Optimization, Characterization, and Ammonia Nitrogen Adsorption Study of Novel PVA-SA-VMT Composite Carrier

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Abstract. To address the low ammonia nitrogen removal efficiency of traditional activated sludge processes under low-temperature conditions, this study developed a novel PVA-SA-VMT composite immobilization carrier using polyvinyl alcohol (PVA), sodium alginate (SA), and vermiculite (VMT). The optimal formulation (7% PVA, 2.5% SA, and 2% VMT) was determined through single-factor experiments. The results indicate that the composite carrier possesses high mechanical strength and excellent chemical stability, with a 24-hour TOC leaching amount of only 14.1 mg/L, 72% lower than that of the pure PVA-SA carrier. The interior of the composite carrier features a porous structure, which enhances the effective diffusion coefficient of ammonia nitrogen. Its adsorption mechanism follows second-order kinetics and the Freundlich isotherm, with vermiculite interlayer ion exchange being a spontaneous endothermic process. The synergistic mechanism of 'scaffold support–adsorption enrichment' provides a solid material foundation for constructing an efficient low-temperature nitrification system in wastewater treatment.

1 Introduction

With the implementation of stricter wastewater discharge standards in China, the traditional activated sludge process is difficult to operate normally in the cold northern winter. Due to the inhibition of nitrifying bacteria activity, the removal rate of ammonia nitrogen is significantly reduced[1]. Microbial immobilization technology has become a promising solution by immobilizing functional microbial communities on specific carriers so that they can withstand low temperature environment and maintain a longer sludge age[2].

The overall efficiency and operational lifespan of microbial immobilization systems are fundamentally dictated by the physicochemical properties of the supporting carrier materials [3,4]. An ideal carrier must provide a protective, biocompatible habitat for microbial communities while facilitating rapid nutrient transport. Currently, traditional single-polymer organic carriers exhibit inherent limitations that severely restrict their large-scale application. For instance, while sodium alginate (SA) offers excellent biocompatibility, it suffers from poor mechanical strength and severe swelling behavior, leading to rapid structural disintegration in actual wastewater environments. Conversely, polyvinyl alcohol (PVA) boasts high structural durability, but its dense, highly cross-linked hydrogel network typically results in poor porogenicity and tremendous mass transfer resistanc [5]. This dense outer shell severely impedes the diffusion of dissolved oxygen and substrate nutrients to the deeply embedded microorganisms.

To resolve the inevitable trade-off between mechanical stability and mass transfer efficiency, incorporating functional inorganic materials into polymeric matrices has emerged as a highly effective strategy. Therefore, this study proposes a novel organic-inorganic composite carrier by introducing vermiculite (VMT)—a naturally abundant, layered silicate mineral—into the blended PVA-SA hydrogel matrix [6,7]. The integration of VMT provides exceptional synergistic benefits. Structurally, the rigid layers of VMT function as a physical "micro-scaffold" within the polymer network, preventing excessive gel shrinkage during cross-linking and significantly enhancing the overall mechanical stability [8]. Functionally, the abundant active sites and interlayer ion-exchange capabilities of VMT confer a strong targeted adsorption capacity. This allows the composite to rapidly enrich surrounding ammonia nitrogen, successfully establishing a localized, high-concentration substrate microenvironment. This targeted enrichment effectively provides a strong chemical driving force that accelerates the internal mass transfer process, which is particularly crucial for overcoming the sluggish biological kinetics typically observed under low-temperature conditions [9,10].

Through the systematic optimization and multidimensional characterization of the preparation parameters such as the concentration ratio of PVA, SA and VMT, this study aims to develop a stable and high porosity carrier. The carrier can be used to verify the synergistic mechanism of "scaffold adsorption enrichment", so as to build a solid foundation for efficient low-temperature wastewater treatment system.

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2 Materials and Methods

2.1 Preparation of the Carrier

Using PVA, SA and VMT as raw materials, the optimal process conditions were determined by orthogonal test. In order to balance the physical stability and biological activity, the formula was further optimized by single factor test (Table 1). According to the evaluation results of key response variables, the optimal carrier composition was determined as 7% PVA, 2.5% SA and 2% VMT. The gel beads were prepared with this optimal ratio, and the PVA-SA carrier without VMT was used as the control group for subsequent tests.

Table 1. Experimental design for carrier optimization and key response variables.

