

NATURAL ALUMINOSILICATES IN WATER PURIFICATION TECHNOLOGIES: A SHORT REVIEW

Ludmila Bogdan¹, Khrystyna Hutsul¹, Viktor Kurylenko¹, Olena Yanushevskaya¹,
Tetiana Dontsova¹

¹National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"

x_gucul1997@ukr.net

DOI: <https://doi.org/10.20535/2218-930032024324430>



The review is devoted to the peculiarities of using natural aluminosilicates, in particular bentonites and zeolites, in water treatment technologies. A description of the general structure of clay materials, their chemical composition, characteristics of their building frameworks, and varieties of forms found in nature is given. Emphasis is placed on the adsorption characteristics of bentonite, which is the most common type of clay, including in Ukraine. In the description of natural zeolites, attention is paid to their spatial structure, namely the ratio of Si:Al in their natural modifications, chemical composition, and structural features that ensure the use of zeolites as adsorbents and catalysts. The expediency of using natural aluminosilicates in adsorption, ion exchange, and photocatalytic processes is shown in the examples of the extraction and degradation of various organic compounds, including petroleum products, phenols, and dyes, etc. Emphasis is placed on the importance of the ion exchange capacity of natural bentonites and zeolites as a tool for their modification and activation, significantly improving their performance in water treatment technologies. The effective properties of natural aluminosilicates, such as the active surface area, its acid-base properties, and non-toxicity, are analysed, which indicates their high potential as a reliable potential alternative to more expensive synthetic materials. Numerous studies confirm that properly modified aluminosilicates can combine high adsorption capacity with catalytic activity, enabling their multifunctional use in advanced water treatment. It has been established that, due to their combination of low cost, environmental safety, wide availability, and high efficiency, natural aluminosilicates represent a promising basis for the development of competitive adsorbents and catalysts within the framework of green water treatment concepts. The use of bentonites and zeolites enables the creation of integrated treatment systems that incorporate both physical and chemical mechanisms for contaminant removal and catalytic degradation. Examples of natural aluminosilicate modification by acid, alkali, surfactant treatment, and metal oxide nanoparticles (e.g., ZnO, TiO₂) are provided, demonstrating the expansion of their functionality in water purification processes.

Keywords: aluminosilicates, bentonite, zeolite, adsorption, modification, photocatalysis, water pollution, water treatment

Received: 10 December 2024

Revised: 26 December 2024

Accepted: 30 December 2024

1. Introduction

The high technological level of modern production facilities and rapid industrialization and urbanization in the world cause environmental problems that provoke several serious consequences and environmental

impacts. Inadequate wastewater treatment and negligence in the maintenance and modernization of water treatment equipment create local environmental problems that quickly turn into total man-made disasters. The spectrum of hazardous pollutants entering water bodies is caused by the presence of

biological and chemical substances of natural and artificial origin, the source of which are agricultural runoff, landfill leachate, industrial and municipal wastewater. These wastewaters contain inorganic salts, mineral acids, heavy metal compounds, complexes of organic compounds with metals, dyes, pathogenic microorganisms, phenol derivatives, dioxins, solvents, antibiotics, pesticides, etc (Shetty et al., 2023). Water pollution causes widespread impacts on human health and aquatic life, including a number of serious illnesses such as cancer, severe poisoning and stomach infections (Mustafa et al., 2024; Khan et al., 2022). Water treatment technologies involve the use of a wide range of physical, chemical and biological methods, namely: coagulation/flocculation, flotation, membrane processes, adsorption, photocatalytic degradation, ion exchange, reagent and biological treatment, etc. (Sharma et al., 2017).

Given the huge scale of water pollution in water bodies (seas, rivers, ponds, reservoirs), cheap and affordable technologies with the lowest energy consumption, the possibility of repeated waste-free use, high efficiency and versatility in terms of pollutants are preferred in water treatment systems. Among the many purification methods, physicochemical methods such as adsorption and photocatalysis stand out, as they allow the use of commercially available natural materials and a minimum of chemicals for their activation and modification. These methods are also easy to operate, do not tend to generate large volumes of secondary wastewater and sludge, and are effective in removing a wide range of contaminants. The effectiveness of adsorption and photocatalytic methods directly depends on the surface characteristics of adsorbents and catalysts, namely: specific surface area, nature and number of surface

acidic and basic active centers, hydrophilicity and hydrophobicity of adsorption/catalytic materials, etc., which can undoubtedly affect the efficiency of pollution removal and ensure the continuity and reliability of technological processes. The study of the surface characteristics of natural materials that can serve as adsorbents, catalysts, and ion exchange agents makes a significant contribution to the development of new methods of their activation and modification with the prospect of further use of such materials in water purification processes from toxic pollutants.

2. Properties of natural aluminosilicate materials: bentonite and zeolite

Low-cost natural materials (adsorbents, catalysts, and ion-exchange materials) can be disposed of after use if they cannot be regenerated. But recently, scientists have been paying more and more attention to the development of new low-cost materials with sorption, catalytic, and ion exchange properties, which are characterized by activity, large surface area, reusability, mechanical and thermal stability, etc., which will help extend their service life and improve regeneration conditions. With the development of high technologies, promising ways of manufacturing materials with a large developed surface and activity are emerging, for example: modified silica and zeolites; clay materials modified with ZnO and TiO₂; metal-organic frameworks; carbon nanomaterials; porous polymers, etc. (Kaykhai et al., 2018). It should be noted that from the perspective of the friendly environmental orientation of the global economy, the trend of using natural materials as a basis for their further activation and modification is not inferior in its priority

and relevance to the synthesis of new artificial high-performance materials, but rather, this friendly environmental approach seems more rational and far-sighted.

