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TiO_2 Encapsulated into Zeolitic Imidazolate Framework (TiO_2@ZIF-8) as an Efficient Nanophotocatalyst for Degradation of Paraquat Herbicide

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Abstract

In this research, preparation, characterization, and evaluation of TiO_2 encapsulated into zeolitic imidazolate framework (TiO_2@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 TiO_2@ZIF-8 nanophotocatalyst. The results showed by increasing the amount of the TiO_2@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, TiO_2@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 TiO_2@ZIF-8 were highlighted and notably showed good reusability in 8 consecutive cycles.

Keywords: TiO_2, Zeolitic Imidazolate Framework, Photocatalyst, Paraquat.

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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 $\mu g.L^{-1}$ exhibits respectively the maximum permissible concentration for drinking water and for surface waters.

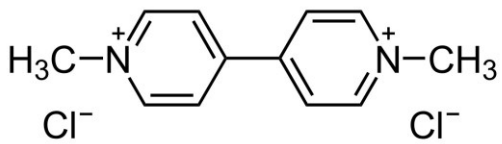

Figure 1. Chemical structure of Paraquat (PQ).

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 TiO_2 nanocatalyst leaches in the treated water. Therefore the TiO_2 nanocatalyst recyclability cannot be acceptable. Hence, the expansion of a simple and efficient separable TiO_2 photocatalyst has recently become an emerging topic of research. To this, several adsorbents have been reported as support for immobilization of TiO_2 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 TiO_2 encapsulated into zeolitic imidazolate framework (TiO_2@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 (TiO_2@ZIF-8)

TiO_2@ZIF-8 nanocomposite was synthesized by in-situ incorporation of TiO_2 NPs (anatase, 20 nm radius) onto the surface of ZIF-8 NPs. To this, zinc chloride ($ZnCl_2$, 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 TiO_2 suspension was prepared by sonicating of TiO_2 NPs (20 mg, 0.25 mmol) in MeOH (10 mL). The prepared TiO_2 suspension was poured slowly to the above mixture. After 30 min stirring, the reaction mixture was left without disturbing overnight. The TiO_2@ZIF-8 product was separated, followed by washing with MeOH several

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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):

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.

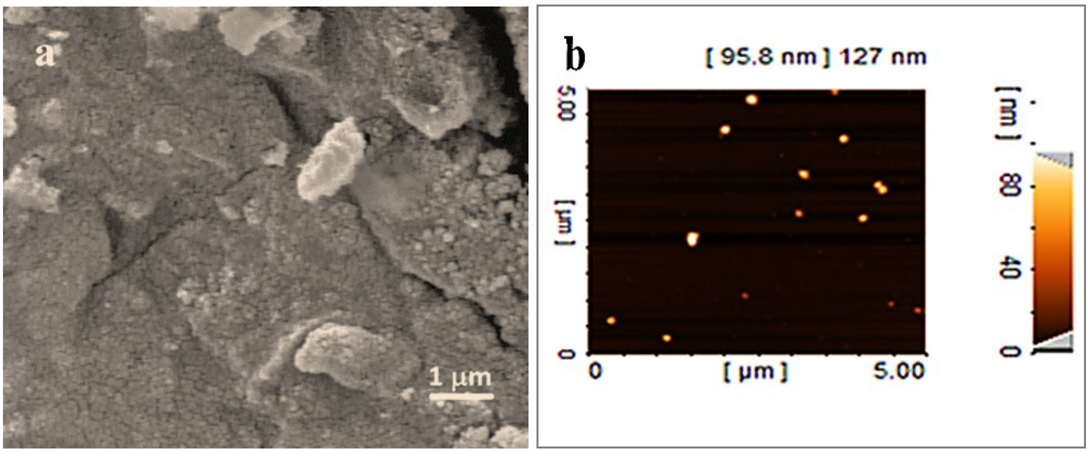

Figure 2. The SEM (a) and AFM (b) images of TiO_2@ZIF-8.

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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 TiO_2@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 TiO_2@ZIF-8 photocatalytic conversion of PQ was affected according to the pH values was. Due to these results, the photocatalytic efficiency of TiO_2@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 TiO_2@ZIF-8 as nano-photocatalyst.

