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ACID-BASE PROPERTIES OF NATURAL AND ACTIVATED ZEOLITES AND THEIR COMPOSITES

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This study investigates the acid-base surface characteristics of natural zeolite samples from the Sokyrnytsia deposit (Ukraine). The samples include untreated natural zeolite, its acid-activated form obtained by treatment with nitric acid (HNO_3, 2 M) at 40 °C under continuous stirring for 4 hours, and zeolite modified with titanium dioxide, both in its natural and acid-activated forms. The acid-base properties of all zeolite forms and composites were studied using the Hammett indicator method, which involves the selective adsorption of acid-base indicators from solutions onto the surface of solid materials. Significant changes in the distribution of Brønsted acid and base sites on the surface of the investigated zeolite-based samples were observed. X-ray diffraction analysis of the acid-activated natural zeolite revealed that acid treatment induced only minor changes in the phase composition while preserving the crystalline structure of the zeolite compared to the untreated material. The influence of pH on fluoride ion removal efficiency by natural zeolite was also investigated to explain the changes in its surface acid-base properties following acid activation. To confirm the potential redistribution of the electronic configuration on the zeolite surface and the possible blocking of its adsorption properties, additional experiments were conducted on the adsorption removal and photocatalytic degradation of Congo Red dye from solutions using the acid-activated zeolite modified with titanium dioxide. The findings demonstrate the feasibility and practicality of utilizing cost-effective natural Ukrainian zeolites for the development of adsorbents and photocatalysts with tunable acid-base surface properties, which could offer competitive advantages in the removal of various pollutants from water.

Keywords: *acid activation, acid-base properties, composite materials, dye photodegradation, natural zeolite, TiO_2 modification*

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1. Introduction

The treatment of wastewater from various sources, as well as natural water purification, requires the implementation of complex technologies, which significantly increases costs. To address urgent water treatment challenges, the use of natural and synthetic zeolitic materials as sorbents remains relevant [1,2]. Zeolites are widely utilized not only as aluminosilicate supports for catalysts but also as standalone catalysts, with extensive applications in petroleum refining, polymer and plastic processing, organic synthesis, and other industrial processes [3,4].

Zeolites are chemically and thermally stable minerals that retain their adsorption and catalytic properties in chemically aggressive environments and at high temperatures without compromising their crystalline framework. A distinctive feature of aluminosilicate materials is their high potential for modification and activation, which significantly alters their properties. Treatment with acidic and alkaline solutions (acids, bases, salt solutions, and certain organic compounds) enables the adjustment of zeolite surface characteristics for specific applications, as such activation allows for the regulation of the acidity and basicity of the aluminosilicate matrix. Consequently, activation and modification of zeolites facilitate the formation of various active sites, including Brønsted and Lewis acid-base centers. These active centers govern the interaction between the adsorbate and the adsorbent and are among the key factors determining the widespread application of zeolites in various processes [5,6]. The formation of acid-activated H-form zeolites is also accompanied by decationization and delocalization processes while preserving the crystalline structure of the mineral.

The modification of zeolites with metal-based species is an effective approach for enhancing their sorption properties, particularly for the removal of heavy metals from aqueous solutions. In a study [7], natural Iranian zeolite (clinoptilolite) was modified with cobalt hexacyanoferrate nanoparticle rods. The adsorption capacity of the modified zeolite toward Cd(II) was reported to be 51 mg/g.

In another study [1], natural zeolites from Georgian deposits (mordenite and clinoptilolite) were treated to improve their adsorption performance for wastewater purification. It was demonstrated that these natural zeolites exhibit high thermal stability and acid resistance even after acid modification, while their synthesized H-forms possess a high concentration of active sites. The obtained results confirmed the effectiveness of acid-activated natural zeolites in the adsorption-based removal of certain pharmaceutically active pollutants from wastewater.

The environmental applications of zeolites were also highlighted in a study [8], where they were utilized for the catalytic conversion of carbon dioxide, which is crucial for carbon capture, storage, and utilization, as well as for reducing CO_2 emissions. The zeolite samples were synthesized via a hydrothermal method using Indonesian kaolin. Their catalytic activity in the CO_2 methanation process was demonstrated to be strongly dependent on the acid-base and textural properties of the zeolites.

