

Prospect of Modification Treatment and Application of Natural Zeolite Materials

Yan Li ^{1, 2, 3, 4}, Nan Lu ^{1, 2, 3, 4}

¹ Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi'an Shaanxi, 710021, China

² Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi'an Shaanxi, 710075, China

³ Key Laboratory of Degraded and Unused Land Consolidation Engineering, Ministry of Natural Resources, Xi'an Shaanxi, 710021, China

⁴ Key Laboratory of Cultivated Land Quality Monitoring and Conservation, Ministry of Agriculture and Rural Affairs, Xi'an Shaanxi, 710021, China

Abstract

The efficient and extensive utilization of natural zeolites is restricted by factors such as pore blockage, weak ion exchange selectivity, and small adsorption capacity. Modifying natural zeolite materials is an important means to enhance their performance and value. Based on existing research results, this paper summarizes the characteristics of inorganic treatment, thermal modification, organic modification, metal loading and composite modification of zeolite materials, as well as their main applicable conditions and influencing factors. Finally, it looks forward to the challenges of large-scale production and application of modified natural zeolites, and proposes to strengthen research and practice in green and efficient modification processes, new functional targeted modification, intelligent manufacturing and application monitoring, etc., to provide scientific references for the high-value utilization of natural zeolite resources.

Keywords

Natural Zeolite; Modified; Mass Production; Application.

1. Introduction

The area of medium and low-yield fields in China accounts for more than 70%. The main obstructive factors are manifested as low nutrient utilization rate, salinization and heavy metal pollution, etc. The current utilization rate of traditional chemical fertilizers is only 20%-35%. Excessive input of chemical fertilizers has exacerbated soil compaction and acidification. Natural zeolite is a kind of hydrated aluminosilicate mineral with a regular pore structure. Its crystal framework is composed of silicon-oxygen and aluminum-oxygen tetrahedra connected by shared oxygen atoms, forming a porous three-dimensional network structure. It has the characteristics of large surface area and abundant pores, and has strong adsorption performance and ion exchange capacity. In an aluminum-oxygen tetrahedron, since aluminum is in the trivalent state, the entire tetrahedron carries a negative charge, which needs to be balanced by alkali metal or alkaline earth metal ions (such as Na^+ , K^+ , Ca^{2+}). These cations have weak binding to the framework and can undergo reversible exchange with other cations in aqueous solution [1]. In fact, although zeolite is abundant in stock, low in cost and easy to obtain, it has disadvantages such as low cation exchange capacity (CEC), low adsorption capacity for anions and organic molecules, small effective specific surface area and limited adsorption capacity due to the presence of non-exchangeable impurities, negative charge and pore

blockage. Therefore, it is necessary to modify and regulate the physical and chemical properties of zeolite, such as expanding the pore size, increasing the specific surface area, introducing active sites or changing the surface charge, which can significantly improve its performance. Through unique crystal structure and surface selective design modification, it provides better value for the modification and efficient utilization of zeolite materials. This paper, in combination with the current research progress, relevant national policies and material application trends, systematically analyzes the methods, application approaches and potential of time-consuming material modification and optimization, providing useful references for the modification of zeolite materials and their planned application in improving the quality of cultivated land.

2. Inorganic Modification Technology of Zeolite Materials

2.1. Acid Modification

Acid treatment is the most classic method for modifying zeolite, and zeolite is usually treated with HCl, H₂SO₄ or HNO₃ solutions. This method is simple to operate and has low cost. It can effectively remove pore impurities, increase the specific surface area and improve the cation exchange capacity. The core mechanism is to replace the cations with larger radii (such as Na⁺ and Ca²⁺) in the zeolite channels through H⁺, thereby expanding the effective space of the channels. At the same time, dissolve some amorphous impurities and unclog the channels. During the treatment process, acid concentration and contact time are key parameters. Moderate acid treatment (1-2 mol/L HCl) can increase the specific surface area by 30%-50%, significantly enhancing the adsorption capacity for ammonia nitrogen and heavy metals [2]. Experimental studies show that the adsorption capacity of zeolite treated with hydrochloric acid for Pb²⁺ has nearly doubled. However, strong acid or prolonged treatment can cause the dissolution of the framework aluminum, destroying the crystal structure and reducing the adsorption capacity instead.

