TiO₂ Encapsulated into Zeolitic Imidazolate Framework (TiO₂@ZIF-8) as an Efficient Nanophotocatalyst for Degradation of Paraquat Herbicide

Fariba Dashtestani[1], Vahid Mohagheghi[1], Leila Ma᾽mani[*1], Kobra Maafi[2]

1- Department of Nanotechnology, Agricultural Biotechnology Research Institute of Iran (ABRII), Agricultural Research Education and Extension Organization (AREEO), Karaj, Iran.

4- Islamic Azad University, West Tehran Branch, Tehran, Iran.

leila.mamani@abrii.ac.ir

Abstract

In this research, preparation, characterization, and evaluation of TiO₂ encapsulated into zeolitic imidazolate framework (TiO₂@ZIF-8) nanophotocatalyst was investigated as an efficient photo-degradation of paraquat (PQ) herbicide from aqueous samples. This study was performed using a ZIF-8-based nanophotocatalyst and a reactor consisting of an ultraviolet (UV) source and a reaction chamber. The effects of various parameters including contaminant concentration, amount of nanophotocatalyst, and pH reaction time were investigated on the removal efficiency of contaminant by the TiO₂@ZIF-8 nanophotocatalyst. The results showed by increasing the amount of the TiO₂@ZIF-8 nanophotocatalyst and pH, the removal of paraquat showed an increase. The optimal condition was found as nanophotocatalyst concentration (0.05 g.L⁻¹), pH (7) at room temperature for 15 min for removal of 99.8% paraquat. According to the results, TiO₂@ZIF-8 emerged as an efficient, robust, and recyclable nanophotocatalyst, which is a potential and environmentally friendly process for the removal of toxic chemical herbicide as hazardous organic contaminants from aqueous samples. The facile fabrication approach and the enhanced photocatalytic activity of TiO₂@ZIF-8 were highlighted and notably showed good reusability in 8 consecutive cycles.

Keywords: TiO₂, Zeolitic Imidazolate Framework, Photocatalyst, Paraquat.

Introduction

Recently, due to the growth of human technology with the increase of agricultural and industrial activities, water and food demand has been increased exponentially. Consequently, the high volume of activities leads to contaminate natural resources such as water and soil. The uncontrolled discharge of the effluents containing large amounts of harmful pollutants threatens human and aquatic life when the tolerance levels exceeds. Hence, these water resources pollutions especially different agrochemicals, drugs, heavy metals, etc. are worldwide concern, which makes serious risks to the environment and human life qualities (1-3). Among different hazardous contaminant, agrochemicals especially pesticides has been recognized as a ubiquitous problem. The pesticide residuals can contaminate our ecosystem and their accumulations are very toxic to biotic and abiotic components of our ecosystem. The elimination of these toxic agrochemical substances residual from water is difficult and requires water treatment. Paraquat (PQ), a bi-pyridinium agrochemical with IUPAC name N,N′-dimethyl-4,4′-bipyridinium dichloride and the chemical formula $[(C_6H_7N)_2]Cl_2$, is known as a non-selective herbicide. Due to the reasonable price and acceptable efficiency, PQ is one of the commonly used herbicides in plantations (rice, sugar cane, coffee, beans, and the other crops) (4-6) as well as in defoliation (grass and weed) (7).

As shown in Figure 1, the presence of the cationic charges on the bi-pyridinium molecule makes PQ water-soluble (620 g.L^{-1} at 25°C), which eradicates plants by interrupting photosynthesis. Nevertheless, PQ is very dangerous for health such as dermal exposure (8), respiratory failure (9), pulmonary fibrosis (10, 11), neurotoxicity (12), damage of digestive apparatus (13) and Parkinson's disease (14, 15). The PQ amount of 35 mg.kg^{-1} displays lethal dose for human being owing to European standards (16). The PQ concentration of 0.1 and 1–3 μg.L^{-1} exhibits respectively the maximum permissible concentration for drinking water and for surface waters.
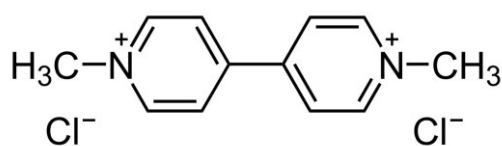

Figure 1. Chemical structure of Paraquat (PQ).