Components	Concentration Ranges (w/v)	Key Response Variables for Optimization
PVA	5%,7%,9%	Spheronization, Mechanical integrity
SA	2%,2.5%,3%	Viscosity, Pelletization performance
VMT	0%,1%,2%,3%	Adsorption capacity, Morphology

2.2 Characterization and Analytical Methods

In order to comprehensively evaluate the performance of the carrier, the following methods were used in this study: the chemical stability was evaluated by the total organic carbon (TOC) dissolved after soaking in water for 24 hours[11]; The micro morphology and pore structure were observed by scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP); The chemical structure was analyzed by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS).

2.3 Adsorption Experiments

To systematically evaluate the ammonia nitrogen removal performance of the prepared composite carrier, batch adsorption experiments were conducted using simulated wastewater. The initial ammonia nitrogen concentration of the solution was precisely adjusted to 50 mg/L. To track the adsorption kinetics, the dynamic changes in the ammonia nitrogen adsorption capacity of the material were continuously monitored at discrete time intervals over a 24-hour period. Furthermore, to investigate the temperature-dependent adsorption behavior and assess the material's feasibility for cold-climate applications, equilibrium adsorption studies were executed across a controlled temperature gradient ranging from 5 °C to 20 °C. The acquired experimental data were subsequently analyzed using classical mathematical frameworks. Specifically, pseudo-first-order and pseudo-second-order kinetic models were employed to elucidate the adsorption rate and rate-limiting steps, while Langmuir and Freundlich isotherm models were utilized to interpret the surface binding mechanisms. Concurrently, based on the temperature-gradient data, essential thermodynamic parameters were calculated to fundamentally determine the spontaneity and energy driving forces of the overall adsorption process[12].

3 Results and Discussion

3.1 Structural and Surface Characterization

The microscopic morphology and internal porous structure of the carriers were systematically investigated using SEM and MIP. As depicted in Fig. 1a–d, the pure PVA-SA matrix originally exhibited a relatively dense and uniform polymer network. However, the incorporation of VMT significantly disrupted this dense configuration. The rigid VMT particles acted as structural modifiers within the polymeric hydrogel, facilitating the formation of a highly interconnected, honeycomb-like hierarchical pore structure. Quantitative MIP analysis (Fig. 1e) further corroborated these morphological changes; compared to the control carrier without VMT, the average pore size of the composite carrier increased significantly to 1019.52 nm. Such an enlarged, macro-porous architecture is highly advantageous, as it alleviates spatial constraints and dramatically reduces the mass transfer resistance for substrates during wastewater treatment. Beyond physical modifications, the surface chemical composition was evaluated to verify the organic-inorganic hybridization. FTIR and XPS analyses (Fig. 1f, g) provided compelling evidence of this successful integration. Specifically, the FTIR spectra of the composite carrier displayed a distinct new characteristic peak near 1000–1040 cm^{-1}, corresponding to the Si–O–Si stretching vibration from the silicate layers of VMT. Concurrently, the XPS survey spectra detected a strong Si 2p orbital signal, which was entirely absent in the pure organic matrix. Collectively, these spectral results unequivocally confirm that the inorganic VMT particles were stably and successfully cross-linked into the PVA-SA polymer network.