2.2. Alkali Modification

Alkali treatment mainly uses NaOH or KOH solutions to selectively dissolve silicon atoms, reducing the silicon-aluminum ratio (Si/Al) of zeolite and forming mesoporous structures. In contrast to acid treatment, alkali treatment reduces the number of cations in the zeolite channels, lowers the electrostatic repulsion to anions, and simultaneously increases the specific surface area and pore volume. This method has relatively low implementation conditions and can significantly increase the mesoporous ratio and enhance the adsorption capacity of macromolecules. It is suitable for the removal of organic pollutants. On the other hand, the alkali treatment must strictly control the alkali concentration (generally <1 mol/L). Excessive treatment will completely destroy the crystal structure, and the dissolution of silicon may cause secondary pollution. Natural clinoptilolite may be transformed into Na-P type zeolite with a low silicon-aluminum ratio after being treated with concentrated alkali. Although the exchange capacity is increased by more than twice, the thermal stability is reduced.

2.3. Salt Exchange Modification

Salt exchange modification alters the types of cations in zeolite channels through ion replacement, and is commonly treated with NaCl and CaCl₂ solutions. After being treated with 98% NaCl solution, the Na⁺ content in zeolite increased significantly, and its adsorption and exchange capacity for ammonia nitrogen could be increased by 30%-50% [3]. This method is particularly suitable for the preparation of single cationic zeolites (such as Na type and Ca type). Among them, the Na type, due to the weakest binding force of Na⁺ with the framework and the easiest exchange by other ions, has become the preferred pretreatment. Salt exchange

modification selectively enhances the specific cation exchange capacity, maintains the original crystal structure of zeolite, and is easy to achieve large-scale mass production.

2.4. Rare Earth Modification

Zeolite was modified by taking advantage of the high coordination ability and amphoteric surface properties of rare earth elements such as lanthanum (La) and cerium (Ce). The zeolite was impregnated with solutions such as LaCl_3 to form metal oxides/hydroxides on its surface. Experiments have shown that under the conditions of LaCl_3 concentration of 8 mg/L and solid-liquid ratio of 1g:30mL, the removal rates of ammonia nitrogen and phosphate by lanthanum-loaded modified zeolite are both above 85%, and the adsorption capacities are 6.5 mg/g and 0.9 mg P/g, respectively [4]. The surface of the modified zeolite is covered with hydroxyl groups, which can easily form surface coordination complexes with cations and anions, achieving the simultaneous removal of ammonia nitrogen and phosphate, broadening the applicable pH range (5.0-9.0), and having high adsorption selectivity. However, rare earth elements are expensive and pose certain ecological risks. The modified zeolite process is relatively complex, which limits mass production and large-scale application.

3. Thermal Modification and Organic Modification Technologies

3.1. Thermal Activation Modification

Thermal modification removes adsorbed water, carbonates and organic impurities in the zeolite channels by controlling the calcination temperature, thereby unclogging the channels and increasing the specific surface area. At an appropriate temperature (200-400°C), zeolite gradually loses bound water, reducing the resistance of the water film to pollutants and enhancing the ion exchange performance. This modification method can effectively remove the blockages in the channels, has a significant synergistic effect with chemical modification, does not introduce chemical reagents, and causes no secondary pollution. The experiment found that the activation of clinoptilolite Jinyun at 400°C could significantly increase its removal rate of Pb^{2+} , because appropriate heating not only purified the pores but also did not damage the crystal structure [5].

However, when the temperature exceeds 300°C, the structure of zeolite begins to change; Hole wall collapse may occur above 500°C, resulting in a reduction in specific surface area. Research shows that the adsorption capacity of zeolite for ammonia nitrogen significantly decreases after calcination at 300°C, indicating structural damage. Thermal modification requires precise temperature control, has high demands on the equipment's high-temperature resistance, consumes a large amount of energy, and has limited room for improving the adsorption capacity of zeolite for pollutants.

3.2. Surfactant Modification

Surfactant modification is achieved by forming an organic coating on the surface of zeolite with cationic surfactants, altering its surface charge properties and transforming the surface charge from negative to positive, thereby realizing anionic adsorption. Commonly used cetyltrimethylammonium bromide (HDTMA) can be loaded onto zeolite through ion exchange, changing its surface from negative charge to positive charge, thereby efficiently adsorbing anionic pollutants (such as Cr(VI), phosphate) and organic molecules (such as phenol).

Studies show that there are two modes of loading HDTMA on the zeolite surface: When the loading is lower than the critical micelle concentration, a single-layer coverage is formed; When the concentration exceeds this level, a double-layer structure is formed, at which point the adsorption capacity for anions is the strongest. Of course, modifying zeolite with surfactants is costly, and there is a high risk of shedding during long-term use or at extreme pH levels, causing secondary pollution.

3.3. Silane Coupling Agent Modification

Silane coupling agent modification introduces functional groups (such as amino and thiol groups) on the surface of zeolite through chemical bonding. This method utilizes the alkoxy groups of silane molecules to react with the hydroxyl groups on the surface of zeolite to form Si-O-Si covalent bonds. The functional groups at the other end provide specific adsorption sites. It has high chemical stability and is not prone to detachment, allowing for the design of adsorbents for specific pollutants.