Up to now, different approaches have been introduced to remove the PQ contaminated water such as physical methods (including adsorption, filtration, and ion exchange), biological method, and chemical methods (including oxidation, photocatalytic degradation, and electrochemical process) (17-25). Among the above-mentioned approaches, the photocatalytic-based methods have been improved as a highly efficient process for eliminating the PQ contaminant from water samples. TiO$_2$ photocatalyst has been found as a promising photocatalyst because of its unique properties including high efficiency, low cost, stability, and nontoxicity. However, TiO$_2$ nanocatalyst

would not be easily separated from the treated water and a part of TiO₂ nanocatalyst leaches in the treated water. Therefore the TiO₂ nanocatalyst recyclability cannot be acceptable. Hence, the expansion of a simple and efficient separable TiO₂ photocatalyst has recently become an emerging topic of research. To this, several adsorbents have been reported as support for immobilization of TiO₂ catalyst including clays, graphene oxide nanosheets, single & multi-walled CNTs, silica, zeolites, and magnetic hybrid nano-sorbent (26-33). Research on the application of nanomaterial in water treatment has experienced strong growth and an enhanced interest in recent decades. These materials has made great impacts in a wide range of fields due to their unique properties in adsorption, catalytic activity, optical, and thermal stability (34, 35). Researchers in science and engineering show an increased interest in the use of nanoparticles due to their physical and chemical properties. Metal organic frameworks (MOFs) (36-39) specially zeolitic imidazolate framework (ZIFs) (40-42), the coordination polymers with proper porosity and high stability, have been appeared as convenient materials for wide applications in different areas such as sensing, catalysis, delivery, immobilizing, separation, and imaging materials. As supporting material, ZIF-8 consisted of a high nanoporous structure; represent more potential over the other traditional materials such as zeolites. This kind of nanoporous material represents an applicable type of supporting material for immobilizing the photocatalyst offering a robust and reusable photocatalyst to remove specific contaminants from water.

The aim of this study was the preparation of TiO₂ encapsulated into zeolitic imidazolate framework (TiO₂@ZIF-8) nanophotocatalyst and evaluation of its potential in the photocatalytic degradation of PQ residual from water samples. The effect of some parameters affecting the process of nano-photocatalysis and adsorption was analyzed.

Materials and Methods

1- General remarks

A stock solution of PQ was provided via dissolving the PQ in double distilled water. Before performing the experiment, the PQ concentration in the stock solution was measured. All the chemicals in this study were of extra pure or analytical grade. The particle size distributions, surface charges of nanoparticles were obtained by dynamic light scattering (DLS) (Brookhaven, USA). SEM technique was applied to determine the size of NPs. The topological characteristics of materials were observed using atomic force microscopy (AFM, DME-Ds95-50 Denmark) in ambient conditions at room temperature. HCl or NaOH was used to adjust the pH solution.

2- Synthesis of Nano-photocatalyst (TiO₂@ZIF-8)

TiO₂@ZIF-8 nanocomposite was synthesized by in-situ incorporation of TiO₂ NPs (anatase, 20 nm radius) onto the surface of ZIF-8 NPs. To this, zinc chloride (ZnCl₂, 0.34 g, 2.5 mmol) with 2-methylimidazole (2-MI, 1.64 g, 20 mmol) in methanol (MeOH, 45 mL) was stirred at room temperature (43). Then, 150 mL of a TiO₂ suspension was prepared by sonicating of TiO₂ NPs (20 mg, 0.25 mmol) in MeOH (10 mL). The prepared TiO₂ suspension was poured slowly to the above mixture. After 30 min stirring, the reaction mixture was left without disturbing overnight. The TiO₂@ZIF-8 product was separated, followed by washing with MeOH several

times, and drying in a vacuum oven at 70°C for 12 h.

3- Photocatalytic Experiment

The removal of PQ from the solution samples was done utilizing a reactor equipped with a 15-watt UV lamp. Briefly, 100 mL solution containing PQ (5, 25, 50 and 100 mg.L^{-1}) with alteration pH (3-11) was mixed with given dosage of TiO2@ZIF-8 (0.005–0.05 g.L^{-1}), and then UV light in the photoreaction apparatus irradiated the suspension for adequate time (5-30 min).

After completion of reaction time, the nano-photocatalyst was removed using an external magnetic field and then washed thoroughly, dried to be ready for using at next run. The changes in the PQ concentration were evaluated using a double beam UV–Vis spectrophotometer at λ_{max} = 257 nm with a calibration curve based on Beer–Lambert law (44). By subtracting the initial and unreduced concentrations of the ions, where, the initial and residual concentrations of PQ shown as C_{in} and C_{out} respectively, the degree of PQ calculated as follow (Eq 1):

$$\text{Equation 1}: R = \frac{c_{in} - c_{out}}{c_{in}} \times 100$$

Results and discussion

The nanophotocatalyst was prepared by immobilizing TiO$_2$ NPs onto the surface of the inorganic support. Forasmuch as catalyst immobilization on the solid surface, the ZIF-8 nano-framework was synthesized and then TiO$_2$ was encapsulated (shown TiO$_2$@ZIF-8 nano-photocatalyst). The TiO$_2$@ZIF-8 nano-photocatalyst structure was characterized by different techniques such as AFM, DLS, and SEM.

