POTENTIAL APPLICATIONS OF TIO$_2$/NATURAL ZEOLITE COMPOSITES FOR DYE REMOVAL

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Water pollution by organic dyes is a critical environmental issue that requires innovative and effective solutions. Photocatalytic materials based on titanium dioxide (TiO_2) can effectively degrade these pollutants; however, their use in suspension form has several drawbacks, such as the difficulty of separation and limited reusability. To overcome these limitations, the use of composites is promising, as they simplify the separation of TiO_2 after the reaction. The aim of this study is to modify natural Ukrainian zeolite and its acid-activated form with TiO_2 nanoparticles and to determine their photocatalytic activity towards anionic dyes. TiO_2/zeolite composites were synthesized by depositing titanium (IV) oxide nanoparticles onto natural zeolite and its acid-activated form, followed by thermal treatment at 500 °C. Characterization of the composites showed that the acid-activated composite achieved a specific surface area of 173.8 m²/g compared to 34.5 m²/g for the natural composite. The photocatalytic activity of the composites was evaluated by the degradation of the anionic dye Congo Red (10 mg/L) under ultraviolet irradiation. The results showed that the acid-activated zeolite modified with TiO_2 nanoparticles achieved a Congo Red degradation efficiency of 65.6% after 30 minutes of ultraviolet exposure, which is 12% higher compared to the natural zeolite modified with TiO_2 under the same conditions. The adsorption efficiency for Congo Red was 33.8%. This indicates that the composite not only facilitates the photocatalytic degradation of the dye but also contributes to its adsorption, enhancing the overall removal efficiency. Thus, the use of inexpensive natural zeolite as a TiO_2 carrier, especially in its acid-activated form, not only simplifies the subsequent separation of the photocatalyst from the purified water but also maintains the photocatalytic efficiency in degrading anionic dyes. The enhanced surface properties and structural characteristics of the acid-activated composite make it highly effective for practical applications. This makes such composites promising candidates for application in industrial wastewater treatment systems, where economic feasibility, operational simplicity, and environmental safety are primary criteria.

Keywords: *acid activation, composite materials, dye photodegradation, natural zeolite, photocatalysis, TiO_2 nanoparticles*

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1. Introduction

Nanostructured semiconductors and composites based on them hold significant potential for environmental remediation due to their ability to photocatalytically oxidize pollutants under solar or ultraviolet light irradiation[1]. The synthesis of new semiconductor-based photocatalysts is of great interest owing to their ability to address a range of issues, such as the decomposition of harmful and colored organic compounds in solutions[2–6] and gases[7–9], bacteriological purification[10], intensification of organic synthesis processes[11–13], and hydrogen production[14]. Titanium(IV) oxide is most commonly used as a photocatalyst because of its high photocatalytic activity, chemical stability, low cost, and non-toxicity[15,16]. However, practical implementation of photocatalytic processes using TiO_2 nanoparticles is complicated due to the difficulty of separating nanosized catalyst particles from the solution after the photocatalysis process. To address these challenges, various methods for immobilizing

TiO_2 nanoparticles onto the surfaces of different supports, such as silicon oxide and fibers[17–19] or zeolites[20], are being explored. It is crucial for such composite materials to retain the high catalytic activity of TiO_2 and the possibility of exhibiting quantum size effects, as well as to select an appropriate support.

Various supports are being investigated for the immobilization of TiO_2 nanoparticles (NPs) to enhance their photocatalytic activity and facilitate catalyst separation post-reaction. For instance, silicon oxide (SiO_2) is used to improve TiO_2 dispersion and more efficiently decompose organic pollutants[19]; activated carbon combines its adsorption properties with the photocatalytic activity of TiO_2 for synergistic pollutant removal[21]; clay minerals like bentonite are cost-effective and enhance photocatalytic stability due to their developed surface area[22–23]; graphene oxides improve electron conductivity and charge transfer in TiO_2 nanocomposites[24]. Among these supports, zeolites stand out due to their high surface area and porous structure, making them particularly effective for TiO_2 immobilization and improved pollutant degradation; therefore, zeolites were chosen for further research[25–28].