Clays are natural sorption materials consisting of fine-grained minerals (about 2–4 microns in diameter) and represent a diverse group of aluminosilicates. The small particle size and high surface area to volume ratio determine a number of unique properties of clays, such as: high cation exchange and anion exchange capacity, good sorption and catalytic properties combined with the absence of toxicity (Huggett et al., 2015).

Clay minerals consist of two main building blocks: a silicon-oxygen tetrahedron (Si_2O_5)²⁻ and an aluminum octahedron (sheet gibbsite). The individual octahedra are arranged in a hexagonal shape and consist of oxygen and hydroxyl anionic groups bonded to Al^{3+} , Mg^{2+} , and Fe^{2+} , which usually act as coordinating cations. Due to their widespread use in nature, clay materials are cheap and readily available, and the list of such materials is quite long: bentonite, clinoptilolite, smectite, sepiolite, montmorillonite, alunite, perlite, etc. (Adeyemo et al., 2017; Akisanmi et al., 2021).

Bentonite is the most common type of clay, which belongs to the group of aluminum phyllosilicate adsorbents and is a complex hydrated aluminum silicate with a layered structure with exchangeable cationic components (Al, Fe, Mg), the empirical formula of which is: $(\text{Na},\text{Ca})_{0.33}(\text{Al},\text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (Fig. 1). The bulk of bentonite is composed of montmorillonite, a clay mineral whose name comes from the small French town (Montmorillon) where it was first discovered. Bentonite is available in calcium (Ca^{2+}) or sodium (Na^+) forms, usually in the

form of the latter (Santos et al., 2019; Kemp et al., 2022).

Fig. 1 illustrates the crystal structure of montmorillonite, the primary mineral phase of bentonite. Montmorillonite is a representative of 2:1 layered aluminosilicates, a structural type where each unit layer consists of two external tetrahedral sheets, typically composed of silicon (Si) atoms with partial substitution by aluminum (Al), and a central octahedral sheet composed mainly of aluminum, magnesium, or iron. Different forms of bentonite are characterised by different Si:Al ratio (Table 1). The “2:1” designation refers to this ratio of two tetrahedral layers to one octahedral layer within the repeating structural unit. The sheets are held together by van der Waals forces and interlayer cations (e.g., Na^+ , K^+ , Ca^{2+}), which can be hydrated and exchanged, granting montmorillonite its swelling and sorption properties.

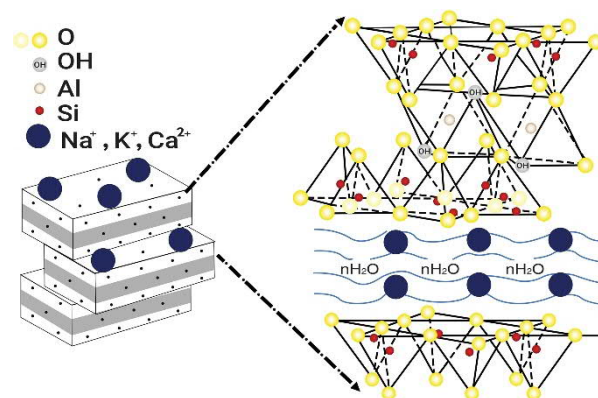


Fig. 1. Structure of bentonite (Pourhakkak P. et al., 2021)

Due to isomorphous substitutions in both tetrahedral and octahedral layers, a permanent negative charge develops, which is balanced by exchangeable cations located in the interlayer space. In addition to these cations, water molecules are also present in the interlayer, enabling the characteristic swelling behaviour of montmorillonite. This swelling

capacity defines the key technological advantages of bentonite, making it invaluable in water purification, soil stabilization, and barrier system construction.

Natural zeolites are minerals that occur in rocks near active or extinct volcanoes and the term “zeolite” appeared about 250 years ago after the Swedish mineralogist Axel Fredrik Cronstedt discovered deposits in Sweden in 1776. The modern classification base of zeolites includes about 230 discrete types of zeolite framework, both natural and synthetic, which are coded by the three-letter system of the International Zeolite Association (Garcia et al., 2022; Baerlocher et al., 2007).

Natural zeolites are highly crystalline-hydrated aluminosilicates of alkaline earth and alkali metal cations, which are built from three-dimensional frameworks of SiO_4^{4-} and

AlO_4^{5-} tetrahedra, which are connected by common oxygen atoms. The empirical formula of zeolites represents the general chemical structure of zeolites, where “x” is always equal to or greater than two, and “M” is a cation with valence “n”: $\text{M}_{2/n}\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$. Differences in the ways of combining SiO_4^{4-} and AlO_4^{5-} tetrahedra in the spatial structure of zeolites, different Si:Al ratio (Table 1), as well as the different nature of substituted cations in natural zeolites, determine the diversity of their forms found in nature (Baerlocher et al., 2024). Oxygen tetrahedra are combined into multistructural rings (four, five, six or more tetrahedra), which are called secondary structural units and which together form channels and cavities of various zeolites (Fig. 2).

