

Review

**PREPARATION AND APPLICATION OF MODIFIED ZEOLITE FROM
INDUSTRIAL WASTE**

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**Maja Nujkić^{1,a*}, Žaklina Tasić^{1,b}, Tanja Kalinović^{1,c}, Dragana Medić^{1,d},
Ana Radojević^{1,e}, Jelena Kalinović^{1,f}, Jelena Jordanović^{1,g}, Stefan Đordjević^{2,h},
Nataša Apostolov¹**

¹ University of Belgrade, Technical Faculty in Bor, Vojske Jugoslavije 12, 19210 Bor, SERBIA

² Mining and Metallurgy Institute Bor, Alberta Ajnštajna 1, 19210 Bor, SERBIA

^a <https://orcid.org/0000-0002-6110-5135> ^b <https://orcid.org/0000-0001-6544-1980>

^c <https://orcid.org/0000-0003-0161-0065> ^d <https://orcid.org/0000-0001-9980-5949>

^e <https://orcid.org/0000-0003-3138-154X> ^f <https://orcid.org/0000-0003-0088-2683>

^g <https://orcid.org/0000-0002-8145-640X> ^h <https://orcid.org/0000-0003-1737-8766>

Abstract

Organic compounds, heavy metals and other pollutants reach the soil, groundwater and surface water, then enter the human body through the food chain, representing a significant environmental and health problem. To develop sustainable and efficient methods for pollutant removal, increasing attention is being paid to the application of zeolites synthesised from industrial waste. Various industrial solid wastes are rich in silicates, crystalline and amorphous silicon, as well as aluminium, making them suitable raw materials for zeolite synthesis. Among the most commonly used waste materials are fly ash from coal, red mud, lithium and steel slag, coal tailings and other by-products of the metallurgical industry. This paper presents an overview of previous researches on the synthesis of zeolites from different types of industrial waste, with particular focus on the advantages and limitations of existing preparation procedures. The application of synthesised zeolites in gas purification, wastewater treatment and soil remediation is also analysed. The results of previous researches indicate the significant potential of these materials in environmental protection and the circular economy.

Keywords: zeolites, industrial solid waste, synthesis methods, environmental protection.

INTRODUCTION

Zeolites are porous, crystalline aluminosilicate materials with a three-dimensional skeletal structure. They occur naturally as a result of volcanic activity (natural zeolites) or are synthesised under controlled laboratory conditions (synthetic zeolites). Their structure is based on the spatial arrangement of TO₄ tetrahedra, where T represents atoms in tetrahedral coordination, most commonly silicon (Si) and aluminium (Al), but also other heteroatoms. The connection of these tetrahedra forms a three-dimensional network of channels and cavities, resulting in significant structural diversity among zeolites. The general structural

* mnujkic@tfbor.bg.ac.rs

formula of zeolite is $M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot \omega H_2O$, where M denotes compensating cations outside the aluminosilicate skeleton, n their valence, and x and y the numbers of aluminium and silicon tetrahedra in the structure. The parameter ω indicates the number of water molecules present in the pores of the crystal lattice [1]. Due to their large specific surface area, developed microporous structure, and ion exchange capacity, zeolites are widely used in various fields, including catalysis, adsorption, gas and liquid separation, filtration, and energy storage [2]. However, compared to synthetic zeolites, natural zeolites often show lower performance due to the complex conditions of their formation, variable chemical composition, and the presence of various impurities. These factors may limit their application in demanding industrial processes. Industrial solid wastes are often rich in silicates, as well as crystalline and amorphous silicon, and may contain various types of slag, including slag from the production of yellow phosphorus, iron and steel, and slag from the smelting of non-ferrous metals. The presence of silicon and aluminum in these materials makes them suitable raw materials for the synthesis of zeolite-type molecular sieves [3].

Current research shows recent scientific results about using of various types of industrial solid waste, such as coal fly ash, red mud, lithium slag, coal tailings, and steel slag, as low-cost alternative raw materials for synthesizing artificial zeolites [2]. This work summarizes and analyzes the advantages and disadvantages of different zeolite preparation methods, based on a literature review. It also presents the applications of various modified zeolites in gas purification, wastewater treatment, and soil remediation.