The SEM image of TiO$_2$@ZIF-8 shows that the modifying and loading process have no impact on the morphology. The average diameter of TiO$_2$@ZIF-8 was around 100 nm, respectively Figure 2a. The AFM imaging of TiO$_2$@ZIF-8 showed in Figure 2b. The uniform morphology with high dispersity occupied for TiO$_2$@ZIF-8. The particle size of TiO$_2$@ZIF-8 was determined using DLS. As seen, the average diameters of TiO$_2$@ZIF-8 was 120 nm.
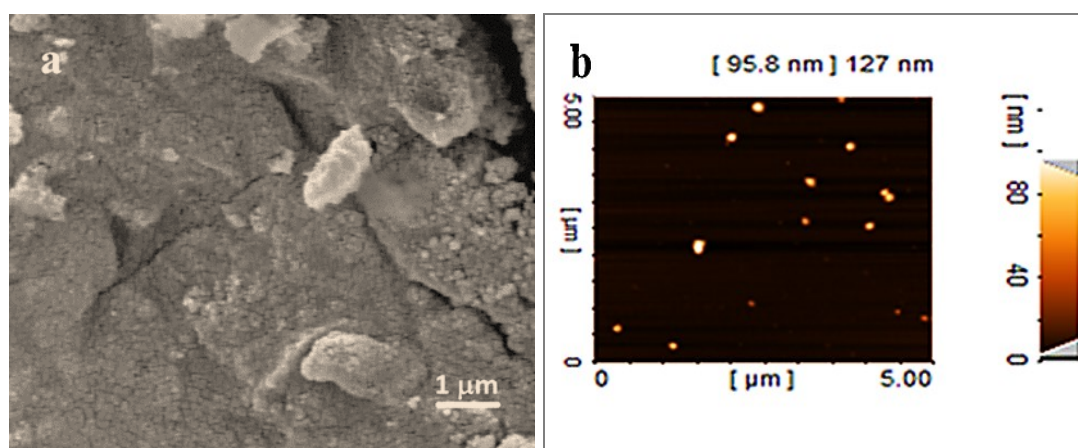

Figure 2. The SEM (a) and AFM (b) images of TiO$_2$@ZIF-8.

Due to the fact of the photocatalytic degradation of PQ is affected by the amount of pH, the different pH value (from 3 to 11) was investigated in the PQ concentration, the amount of TiO₂@ZIF-8 nano-photocatalyst, and the irradiation time were 50 mg.L^{-1}, 0.5 g.L^{-1}, and 15 min, respectively. Figure 3 illustrated the efficiency of TiO₂@ZIF-8 photocatalytic conversion of PQ was affected according to the pH values was. Due to these results, the photocatalytic efficiency of TiO₂@ZIF-8 was obtained at the highest level at pH of 7 and the lowest level at pH of 3. In accordance with this result, the remarked increase in efficiency was reported by increasing the pH value from 6.5 to 11 (45-47). Rationally, in aqueous solution of the hydroxyl radical production maximizes at neutral and alkaline pH values, which helps to enhance the photocatalytic conversion of PQ. With decreasing pH value from 9 to 7, the photocatalytic efficiency is shown a negligible decrease. Because the pH of wastewaters is about 8 which it consider as nearly neutral (48), and based on our results, pH value of 7 was selected as the optimal and eco-friendly value for keeping on the further investigations of TiO₂@ZIF-8 as nano-photocatalyst.
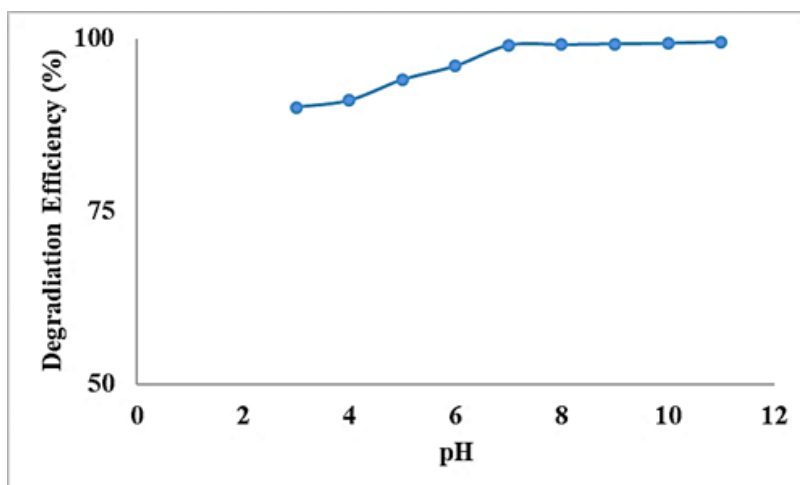

Figure 3. The effect of the pH value of the reaction mixture, while the PQ concentration, the amount of TiO₂@ZIF-8 nano-photocatalyst, and the irradiation time were 50 mg.L^{-1}, 0.05g.L^{-1} and 15 min, respectively.