Table 1. The Si:Al ratios for different types of natural zeolites and bentonites

№	Zeolite type	Si:Al ratio range
1.	Analcite	1.00 – 3.00 (Baerlocher et al., 2024)
2.	Metakaolinite, kaolinite	1.00 – 1.2 (Montalvo et al., 2012; Villaquiran-Caicedo et al., 2015)
3.	Smectite	2.4 – 2.6 (Montalvo et al., 2012)
4.	Clinoptilolite	2.92 – 5.04 (Baerlocher et al., 2024)
5.	Erionite	3.05 – 4.5 (Baerlocher et al., 2024; Patel et al., 2022)
6.	Ferrierite	3.5 – 6.5 (Baerlocher et al., 2024; Catizzone et al., 2020)
7.	Laumontite	1.95 – 2.25 (Baerlocher et al., 2024)
8.	Mordenite	4.19 – 5.79 (Baerlocher et al., 2024)
9.	Bentonite	2.0 – 5.0 (Montalvo et al., 2012; Dorah et al., 2021)
10.	Montmorillonite	2.4 – 3.0 (Montalvo et al., 2012)

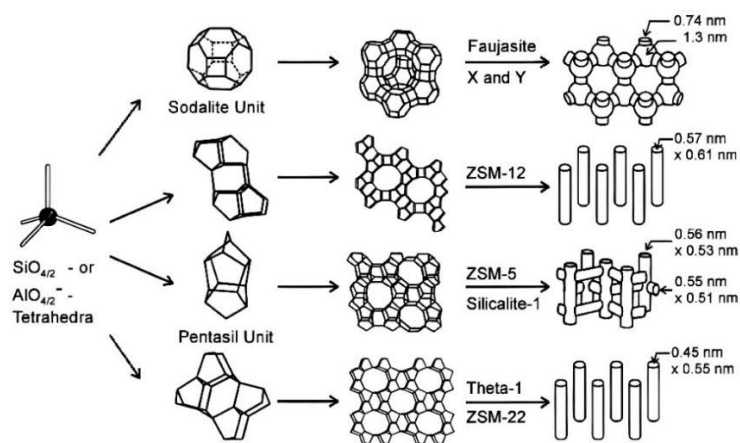


Fig. 2. Structural diversity of zeolites (Weitkamp J., 2000)

Fig. 2 presents the structural diversity of zeolites, highlighting their pore systems and the basic building units from which they are formed. All these zeolites comprise tetrahedral SiO_4^{4-} or AlO_4^{5-} units, which connect into larger secondary structural units. The sodalite unit, shown at the top, is formed by fused 4- and 6-membered rings and serves as the structural element of faujasite (zeolites X and Y), which contains large pores with diameters of 0.74 nm and 1.3 nm. The second unit from the top, which is a truncated cuboctahedron, is composed of linked 5-membered rings and forms the framework of ZSM-12, characterized by unidimensional, slightly elliptical pores of 0.57×0.61 nm. The pentasil unit is also built from 5-membered rings and serves as the building block for ZSM-5 and its silica analogue silicalite-1. These zeolites have one straight and the other sinusoidal intersecting 10-membered ring pores. The

bottom unit, which is Theta-1 (ZSM-22), has a framework formed from unidimensional 10-membered ring pores with a size of 0.45×0.55 nm, and it shares structural similarity with ZSM-5. The abbreviation ZSM stands for Zeolite Socony Mobil, referring to the company that first synthesized these materials in the 1970s. ZSM-type zeolites represent a family of high-silica aluminosilicates characterized by well-defined pore structures and distinct framework topologies. The number following the abbreviation (e.g., ZSM-5, ZSM-12, ZSM-22) indicates a specific structural type, each with unique channel systems, pore dimensions, and sorption characteristics.

The comparative Table 2 summarizes the key physicochemical properties of bentonite and zeolites relevant to their effectiveness in water treatment processes.

Table 2. Comparative Characteristics of Bentonite and Zeolites

Parameter	Bentonite	Zeolite
Structure	Layered structure with interlayer spaces	Porous framework structure with channels
Main chemical elements	Si, Al, Mg, Fe, Na, Ca	Si, Al, Na, K, Ca
Ion exchange capacity	High	High
Acid-base properties	Moderate acidity, flexible for modification	High acidity (Brønsted and Lewis centres)
Mechanical strength	Low (prone to swelling)	High
Application in water treatment	Adsorbent, ion exchanger, base for catalysts	Adsorbent, molecular sieve, catalyst
Disadvantages	Swelling, reduction of mechanical strength after repeated use	Need for modification to extend the spectrum of action

Natural zeolites are characterized by the ability to lose and adsorb water; adsorb or retain molecules of a suitable diameter (adsorption property or “molecular sieve” effect) and exchange metal cations in their composition without changing their structure

(ion exchange property) (Baerlocher et al., 2024). The uniqueness of zeolites is due to their physical and structural properties, which contribute to their diverse applications in membrane separation, water purification, catalysis, drug delivery and many other

environmental technologies (Werling et al., 2022).

3. Features of the use of natural bentonite and zeolites in water treatment

The scientific literature contains a sufficient number of examples of the use of native (raw) clay materials as sorbents. Effective properties of clays, such as a large active surface area, its acid-base chemical composition, surface charge, layered structure, non-toxicity and their high ion exchange potential have been used as a potential alternative to activated carbon in the processes of removing various types of dyes (acidic, basic, reactive) from wastewater of various origins.

