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Application of mineral porous materials in soil pollution remediation

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Abstract

Rapid urban development and economic structure transformation and upgrading process produces a large amount of contaminated land, which has a non-negligible impact on soil, air and other habitat environment and human health, and remediation treatment of contaminated soil is a necessary choice for efficient use of limited land resources. Modified porous materials are widely used in soil pollution remediation as materials with rich pores and large specific surface area. The paper summarized the modification and enhancement of minerals to porous materials, and sorted out the effect of mineral modified porous materials on the passivation and fixation of heavy metals in soil, and the enhancement of soil quality. It also provides an outlook on the modification methods and technologies of porous materials and the research and development in integrated remediation materials.

Keywords

Porous materials, modified modifications, heavy metals, remediation treatment.

1. Introduction

Porous materials have unique structures such as high specific surface area, strong electron exchangeability, structural stability, porosity and abundant carbonaceous components, and have advantages such as low production cost and renewable, which are excellent performance materials for remediation of contaminated soil and cheap alternatives to expensive materials with important economic and application values [1]. Studies have shown that the physicochemical properties of porous materials determine their application value, and the adsorption efficiency of soil organic pollutants matches the polarity, aromaticity and molecular size of organic pollutants to achieve better adsorption and fixation [2]. In addition, different pollutant properties, the amount of porous materials applied and the adsorption environment such as adsorption medium and pH also have some influence on the adsorption mechanism and adsorption effect [3]. At present, porous materials are mainly applied to improve soil properties, reduce the content of heavy metals and organic matter in soil, reduce their mobility and accumulation in soil and plants, and improve crop yield and food security.

2. Mineral modification of porous materials

As a waste-derived soil amendment, porous materials have received much attention for their ability to improve soil fertility/health by removing or immobilizing contaminants from soil, water, and air. In order to produce engineered porous materials with excellent properties, new trends in porous material pyrolysis production and modification strategies have emerged [4]. Porous materials prepared from different raw materials and methods vary greatly in their ability to adsorb pollutants [5], and because of the unstable physicochemical properties of porous materials, their negatively charged surfaces lead to low anion exchange, unstable adsorption, and easy decomposition to release pollutant ions and cause secondary pollution, all these characteristics greatly limit the application of porous materials in environmental pollution management. Therefore, how to modify them and prepare porous material composites with high efficiency, stability and excellent adsorption performance is a hot spot in the current research on the application of porous materials.

2.1. Mineral-modified porous materials

The stability of porous materials is the most critical factor in determining their carbon sequestration potential, and mineral modification can effectively improve the stability of porous materials. It has been shown that the stability and yield of vermiculite modified porous materials are significantly improved, and the mineral contents such as Fe and Si on the surface of the modified porous materials are significantly increased, which provides options for the research and development of functional porous materials and their applications in carbon sequestration [6]. Mineral modification can improve the stability of porous materials in use and make porous materials add some trace mineral elements to improve the possibility of their scale application.

2.2. Metal-reinforced modified porous materials

Porous materials are mixed with solutions containing metals in different proportions by impregnation, and after the reaction, the metals can be loaded on the surface of porous materials. After loading the porous material with metal, the specific surface area becomes smaller and the adsorption capacity increases. This is because the adsorption mechanism of the unmodified porous material is mainly the physical adsorption of pollutants by the pores on the surface of the porous material, while the metal loading increases the nature of the metal, and the adsorption is a synergistic effect of chemisorption and physical adsorption, which has a stronger adsorption effect on the target ions. It was shown that the adsorption was increased 20-fold by corn cob porous material modified with Fe^{3+} [7]. The adsorption capacity of pollutants in pig wastewater was increased 6-fold and 3-fold by pine bark porous material modified with Fe^{3+} and Ga^{2+}, respectively [8]. This indicates that the porous materials modified with metal elements have strong adsorption performance for pollutant adsorption. The metal modification method is the most used research method, which is simple, convenient and easy to operate, and has great potential for application.

2.3. Clay-modified porous materials

Clay is a promising adsorbent material due to its large surface area, high cation exchange capacity, good chemical and mechanical stability, and its layered structure [9]. The main role component of clay is montmorillonite, combining porous material with montmorillonite can effectively enhance the adsorption performance of porous material, and the maximum adsorption of nitrate is about 5 mg/g, while the adsorption of nitrate by porous material/montmorillonite composite can reach 9 mg/g, and the adsorption effect of the composite is significantly improved [10]. In addition, clay composites combine porous materials and clay components, which is a new research direction, but such research is less.

3. Characterization and analysis of modified porous materials

Porous material characterization methods are mainly performed using FTIR, XRD, SEM+EDS and BET, which can determine the properties of surface morphology, crystal structure, elemental composition, surface functional groups, porosity and valence changes of porous materials to analyze the modification mechanism of porous materials and their repair mechanism [11].

Table 1 Characterization analysis of modified porous materials

Characterization methods	Properties and effects
X-ray diffraction (XRD)	Testing the crystalline structure of porous materials and their composite material phase composition
X-ray photoelectron spectroscopy (XPS)	Valence and content of elements on the surface of porous materials and their composites
Fourier infrared spectrometer (FTIR)	Testing the absorption of infrared spectrum of porous materials
Nitrogen isothermal adsorption and desorption test	Testing the specific surface area and porosity of samples
Elemental analysis	Testing of porous materials for C, H, O, N and other elements
Scanning electron microscopy and energy spectrum testing	Characterize the morphology and micro-zone element distribution of porous materials and their composites
Atomic absorption test	Test the content of metallic elements in porous materials

4. Mineral modified porous materials for soil contamination treatment

4.1. Modified porous materials for remediation of heavy metal pollution

The remediation of soil heavy metals by modified porous materials is mainly achieved through direct and indirect effects. Among them, the passivation mechanism of porous materials on heavy metals directly affects their remediation efficiency, which is mainly determined by the surface physicochemical properties of the materials. The selection of raw materials, preparation conditions and modification methods determine the differences of surface physicochemical properties of porous materials, so the fixation mechanisms of porous materials are also very different, and can be broadly classified into adsorption, complexation reaction, co-precipitation and ion exchange mechanisms.