Figure 4 presents the effects of the initial concentration of PQ, as the target contaminant, on the nanophotocatalytic efficiency of TiO₂@ZIF-8 nanophotocatalyst. To this, the initial PQ concentration was varied between 5-100 mg.L^{-1}, while the photocatalytic reaction time, pH value, and the amount of TiO₂@ZIF-8 nanophotocatalyst were 15 min, and 7, and 0.5 g.L^{-1}, respectively. Based on the obtained results, the TiO₂@ZIF-8 nano-photocatalyst efficiency was decreased by increasing the initial concentration of PQ. In fact, the high contaminant concentrations lead to turbidity and reduce the transparency of the reaction media. So, the efficiency of the nanophotocatalyst would be decreased because of the lower adsorption of source light irradiation by the photocatalyst and subsequently the lower level of hydroxyl radical. It was reported that as the level of generated radicals is

75

constant during a photocatalysis process, the photocatalyst efficiency decreases with growing the initial contaminant concentration (49). As a limitation, with increasing the initial PQ concentrations the competition reactions are more possible due to producing higher amounts of intermediates (50, 51). According to these results, the initial PQ concentration of 50 mg.L^{-1} was chosen as favorite value for further studies.
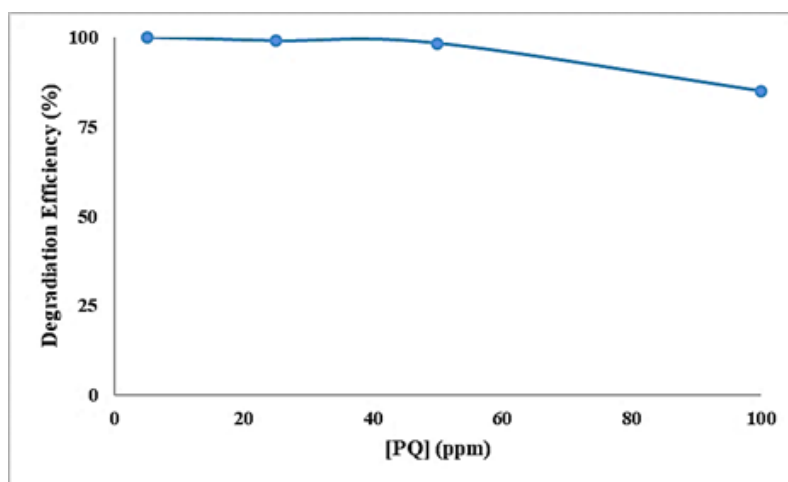

Figure 4. The effect of the PQ concentration, while the amount of TiO$_2$@ZIF-8 nano-photocatalyst, pH, and the irradiation time were 0.05 g.L^{-1}, 7 and 15 min, respectively.

The effects of the amount of TiO$_2$@ZIF-8 as nanophotocatalyst on the photocatalytic efficiency within a reaction time of 10 min and pH 7 is shown in Figure 5. The results indicated that the optimal dosage of the nanophotocatalyst was 50 mg.L^{-1}. Additional amounts of the semiconductor materials makes energy loss, which leads to more activity (52).
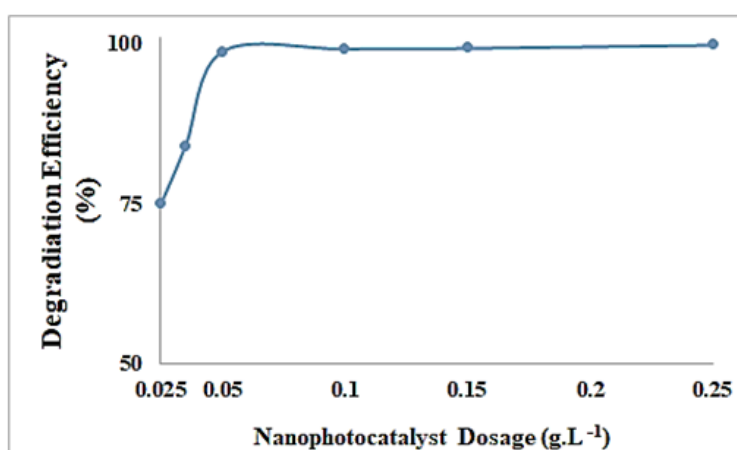

Figure 5. The effect of the amount of TiO$_2$@ZIF-8 nano-photocatalyst, while the PQ concentration, pH, and the irradiation time were 50 mg.L^{-1}, 7 and 15 min, respectively.

Figure 6 also shows the effects of the reaction time on the efficiency of TiO$_2$@ZIF-8 nanophotocatalyst. In this step, the initial PQ concentration, pH value, and nanophotocatalyst dosage were adjusted to 50 mg.L^{-1}, 7 and 0.05 g.L^{-1}, respectively. As the time increased the nanophotocatalyst efficiency enhanced, therefore the best results were taken between 15 min.
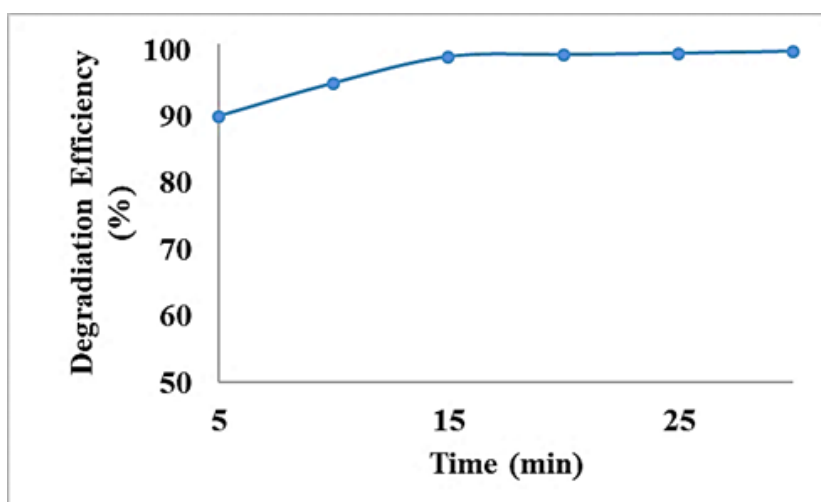