SYNTHESIS METHODS OF ZEOLITES

The zeolite crystallization process involves the dispersion, recombination, and polymerization of silicate and aluminate species. Industrial solid wastes are complex, heterogeneous systems containing a significant proportion of inert components, which affect the kinetics and mechanism of zeolite formation from these raw materials. Zeolite synthesis from solid waste typically proceeds through four consecutive stages [3].

In the first phase, chemical pretreatment of the raw material is performed, most often using an HCl solution, to remove impurities such as Fe_2O_3 and CaO. This step increases the reactivity of the precursor and homogenizes the system. The second phase involves alkaline decomposition or alkaline fusion, during which amorphous silicon and aluminium phases dissolve. Stable crystalline components, such as corundum, have significantly lower solubility. The presence of OH^- ions in alkaline solutions or melts is crucial for increasing the solubility of Si and Al species. In this phase, the aluminosilicate structure breaks down, and Si–O and Al–O tetrahedra dissociate and form in the alkaline medium.

The third phase involves restructuring the aluminosilicate gel, during which the TO_4 tetrahedra are reorganized to form short-range structures. When the concentration of these structural units reaches a critical value, nucleation and the formation of ordered nanocrystalline cores occur. This process initiates further polymerization and recombination of tetrahedra on the surface of the cores.

In the final stage, crystal growth occurs as TO_4 tetrahedra are incorporated onto the surface of the cores according to specific crystallographic rules. Continuous growth leads to the formation of a stable zeolite structure with defined porosity and morphology [4–6].

Conventional hydrothermal method

The conventional one-step hydrothermal method enables the direct conversion of pretreated raw materials into zeolites. First, the materials are dissolved in an alkaline solution (NaOH or KOH), which dissolves silicates and aluminates. Then, by mixing and controlled aging of the solution – with the possible addition of silicon and aluminium sources to adjust the molar ratio – a silicoaluminate gel forms. The gel is subjected to hydrothermal crystallization, typically at temperatures of 80–200 °C for 12–48 hours, resulting in zeolite crystals. The final product is obtained after drying or calcination [4].

In the study by Constantin *et al.* [7], zeolite was synthesized from fly ash using combined alkaline and hydrothermal methods. The resulting material had an adsorption capacity of approximately 17 mg/g for Cd^{2+} ions, with the adsorption process reaching equilibrium quickly and following the Langmuir model. The adsorbent could be reused for multiple cycles without significant loss of efficiency. These results indicate that hydrothermally synthesized zeolites from fly ash provide a sustainable and effective solution for removing heavy metals from aquatic environments.

Alkaline fusion hydrothermal method

A key aspect of the alkaline fusion method is the calcination of the raw material with a solid alkaline compound at high temperature. During this process, resistant components of crystalline aluminosilicates, such as mullite and quartz in the raw material, are activated and decomposed. This stage produces a reactive precursor for the subsequent synthesis steps. After cooling the calcined material, deionized water is added, and the mixture is stirred at room temperature to form an intermediate gel, rich in silicon and aluminum. The gel is crucial because it ensures proper distribution of the active components and forms the foundation for crystallization. The final zeolite is produced by hydrothermal crystallization, in which the gel is subjected to controlled temperature and environmental conditions, resulting in the formation of the desired crystal structure and porous material. This method combines efficient activation of raw materials with precise control of crystallization, enabling the production of zeolites with high purity and well-defined properties [8].

Buzukashvili *et al.* [9] synthesized zeolite from fly ash using a combination of fusion and hydrothermal methods, producing a material with strong adsorption properties for removing heavy metals from aqueous solutions. The maximum adsorption capacities were 495 mg/g for Pb^{2+} , 248 mg/g for Cu^{2+} , 177 mg/g for Zn^{2+} , and 130 mg/g for Ni^{2+} ions. The adsorption process followed the Langmuir isotherm model and pseudo-second-order kinetics. The developed magnetic zeolite also enables easy extraction of the adsorbent from the solution after treatment, further increasing its practical significance in water purification processes.

Ultrasonic assistance in the hydrothermal synthesis of zeolites

Ultrasonic assistance is an effective method for synthesizing zeolites from raw materials containing inert substances. First, the raw materials are mixed with an alkaline solution, and the mixture undergoes ultrasonic treatment. Ultrasonic waves deliver high energy to

molecules through cavitation and mechanical effects, increasing molecular movement, accelerating chemical reactions, and facilitating the dissolution of silico-alumina oxides from solid waste. Microbubbles generated by ultrasound further promote the formation of zeolite crystals. After ultrasonic treatment, zeolites are produced by hydrothermal crystallization [2]. In recent years, significant progress has been made in this area.