This study explores the potential application of natural Ukrainian zeolite (clinoptilolite) from the Sokyrnytsia deposit (Sokyrnytsia Zeolite Plant LLC), which possesses high mechanical strength and serves as a cost-effective raw material, highlighting its economic feasibility. The research focuses on the properties of natural Ukrainian zeolite (Zeo-0), its acid-activated form (Zeo-1), as well as powders modified with TiO_2 nanoparticles – Zeo-0 and Zeo-1 (composites TiO_2/Zeo-0 and TiO_2/Zeo-1, respectively). The acid-base characteristics of these materials were investigated using the Hammett indicator adsorption method.

2. Materials and Methods

A natural zeolite from a Ukrainian deposit (LLC "Sokyrnytsia Zeolite Plant") with a particle size of up to 1 mm, containing up to 85% clinoptilolite, was used in this study.

The acid activation of the natural zeolite was performed by treating a dry aluminosilicate material with a 2 M nitric acid (HNO_3) solution at 40°C under continuous stirring for 4 hours. Following the treatment, the sample was thoroughly washed with distilled water until a neutral pH of the rinsing water was achieved. The sample was then dried at 105°C for 24 hours to remove residual moisture, resulting in acid-activated zeolite (Zeo-1). The synthesis of TiO_2/Zeo composites via hydrolysis of titanium isopropoxide is described in a previous publication dedicated to photocatalysis [9].

The acid-base properties of the composites were investigated using the Hammett indicator method [10], which involves the selective adsorption of acid-base indicators. The set of indicators with predefined pKa transition values used in this study was identical to that reported [11]. Changes in the optical density of indicator solutions were measured spectrophotometrically. The optical density of the initial indicator solution (D_0) was recorded using a spectrophotometer. Subsequently, a suspension of the photocatalyst in the respective indicator solutions was prepared (sample mass: 0.02 g; indicator solution volume: 10 ml). The concentration of acid sites (q, mol/g), equivalent to the amount of adsorbed indicator q_{pKa}, was calculated using the following equation:

$$q_{pK_a} = \frac{C_{ind}V_{ind}}{D_0}\left[\frac{|D_0-D_1|}{\alpha_1} \pm \frac{|D_0-D_2|}{\alpha_2}\right],$$

where C_{ind} and V_{ind} are the concentration and volume of the indicator, respectively; α_1 and α_2 are the sample masses used in the D_1 and D_2 measurements. The "–" sign corresponds to unidirectional changes in D_1 and D_2 relative to D_0, while the "+" sign corresponds to bidirectional changes.

The surface acidity function H_0 was determined from the adsorption center distribution spectra using the following equation:

$$H_0 = \frac{\Sigma(pK_a \cdot q_{pK_a})}{\Sigma q_{pK_a}}.$$

Adsorption experiments were conducted using natural zeolite under different initial fluoride concentrations and pH values, with fluoride ion measurements performed via potentiometric analysis; all materials and methodological details are provided in a previous publication dedicated to fluoride adsorption [12].

The photocatalytic properties of the samples were assessed based on the photodegradation efficiency of Congo Red under UV irradiation, with all methodological details provided in a previous publication dedicated to photocatalysis [9].

The phase composition of the samples was identified using X-ray diffraction (XRD) analysis performed on a Rigaku Ultima IV diffractometer (Japan) with CuKα radiation (20-60 kV, 2-60 mA). The phase composition was determined using the Profex software based on standard reference patterns and the COD database.

3. Results and Discussion

X-ray diffraction (XRD) analysis was performed on both the native and acid-activated natural zeolite (clinoptilolite) samples [12], and the results are presented in Figure 1.