Soil heavy metal pollution is complex and diverse, and usually exists in the form of multi-metal complex pollution. Numerous scholars have used modified porous materials for passivation remediation of soil heavy metal lead, cadmium and arsenic contamination, and have achieved a series of research results. Studies have shown that Fe-modified porous materials solidify soil heavy metals through surface adsorption, electrostatic interaction, and precipitation. Due to the large specific surface area and high porosity of iron-modified porous materials, heavy metal ions can be immobilized by surface adsorption. The surface charge reversal phenomenon may occur after adsorption of Cd^{2+} and affect its adsorption of As. Some heavy metal ions will be immobilized by precipitation in the form of hydroxide, carbonate or phosphate bound [12]. The application of iron sulfide modified porous material increased the soil pH and Cd was immobilized by binding with CO_3^{2-} and PO_4^{3-} to form precipitates [13], which significantly reduced the content of Cd in the exchangeable state of the soil. On the other hand, Fe-modified porous materials reduce the mobility of soil heavy metals through ion exchange and

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complexation, and also reduce the effectiveness of heavy metals through redox and co-precipitation. In general, the synergistic effect of porous materials and iron nanoparticles can effectively improve the removal ability of the composite materials for pollutants, and the iron-modified porous materials have good reactivity and stability, and are increasingly used in the remediation of heavy metal-contaminated soils, but the corresponding environmental functions and the resulting effects are somewhat different due to different sources of porous materials, different methods of iron modification, and different types of heavy metals.

4.2. Soil quality improvement by modified porous materials

The research on the effect of porous materials to improve soil quality is a hot topic in the field of environment and agricultural production. The improvement of soil by porous materials mainly includes the improvement of physical and chemical properties such as soil acidity and alkalinity, organic matter, water nutrients, and capacity, and the biological properties such as soil microbial community structure, physical biodiversity, and soil enzyme activity. As shown in Table 1, acidity and alkalinity are the key factors influencing soil properties, fertility and plant growth. Applying the right amounts of porous materials can well improve the pH of acidic soil, alleviate soil acidification, and promote the precipitation and adsorption of heavy metals in the soil. In addition, porous materials play an important role in soil nutrient retention, which can significantly improve soil fertility in the tillage layer, increase soil organic carbon content, improve the carbon to nitrogen ratio, and have a positive effect on stabilizing the amount of soil carbon pool and the content of nutrients such as nitrogen, phosphorus and potassium.

Porous materials influence soil acidity, water content, permeability and temperature, and thus have an impact on soil microbial metabolism (Table 2). The type and nature of the porous material and the amount of application directly affect the soil microbial community structure, diversity and enzyme activity. For example, exogenous porous materials provide a rich source of carbon for soil microbial metabolism, which increases the number and species of microorganisms in the soil and significantly increases the number, abundance and Shannon index of microorganisms in agricultural soils containing chemical and biological fertilizers [14].

Table 2 Analysis of the effect of biochar on soil improvement

Soil		Effects
Soil properties	Soil acidity and alkalinity	Increase acidic soil pH, good neutralizing and improving effect, no significant effect on neutral and alkaline soil.
	Soil organic matter	Significantly increase soil organic carbon content, improve carbon to nitrogen ratio, improve soil quality and increase productivity. The improvement effect is related to the nature and amounts of porous materials.
	Soil moisture	Promote soil nutrient cycling, favor soil water retention and water holding.
	Soil nutrients	Carbon sequestration and emission reduction, reducing soil nutrient loss, depending on the nature, type and freshness of porous materials.
	Soil capacity	Porous material capacity and addition are inversely proportional to soil capacity and positively proportional to total soil porosity and capillary porosity
Soil microorganisms	Microbial population structure	Optimization of bacterial community structure, the type of porous material and the amount of addition had a large variation on soil microbial species and communities.

	Microbial diversity	Enrichment biodiversity, increase bacterial number, abundance, Shannon index.
	Soil enzyme activity	Inhibition of soil peroxidase activity, increase in sucrase activity, and increase in soluble organic carbon

5. Conclusion

Porous materials have been one of the important materials in the field of ecological environmental protection and treatment. Numerous studies have been conducted to test methods and techniques to enhance the properties of porous materials such as pore structure, functional groups, and specific surface area, and to promote low-cost modification of porous materials, mass production and large-scale application research. Future research on porous materials can also be carried out in the following aspects.

(1) The continuous development of sustainable and green modification technologies, such as minerals and metal oxides and other metal-rich materials become the choice of new modification technologies.

(2) Continuous innovation of porous preparation technologies and methods to expand the application of materials and applicable environmental conditions, and to reduce the cost of material applications and the risk of derivative pollution and secondary pollution in the process.

(3) Accelerate the research on the promotion and application of materials and technologies in the field of wastewater treatment in soil pollution remediation and ecological restoration, focusing on the prediction of energy efficiency and potential ecological risks of their application, and research on reducing potential negative impacts and improving utilization efficiency.

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