For example, applying ultrasound in the synthesis of zeolite RHO reduced the crystallization time from 7–8 days with the conventional method to about 2 days with ultrasound, while maintaining high crystallinity and characteristic crystal morphology. This demonstrates ultrasound's ability to accelerate nucleation and growth of the crystalline phase [10].

In another case, ultrasound-pretreated hydrothermal synthesis of zeolite CHA enabled the transformation of zeolite T into a less dense CHA phase without the need for an organic template or seeds, and with improved CO₂ adsorption capacity. This highlights the use of ultrasound in manipulating interfacial conversions and enhancing product properties [11].

These examples show that ultrasonic assistance not only accelerates crystallization kinetics and shortens synthesis time, but also improves control over the morphology and properties of zeolite materials. This creates opportunities for broader application of this method in industrial processes such as catalysis, adsorption, and separation, especially when using raw materials with a high content of inert substances.

Microwave- assisted synthesis method

The microwave-assisted synthesis method is among the most advanced techniques for accelerating the hydrothermal crystallization of zeolites, due to the direct interaction of microwave radiation with the reaction mixture. Over the past decade, this method has attracted considerable attention because it can drastically reduce synthesis time, improve control over nucleation and crystal growth, and produce materials with enhanced functional properties. Compared to conventional hydrothermal procedures, microwave heating enables rapid and uniform attainment of the target temperature throughout the entire system, which intensifies crystallization kinetics.

Recent research further confirms the potential of this method for valorizing industrial waste. For example, Zang *et al.* [12] work reported the microwave-assisted synthesis of Na-P1-type zeolites and sodalite from fly ash, with the resulting materials demonstrating high efficiency in removing Pb²⁺ and Cd²⁺ ions from aqueous solutions (adsorption capacities exceeding 100 mg/g, depending on synthesis conditions). Under optimized conditions, zeolite with high crystallinity (~51.7%) and significantly increased ion exchange capacity (CEC ≈ 2.58 meq/g) was obtained, which is more than 100 times higher than that of the starting ash. This approach not only supports the development of efficient adsorbents but also enables sustainable waste management by converting waste into high-value-added materials.

Table 1 presents representative results for the adsorption of various pollutants using zeolites derived from different waste raw materials, with particular reference to adsorption capacity, selectivity, and stability during cyclic use.

Table 1 Representative results of pollutant adsorption by solid waste-based zeolites

Type of pollutant	Synthetic material	Name of zeolite	Adsorption capacity/ Removal efficiency	Synthesis method	Ref.
Toluen	Coal fly ash	Plasma-modified iron-enriched zeolite	98%	Ultrasonic-assisted, double stage fusion-hydrothermal synthesis	[13]
CO ₂	Waste coal fly ash	Na-Ca ²⁺	0.4–0.8 mmol/g	Hydrothermal treatment	[14]
Benzen	Fly ash, natural clinoptilolite (ZN-C) and diatomite	Na-P1	1.40 µmol/g	Alkali hydrothermal method	[15]
Toluen			10.52 µmol/g		
o-ksilen			26.22 µmol/g		
m-ksilen			25.96 µmol/g		
Benzen	Fly ash, natural clinoptilolite (ZN-C) and diatomite	Na-X	383.67 µmol/g	Alkali hydrothermal method	[15]
Toluen			525.03 µmol/g		
o-ksilen			545.26 µmol/g		
m-ksilen			563.82 µmol/g		
NH ₃	Waste fly ash, with vermiculite and unburned coal	NaX–Ver	38.46 mg/g	Hydrothermal syntheses	[16]
		NaX–FA	40.00 mg/g		
		NaX–C	21.05 mg/g		
Hg ^o	Fly ash, red mud and steel slag	M-8FA2SS	99%	Supercritical hydrothermal synthesis	[17]
		M-4FA4RM2SS	97%		
		M-8RM2SS	92%		
Ni	Hard kaolin and industrial solid waste red mud	MZA	80.71 mg/g	Ultrafast Joule Heating (UJH) combined with Hydrothermal method	[18]
Co			82.73 mg/g		
Mn			85.91 mg/g		
Cu			207.20 mg/g		

APPLICATION OF ZEOLITE FOR GAS PURIFICATION

The purification of volatile organic compounds (VOC_s) is among the most important and dynamic areas of zeolite application, especially given increasingly strict environmental regulations and the need to decarbonize industrial processes.