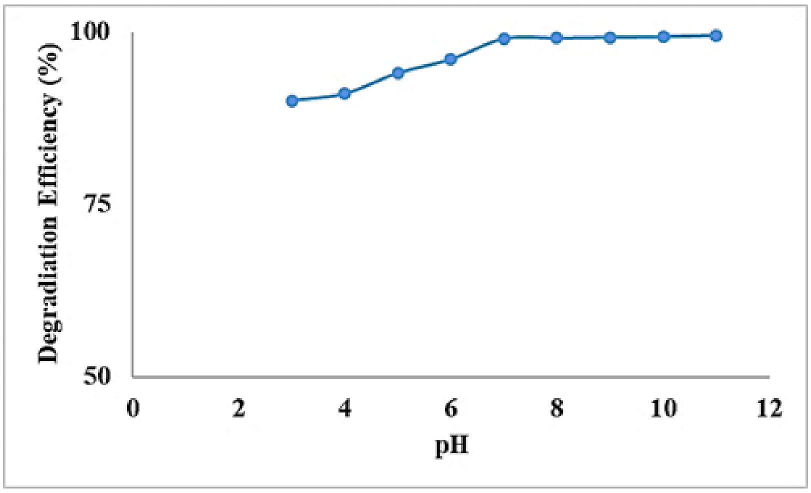

Figure 3. The effect of the pH value of the reaction mixture, while the PQ concentration, the amount of TiO_2@ZIF-8 nano-photocatalyst, and the irradiation time were 50 $mg.L^{-1}$, 0.05$g.L^{-1}$ and 15 min, respectively.

Figure 4 presents the effects of the initial concentration of PQ, as the target contaminant, on the nanophotocatalytic efficiency of TiO_2@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 TiO_2@ZIF-8 nanophotocatalyst were 15 min, and 7, and 0.5 $g.L^{-1}$, respectively. Based on the obtained results, the TiO_2@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

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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.

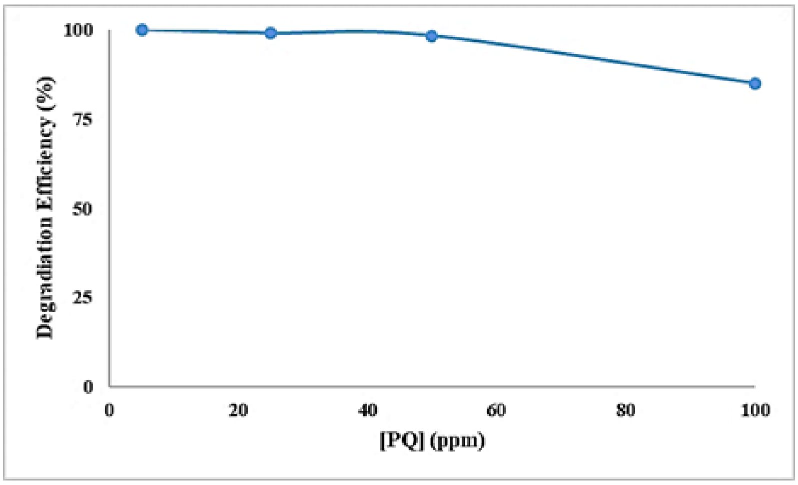

Figure 4. The effect of the PQ concentration, while the amount of TiO_2@ZIF-8 nano-photocatalyst, pH, and the irradiation time were 0.05 $g.L^{-1}$, 7 and 15 min, respectively.

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).

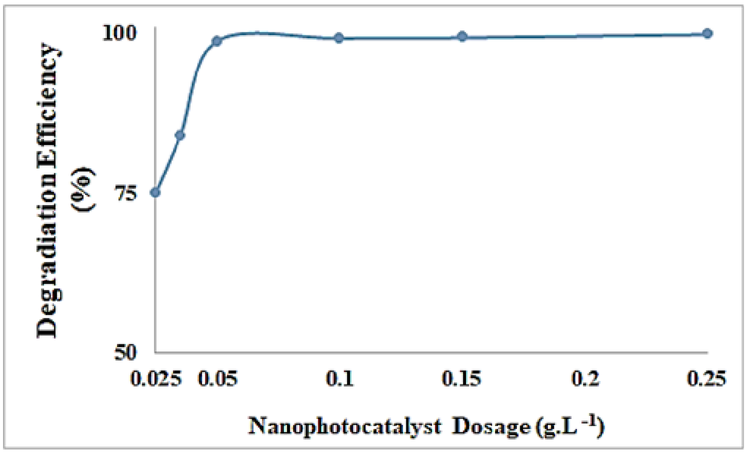

Figure 5. The effect of the amount of TiO_2@ZIF-8 nano-photocatalyst, while the PQ concentration, pH, and the irradiation time were 50 $mg.L^{-1}$, 7 and 15 min, respectively.

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.