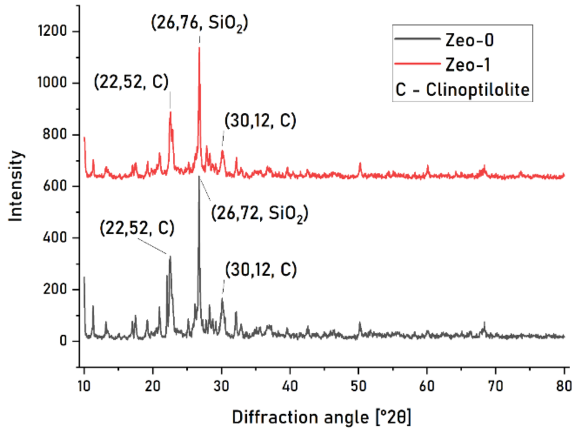
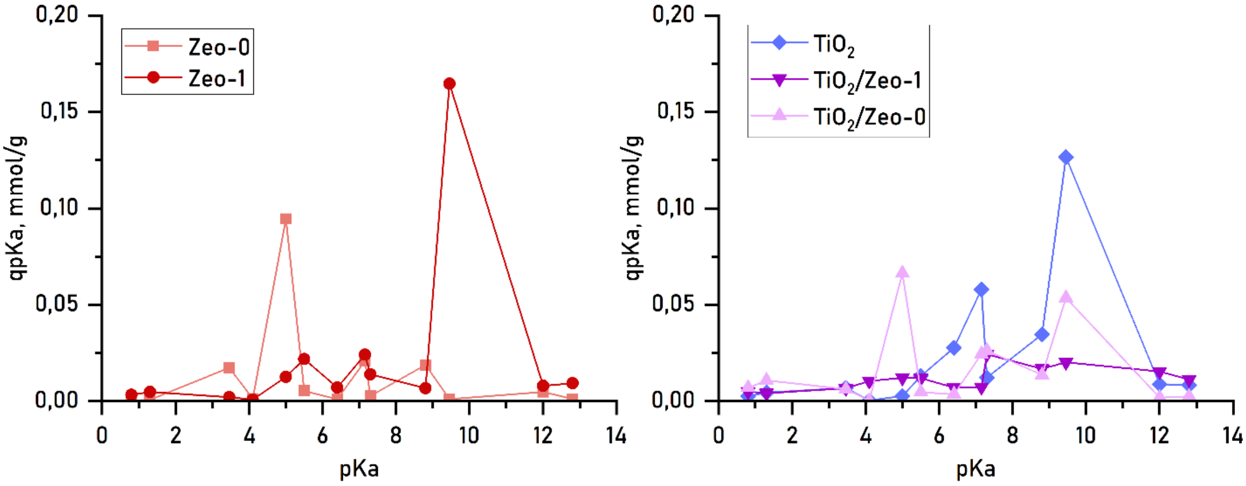


Fig. 1. *X-ray phase analysis of natural and acid-activated zeolite*

The obtained XRD results indicate that acid activation has a minimal impact on the structural and compositional properties of natural zeolite. The quantity of clinoptilolite-

Na slightly decreases from 73.7% to 69.6%, while the quartz content exhibits a minor increase (30.4% in Zeo-1 compared to 23.2% in Zeo-0), whereas cristobalite is completely absent in Zeo-1. R_{wp} values (22.6 for Zeo-0 and 23.4 for Zeo-1) and χ^2 values (1.6 for Zeo-0 and 1.7 for Zeo-1) confirm that structural changes remain negligible.

The results of the investigation into the acid-base properties of the surface of native and acid-activated zeolite samples are presented in Figure 2.



a) b)

Fig. 2. *Distribution of surface centers of zeolite-based samples according to acidity: (a) natural and acid-activated zeolites; (b)* TiO_2 *and its composites with natural and acid-activated zeolites.*

The Hammett indicator adsorption method was employed to evaluate the acid-base characteristics of zeolite surfaces, as reflected in the obtained pKa distributions and surface acidity function (H_0) values. Natural zeolite Zeo-0 exhibits two primary regions of acid-base activity, at pKa 5.0 and 9.45 (Figure 2a). The pronounced peak at pKa 5.0 corresponds to Brønsted acid sites, which are formed by Si(Al)-OH hydroxyl groups capable of donating protons [13]. A smaller peak at pKa 9.45 is associated with Brønsted basic sites, likely attributed to the presence of oxide ions or dissociated surface groups [14].

Surface acidity calculations based on the distribution of acid-base centers in the studied samples (Section 2) yielded the values listed in the table.

Table 1. *H_0 values for natural, activated, and modified zeolites*

Sample	**H_0**
Zeo-0	5,8
Zeo-1	8,4
TiO_2	8,2
TiO_2/Zeo-0	6,6
TiO_2/Zeo-1	7,5

The overall H_0 value of 5.8 for Zeo-0 indicates a predominance of acidic centers on the surface, confirming its general acidity.