Modifying natural zeolites to enhance photocatalytic activity is a relevant research direction due to the growing need for efficient and sustainable methods to combat environmental pollution. The use of natural and economically advantageous materials, such as zeolites, for photocatalysis offers significant benefits in terms of environmental and economic sustainability.

The aim of this work is to investigate the modification of natural Ukrainian zeolite and its acid-activated form with TiO_2 nanoparticles (composites TiO_2/Zeo-0 and TiO_2/Zeo-1, respectively) and to determine their photocatalytic activity towards an anionic dye.

2. Materials and Methods

Natural zeolite (LLC "Sokyrnytsky Zeolite Plant") with a particle size up to 1 mm, containing up to 85% clinoptilolite, was used. The zeolite (Zeo-0) was subjected to acid activation by treating it with a 2 M nitric acid (HNO_3) solution at a temperature of 40 °C under intensive stirring for 4 hours. After treatment, the sample was thoroughly washed with distilled water until the pH of the wash water reached 6–7, then dried at 105 °C for 24 hours to remove moisture completely, resulting in acid-activated zeolite (Zeo-1).

Synthesis of TiO_2/Zeo Composites

The method for synthesizing TiO_2 NP is based on the procedure described by Ariza-Tarazona[29]. TiO_2 NP were obtained by hydrolysis of titanium isopropoxide: 4 g of zeolite were added to 250 mL of distilled water in a 500 mL flask with a magnetic stirrer, and the suspension was adjusted to pH 2, 2 mL of titanium isopropoxide, previously dissolved in 15 mL of isopropanol, was added dropwise to the suspension, heated to 80 °C, and stirred for 3 h. The suspension was then evaporated to dryness and calcined at 500 °C for 2 hours.

The structural and adsorption properties of the catalysts were studied using a JWGB Meso 112 specific surface area and porosity analyzer (China). The analysis of low-temperature nitrogen adsorption-desorption isotherms allowed determination of the pore size distribution, surface area, and hysteresis type, which is important for evaluating the efficiency of adsorption processes and the availability of active sites for photocatalytic reactions.

The method for studying the acid-base properties of the samples involved determining the change in pH of a neutral solution upon adding the sample[30]. Distilled water was adjusted to pH 7 by adding 0.1 M HCl under stirring. Then, 99 mL of the solution was taken, and 1 g of the sample was added. The pH change was observed over 10 minutes at 30-second intervals using a pH meter.

The photocatalytic properties of the samples were evaluated by assessing the efficiency of photodegradation of Congo Red (CR), an anionic dye, with an initial concentration of 10 mg/L under UV irradiation. Two doses of photocatalysts (0.5 and 1 g/L) were tested. For photocatalytic studies, the sample was dispersed in 50 mL of the dye solution and left to reach adsorption equilibrium under constant stirring and room temperature for 30 minutes. Photocatalytic experiments were conducted using an Arc Lamp Housing, Research, 50–500 W, Plano-Convex 66901 with frontal irradiation through quartz glass. After the photocatalytic process, the suspensions were filtered through a membrane filter. Pore sizes were selected to allow dye molecules to pass freely while retaining zeolite particles with modified by TiO_2. The immobilization of TiO_2 on zeolite significantly facilitated this process, enabling more efficient separation of the catalyst from the solution. Furthermore, to account for the potential adsorption of the dye on the membrane filter during the filtration of water samples, the degree of dye removal was calculated relative to the dye concentration after filtration. This approach ensures that the adsorption by the filter does not skew the results of the photocatalytic degradation. The residual dye concentration was determined spectrophotometrically using a Shimadzu UV 2600i. An anionic dye, Congo Red, was specifically chosen for this study because cationic dyes exhibited very intense adsorption on zeolite even in the absence of photocatalysis. By selecting an anionic dye, which has lower inherent adsorption on the zeolite support, the true photocatalytic activity could be more effectively evaluated.