For example, work (Chatterjee et al., 2021) shows the ability of bentonite to remove Malachite Green dye from aqueous solutions with different concentrations, with variation in adsorbent dose, shaking time, pH, and process temperature. It was found that the removal of the dye by 90 % can be obtained by using small doses of bentonite with the equilibrium state between the dye and bentonite being reached after 10 min. The adsorption capacity of bentonite increased from 29% to 91% with increasing solution pH from 2.0 to 9.0, which is explained by a change in the surface charge on the adsorbent, which, in turn, depends on the pH of the solution. The pH_{pzc} value (pH at the zero-charge point) for bentonite was 2.2. The removal of the dye Congo Red from aqueous solutions using native Ca-bentonite as a sorbent was also shown. An increase in temperature led to an increase in the absorption of the dye by Ca-bentonite, and at a temperature of 50 °C, the degree of dye removal reached a maximum percentage of 95.92 %. This characterizes the adsorption

process as endothermic and provides prospects for using the thermodynamic properties of the bentonite surface as a regulator of its adsorption activity and selectivity.

Thus, for effective adsorption of dyes, raw bentonite is often used, which is a cheap sorbent and is freely available in many regions (Bentonite Global Market Report), but natural raw bentonite has low mechanical strength and a high swelling ability. The ability of clays to swell hinders their use in fixed beds for the removal of dyes on an industrial scale. To improve adsorption properties, mechanical stability and selectivity, raw clay materials are subjected to heat treatment and modification.

For example, in (Akisanmi, et al., 2021), the adsorption of a dye, Rodamine B, was realized using bentonite clay that was subjected to heat treatment. Thus, the prospect of using bentonite after heat treatment as a cheap and reliable adsorbent in the processes of decolorization of large volumes of polluted wastewater was shown.

In (Keshmir-Naqab et al., 2024), in order to improve the absorption capacity of Na-bentonite in relation to the azo dye Acid Orange 7 ($C_{16}H_{11}N_2NaO_4S$), it was modified with a surfactant, hexadecyltrimethylammonium bromide (HDTMA), to improve the absorption capacity of Na-bentonite. FTIR analysis showed the appearance of new peaks of intercalation of surfactant molecules between silica layers in the modified bentonite, which led to changes in surface functional groups and hydrophobicity of the clay material. The HDTMA-modified bentonite showed a significantly higher degree of dye removal (on average 90 %) in contrast to the original Na-bentonite (removal rate of 10 %), which proves the obvious prospects of using modified clay materials as alternative adsorbents for the

removal of dyes from aqueous solutions. Therefore, modified natural bentonites are becoming increasingly popular in wastewater decolorization processes.

In work (Shaban et al., 2018), bentonite from a bentonite quarry in Egypt (54,82 % SiO₂; 17,56 % Al₂O₃; 9,5 % Fe₂O₃; 2,6 % Na₂O; 2,5 % MgO; 2,4 % CaO; 1,45 % TiO₂) was subjected to hydrothermal synthesis in the presence of synthetic NaP-zeolite after thermal and alkaline treatment. The resulting bentonite/zeolite-NaP composite demonstrated high efficiency of removal of Methylene Blue – 94 % and Congo Red (CR) – 93 % from aqueous solution (initial concentration of dyes was 5 mg·L⁻¹).

A somewhat different approach (using the ion exchange ability of bentonite to activate and modify natural bentonite B) was presented in (Hashemian et al., 2007), in which the solid phase of bentonite was saturated with sodium ions (Na⁺ was introduced by 24-hour stirring with a solution of sodium chloride, 1 mol·L⁻¹) and hydrogen ions (H⁺ was introduced by 24-hour stirring with a solution of hydrochloric acid, 1 mol·L⁻¹). Accordingly, sodium-exchanged bentonite Na-B and hydrogen-exchanged bentonite H-B were obtained. The degree of removal of the synthetic textile dye CAB (4-anilino-5-sulfo-1-naphthylazo)-1-naphthol-(3,6-disulfonic acid trisodium salt) from aqueous solution using the Na-B sample was higher (65.2%) compared to the unactivated bentonite B (39.0%) and the H-B sample (43.7%). The surface area increased in a number of samples: B→H-B→Na-B from 52 m²·g⁻¹ for B to 93.6 m²·g⁻¹ for Na-B.

Due to the high ion exchange capacity of bentonite, it is modified with metal oxides, such as TiO₂, ZnO, SnO₂, ZrO₂, and MnO₂ (Dontsova et al., 2022) for use in wastewater treatment processes and has gained wide

popularity. These oxides are known for their photocatalytic properties, chemical stability, and low water solubility. It has been proven that the catalytic activity of these oxides can be enhanced by modifying clays, in particular, bentonite. For example, in (Chakraborty et al., 2019), pure ZnO nanoparticles (ZnO-NPs) were synthesized for the subsequent synthesis of a bentonite-based nanocomposite – ZnO-NPs@bentonite. The synthesis consisted of the steps of mixing pure ZnO-NPs with purified bentonite clay in distilled water for 36 hours, washing the solid phase with distilled water, and drying the resulting material under vacuum. The ZnO-NPs@bentonite nanocomposite showed acceptable efficiency in the photocatalytic degradation of organic contaminants in aqueous solutions, namely phenol, dyes, and the removal of Cr⁶⁺ ions. A 200 W tungsten lamp (≥ 410 nm) and 1(M) NaNO₂ solution were taken as a light source and UV cut off filter, respectively. The results of photocatalytic studies showed an increase in the degradation rate of pollutants when using a bentonite-based nanocomposite containing 1 % ZnO, which indicates the high efficiency of such composites.