Following acid activation, represented by Zeo-1, significant changes occur in the distribution of acid-base centers (Figure 2a). The most notable effect is a decrease in the peak at pKa 5.0, accompanied by a shift towards pKa 5.5. This phenomenon may be attributed to a reduction in the electron-acceptor strength of the zeolite surface due to the replacement of exchangeable metal cations with hydrogen ions, forming the H-zeolite during acid activation. Simultaneously, an increase in the peak intensity at pKa 9.45 suggests that during the formation of H-zeolites, acid treatment induces parallel de-cationization processes. The removal of Al^{3+} from the aluminosilicate framework generates an excess negative surface charge, enhancing the electron-donor properties of the material and leading to the formation of Brønsted basic sites [15]. The increase in H_0 to 8.4 is consistent with the observed redistribution of active sites, specifically the reduction in acid sites at pKa 5.0 and the enhancement of basic sites at pKa 9.45.

An indirect confirmation of this redistribution of acid-base properties in native clinoptilolite (Zeo-0) can be found in its adsorption characteristics (Figure 3).

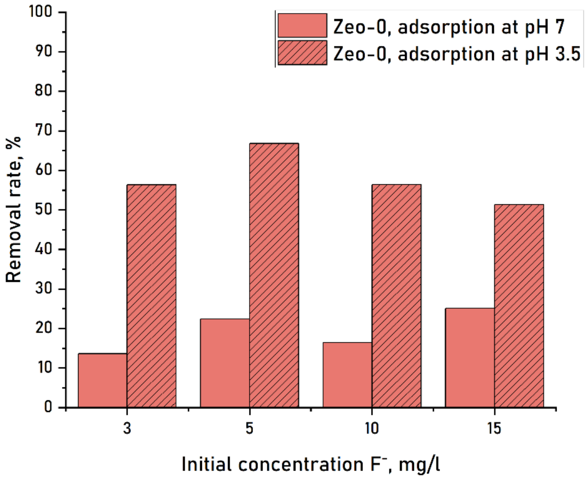


Fig. 3. *Comparison of fluoride ion adsorption efficiency by natural zeolite at different pH levels*

Figure 3 demonstrates that as the pH of the medium decreases, meaning an increase in H^+ concentration, the fluoride ion adsorption activity of Zeo-0 significantly increases. This can be explained by the redistribution of electron density and the enhancement of electron-donor properties at the surface due to partial protonation at electron-donor sites, facilitating electron transfer from F^- to electron-acceptor centers.

Modification of natural zeolite with titanium dioxide leads to substantial alterations in the distribution of active sites, as observed in the TiO_2/Zeo-0 sample (Figure 2b). Unlike the original Zeo-0, the peak intensity at pKa 9.45 increases, indicating a higher concentration of Brønsted basic sites. This may result from the partial formation of additional Ti-O surface groups. Simultaneously, the peak intensity at pKa 5.0 decreases, signifying a reduction in weak Brønsted acid sites. This change may be attributed to the reduced availability of silanol groups due to TiO_2 coating, which induces a surface blocking effect. The H_0 value of 6.6 confirms the shift in acid-base properties toward a reduction in overall acidity.

The most significant changes are observed in the TiO_2/Zeo-1 sample, where both acid activation and TiO_2 modification occur simultaneously. The complete disappearance of peaks at pKa 5.5 and 9.45 suggests that titanium dioxide not only alters the distribution of acid-base sites but also blocks them. This phenomenon may be explained by the formation of new surface bonds that modify the electronic configuration of the zeolite and its interactions with acidic or basic molecules. Simultaneously, the overall acidity increases, as evidenced by the reduction of H_0 to 7.5 compared to Zeo-1 and TiO_2.

The acid-base surface behavior of the TiO_2/Zeo-1 sample can be further explained by its adsorption and photocatalytic characteristics concerning Congo Red dye in the presence of TiO_2/Zeo-1 (Figure 4).

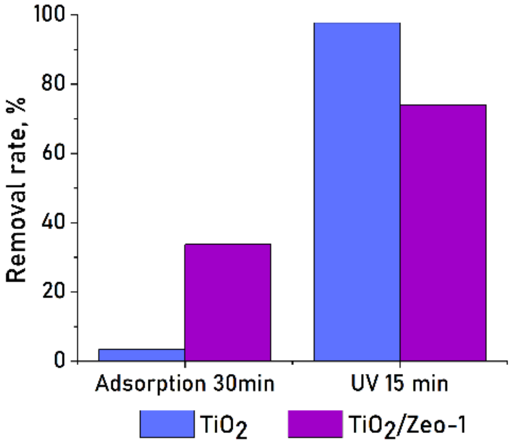


Fig. 4. *Comparison of the adsorption and photocatalytic activity of TiO_2 and its zeolite-based composite*

Figure 4 shows that the adsorption capacity of TiO_2 is minimal, indicating that TiO_2 itself exhibits negligible adsorption ability for Congo Red dye but demonstrates significant photocatalytic activity. Additionally, the TiO_2/Zeo-1 sample exhibits high photocatalytic performance, suggesting that the active photocatalytic TiO_2 phase is exposed at the surface and accessible to light irradiation. This, in turn, implies that the active acid-base centers, which serve as adsorption sites, are blocked.