This type of modified zeolite has molecular recognition ability for specific pollutants: amino-modified zeolite has enhanced coordination ability for heavy metal ions (such as Cu^{2+} , Cd^{2+}); Thiol-modified zeolite has a specific adsorption capacity for mercury (Hg^{2+}) [6]. However, the salinization reaction requires strict control of moisture and temperature, and the process is complex, making it difficult to achieve large-scale mass production.

4. Metal Loading and Composite Modification

4.1. Metal/Metal Oxide Loading

Loading metals or metal oxides is an efficient means to enhance the functionality of zeolite. Iron, lanthanum, zinc, etc. are introduced into the surface of zeolite through ion exchange, impregnation or co-precipitation methods. These metals exist in the form of nanoparticles or oxide coatings and enhance the pollutant removal capacity through electrostatic attraction, coordination complexation or REDOX reactions.

The clinoptilolite modified with $\text{Fe}(\text{NO}_3)_3$ was used to adsorb the drug dipipanone. The maximum adsorption capacity reached 23.37 mg/g at 318K, and the efficiency remained above 85% after 5 cycles. Iron-based zeolites can also degrade organic pollutants through the Fenton reaction, achieving the synergy of "adsorption - oxidation". The adsorption capacity of lanthanum hydroxide supported zeolite for phosphate can reach 3.58 mg P/g (powder) and 1.56 mg P/g (sphere), and efficient phosphorus removal is achieved through the formation of LaPO_4 precipitate [7]. However, lanthanum is expensive and may dissolve in an acidic environment. After zinc/titanium modified zeolite, the positive charge on its surface increased, and the adsorption capacity for humic acid (HA) reached 60 mg/g. In particular, TiO_2 modified zeolite also has photocatalytic properties and can simultaneously adsorb and degrade organic substances.

4.2. Composite Modification Technology

Composite modification integrates the advantages of each method through multi-step combination to solve the limitations of single modification. For example, the use of NaOH melting (600°C) combined with lanthanum-loaded modified zeolite increased the specific surface area by three times, and simultaneously removed ammonia nitrogen (23.88 mg/g) and phosphate (3.58 mg P/g). In the melting stage, all silicon-aluminum minerals (including impurities) are dissolved. In the hydrothermal stage, they are reorganized into a new zeolite structure, and the purity of the product is extremely high. The acid-surfactant composite modified zeolite is first treated with acid to unblock the channels and then loaded with HDTMA. Compared with the single modification, its adsorption capacity for Cr(VI) is increased by more than 40%.

The core value of composite modification lies in the synergistic effect: alkali melting solves the problem of impurities, metal loading introduces active sites, and granulation molding (such as zeolite-bentonite spheres) enhances the engineering applicability. Chen Xianhong's research confirmed that after the modified zeolite powder was granulated into balls (with a ratio of zeolite powder: bentonite: steel slag = 10:6:7), the loss rate was only 7.46%, and after being

reused for five times, the removal rates of ammonia nitrogen and phosphorus were still over 75%.

5. Influencing Factors of Modified Zeolite Performance

5.1. The Influence of Adsorbent Properties

The adsorption performance of zeolite primarily depends on its physical and chemical properties. Secondly, characteristics such as specific surface area and pore size distribution, types and quantities of active groups, and the silicon-aluminum ratio (Si/Al) directly affect the intensity of interaction with pollutants. The specific surface area and pore size distribution of zeolite determine the contact probability between pollutant molecules and active sites. Acid/base modification can increase the specific surface area from 400 m²/g to over 1000-5000 m²/g, and the increase in the proportion of mesopores is conducive to the diffusion of macromolecules [8]. However, some metal oxide loads may clog the micropores. Although the specific surface area is reduced, the adsorption efficiency per unit area is improved due to the addition of new active sites.

The types and quantities of surface-active functional groups (such as quaternary ammonium salts, hydroxyl groups, and metal oxides) directly affect the adsorption selectivity and capacity. Hdtma-modified zeolite adsorbed anions through quaternary ammonium groups. When the loading reached 1.07×10⁻⁴ mol/g, the adsorption capacity for Congo red reached 33.11 mg/g². Rare earth modified zeolites specifically bind phosphate ions through the coordination site of La(OH)₃. The low-Si /Al zeolite framework has a high charge density and a large cation exchange capacity, but poor hydrophobicity. High Si/Al zeolite is the opposite. Usually, alkaline treatment reduces Si/Al by dissolving silicon to enhance hydrophilicity and ion exchange capacity.