3. Results and Discussion

The obtained photocatalytic systems (Zeo-0, Zeo-1, TiO_2/Zeo-0, and TiO_2/Zeo-1) were investigated using low-temperature nitrogen adsorption-desorption to determine their porous structures – specifically, pore size distribution, surface area, and hysteresis type – which are crucial for evaluating the efficiency of adsorption processes and the availability of active sites for photocatalytic reactions. Analysis of the adsorption-desorption isotherms (Figure 1) allowed us to determine these parameters for each sample according to the IUPAC classification.

Data on the porous characteristics of Zeo-0 (Figure 1) indicate the presence of H3-type hysteresis, characteristic of materials with slit-shaped pores. The average pore diameter was 6.5 nm, suggesting the predominance of mesopores. The external surface area was 18.8 m^2/g. The isotherm of the Zeo-1 demonstrates H4-type hysteresis, indicating the dominance of micropores. The average pore diameter was 4.1 nm, and the surface area was 39.0 m^2/g, explained by the presence of micropores (29.3 m^2/g).

After modifying the zeolite samples by depositing TiO_2 nanoparticles, the porous structure of both the natural and acid-activated zeolites changed significantly. Data on the porous characteristics of TiO_2/Zeo-0 indicate the presence of H1-type hysteresis on the isotherms, characteristic of the formation of more uniform cylindrical mesopores. The average pore diameter increased to 8.8 nm, and the external surface area was 39.4 m^2/g.