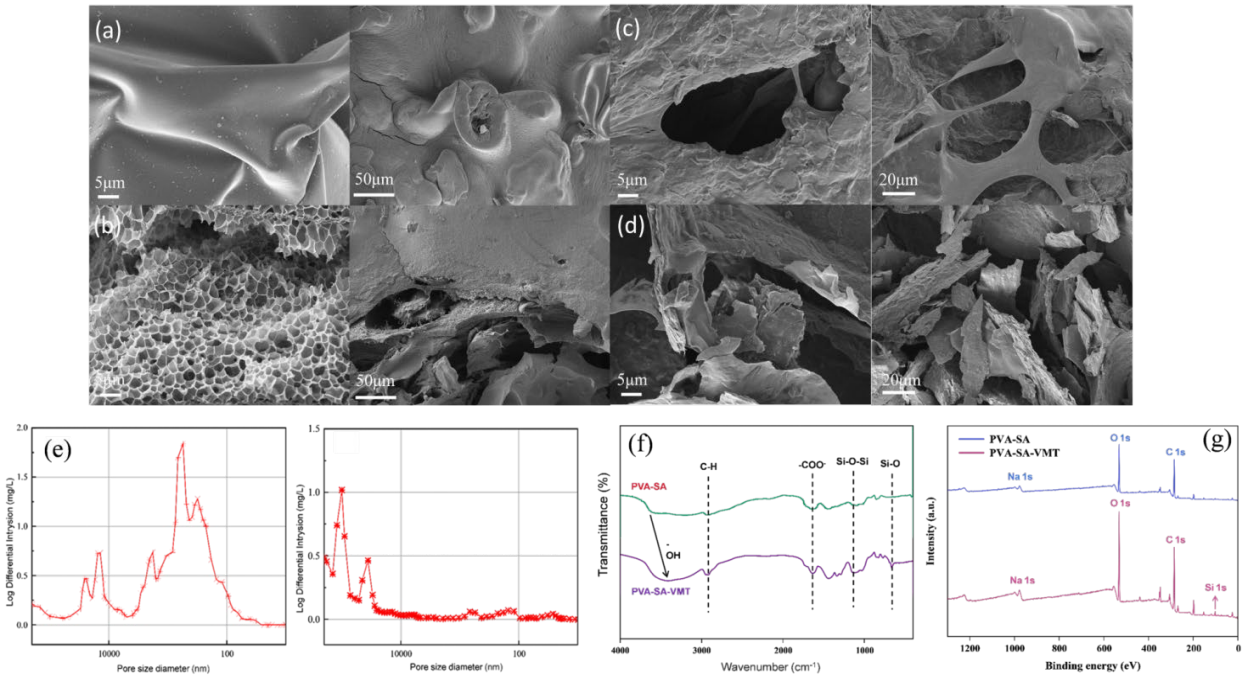

Fig. 1. Surface morphology and chemical composition of the carriers. (a,b) SEM image of the pure PVA-SA carrier; (c,d) SEM image of the PVA-SA-VMT composite carrier; (e) Pore size distribution of PVA-SA-VMT carrier and PVA-SA carriers; (f) FTIR spectra of the immobilized composite carriers; (g) XPS survey spectra of the PVA-SA and PVA-SA-VMT carriers.

3.2 Chemical Stability

The optimized PVA-SA-VMT composite carriers (comprising 7% PVA, 2.5% SA, and 2% VMT) demonstrated exceptional chemical stability, which is a critical prerequisite for maintaining a long operational lifespan in wastewater treatment systems. As illustrated in Figure 2, the incorporation of VMT significantly mitigated the leaching of uncrosslinked organic components. After a 24-h soaking period, the equilibrium total organic carbon (TOC) dissolution concentration of the composite carrier dropped sharply to only 14.1 mg/L. This represents a remarkable 72% reduction compared to the pure PVA-SA control carrier, indicating that VMT effectively enhances the structural cohesion of the polymer network and minimizes the risk of secondary organic pollution to the water body[13].

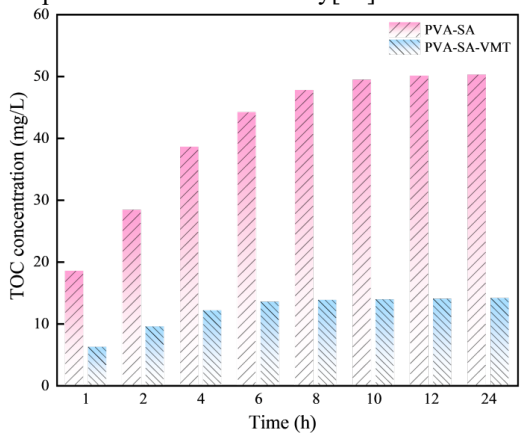

Fig. 2. Chemical stability evaluation.

Mechanistically, the structurally rigid VMT particles function as internal, physical "micro-scaffolds" dispersed throughout the hydrogel matrix. Traditional pure organic gels are highly susceptible to severe volume shrinkage and pore collapse during the cross-linking phase, which typically leads to the formation of a dense, impermeable outer shell. However, the embedded VMT skeleton successfully counteracts this inward contraction stress, preserving the volumetric integrity and preventing excessive gel shrinkage. Consequently, this robust structural support maintains open and interconnected internal pore channels. By preserving this well-developed porosity, the composite carrier effectively minimizes internal mass transfer resistance, providing highly accessible pathways for target substrates—such as ammonia nitrogen and dissolved oxygen—to rapidly diffuse into the carrier's deep interior.