The acid-base nature of the surface of aluminosilicates is due to the presence of a certain number of Si⁴⁺ substitutions for Al³⁺ in the silica lattice structure, resulting in the formation of Lewis-type AlO⁴⁺ centers, which require a compensating negative charge generated by forming Brønsted -type acid centers, provided that hydrogen is such a compensator. For aluminosilicates, the Brønsted acidity decreases in the order zeolite→clay→amorphous silica→aluminosilicate, i.e., zeolites are believed to have stronger Brønsted acid centers than clays and amorphous silica materials. However, studies (Yue et al., 2016) have shown that the

introduction of metal ions into the structure of clay materials can radically change the acidity of their surface, which opens up great prospects for the use of such composites as acid catalysts in the reaction of paraffin hydroisomerization. The inclusion of Ni^{2+} in the structure of SMM (substituted synthetic mica-montmorillonite clays) mainly occurs by isomorphic replacement of octahedral Al^{3+} ions with Ni^{2+} ions to form Ni-SMM composites. The IR-spectra of Ni-SMM samples with different probe molecules (pyridine and CO as basic probes) showed that they contain two types of acidic Brønsted centers that exhibit much stronger acidity than zeolites (H-ZSM-5 and H-USY). The calculations confirmed that the replacement of octahedral $[\text{Al}^{3+}\text{-O}]^+$ by $[\text{Ni}^{2+}\text{-F}]^+$ causes a high acidity of the interlayer proton associated with the tetrahedron occupied by aluminium.

In (Amaya et al., 2020), bentonite was subjected to the delamination process (BD) and incorporation of the AlZr or AlCe phases (B-AlZr and B-AlCe for the minerals modified with AlZr and AlCe, respectively) with the subsequent determination of the effect of such modifications on the acid-base characteristics of the surface of the resulting composites. The results of acidity studies, which were obtained using the probe molecule NH_3 , indicate that in both cases (delamination and incorporation of phases), the natural mineral bentonite (BN) had a much lower acidity than the BD, B-AlZr, and B-AlCe samples. For comparison, the total acidity of BN was $56 \mu\text{mol NH}_3 \cdot \text{g}^{-1}$, which corresponds to the intrinsic acid properties of bentonite, the acidity of BD was $110 \mu\text{mol NH}_3 \cdot \text{g}^{-1}$, and the acidity of B-AlZr and B-AlCe was $171 \mu\text{mol NH}_3 \cdot \text{g}^{-1}$ and $141 \mu\text{mol NH}_3 \cdot \text{g}^{-1}$, respectively. According to the authors, the increased acidity of the BD sample is associated with the appearance of a larger

number of available acid centers after structural changes in delamination, which involve an increase in surface area, and in the case of incorporation of AlZr or AlCe phases into the bentonite structure, new acid centers are formed. The increase in acidity with the use of Zr can be explained by the protonation of the Si-O(H)-Al bond caused by the characteristic decrease in the pH of solutions of Zr compounds. In the case of Ce, the higher acidity is most likely due to the stabilization of Brønsted-type acid centers.

Thus, the acid-base properties of the surface of natural bentonites play a crucial role in determining their adsorption efficiency. Bentonite, due to its layered aluminosilicate structure, exhibits moderate Brønsted acidity, which can be significantly altered through ion exchange and modification processes. As shown in various studies, thermal treatment, surfactant modification, and incorporation of metal oxides (ZnO , TiO_2) not only enhance the adsorption capacity of bentonite but also introduce new surface functionalities, enabling its use as both an adsorbent and photocatalyst. This flexibility makes bentonite a particularly attractive material for removing dyes, phenols, and heavy metals from wastewater.

The use of natural aluminosilicates, in particular bentonite and zeolites, in water purification processes is based on their unique structural properties, high ion exchange capacity, and surface reactivity. These materials are widely used as adsorbents for removing organic and inorganic contaminants, including dyes, heavy metals, petroleum products, and pharmaceuticals (Kurylenko et al., 2024). Their low cost, environmental safety, and wide availability make them promising candidates for use in both industrial and municipal water treatment systems. The efficiency of natural zeolites in water

purification is closely related to the peculiarities of their crystal lattice, the Si:Al ratio, and the nature of exchangeable cations present in their structure. As shown in the work (Velarde et al., 2023), natural clinoptilolite demonstrates high sorption capacity for heavy metals (As, Cd, Cr, Pb, Hg, Ni), which can be significantly enhanced through surface modification techniques, such as acid activation, surfactant treatment, and metal ion impregnation. These modification strategies enhance the selectivity and binding strength towards specific pollutants, expanding the practical applicability of natural zeolites in modern water treatment technologies.

The catalytic properties of natural zeolites are also of particular interest for advanced oxidation processes, such as photocatalysis. According to (Liaquat et al., 2024), hybrid materials based on natural zeolites, doped with photocatalytic metal oxides, combine adsorption and catalytic activity, creating multifunctional materials capable of both capturing and degrading organic pollutants. These composites demonstrate high efficiency in removing dyes, pharmaceuticals, and even volatile organic compounds (VOCs), confirming the potential of zeolite-based materials in integrated water purification technologies.