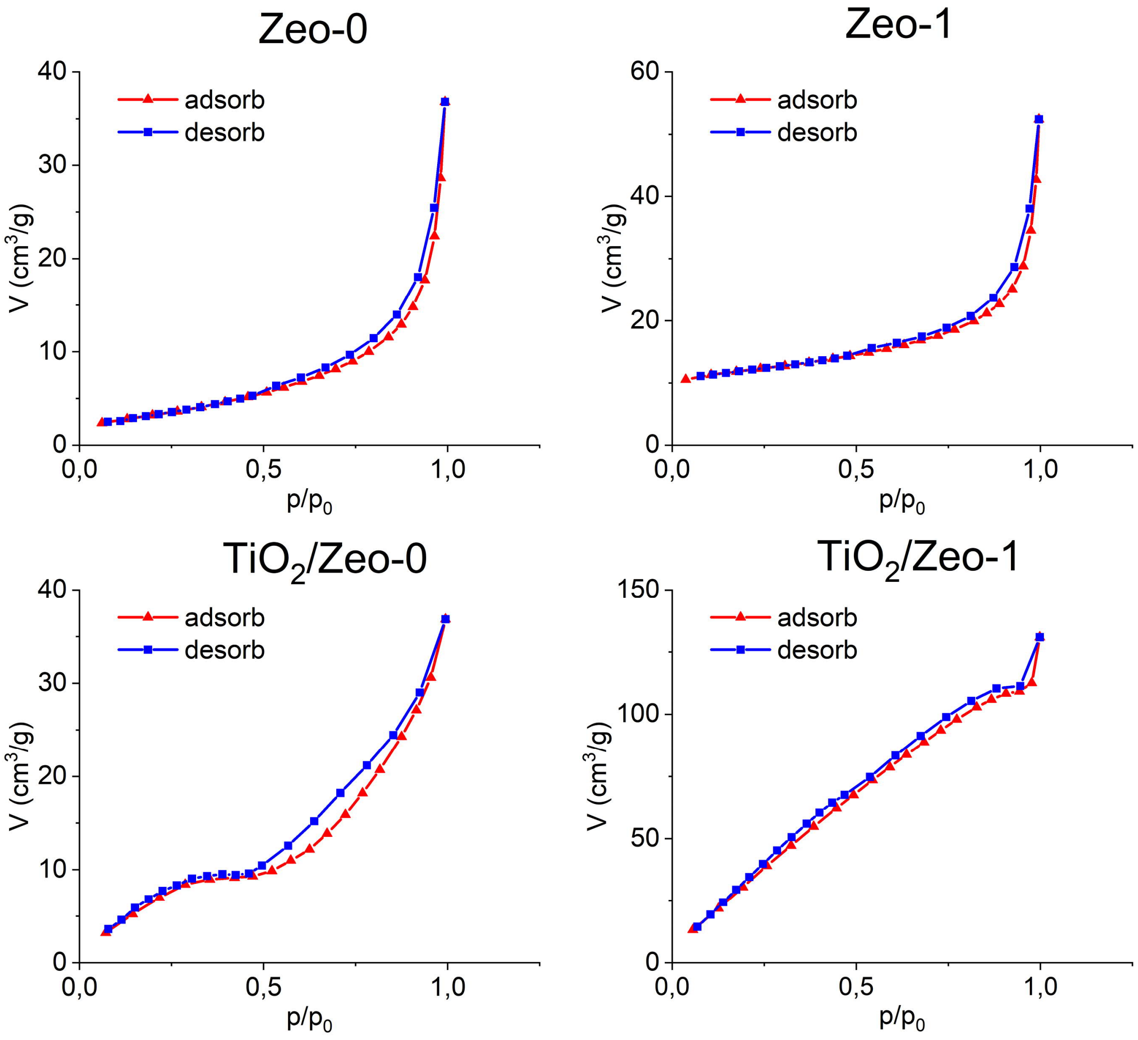

Figure 1. *Low-temperature nitrogen adsorption-desorption isotherms of the samples.*

The adsorption-desorption isotherm of the modified sample TiO_2/Zeo-1 shows H2-type hysteresis, characteristic of structures with narrow necks and wide cavities ("ink-bottle" pores). The average pore diameter was 3.9 nm, and the surface area increased significantly to 173.8 m^2/g.

Comparison of the modified and unmodified samples showed that TiO_2 modification primarily improves the structural and adsorption properties (Table 1). In the Zeo-0 samples, the pore structure changed from H3 to H1, indicating the creation of a uniform porous structure. In Zeo-1, modification with titanium (IV) oxide caused a change in hysteresis type from H4 to H2 and significantly increased the specific surface area, likely due to the creation of a secondary porous structure on the surface of Zeo-1.

A previously conducted X-ray phase analysis of the Zeo-0 (natural zeolite) and Zeo-1 (acid-activated zeolite) samples showed[31] that acid activation has minimal impact on structural and compositional properties: the amount of clinoptilolite-Na decreased slightly from 73.7% to 69.6%, and the quartz content remained stable (30.4% in Zeo-1 versus 23.2% in Zeo-0), while cristobalite completely disappeared in Zeo-1. The R_{wp} values (22.6 for Zeo-0 and 23.4 for Zeo-1) and χ^2 (1.6 for Zeo-0 and 1.7 for Zeo-1) confirm that structural changes are negligible.

Table 1. *Structural characteristics of the samples.*

Sample	Hysteresis Type	Average Pore Diameter (nm)	BET Surface Area (m^2/g)	Micropore Surface Area (m^2/g)	External Surface Area (m^2/g)
Zeo-0	H3	6,5	34,5	15,7	18,8
Zeo-1	H4	4,1	39,0	29,3	25,0
TiO_2/Zeo-0	H1	8,8	34,5	0,0	34,5
TiO_2/Zeo-1	H2	3,9	173,8	0,0	173,8

An analysis of the acid-base properties of the samples was conducted (Table 2). The Zeo-1 sample, which underwent acid activation, demonstrated the highest concentration of acidic sites, amounting to 0.014 mmol/g. The unmodified Zeo-0 had a significantly lower number of acidic sites – $2{,}34\cdot10^{-4}$ mmol/g.

