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Research Paper

Preparation and Characterization of Clinoptilolite Impregnated with Titanium Dioxide Nanoparticles to Remove Agricultural Pesticides

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Abstract: Removal of bentazone herbicide through photodegradation process using nanostructured TiO_2/Clinoptilolite composite was studied to investigate the potential of clinoptilolite natural support and the effect of the loaded TiO_2 content on the process efficiency. For this purpose, TiO_2/Clinoptilolite photocatalysts containing different amounts of titania (10, 20, 30, 40 wt.%) were synthesized using a simple and inexpensive wet impregnation method and characterized by XRD, FESEM, EDX, BET, PL, and UV-vis analyses. The characterization results confirmed the successful synthesis of nanocomposite samples and showed that the use of zeolitic support, reducing the recombination rate of electron-hole pairs, improves the dispersion of titania nanoparticles and reduces the accumulation of these particles. The performance results showed that by increasing the TiO_2 loading up to 30 wt.%, the removal efficiency of bentazone increases, which is due to the greater number of available active sites. By further increasing the amount of TiO_2 loading, the percentage of photocatalytic removal decreases because of the increment in the number of agglomerations on the catalyst surface and the decrement in the adsorption capacity. Also, the kinetic studies show a higher rate of bentazone degradation over the sample containing 30 wt.% of titania and the results follow the first-order kinetic reaction. In order to ensure the efficiency of the selected photocatalyst in the removal of other agricultural pesticides, its efficiency in the photocatalytic removal of paraquat herbicide was also evaluated, which showed good performance. Thus, it can be concluded that the immobilization of the optimal amount of titania on clinoptilolite, in addition to better and easier separation, leads to improved optical and structural properties, and ultimately increased photocatalytic performance.

Keywords: Photodegradation, Bentazone, Paraquat, Clinoptilolite, Kinetic studies.

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INTRODUCTION

Agriculture activities may be caused serious negative impacts on the quality of surface and underground water due to the release of pesticides. The presence of pesticides in water could be dangerous for humans and animals due to their toxicity properties and causes death. Thus, the removal of pesticides from aquatic systems is considered a crucial issue [1]. There are several methods for pesticides removal from solution. However, photocatalytic degradation is considered one of the low-cost, safe, and environment-friendly methods to degrade pesticides from the aqueous phase [2]. TiO_2 is the most commonly used semiconductor because of its strong oxidizing abilities, high photoactivity, inexpensive, non-toxic, and good chemical and thermal stability [3]. However, there are still some inherent drawbacks such as rapid charge carrier recombination, low separation probability of electron, poor adsorption, difficult recovery, separation, and agglomeration which lead to limitations in its photocatalytic efficiency. To overcome these challenges, one of the effective strategies is the immobilization of TiO_2 nanoparticles on a highly porous support such as zeolitic material .Considering the cost effectiveness, abundance, easily available, and high chemical stability, clinoptilolite seems to be efficient support applicable for photocatalytic wastewater treatment [4]. Therefore, the current research is emphasized studying the effect of clinoptilolite usage as a low-cost and available support, the amount of TiO_2 loading and further discovers the potential of clinoptilolite supported TiO_2 photocatalyst in the degradation of bentazone and paraquat pesticides.

METHODS

Preparation of photocatalysts:

At first, the clinoptilolite tuff was crushed and sieved to obtain a particulate size of approximately 44–53 µm. Then, it was washed to remove the water-soluble residues and other undesirable materials and dried at 110 °C for 24h. Afterwards, the titanium (IV) tetraisopropoxide was added to the clinoptilolite-suspended isopropanol solution and mixed until the dispersing agent was evaporated. After drying at 110°C overnight, the samples were calcined in the static air at 500°C for 6h.

FINDINGS AND ARGUMENT

Photocatalyst characterization

The XRD analysis confirmed the existence of crystalline phases of TiO_2 and clinoptilolite in all the synthesizedTiO_2/Clinoptilolite photocatalysts. Moreover, the crystallinity of TiO_2 increments while that of clinoptilolite decrements by gradually increasing TiO_2 content over clinoptilolite structure. This reduction can be attributed to a dilution effect of the zeolite matrix in the photocatalyst and might be a sign of surface coverage of zeolite by TiO_2 nanoparticles. Accordingly, it seems that the severe surface coverage of zeolite occurred in the TiO_2 rich composites (containing more than 30 wt.%) which is in good agreement with the FESEM analysis. A close examination of the FESEM results also revealed that more agglomerations appear by further increasing TiO_2 loading. The recorded EDX spectra confirmed the presence of all elements used in the synthesis of all samples and the absence of any impurities in their structure. Based on the UV-Vis analysis, the bandgap calculated for supported TiO_2 (T30-Clin) was higher (3.4 eV) than that of bare TiO_2, commensurate with decreasing in TiO_2 cluster size and agglomeration numbers. According to PL analysis, the separation efficiency of electron-hole pairs was enhanced when TiO_2 nanoparticles were dispersed on clinoptilolite.