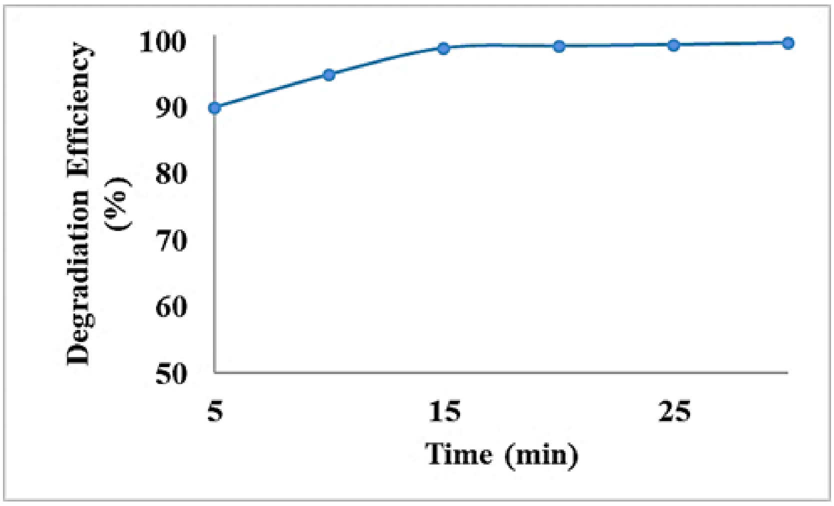

Figure 6. The effect of the irradiation time, while the PQ concentration, the amount of TiO_2@ZIF-8 nano-photocatalyst and pH were 50 mg.L^{-1}, 0.05 g.L^{-1} and 7, respectively.

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).

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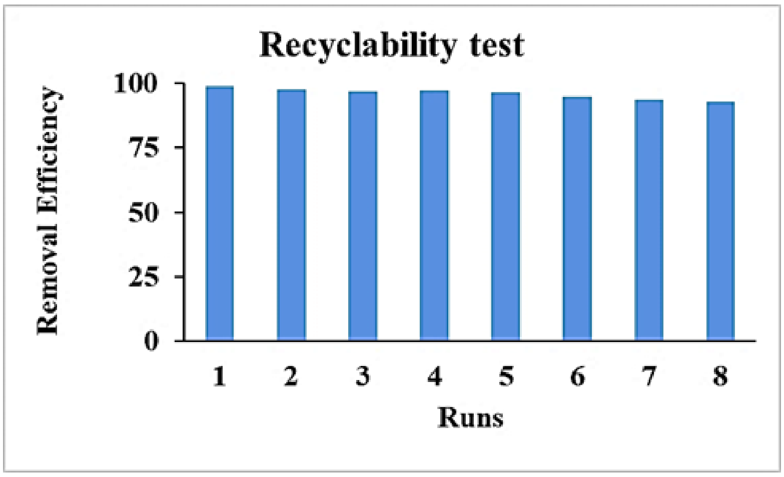

Figure 7. The recyclability test of TiO_2@ZIF-8 nano-photocatalyst in the optimal condition.

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.

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TiO_2 انکپسوله‌شده بر پایه چارچوب زیولیتی ایمیدازولیوم (TiO_2@ZIF-8) به عنوان یک نانوفتوکاتالیزور مؤثر برای تجزیه علف‌کش پاراکوآت

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صفحه ۸۲-۷۱

چکیده

در این تحقیق، تهیه، مشخصه‌یابی و ارزیابی پتانسیل نانوفتوکاتالیزور TiO_2 انکپسوله‌شده بر پایه چارچوب زیولیتی ایمیدازولیوم (TiO_2@ZIF-8) تخریب کارآمد علف‌کش پاراکوات مورد بررسی قرار گرفت. این مطالعه با استفاده از یک نانوفوتوکاتالیزور برپایه ZIF-8 و یک راکتور متشکل از منبع ماوراء بنفش (UV) و محفظه واکنش انجام شد. برای تعیین راندمان حذف آلاینده پاراکوآت توسط نانوفتوکاتالیزور TiO_2@ZIF-8، اثر پارامترهای مختلف شامل غلظت آلاینده، مقدار نانوفتوکاتالیزور، pH و زمان واکنش مورد بررسی قرار گرفت. نتایج نشان داد که با افزایش مقدار نانوفوتوکاتالیزور TiO_2@ZIF-8 و pH، حذف پاراکوآت افزایش یافته است. حداکثر راندمان تخریب و حذف پاراکوآت در مقدار ۰/۰۵ گرم در لیتر نانوفوتوکاتالیزور TiO_2@ZIF-8و pH برابر با ۷ و ۱۵ دقیقه بدست آمد که برابر با ۹۹/۸ بود. با توجه به نتایج، TiO_2@ZIF-8 به‌عنوان یک نانوفوتوکاتالیزور کارآمد، مقاوم و قابل بازیافت ظاهر شد، که روشی توانمند و سازگار با محیط زیست برای از بین بردن بقایای این علف‌کش شیمیایی به‌عنوان آلاینده‌ای خطرناک در نمونه‌های آبی ارائه می‌کند. روش تهیه آسان و فعالیت فوتوکاتالیستی افزایش‌یافته از نکات برجسته این کاتالیزور بوده و قابل توجه است که TiO_2@ZIF-8 قابلیت بازیافت و بکارگیری مجدد نسبتاً خوبی را در ۸ دوره متوالی بکارگیری نشان داد.

واژه‌های کلیدی: TiO_2، چارچوب زیولیتی ایمیدازولیوم، فوتوکاتالیزور، پاراکوآت.