Table 2. *Acid-base properties of the samples.*

Sample	pH	Acidic Sites (mmol/g)
Zeo-1	3,7	$1{,}41\cdot10^{-2}$
Zeo-0	6,6	$2{,}34\cdot10^{-4}$
TiO_2/Zeo-1	5,1	$8{,}91\cdot10^{-4}$
TiO_2/Zeo-0	7,3	$4{,}79\cdot10^{-5}$

Modification of the zeolite samples with TiO_2 reduced the number of acidic sites – to $8{,}91\cdot10^{-4}$ mmol/g in TiO_2/Zeo-1 and to $4{,}79\cdot10^{-5}$ mmol/g in TiO_2/Zeo-0.

The photocatalytic efficiency of the modified zeolites was investigated using Congo Red dye. The photocatalyst dosages were 0.5 g/L and 1 g/L, with an initial dye concentration of 10 mg/L. The influence of the presence or absence of thermal treatment (calcination at 500 °C) after modifying Zeo-1 with titanium (IV) oxide on the photocatalytic activity of the composites was preliminarily studied. The increase in photocatalytic activity observed after calcination at 500 °C can be attributed to the crystallisation of TiO_2 into the anatase phase, which is known for its superior photocatalytic properties. According to the article [32], TiO_2 remains in the anatase form at 500 °C, with the transformation to the rutile phase occurring at temperatures above 600 °C. Thermal treatment at 500 °C facilitates the formation of well crystallised anatase TiO_2, reduces the number of surface defects and improves the adhesion of TiO_2 to the zeolite support. Together, these factors enhance the efficiency of active radical generation during photocatalysis, resulting in increased photocatalytic activity of the composites. Figure 2 presents data on the degree of Congo Red removal by the thermally treated and untreated TiO_2/Zeo-1 samples.

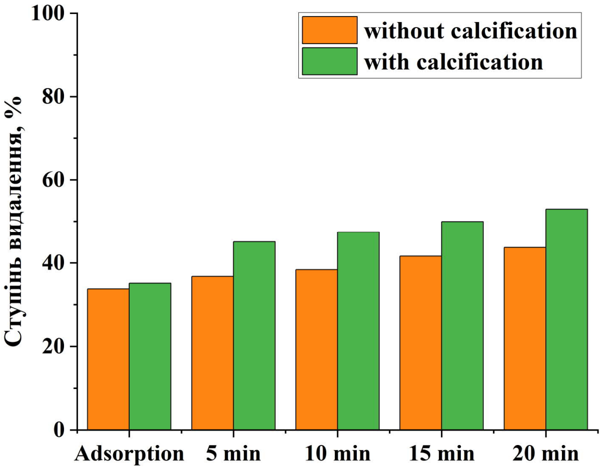

Figure 2. *Effect of calcination on photocatalytic efficiency using TiO_2/Zeo-1 at a dosage of 0.5 g/L*

The results showed that for samples without thermal treatment, the degree of dye removal increased with the duration of UV irradiation, starting from 36.8% after 5 minutes and reaching 43.7% at 20 minutes. High adsorption capacity of Zeo-1 towards CR achieved 33.8% without UV irradiation. Samples that were calcined at 500 °C exhibited increased photocatalytic efficiency – from 45.1% after 5 minutes of UV irradiation to 53.0% after 20 min. Thus, additional thermal treatment of the composite increases its photocatalytic activity towards Congo Red by 8-10%. Subsequent experiments were conducted with thermally treated samples.

The effect of photocatalyst dosage was investigated using the TiO_2/Zeo-0 sample at two different dosages: 0.5 g/L and 1 g/L. The results showed that for the sample with a concentration of 0.5 g/L, the degradation efficiency of Congo Red increased from 22.7% after 5 minutes of UV irradiation to 39.5% at 20 minutes (Figure 3). This indicates an improvement in photocatalytic activity with irradiation time, consistent with expectations regarding increased generation of active radicals with longer exposure. For samples with a higher photocatalyst concentration (1 g/L), significantly higher degradation efficiency was observed, reaching 37.2% after just 5 minutes of UV irradiation and gradually increasing to 62.2% at 20 minutes.