In parallel, the work (Khudhur et al., 2023) demonstrated the ability of synthetic zeolite NaX to remove anionic azo dyes from aqueous solutions effectively. Under optimised conditions (pH = 2, initial dye concentration 5 mg/L, adsorbent dose 0.3 g, shaking speed 180 rpm), a removal efficiency of 72.34 % was achieved. The adsorption process followed the Langmuir isotherm model, indicating the formation of a uniform monolayer of dye molecules on the surface of zeolite NaX. Kinetic studies confirmed that the

adsorption proceeds according to the pseudo-first-order model, reflecting the dominance of surface interactions in the early stages.

In the context of acid-base surface properties, the study by (Grifoni et al., 2021) provided critical insights into the behavior of Brønsted acid sites in hydrated zeolite pores. It was established that increasing water content leads to the formation of hydronium ion clusters, which gradually alter the proton-donating ability of the zeolite. This fundamental understanding is essential for designing zeolite-based catalysts for water purification processes that involve acidic or proton transfer reactions. The relationship between hydration degree, pore confinement, and acid strength highlights the need for careful control of operational conditions when employing zeolites in real water treatment applications.

So, the combination of high cation exchange capacity, tunable surface acidity, and structural versatility defines the unique advantages of natural aluminosilicates in water treatment technologies. These materials can be adapted through proper modification strategies to address diverse water pollution challenges, from conventional adsorption of heavy metals to advanced photocatalytic degradation of organic pollutants.

4. Conclusions

The article considers the peculiarities of the use of natural aluminosilicates, namely bentonites and zeolites, in water purification processes, which are cheap and environmentally friendly materials. It has been shown that natural bentonites and zeolites are promising materials for the creation of adsorbents and catalysts based on them, in particular, photocatalysts, for use in water purification technologies from organic

compounds. The possibilities of improving the sorption and catalytic characteristics of natural aluminosilicates by acid activation, modification with metals (Zr, Se, Fe), metal oxides (TiO₂, ZnO), and surfactants (HDTMA) are outlined. Prospects for the synthesis of complex composites based on natural bentonites and zeolites are shown, due to their inherent high ion exchange capacity, layered structure, hydrophilicity, and acid-base nature of their developed surface. It is noted that the modification of natural bentonites and zeolites allows manipulating their structure and properties, which gives the prospect of their multifunctional use.

The development of hybrid materials based on natural aluminosilicates, especially those with enhanced photocatalytic properties, represents a promising direction for the creation of sustainable and energy-efficient technologies for treating complex wastewater streams. Given their wide availability and low cost, natural aluminosilicates can form the basis for innovative "green" technologies to protect water resources and ensure environmental safety in industrial and municipal sectors.

Acknowledgments

We are grateful for project of fundamental scientific research, applied research and scientific and technical (experimental) developments of young scientists of Ministry of Education and Science of Ukraine for funding the project 0124U001100 "The novel selective indicator systems for assessing the state of the marine environment in Ukraine" and the applied research project "Chemically modified membranes for rapid detection of nitrogen compounds in natural waters as explosives

markers" funded by the State Budget of Ukraine (State registration number 0124U001095), as well as the National Research Foundation of Ukraine for funding the project "Scientific basis for the synthesis of advanced ceramic membranes using 3D printing technologies" (project registration number 2023.03/0178 within the framework of the call 2023.03 Advanced Science in Ukraine).

References

1. Adeyemo, A. A.; Adeoye, I. O.; Bello, O. S. Adsorption of Dyes Using Different Types of Clay: A Review. *Appl. Water Sci.* 2017, 7, 543–568. <https://doi.org/10.1007/s13201-015-0322-y>.
2. Akisanmi, P. Classification of Clay Minerals. *Intech Open* 2021. <https://doi.org/10.5772/intechopen.103841>.
3. Amaya, J.; Bobadilla, L.; Azancot, L.; Centeno, M.; Moreno, S.; Molina, R. Potentialization of Bentonite Properties as Support in Acid Catalysts. *Mater. Res. Bull.* 2020, 123, 110728.
4. Baerlocher, C.; McCusker, L. B. Database of Zeolite Structures. <https://www.iza-structure.org/databases/> (accessed 2024-12-20).
5. Baerlocher, C.; McCusker, L. B.; Olson, D. H. Introduction and Explanatory Notes. In *Atlas of Zeolite Framework Types*, 6th ed.; Baerlocher, C., McCusker, L. B., Olson, D. H., Eds.; Elsevier Science B.V.: Amsterdam, 2007; pp 3–11. <https://doi.org/10.1016/B978-044453064-6/50187-0>.
6. Bentonine Global Market Report. <https://www.thebusinessresearchcompany.com/report/bentonite-global-market-report> (accessed 2025-03-03).
7. Borah, D.; Nath, H.; Saikia, H. Modification of Bentonite Clay & Its Applications: A Review. *Rev. Inorg. Chem.* 2021. <https://doi.org/10.1515/revic-2021-0030>.
8. Catizzone, E.; Migliori, M.; Mineva, T.; van Daele, S.; Valtchev, V.; Giordano, G. New Synthesis Routes and Catalytic Applications of Ferrierite Crystals. Part 1: 1,8-Diaminooctane as a New OSDA. *Microporous Mesoporous Mater.* 2020, 296, 109987. <https://doi.org/10.1016/j.micromeso.2019.109987>.
9. Chakraborty, T.; Chakraborty, A.; Shukla, M.; Chattopadhyay, T. ZnO-Bentonite Nanocomposite: An

Efficient Catalyst for Discharge of Dyes, Phenol and Cr(VI) from Water. *J. Coord. Chem.* 2019. <https://doi.org/10.1080/00958972.2018.1560429>.