Overall, the analysis of the obtained data suggests that acid activation leads to substantial structural changes, particularly the loss of Brønsted acid sites at pKa 5.0 and an increase in basic sites at pKa 9.45. Modification with titanium dioxide induces further transformations, including surface blocking and changes in basic site activity, as confirmed by shifts in H_0 values and the results of adsorption and photocatalytic studies of zeolite-based samples.

4. Conclusions

The acid-base properties of natural and modified zeolites were investigated using the Hammett indicator adsorption method. It was determined that natural zeolite (Zeo-0) has an H_0 value of 5.8, indicating moderate surface acidity, whereas acid activation increases H_0 to 8.4, signifying a substantial enhancement of surface basicity. The incorporation of TiO_2 into natural zeolite (TiO_2/Zeo-0) alters the distribution of acid-base centers, leading to an increase in basic site concentration and a decrease in H_0 to 6.6. In the case of acid-activated zeolite modified with TiO_2 (TiO_2/Zeo-1), the H_0 value decreases to 7.5, indicating an increase in overall acidity compared to Zeo-1, while remaining higher than that of the original zeolite.

Spectrophotometric measurements and acid-base characterization confirmed that acid activation of natural zeolite reduces Brønsted acid centers at pKa 5.0 while enhancing basic centers at pKa 9.45. The introduction of TiO_2 further modifies the surface properties, decreasing overall basicity and altering the electronic structure of the zeolite. The obtained results are essential for the future application of modified zeolite materials in catalytic conversion, adsorption, and water purification processes, as controlling the acid-base characteristics of their surfaces enables optimization of their functional properties.

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КИСЛОТНО-ОСНОВНІ ВЛАСТИВОСТІ ПРИРОДНОГО І АКТИВОВАНОГО ЦЕОЛІТІВ ТА КОМПОЗИТІВ НА ЇХ ОСНОВІ

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У роботі проведено дослідження поверхневих кислотно-основних характеристик зразків природного цеоліту Сокирницького родовища (Україна) без попередньої обробки; його кислотно-активованої форми, яку отримували шляхом додавання нітратної кислоти (HNO_3, 2 М) за температури 40 °С та інтенсивного перемішування протягом 4 годин; і модифікованих титан(IV) оксидом природного цеоліту без обробки та кислотно-активованого цеоліту. Дослідження кислотно-основних властивостей всіх форм цеоліту та композитів проводили з використанням індикаторного методу Гаммета, який полягає в селективній адсорбції кислотно-основних індикаторів з розчинів на поверхні твердих матеріалів. Виявлено суттєві зміни розподілу кислотних та осно́вних центрів (кислотні та осно́вні центри Бренстеда) на поверхні досліджених зразків на основі цеоліту. За допомогою рентгенофазового дослідження кислотно-активованого природного цеоліту встановлено, що під час кислотної активації у фазовому складі цеоліту відбуваються несуттєві зміни та спостерігається збереження його кристалічної структури у порівнянні з нативним цеолітом. Проведено дослідження впливу pH середовища на ефективність видалення фторид-іонів у присутності з метою отримання пояснення щодо зміни його кислотно-основних характеристик поверхні після кислотної активації. Для підтвердження ефекту можливого перерозподілу електронної конфігурації на поверхні цеоліту та можливого блокування його адсорбційних властивостей проведені досліди з адсорбційного вилучення та фотокаталітичної деструкції барвника Конго червоного з розчинів для зразку модифікованого титан(IV) оксидом кислотно-активованого цеоліту. Показано перспектива і доцільність використання дешевих природних цеолітів українського видобутку для створення адсорбентів та фотокаталізаторів з регульованими кислотно-основними властивостями поверхні, які можуть стати конкурентно спроможними у процесах очищення води від полютантів різної природи.

Ключові слова: *кислотна активація, кислотно-основні властивості, композиційні матеріали, модифікація TiO_2, природний цеоліт, фотодеградація барвників*