Figure 6. The effect of the irradiation time, while the PQ concentration, the amount of TiO$_2$@ZIF-8 nano-photocatalyst and pH were 50 mg.L^{-1}, 0.05 g.L^{-1} and 7, respectively.

The nanophotocatalyst was recycled eight times with a negligible loss of phocatalytic activity (Figure 7). TiO$_2$@ZIF-8 nanophotocatalyst is appeared as a boosted and eco-friendly nanophotocatalyst that showed an excellent robustness and catalytic efficiency in removal of PQ. To rule out the leaching phenomena and existence of the homogeneous Ti species, 5 mg of the TiO$_2$@ZIF-8 nanophotocatalyst was prepared as optimal condition, and at the half of the reaction time, the nanophotocatalyst was separated magnetically. It was found that the amount of leached titanium ion was less than 1 mg.L^{-1} for the separated liquid (measured by ICP-AES).
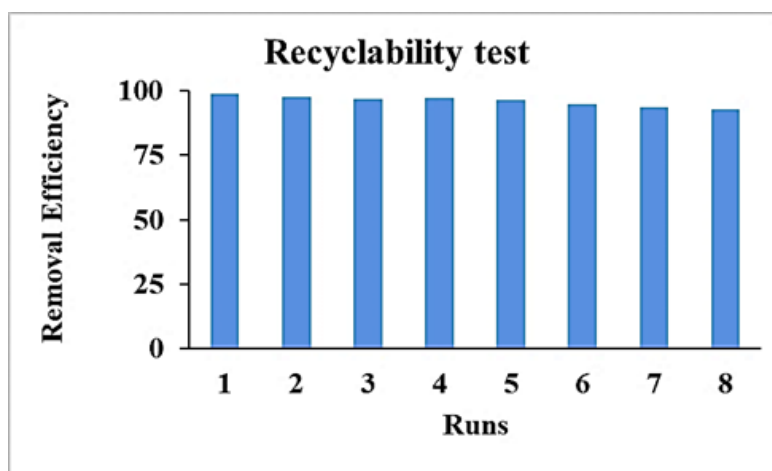
77

Figure 7. The recyclability test of $TiO_2@ZIF-8$ nano-photocatalyst in the optimal condition.

Conclusions

Summary, it can be concluded that, the simple recyclable encapsulated TiO_2 NPs within ZIF-8 nanopores provided a desirable mode of employing TiO_2 NPs for the photocatalytic degradation of agrochemicals as here the efficiency and robustness of the photocatalysis process can enhance as well as the ability to reuse this nanoparticle-ZIF nanocomposite for several cycles improved much higher.

References   منابع

1. Gola D., Malik A., Shaikh Z.A. and Sreekrishnan T.R. (2016). Impact of heavy metal containing wastewater on agricultural soil and produce: relevance of biological treatment. Environ. Process. 3: 1063–1080.
2. Masindi V. and Muedi K.L. (2018). Environmental contamination by heavy metals. Heavy Metals. edited by Hosam El-Din M. Saleh and Refaat F. Aglan. In Tech Open.
3. Suvarapu L.N., Baek S.O. (2016). Determination of heavy metals in the ambient atmosphere: A review. Toxicol. Ind. Health. 33: 79–96 .
4. Nanseu-Njiki C.P., Dedzo G.K. and Ngameni E. (2010). Study of the removal of paraquat from aqueous solution by biosorption onto Ayous (*Triplochiton scleroxylon*) sawdust. J Hazard Mater. 179: 63–71.
5. Mhammedi M.A.E., Bakasse M. and Chtaini A. (2007). Electrochemical studies and square wave voltammetry of paraquat at natural phosphate modified carbon paste electrode. J Hazard Mater. 145: 1–7.

6. Recena M.C.P., Caldas E.D., Pires D.X. and Pontes E.R.J.C. (2006). Pesticides exposure in Culturama, Brazil-knowledge, attitudes, and practices. Environ Res. 102: 230–236.

7. Núñez O., Kim J.B., Moyano E., Galceran M.T. and Terabe S. (2002). Analysis of the herbicides paraquat, diquat and difenzoquat in drinking water by micellar electrokinetic chromatography using sweeping and cation selective exhaustive injection. J Chromatogr A. 961: 65–75.