10. Chatterjee, S.; Jeevanandham, S.; Mukherjee, M.; Vo, D. N.; Mishra, V. Significance of Re-Engineered Zeolites in Climate Mitigation – A Review for Carbon Capture and Separation. *J. Environ. Chem. Eng.* 2021, 9 (5), 105957. <https://doi.org/10.1016/j.jece.2021.105957>.

11. Dontsova, T.; Kyrii, S.; Yanushevskaya, O.; Suprunchuk, V.; Kosogina, I. Physicochemical Properties of TiO₂, ZrO₂, Fe₃O₄ Nanocrystalline Adsorbents and Photocatalysts. *Chem. Pap.* 2022. <https://doi.org/10.1007/s11696-022-02433-4>.

12. García, D. B.; Sanchez, M. C.; Bacigalupe, A.; Escobar, M. M.; Mansilla, M. A. Green Rubber Composites. In *Green Sustainable Process for Chemical and Environmental Engineering and Science*; Elsevier, 2022; pp 273–312. <https://doi.org/10.1016/B978-0-323-99643-3.00008-5>.

13. Grifoni, M.; Agostini, G.; Giuntini, A.; Civiero, P.; Mino, L.; Lamberti, C.; Nale, A.; Bordiga, S.; Zecchina, A.; Ricchiardi, G. Acid Strength and Confinement Effects in Zeolites: The Role of Water in Modifying the Brønsted Acidity of H-ZSM-5 and H-SSZ-13. *Nat. Commun.* 2021, 12, 6034. <https://doi.org/10.1038/s41467-021-22936-0>.

14. Hashemian, S. Study of Adsorption of Acid Dye from Aqueous Solutions Using Bentonite. *Main Group Chem.* 2007, 6 (2), 97–107. <https://doi.org/10.1080/10241220701837462>.

15. Huggett, J. M. *Clay Minerals. Ref. Modul. Earth Syst. Environ. Sci.* 2015. <https://doi.org/10.1016/B978-0-12-409548-9.09519-1>.

16. Kaykhani, M.; Sasani, M.; Marghzari, S. Removal of Dyes from the Environment by Adsorption Process. *Chem. Mater. Eng.* 2018, 6 (2), 31–35. <https://doi.org/10.13189/cme.2018.060201>.

17. Kemp, B.; Marangon, M.; Curioni, A.; Waters, E.; Marchal, R. New Directions in Stabilization, Clarification, and Fining. In *Managing Wine Quality*, 2nd ed.; Woodhead Publishing: 2022; pp 245–301. <https://doi.org/10.1016/B978-0-08-102065-4.00002-X>.

18. Keshmir-Naqab, R.; Keshmiri-Naghab, S.; Taghavijeloudar, M. Efficient Removal of Dye from Industrial Wastewater Using Modified-Clay as an Eco-Friendly Adsorbent: Characterization and Adsorption Isotherm. In *5th Int. Congr. Eng. Technol. Appl. Sci.*, Feb 2024, Auckland, New Zealand. <https://hal.science/hal-04543154>.

19. Khan, W. A.; Ali, S.; Shah, S. A. Water Pollution: Sources and Its Impact on Human Health, Control and Managing. *J. Int. Coop. Dev.* 2022, 5 (1), 69. <https://doi.org/10.36941/jicd-2022-0005>.

20. Khudhur, R. H.; Ali, N. S.; Khader, E. H.; Abbood, N. S.; Salih, I. K.; Albayati, T. M. Adsorption of Anionic Azo Dye from Aqueous Wastewater Using Zeolite NaX as an Efficient Adsorbent. *Desalination Water Treat.* 2023, 306, 245–252. <https://doi.org/10.5004/dwt.2023.29861>.

21. Kurylenko, V.; Dontsova, T. Potential Applications of TiO₂/Natural Zeolite Composites for Dye Removal. *Water Water Purif. Technol. Sci. Tech. News* 2024, 38 (1), 27–37.

22. Liaquat, I.; Hasan, N.; Gilani, S. R.; Ayub, S.; Hussain, S.; Rehman, F. The Role of Zeolite-Based Composites in Wastewater Treatment Technologies: Current Trends and Future Perspectives. *Environ. Pollut.* 2024, 338, 123867. <https://doi.org/10.1016/j.envpol.2024.123867>.

23. Montalvo, S.; Guerrero, L.; Borja, R.; Sánchez, E.; Milán, Z.; Cortés, I.; Rubia, M. A. de la. Application of Natural Zeolites in Anaerobic Digestion Processes: A Review. *Appl. Clay Sci.* 2012, 58, 125–133. <https://doi.org/10.1016/j.clay.2012.01.013>.

24. Mustafa, B. M.; Hassan, N. E. Water Contamination and Its Effects on Human Health: A Review. *J. Geogr. Environ. Earth Sci. Int.* 2024, 28 (1), 38–49. <https://doi.org/10.9734/jgeesi/2024/v28i1743>.

25. Pourhakkak, P.; Taghizadeh, M.; Taghizadeh, A.; Ghaedi, M. Adsorbent. *Y Interface Science and Technology*; Elsevier, 2021; c 71–210. <https://doi.org/10.1016/b978-0-12-818805-7.00009-6>.