3.3 Adsorption Kinetics and Thermodynamics

To fundamentally understand the interaction mechanism between the pure carrier (evaluated strictly without fixed bacteria to isolate physical and chemical adsorption effects) and the target pollutants, the adsorption behaviors were systematically evaluated. As illustrated in Figure 3(a), the experimental data points demonstrated a remarkably higher fitting accuracy when applied to the pseudo-second-order kinetic model compared to the pseudo-first-order model. This excellent alignment strongly indicates that the overall adsorption rate is governed predominantly by chemisorption rather than physical diffusion. Specifically, the vigorous ion-exchange reaction between NH_4^+ in the bulk solution and the inherent exchangeable cations located within the interlayer spacing of the VMT structure plays the leading and rate-limiting role throughout the reaction cycle.

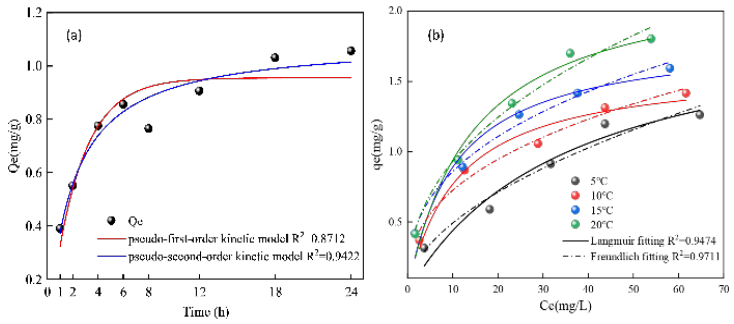

Fig. 3. Adsorption kinetics and isotherms of ammonia nitrogen on the PVA-SA-VMT composite carrier. (a) Comparison of pseudo-first- and pseudo-second-order kinetic fits; (b) Nonlinear fits of the adsorption data to Langmuir and Freundlich equations at different temperatures.

Furthermore, the equilibrium isotherm data, collected at a fixed carrier dosage of 20 g/L, provided deeper insights into the surface binding affinities. As depicted in Figure 3(b), the nonlinear fitting reveals that the Freundlich model exhibits a significantly better correlation with the experimental data than the Langmuir model. This superior fitting effect confirms that the adsorption of ammonia nitrogen does not occur as a simple monolayer on a uniform surface. Instead, it is a complex, multi-point adsorption process taking place on the highly heterogeneous surface of the composite carrier, utilizing the abundant active sites introduced by the VMT integration. To elucidate the energy changes associated with this mechanism, thermodynamic calculations were performed over the evaluated temperature gradient from 5°C to 25°C. The calculated parameters yielded a negative standard Gibbs free energy ($\triangle G° < 0$) coupled with a notably large positive standard enthalpy change ($\triangle H° >$ 20 kJ/mol). The negative $\triangle G°$ mathematically validates the inherent thermodynamic spontaneity of the NH_4^+ uptake, while the large positive $\triangle H°$ unambiguously classifies the adsorption onto the composite as a robust, endothermic process. Together, these thermodynamic indicators solidify the conclusion that the ammonia capture is a spontaneous, energy-consuming phenomenon driven by intense chemical ion-exchange interactions.

4. Conclusions

In order to solve the bottleneck problem of nitrogen removal at low temperature, the PVA-SA-VMT composite carrier was developed in this study, and the proportion of PVA, SA and VMT was optimized to be 7%, 2.5% and 2% respectively. The addition of VMT formed a hierarchical cellular network, which was used as a rigid "micro scaffold", which could prevent gel shrinkage and improve mechanical stability. Spectral analysis further confirmed the successful organic-inorganic hybrid, VMT introduced a wealth of siloxane active sites.The adsorption experiment results showed that the kinetics and isotherm fit the pseudo second-order equation and Freundlich isotherm model respectively, revealing an endothermic chemisorption mechanism dominated by multicenter ion exchange. Finally, this study verified the "scaffold adsorption enrichment" synergistic mechanism of PVA-SA-VMT carrier. Although the above-mentioned superior physical and chemical properties show that the carrier has great potential in low-temperature wastewater treatment, subsequent biological immobilization tests are still needed to comprehensively evaluate its long-term nitrification performance.

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