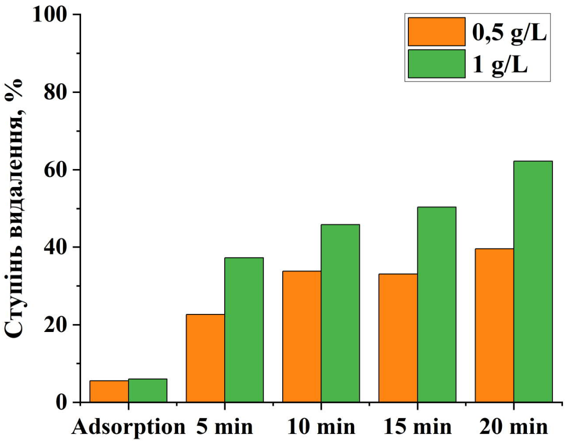

Figure 3. Effect of TiO_2/Zeo-0 dosage on CR removal efficiency

Comparison of the photocatalytic activity towards CR of thermally treated samples TiO_2/Zeo-0 and TiO_2/Zeo-1 at a dosage of 0.5 g/L indicates significantly higher photocatalytic activity of TiO_2/Zeo-1. Specifically, the maximum removal degree of Congo Red for TiO_2/Zeo-0 reached 39.5% (Figure 3), while under the same conditions, the removal degree for TiO_2/Zeo-1 was 53.0% (Figure 2).

To further investigate, the photocatalytic activity of TiO_2/Zeo-0 and TiO_2/Zeo-1 towards Congo Red was studied at a dosage of 1 g/L (Figure 4). The results showed that the adsorption degree of the TiO_2/Zeo-0 sample was only 9.4%, and the photocatalytic activity after 15 minutes of UV irradiation was 12.3%, increasing to 23.4% at 30 minutes. In contrast, TiO_2/Zeo-1 demonstrated higher sorption capacity: the adsorption degree was 36.5%, and the photocatalytic activity increased to 57.8% after 15 minutes of UV irradiation, reaching 65.6% at 30 minutes. These results confirm that TiO_2-modified Zeo-1 significantly surpasses Zeo-0 in both adsorption and photocatalytic properties.

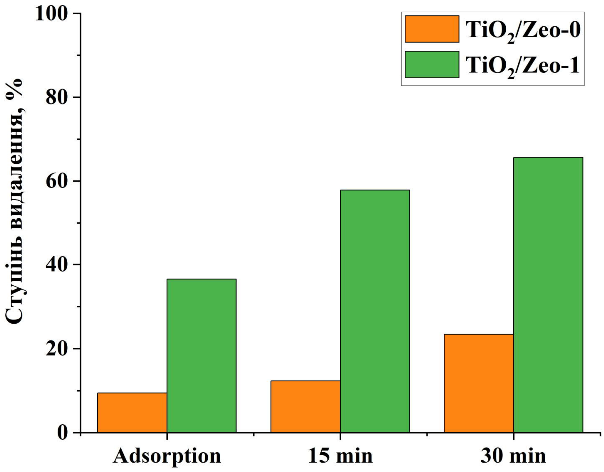

***Figure 4.** Adsorption efficiency and photocatalytic activity of TiO_2/Zeo-0 and TiO_2/Zeo-1 samples at a dosage of 1 g/L*

These findings demonstrate that TiO_2-modified Zeo-1 exhibits superior performance compared to Zeo-0, owing to its enhanced adsorption capacity and photocatalytic activity, likely resulting from its optimized porous structure and increased specific surface area due to acid activation.

4. Conclusions

In this study, photocatalysts based on natural zeolite (Zeo-0) and its acid-activated form (Zeo-1), modified with TiO_2 nanoparticles, were successfully synthesized and analyzed. The modification of zeolites with TiO_2 nanoparticles significantly improved their structural, adsorption, and photocatalytic properties. The porous structure of the zeolites was substantially altered upon modification. The TiO_2/Zeo-1 sample exhibited a significant increase in specific surface area to 173.8 m^2/g and a change in pore structure, which enhanced adsorption properties and provided greater accessibility of active sites for photocatalytic reactions. This indicates that acid activation and subsequent TiO_2 modification create a more favorable porous structure for photocatalysis.