26. Santos, F. R.; Bruno, H. C. O.; Melgar, L. Z. Use of Bentonite Calcined Clay as an Adsorbent: Equilibrium and Thermodynamic Study of Rhodamine B Adsorption in Aqueous Solution. *Environ. Sci. Pollut. Res.* 2019, 26, 28622–28632. <https://doi.org/10.1007/s11356-019-04641-0>.

27. Sharma, S. K.; Bhattacharya, A. Drinking Water Contamination and Treatment Techniques. *Appl. Water Sci.* 2017, 7 (3), 1043–1067. <https://doi.org/10.1007/s13201-016-0455-7>.

28. Shetty, S. S.; Deepthi, D.; Harshitha, S.; Sonkusare, S.; Naik, P. B.; Kumari, S. N.; Madhyastha, H. Environmental Pollutants and Their Effects on Human Health. *Heliyon* 2023, 9 (9), e19496. <https://doi.org/10.1016/j.heliyon.2023.e19496>.

29. Velarde, M.; Limachi, R.; Aliaga, C.; Choque, R.; Velarde, M.; Chura, J.; Mendez, C. Natural

Zeolite and Its Modification for Heavy Metal Removal from Aqueous Solutions: A Review. *Chemosphere* 2023, 319, 137972. <https://doi.org/10.1016/j.chemosphere.2023.137972>.

30. Villaquirán-Caicedo, M. A.; de Gutiérrez, R. M.; Sulekar, S.; Davis, C.; Nino, J. C. Thermal Properties of Novel Binary Geopolymers Based on Metakaolin and Alternative Silica Sources. *Appl. Clay Sci.* 2015, 118, 276–282. <https://doi.org/10.1016/j.clay.2015.10.005>.

31. Werling, N.; Kaltenbach, J.; Weidler, P. G.; Schuhmann, R.; Dehn, F.; Emmerich, K. Solubility of Calcined Kaolinite, Montmorillonite, and Illite in High

Molar NaOH and Suitability as Precursors for Geopolymers. *Clays Clay Miner.* 2022, 70 (2), 270–289. <https://doi.org/10.1007/s42860-022-00185-6>.

32. Yue, C.; Liu, C.; Mezari, B.; Brückner, A.; Pidko, E. A.; Rigutto, M. S.; Hensen, E. J. M. The Nature of Strong Brønsted Acidity of Ni-SMM Clay. *Appl. Catal., B* 2016. <https://doi.org/10.1016/j.apcatb.2016.03.006>.

33. Zeng, B.-J.; Wu, S.-M.; Antonietti, M.; Janiak, C.; Terasaki, O.; Yang, X.-Y. Hierarchy Design of Zeolite Mesocrystals. *Chem. Eng. J.* 2025, 505, 159282. <https://doi.org/10.1016/j.cej.2025.159282>.

ПРИРОДНІ АЛЮМОСИЛКАТИ У ТЕХНОЛОГІЯХ ОЧИЩЕННЯ ВОДИ: КОРОТКИЙ ОГЛЯД

Людмила Богдан¹, Христина Гуцул¹, Віктор Куриленко¹, Олена Янушевська¹,

Тетяна Донцова¹

¹ Національний технічний університет України «Київський політехнічний інститут імені

Ігоря Сікорського»

x_gucul1997@ukr.net



Огляд присвячено особливостям застосування природних алюмосилікатів, зокрема бентонітів і цеолітів, у технологіях очищення води. Описано загальну будову глинистих матеріалів, їх хімічний склад, характеристики структурних каркасів та різноманіття природних форм. Особливу увагу приділено адсорбційним характеристикам бентоніту, який є найбільш поширеним типом глини, зокрема в Україні. У контексті природних цеолітів розглянуто їх просторову структуру, співвідношення Si:Al у природних модифікаціях, хімічний склад та структурні особливості, що забезпечують застосування цеолітів як адсорбентів та каталізаторів. Показано доцільність використання природних алюмосилікатів в адсорбційних, іонообмінних та фотокаталітичних процесах на прикладі вилучення й деградації органічних сполук, зокрема нафтових продуктів, фенолів, барвників. Особливо наголошено на ролі іонообмінної ємності природних бентонітів та цеолітів як інструменту для їх модифікації й активації, що суттєво підвищує ефективність у водоочищенні. Проаналізовано ефективні властивості природних алюмосилікатів, зокрема розвинену питому поверхню, кислотно-основні характеристики та нетоксичність, що підтверджує їх високий потенціал як надійної й економічно вигідної альтернативи дорогим синтетичним матеріалам. Встановлено, що завдяки поєднанню низької вартості, екологічної безпечності, широкої доступності та ефективності природні алюмосилікати можуть стати основою конкурентних адсорбентів і каталізаторів у концепціях «зеленого» водоочищення. Використання бентонітів і цеолітів дає змогу створювати комбіновані системи очищення, які поєднують фізико-хімічні механізми вилучення забруднень та каталіз їхньої деградації. Наведено приклади модифікації природних алюмосилікатів шляхом обробки кислотами, лугами, ПАР та наночастинками оксидів металів (ZnO, TiO₂), що розширює їх функціональність у водоочищенні.

Ключові слова: алюмосилікати, бентоніт, цеоліт, адсорбція, модифікація, фотокаталіз, забруднення води, очищення води