5.2. The Influence of Environmental Parameters

The solution conditions significantly regulate the adsorption process. The main influencing factors include pH value, temperature, coexisting ions and other factors. Among them, temperature affects the adsorption kinetics and thermodynamic equilibrium. The pH value not only alters the existence form of pollutants but also affects the surface charge of zeolite. Most modified zeolites perform best within the pH range of 5 to 9: at low pH, H⁺ competes for cationic adsorption sites, while at high pH, anionic pollutants (such as PO₄³⁻) are converted into OH⁻ competing forms. ZnO modified zeolite has the maximum adsorption capacity for humic acid at pH=7 [9]. Therefore, at this time, HA is fully ionized and the positive charge density on the surface of the adsorbent is high.

6. Conclusion and Prospects

Although the modification technology of natural zeolite has made remarkable progress and shown great potential in the field of adsorption, poor regeneration economy, difficulty in scaling up the preparation process and environmental safety concerns also restrict mass production and large-scale application. Firstly, the regeneration cost is high. After the zeolite material reaches adsorption saturation, it needs to rely on chemical regeneration costs, which can account for 40% to 60% of the total operating costs. However, surface-active activator-modified zeolite requires organic solvents (such as ethanol) for desorption. Although the desorption rate is as high as 96%, its economic efficiency is significantly reduced. Secondly, large-scale production is difficult. Efficient modification techniques in the laboratory (such as salinization, alkali melting, and metal loading) encounter multiple difficulties when being produced on a large scale, including equipment corrosion caused by strong acid/alkali treatment, huge energy consumption burden brought by high-temperature calcination, and

unstable material properties due to uneven metal loading. Finally, the potential environmental risks have not yet been resolved. Metal-modified zeolites (such as those loaded with lanthanum, iron and other ions) may undergo ion dissolution under acidic conditions, causing secondary pollution of heavy metals. Meanwhile, surfactant modifiers have the risk of shedding after long-term use, and their residues may have toxic effects on the ecosystem.

There is still huge room for development in the precision of natural zeolite modification design, the greening of the process and the intelligence of application. Future breakthroughs require the integration of multiple disciplines such as materials science, environmental engineering, and artificial intelligence, focusing on the development of low-energy consumption green recycling technologies, designing zeolite modified structures in a targeted manner based on the characteristics of pollutants or target requirements, constructing an integrated adsorption-catalysis system for modified zeolite functional materials, optimizing material formulas and processes based on machine learning, and developing intelligent application technologies, etc. Work together to promote the development of zeolite materials towards high efficiency, precision and sustainability.

Acknowledgments

This research was funded by Shaanxi Provincial Land Engineering Construction Group internal research project (DJNY-ZD-2023-4), Pre-research Project of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd (2024-NBYY-01), the Technology Innovation Center for Land Engineering and Human Settlements, Shaanxi Land Engineering Construction Group Co., Ltd and Xi'an Jiaotong University (2024WHZ0235).

References

- [1] Li X Y. Study on the adsorption of natural zeolite and modified zeolite to selenium (IV) and its reuse in soil and plants [D]. Beijing: Beijing Forestry University,2020.
- [2] Fu J X, Zhang Y P, Li S, et al. Preparation of modified zeolite ammonia nitrogen adsorbent and its application in domestic sewage treatment [J]. Bulletin of the Chinese Ceramic Society,2021, 40 (5): 1728-1734.
- [3] Chen X H. Study on modification of natural zeolite and its nitrogen and phosphorus removal performance [D]. Guangzhou: Guangzhou University,2022.
- [4] Ma Y, Zheng X, He S, et al. Nitrification, denitrification and anammox process coupled to iron redox in wetlands for domestic wastewater treatment[J]. Journal of Cleaner Production,2021,300(10): 126953.
- [5] Lidimara, Suzin, Fabiane, et al. Chemical removal of phosphorus from swine effluent: The impact of previous effluent treatment technologies on process efficiency[J]. Water Air & Soil Pollution, 2018, 229(11):341.1-341.9.
- [6] Sakineh H, Gholamreza N B, Nasser M. Nitrogen removal from wastewater through microbial electrolysis cells and cation exchange membrane[J]. 2020,12(1):48.
- [7] Xu Y H.Modified Zeolite Synergistic Thermal Desorption Repair Research on DDTs] Poluted Soil and Its Tail Gas Disposal[D]. Hangzhou: Hangzhou Dianzi University,2023.
- [8] Pour A A, Sharifnia S, Neishaborisalehi R, et al. Adsorption separation of CO₂/CH₄ on the synthesized NaA zeolite shaped with montmorillonite clay in natural gas purification process[J]. Journal of Natural Gas Science & Engineering, 2016: 630-643.
- [9] He L, Yao Q X, Sun M, et al. Progress in Preparation and Catalysis of Two-dimensional (2D) and Three-dimensional (3D) Zeolites [J]. Acta Chimica Sinica,2022,80(2):19.