Thermal treatment of the composites at 500 °C positively affected their photocatalytic activity. Calcination facilitated the crystallization of TiO_2 nanoparticles into a more active form and reduced the number of surface defects, leading to an 8–10% increase in the efficiency of Congo Red degradation compared to non-calcined samples. This underscores the importance of thermal treatment in forming active photocatalysts.

The influence of photocatalyst dosage was also investigated. Increasing the dosage from 0.5 g/L to 1 g/L resulted in a significant enhancement of dye degradation efficiency. For the TiO_2/Zeo-1 composite, the degree of Congo Red degradation reached 65.6% after 30 minutes of ultraviolet irradiation at a dosage of 1 g/L, substantially exceeding the performance at the lower dosage. This can be attributed to the increased number of active sites and more intensive generation of reactive radicals under UV irradiation.

Overall, the TiO_2/Zeo-1 sample demonstrated higher photocatalytic activity compared to TiO_2/Zeo-0. The enhanced performance is associated with the optimized porous structure, higher specific surface area, and increased number of active sites resulting from acid activation of the zeolite. These results indicate the prospect of using modified TiO_2/zeolite composites, particularly those based on acid-activated zeolite, for the effective removal of anionic organic dyes from aqueous solutions.

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ПЕРСПЕКТИВИ ВИКОРИСТАННЯ КОМПОЗИТІВ TiO_2/ПРИРОДНИЙ ЦЕОЛІТ ДЛЯ ВИДАЛЕННЯ БАРВНИКІВ

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Забруднення води органічними барвниками є важливою екологічною проблемою, яка потребує інноваційних та ефективних рішень. Фотокаталітичні матеріали на основі діоксиду титану (TiO_2) можуть ефективно розкладати ці забруднювачі, однак їх використання у вигляді суспензії має ряд недоліків, таких як складність розділення та обмежена можливість повторного використання. Для подолання цих обмежень перспективним є використання композитів, оскільки вони спрощують відокремлення TiO_2 після реакції. Метою цього дослідження є модифікація природного українського цеоліту та його кислотно-активованої форми наночастинками TiO_2 і визначення їхньої фотокаталітичної активності по відношенню до аніонних барвників. Композити TiO_2/цеоліт були синтезовані шляхом осадження наночастинок титан (IV) оксиду на природний цеоліт та його кислотно-активовану форму з подальшою термічною обробкою при 500 °C. Характеристика композитів показала, що кислотно-активований композит досяг питомої поверхні 173,8 $м^2/г$ порівняно з 34,5 $м^2/г$ для природного композиту. Фотокаталітичну активність композитів оцінювали за деградацією аніонного барвника конго червоного (10 $мг/дм^3$) під дією ультрафіолетового (УФ) опромінення. Результати показали, що кислотно-активований цеоліт, модифікований наночастинками TiO_2, досягнув ефективності деградації конго червоного 65,6% після 30 хвилин УФ-опромінення, що на 12% вище порівняно з природним цеолітом, модифікованим TiO_2 за тих же умов. Ефективність адсорбції для червоного конго склала 33,8%. Це свідчить про те, що композит не тільки полегшує фотокаталітичну деградацію барвника, але й сприяє його адсорбції, підвищуючи загальну ефективність видалення. Таким чином, використання недорогого природного цеоліту як носія TiO_2, особливо в його кислотно-активованій формі, не тільки спрощує подальше відділення фотокаталізатора від очищеної води, але й зберігає фотокаталітичну ефективність деградації аніонних барвників. Покращені поверхневі властивості та структурні характеристики кислотно-активованого композиту роблять його високоефективним для практичного застосування. Це робить такі композити перспективними кандидатами для застосування в промислових системах очищення стічних вод, де економічна доцільність, простота експлуатації та екологічна безпека є першочерговими критеріями.

Ключові слова: *кислотна активація, композиційні матеріали, наночастинки TiO_2, природний цеоліт, фотокаталіз, фотодеструкція барвників*