8. Brown R., Clapp M., Dyson J., Scott D., Wheals I. and Wilks M. (2004). Paraquat in perspective. Outlooks Pest Manag. 15: 259–26.

9. Dinis-Oliveira R.J., Duarte J.A., Sánchez-Navarro A., Remião F., Bastos M.L. and Carvalho F. (2008). Paraquat poisonings: mechanisms of lung toxicity, clinical features, and treatment. Crit Rev Toxicol. 38: 13–71.

10. Lacerda A.C.R., Rodrigues-Machado M.D.G., Mendes P.L., Novaes R.D., Carvalho G.M.C., Zin W.A., Gripp F. and Coimbra C.C. (2009). Paraquat (PQ)-induced pulmonary fibrosis increases exercise metabolic cost, reducing aerobic performance in rats. J Toxicol Sci. 34: 671–679.

11. Cho I.K., Jeong M, You A.S. and Li Q.X. (2015). Pulmonary proteome and protein networks in response to the herbicide paraquat in rats. J Proteomics Bioinform. 8: 67–79.

12. Smeyne R.J., Breckenridge C.B., Beck M., Jiao Y., Butt M.T., Wolf J.C., Zadory D., Minnema D.J., Sturgess N.C., Travis K.Z., Cook A.R., Smith L.L. and Botham P.A. (2016). Assessment of the effects of MPTP and paraquat on dopaminergic neurons and microglia in the substantia nigra pars compacta of C57BL/mice. PLoS ONE. 11: e0164094.

13. Zhang X., Thompson M. and Xu Y. (2016). Multifactorial theory applied to the neurotoxicity of paraquat and paraquat-induced mechanisms of developing Parkinson's disease. Lab Invest. 96: 496–50.

14. Dinis-Oliveira R.J., Remião F., Carmo H., Duarte J.A., Navarro A.S., Bastos M.L. and Carvalho F. (2006). Paraquat exposure as an etiological factor of Parkinson's disease. NeuroToxicol. 27: 1110–112.

15. Hamadi N.K., Swaminathan S. and Chen X.D. (2004) Adsorption of Paraquat dichloride from aqueous solution by activated carbon derived from used tires. J Hazard Mater. 112: 133–141.

16. Akhtar M., Hasany S.M., Bhanger M.I. and Iqbal S. (2007). Low cost sorbents for the removal of methyl parathion pesticide from aqueous solutions. Chemosphere. 66: 1829–1838.

17. Zayats M.F., Leschev S.M., Petrashkevich N.V., Zayats M.A., Kadenczki L., Szitás R., Dobrik H.S. and Keresztény N. (2013). Distribution of pesticides in n-hexane/water and n-hexane/acetonitrile systems and estimation of possibilities of their extraction isolation and preconcentration from various matrices. Anal Chim Acta. 774: 33–43.

18. Dehghani Z., Sedghi-Asl M., Ghaedi M., Sabzehmeidani M.M. and Adhami E. (2021). Ultrasound-assisted adsorption of paraquat herbicide from aqueous solution by graphene oxide/mesoporous silica. Journal of Environmental Chemical Engineering. 9(2): 105043.

19. Sorolla M.G., Dalida M.L., Khemthong P. and Grisdanurak N. (2012). Photocatalytic degradation of paraquat using nano-sized Cu-TiO₂/SBA-15 under UV and visible light. J Environ Sci. 24: 1125–1132.

20. Santos M.S.F., Alves A. and Madeira L.M. (2011). Paraquat removal from water by oxidation with Fenton's reagent. Chem Eng J. 175: 279–290.

21. Dhaouadi A. and Adhoum N. (2010). Heterogeneous catalytic wet peroxide oxidation of paraquat in the presence of modified activated carbon. Appl Catal B Environ. 97: 227–235.

22. Dhaouadi A. and Adhoum N. (2009). Degradation of paraquat herbicide by electrochemical advanced oxidation methods. J Electroanal Chem. 637: 33–42.

23. Carr R.J., Bilton R.F. and Atkinson T. (1985). Mechanism of biodegradation of paraquat by Lipomyces starkeyi. Appl Environ Microbiol. 49: 1290–1294.

24. Nakamura T., Kawasaki N., Ogawa H., Tanada S., Kogirima M. and Imaki M. (1999). Adsorption removal of paraquat and diquat onto activated carbon at different adsorption temperature. Toxicol Environ Chem. 70: 275–280.

25. Tsai W.T. and Chen H.R. (2013). Adsorption kinetics of herbicide Paraquat in aqueous solution onto a low-cost adsorbent, swinemanure-derived biochar. Int J Environ Sci Technol. 10(6): 1349–1356.

26. Ajmal A., Majeed I., Malik R.N., Idrissc H. and Nadeem M.A. (2014). Principles and mechanisms of photocatalytic dye degradation on TiO₂ based photocatalysts: a comparative overview. R. Soc. Chem. Adv. 4: 37003–37026.