Photocatalyst performance

The photocatalytic activities of TiO_2/clinoptilolite composites containing different amounts of titania toward bentazone degradation as a function of reaction time are illustrated in Figure 1. As can be seen, improved photocatalytic activity is achieved for the TiO_2/clinoptilolite nanocomposites in comparison with that of pure TiO_2. This can be attributed to the low recombination of electron-hole pairs, better distribution of TiO_2 particles, and lower agglomerations, in accordance with PL, UV-vis, and FESEM analyses. Among the various TiO_2-based nanocomposites, T30-Clin shows the highest efficiency during the photocatalytic reaction. By further increasing TiO_2 loading, the removal efficiency decreases due to the agglomerations of TiO_2 particles on the zeolite matrix and the severe coverage of the clinoptilolite surface which weakened the contact between clinoptilolite and TiO_2 and also the separation efficiency of electron-hole pairs. Moreover, the results of the kinetic models revealed that the photodegradation of bentazon is in accordance with the pseudo-first-order kinetics according to the Langmuir–Hinshelwood model (Figure 2). In addition, it was found that the optimum dosage of T30-Clin for the photodegradation of bentazon is 0.25g/L. To further investigate the performance of T30-Clin, as an optimum sample, in the decomposition of other pesticides, the photodegradation process for paraquat was also done. Due to higher adsorption capacity, T30-Clin exhibits better removal efficiency for paraquat.

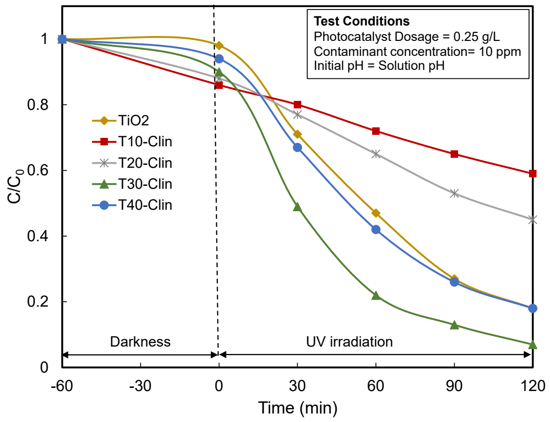

Figure 1. Performance of TiO_2/Clinoptilolite nanocomposites in the degradation of bentazone

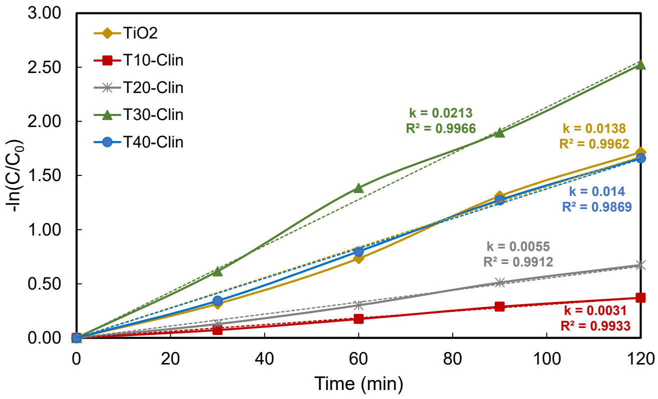

Figure 2. Kinetic consideration of TiO_2/Clinoptilolite nanocomposites in the degradation of bentazone

CONCLUSIONS

The clinoptilolite utilization could not only reduce the recombination of electron-hole pairs but also promote the distribution and reduce agglomerations of TiO_2 particles. The level of the synergetic effect of clinoptilolite strongly depends on TiO_2 loading. These features are more prominent when 30 wt.% of TiO_2 is added. However, the promoting effects of clinoptilolite utilization are weakened with the further addition of TiO_2. The excessive loading of TiO_2 (40 wt.%) severely covered the surface of clinoptilolite, afforded the aggregations, and weakened the contact between clinoptilolite and TiO_2, resulting in a decrease in metallic dispersion and the separation efficiency of electron–hole pairs. T30-Clin showed the highest photocatalytic removal efficiency for bentazone which alongside better performance for paraquat degradation, making it a good choice for photocatalytic removal of pesticides. The photocatalytic degradation of bentazone followed the pseudo-first-order kinetics according to the Langmuir–Hinshelwood model.

REFERENCES

[1] Shemeena, M., and Binitha, N. (2020). *"Visible light active ZnO–g-C_3N_4 photocatalyst for dye pollutant degradation"*. Materials Today: Proceedings, 25: 107-10.

[2] Wei, X., Wang, X., Pu, Y., Liu, A., Chen, C., Zou, W., Zheng, Y., Huang, J., Zhang, Y., and Yang, Y. (2021). *"Facile ball-milling synthesis of CeO_2/g-C_3N_4 Z-scheme heterojunction for synergistic adsorption and photodegradation of methylene blue: characteristics, kinetics, models, and mechanisms"*. Chemical Engineering Journal, 420: 127719.

[3] Berberidou, C., Kitsiou, V., Kazala, E., Lambropoulou, D. A., Kouras, A., Kosma, C. I., Albanis, T. A., and Poulios, I. (2017). *"Study of the decomposition and detoxification of the herbicide bentazon by heterogeneous photocatalysis: Kinetics, intermediates and transformation pathways*. Applied Catalysis B: Environmental, 200: 150-163.

[4] Khodadoust, S., Sheina, A., and Armand, N. (2012). *"Photocatalytic degradation of monoethanolamine in wastewater using nanosized TiO_2 loaded on clinoptilolite"*. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 92: 91-95.