)/TiO_2 nanocomposite. ***NanoSci.Technol. J.*, 2023**, 1(1), 38-48. https://doi.org/10.22034/nstj.2023.707804

[4]. Mirhoseini, F., Salabat, A., Ionic liquid based microemulsion method for fabrication of poly(methyl methacrylate)–TiO_2 nanocomposite as highly efficient visible light photocatalyst, ***RSC Advanced*, 2015**, 5, 12536–12545. https://doi.org/10.1039/c4ra14612c

[5]. Salabat, A., Mirhoseini, F., Applications of a new type of poly(methyl methacrylate)/TiO_2 nanocomposite as an antibacterial agent and a reducing photocatalyst. ***Photochemistry & Photobiological Science*, 2015**, 14(9) 1637–1643. https://doi.org/10.1039/c5pp00065c

[6]. Mirhoseini, F., Salabat, A., Polymer nanocomposite based composition and method for controlling water hardness, ***United States patent*** 11136247.

[7]. Mirhoseini, F., Salabat, A., **Photocatalytic filter, United States patent** 10828629.

[8]. Salabat, A., F. Mirhoseini, F., Polymer-based nanocomposites fabricated by microemulsion method, Polym. ***Composites*, 2022**, 43 1282–94. https://doi.org/10.1002/pc.26504

[9]. Mahu, E., Ignat, M., Cojocaru, C., Samoila, P., Coromelci, C., Asaftei, I., Harabagiu, V., Development of Porous Titania Structure with Improved Photocatalytic Activity: Response Surface Modeling and Multi-Objective Optimization. ***Nanomaterials.*** **2020**,10(5), 998. https://doi.org/10.3390/nano10050998

[10]. Salabat, A., Mirhoseini, F., Nouri, F.H., Microemulsion strategy for preparation of TiO_2–Ag/poly(methyl methacrylate) nanocomposite and its photodegradation application. ***Journal of Iranian***

Chemical Society, **2022**, 20 599–608. https://doi.org/10.1007/s13738-022-02693-7.

[11]. Salabat, A., Mirhoseini, F., A novel and simple microemulsion method for synthesis of biocompatible functionalized gold nanoparticles, ***Journal of Molecular Liquids,*** **2018**, 268 849–853. https://doi.org/10.1016/j.molliq.2018.07.112

[12]. Salabat, A., Mirhoseini, F., Masoumi, Z., Mahdie, M., Preparation and characterization of polystyrene-silver nanocomposite using microemulsion method and its antibacterial activity, ***JNS,*** **2014**, 4, 377-382.

[13]. Salabat, A., Mirhoseini, F., Abdoli, K., A microemulsion route to fabrication of mono and bimetallic Cu/Zn/γ-Al_2O_3 nanocatalysts for hydrogenation reaction. ***Scientia Iranica,*** **2018**, 25, 1364-1370.https://doi.org/10.24200/sci.2018.5023.1048

[14]. Salabat, A., Mirhoseini, B.S., Mirhoseini, F., Ionic liquid based surfactant-free microemulsion as a new protocol for preparation of visible light active poly(methyl ethacrylate)/TiO_2 nanocomposite. **Scientific Reports, 2024**, 14, 15676.

https://doi.org/10.1038/s41598-024-66872-7

[15]. Salabat, A., Mirhoseini, F., Valirasti, R., Engineering poly(methyl methacrylate)/Fe_2O_3 hollow nanospheres composite prepared in microemulsion system as a recyclable adsorbent for removal of benzothiophene, ***Industrial & Engineering Chemistry Research,*** **2019**, 58,17850-1785.

https://doi.org/10.1021/acs.iecr.9b04322

[16]. Salabat, A., Mirhoseini, F., Mahdieh, M., H. Saydi, H., A novel nanotube-shaped polypyrrole-Pd composite prepared using reverse microemulsion polymerization and its evaluation as an antibacterial agent, ***New Journal of Chemistry,*** **2015**, 39 (5), 4109–4114. https://doi.org/10.1039/c5nj00175g

[17]. Salabat, A., Mirhoseini, F., Arjomandzadegan, M., Jiryaei, E., A novel methodology for fabrication of Agpolypyrrole core-shell nanosphere using microemulsion system and evaluation of its antibacterial application, ***New Journal of Chemistry,*** **2017**, 41(21), 12892–12900. https://doi.org/10.1039/c7nj00678k

[18]. Salabat, A., Mirhoseini, F., Photo-induced hydrophilicity study of poly (methyl methacrylate)/TiO_2 nanocomposite prepared in ionic liquid based microemulsion system. ***Current Applied Polymer Science,*** **2018**, 2(2), 112–120. https://doi.org/10.2174/2452271602666180803141554F

[19]. Mirhoseini, F., Salabat, A., Antibactrial activity based poly (methyl methacrylate) supported TiO_2 photocatalyst film nanocomposite, ***Technical Journal of Engineering and Applied Science***, 2015, 5,115-118.

[20]. Kamali, F., Faghihi, K., Mirhoseini, F., High antibacterial activity of new eco-friendly and biocompatible polyurethane nanocomposites based on Fe_3O_4/Ag and starch moieties. ***Polymer Engineering and Science,*** **2022**, 62(5), 1444- 1462. https://doi.org/10.1002/pen.25934

[21]. Mirhoseini, F., Salabat, A., Iinvestigation of operational parameters on the photocatalytic activity of a new type of poly (methyl methacrylate)/ionic liquid-TiO_2 nanocomposite, ***Iranian Journal of Chemistry and Chemical Engineering,*** **2019**, 38, 101-114. https://doi.org/10.30492/IJCCE.2019.37613

[22]. Mirhoseini, F., Salabat, A., Removal of methyl tert -butyl ether as a water pollutant by photodegradation over a new type of poly (methyl methacrylate)/TiO_2 nanocomposite. ***Polymer Composites,*** **2018**, 39(4), 1248–1254. https://doi.org/10.1002/pc.24059.