27.   Houas A., Lachheb H., Ksibi M., Elaloui E., Guillard C. and Herrmann J.M. (2001). Photocatalytic degradation pathway of methylene blue in water. Appl. Catal. B. 31: 145–157.

28.   Wang M., Ioccozia J., Sun L., Lin C. and Lin Z. (2014). Inorganic-modified semiconductor TiO2 nanotube arrays for photocatalysis. Energy Environ. Sci. 7(7): 2182–2202 .

29.   Yeganeh M., Charkhloo E., Sobhi HR., Esrafili A., Gholami M. (2021). Photocatalytic processes associated with degradation of pesticides in aqueous solutions: Systematic review and meta-analysis. Chem. Eng. J. 130081.

30.   Chandra R., Mukhopadhyay S. and Nath M. (2016). TiO2@ ZIF-8: A novel approach of modifying micro-environment for enhanced photo-catalytic dye degradation and high usability of TiO2 nanoparticles. Mat. Lett. 164: 571-574.

31.   Daghrir R., Drogui P., Robert D. (2013). Modified TiO2 for environmental photocatalytic applications: a review. Indus. and Eng. Chem. Res. 52(10): 3581-3599.

32.   Park K.S., Ni Z., Co A.P., Choi J.Y., Huang R., Uribe-Romo F.J., Chae H.K., O'Keeffe M. and Yaghi O.M. (2006). Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. Proc. Natl. Acad. Sci. 103(27): 10186-10191.

33.   Hadei M., Mesdaghinia A., Nabizadeh R., Mahvi A.H., Rabbani S. and Naddafi K. (2021). Environmental A comprehensive systematic review of photocatalytic degradation of pesticides using nano TiO2. Environ Sci Pollut R. 1-17.

34.   Dave P.N. and Chopd L.V. (2014). Application of Iron oxide nanomaterials for the removal of heavy metals. Journal of Nanotechnology. 398569.

35.   Wang X., Pehkonen S.O., Rämö J., Väänänen M., Highfielde J.G. and Laasonen K. (2012). Experimental and computational studies of nitrogen doped Degussa P25 TiO2: application to visible-light driven photo-oxidation of As (III). Catal. Sci. Technol. 2: 784–793.

36.   Wen Y., Feng M., Zhang P., Zhou H.C., Sharma V.K. and Ma X. (2021). Metal Organic Frameworks (MOFs) as Photocatalysts for the Degradation of Agricultural Pollutants in Water. ACS ES&T Engineering. 1(5): 804-26.

37.   Yuan S., Feng L., Wang K., Pang J., Bosch M., Lollar C., Sun Y., Qin J., Yang X., Zhang P., Wang Q., Zou L., Zhang Y., Zhang L., Fang Y., Li J. and Zhou H.C. (2018). Stable metal–organic frameworks: design, synthesis, and applications. Advanced Materials. 30: 1704303 .

38.   Cao C.C., Chen C.X., Wei Z.W., Qiu Q.F., Zhu N.X., Xiong Y.Y., Jiang J.J., Wang D. and Su C.Y. (2019). Catalysis through dynamic spacer installation of multivariate functionalities in metal–organic frameworks. J. Am. Chem. Soc. 141: 2589–2593.

39.   Golmohamadpour A., Bahramian B., Shafiee A. and Ma'mani L. (2018). Slow released delivery of alendronate using β-cyclodextrine modified FE–MOF encapsulated porous hydroxyapatite. Journal of Inorganic and Organometallic Polymers and Materials. 28: 3456789 .

40.   Chandra R., Mukhopadhyay S. and Nath M. (2016). TiO2@ ZIF-8: A novel approach of modifying micro-environment for enhanced photo-catalytic dye degradation and high usability of TiO2 nanoparticles. Mat. Lett. 164:571-574.

41.   Yu B., Wang F., Dong W., Huo J. and Lu P. (2015). Self-template synthesis of core–shell ZnO@ ZIF-8 nanospheres and the photocatalysis under UV irradiation. Mat. Lett. 156: 50-53.

42.   Sun D.W., Huang L., Pu H. and J. Ma. (2021). Introducing reticular chemistry into agrochemistry. Chem. Soc. Rev. (In Press).

43.   Chandra R., Mukhopadhyay S. and Nath M. (2016). TiO2@ZIF-8: A novel approach of modifying micro-environment for enhanced photo-catalytic dye degradation and high usability of TiO2 nanoparticles, Materials Letters. 164: 571- 574.

44.   Khodkar A., Khezri S.M., Pendashteh A.R., Khoramnejadian S. and Maˈmani L. (2019). A designed experimental approach for photocatalytic degradation of paraquat using α-Fe2O3@MIL-101 (Cr)@TiO2 based on metal–organic framework. Int. J. Environ. Sci. Techno. l16: 5741–5756 .