To address this persistent problem, metal-modified zeolite catalysts have demonstrated exceptional performance due to their high specific surface area, well-developed microporosity, adjustable acidity, and pronounced thermal and chemical stability. These properties enable efficient use in both adsorption and catalytic decomposition of VOC_s, making them key materials in modern emission control technologies.

The removal of VOCs using zeolite catalysts relies primarily on a combination of adsorption and catalytic oxidation processes. The classical mechanism involves three main steps: (i) adsorption of VOC molecules on acidic active sites of the zeolite, (ii) activation of molecular oxygen on metal centers (such as Pt, Pd, Cu, or Mn), and (iii) oxidation of adsorbed organic molecules to end products, mainly CO₂ and H₂O. This synergistic effect between the zeolite support and the active metal phase is essential for achieving high conversion at relatively low temperatures.

A significant trend is the increasing use of zeolites synthesized from solid waste for VOC purification, supporting the principles of the circular economy. These materials not only reduce production costs but also help address waste management challenges [19].

APPLICATION OF ZEOLITE IN WASTEWATER TREATMENT

Water pollution by heavy metals is a serious environmental problem that requires efficient and sustainable solutions. Zeolites have emerged as highly effective adsorbents (Table 1), primarily due to their well-developed porous structure, high ion exchange capacity, and strong electrostatic interactions, which are the main mechanisms for metal ion binding.

Recent research has focused on zeolites synthesized from municipal waste ash under low pH conditions. After appropriate chemical or thermal modification, these materials can exhibit improved stability in acidic media and increased selectivity for certain metal ions. For example, one study found that zeolites produced by alkaline activation of municipal waste ash and subsequent surface modification retain significant adsorption capacity even at pH values below 4. Under these conditions, despite increased competition from H^+ ions, efficient removal of ions such as Pb^{2+} and Cu^{2+} occurs, attributed to the stabilization of active centers and increased specific surface area of the material. These results suggest that properly engineered zeolites from secondary raw materials, such as municipal waste ash, can provide a sustainable and economical solution for treating acidic industrial wastewater, especially where conventional adsorbents are less efficient [20].

APPLICATION OF ZEOLITE IN POLLUTED SOIL TREATMENT

Zeolite adsorbents have exceptional ion exchange and adsorption capacities, making them highly effective for remediating polluted soils. Their stable crystal structure, long-term effectiveness, resistance to pH changes, good permeability, and environmental friendliness make zeolites an increasingly sustainable solution for soil protection without the risk of secondary pollution. Their use in soils contaminated with heavy metals relies primarily on ion exchange, surface adsorption, and chemisorption. These processes bind toxic ions (e.g., Pb^{2+} , Cu^{2+} , Cd^{2+}), reducing their mobility and bioavailability and preventing their accumulation in plants and entry into the food chain. For example, Zhang *et al.* [21] synthesized MnO_2 -modified clinoptilolite, in which the zeolite surface is enriched with manganese oxide phases that have a strong affinity for heavy metals. Applying this material to soil contaminated with Cd^{2+} and Pb^{2+} ions significantly reduced their bioavailability and mobility, decreasing plant accumulation by 42–68%. Additionally, improvements in soil chemical properties were observed, including increased pH and cation exchange capacity, which further contribute to contaminant stabilization. These results confirm the effectiveness of MnO_2 -modified zeolites as promising materials for remediating soils contaminated with heavy metals [21].

CONCLUSION

Previous research shows that zeolites synthesized from solid waste are highly promising green functional materials with broad potential for environmental protection. Their use has demonstrated significant potential in adsorption processes, water and gas purification, and soil remediation. However, despite encouraging results, several challenges still limit their wider industrial application. It is necessary to investigate more thoroughly the mechanisms of interaction between zeolites and soil, and to develop more efficient hydrophobic zeolites and materials for gas and water purification. Another issue is that current methods of zeolite

regeneration mainly rely on thermal treatments or chemical reagents, which increase process costs and may cause secondary pollution. Research on zeolites derived from solid waste is currently mostly limited to the laboratory, while industrial application remains underdeveloped. Therefore, further research is essential to improve their performance, reduce production and regeneration costs, and enable broader commercial and sustainable use of these materials in the future.

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