45.   Wang T., Ye F., Wu S., Chen S., Yu H. and Quan X. (2021). Efficient Light-Driven Fuel Cell with Simultaneous Degradation of Pollutants on a TiO_2 Photoanode and Production of H2O2 on a Gas Diffusion Electrode Cathode. ACS ES&T Engineering. In Press. https://doi.org/10.1021/acsestengg.1c00083.

46.   Deepracha S., Ayral A. and Ogawa M. (2021). Acceleration of the photocatalytic degradation of organics by in-situ removal of the products of degradation. Applied Catalysis B: Environmental. 284: 119705.

47.   Tang C. and Chen V. (2004). The photocatalytic degradation of reactive black 5 using TiO2/UV in an annular photoreactor, Water Res. 38: 2775–2781.

48.   Hussain S.M., Hussain T., Faryad M., Ali Q., Ali S., Rizwan M. and Chatha S.A. (2021). Emerging aspects of photo-catalysts (TiO₂ & ZnO) doped zeolites and advanced oxidation processes for degradation of azo dyes: A Review. Curr. Anal. Chem. 17(1): 82-97.

49.   . Lee J.M, Kim M.S., Hwang B., Bae W. and Kim B.W. (2003). Photodegradation of acid red 114 dissolved using a photo-Fenton process with TiO2, Dyes Pigm. 56: 59–67.

50.   Chakrabarti S. and Dutta B.K. (2004). Photocatalytic degradation of model textile dyes in wastewater using ZnO as semico doctor catalyst, J. Hazard. Mater. 112: 269–278.

51.   Bairam C., Yalçın Y., Efkere H.İ., Çokduygulular E., Çetinkaya Ç., Kınacı B. and Özçelik S. (2021). Structural, morphological, optical and electrical properties of the Ti doped-ZnO (TZO) thin film prepared by RF sputter technique. Phys. B: Condens. Matter. 616: 413126.

52.   Luo J., Zhu X., Chen G., Zeng F. and Pan F. (2012). The electrical, optical and magnetic properties of Sidoped ZnO films, Appl. Surf. Sci. 258: 2177–2181.

81

TiO2 انکپسوله‌شده بر پایه چارچوب زیولیتی ایمیدازولیوم (TiO2@ZIF-8) به عنوان یک نانوفتوکاتالیزور مؤثر برای تجزیه علف‌کش پاراکوآت

فریبا دشتستانی¹، وحید محققی¹، لیلا مأمنی¹*، کبری مافی²

۱- بخش نانوتکنولوژی، پژوهشگاه بیوتکنولوژی کشاورزی (ABRII)، سازمان تحقیقات، آموزش و ترویج کشاورزی(AREEO)، البرز، ایران

۲- دانشگاه آزاد اسلامی– واحد تهران غرب، تهران، ایران

leila.mamani@abrii.ac.ir

چکیده

در این تحقیق، تهیه، مشخصه‌یابی و ارزیابی پتانسیل نانوفتوکاتالیزور TiO2 انکپسوله‌شده بـر پایـه چارچوب زیولیتی ایمیدازولیوم (TiO2@ZIF-8) تخریب کارآمد علف‌کش پـاراکوات مـورد بررسـی قرار گرفت. این مطالعه با استفاده از یک نانوفتوکاتالیزور برپایه ZIF-8 و یک راکتور متشکل از منبع ماوراء بنفش (UV) و محفظه واکنش انجام شد. برای تعیین راندمان حذف آلاینده پـاراکوآت توسـط نانوفتوکاتالیزور TiO2@ZIF-8، اثر پارامترهای مختلف شامل غلظت آلاینده، مقدار نانوفتوکاتالیـزور، pH و زمان واکنش مورد بررسی قرار گرفت. نتایج نشان داد که بـا افـزایش مقـدار نانوفتوکاتـالیزور TiO2@ZIF-8 و pH، حذف پـاراکوآت افـزایش یافتـه اسـت. حـداکثر رانـدمان تخریـب و حـذف پاراکوآت در مقدار ۰/۰۵ گرم در لیتر نانوفوتوکاتـالیزور TiO2@ZIF-8و pH برابـر بـا ۷ و ۱۵ دقیقـه بدست آمد که برابر با ۹۹/۸ بود. با توجه به نتـایج، TiO2@ZIF-8 بـه‌عنوان یـک نانوفوتوکاتـالیزور کارآمد، مقاوم و قابل بازیافت ظاهر شد، که روشی توانمند و سازگار با محیط زیسـت بـرای از بـین بردن بقایای این علف‌کش شیمیایی به‌عنوان آلاینده‌ای خطرناک در نمونه‌های آبی ارائه می‌کنـد. روش تهیه آسان و فعالیت فوتوکاتالیستی افزایش‌یافته از نکات برجسته این کاتـالیزور بـوده و قابـل توجـه است کـه TiO2@ZIF-8 قابلیـت بازیافـت و بکـارگیری مجـدد نسـبتاً خـوبی را در ۸ دوره متـوالی بکارگیری نشان داد.

واژه‌های کلیدی: TiO2، چارچوب زیولیتی ایمیدازولیوم، فوتوکاتالیزور، پاراکوآت.