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Development of Pollutant-Targeted Recognition Slow-Release Materials and Research on Petrochemical Wastewater Treatment

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Abstract **-** In response to the trailing and rebounding problems caused by conventional remediation technologies for NAPL pollutants in groundwater at petrochemical contaminated sites, this study developed a modified cellulose as a safe, non-toxic and biodegradable embedding matrix, and combined it with advanced oxidants such as potassium permanganate, persulfate, and nZVI-activated persulfate as active remediation agents. The effective embedding of advanced oxidants was achieved by using organic phase separation method to achieve sustained release of oxidants, and targeted recognition and directional enrichment of organic pollutants. A solvent recycling process for the organic phase separation assembly system was constructed to significantly reduce the production cost of pollutant-targeted recognition slow-release materials. The surface properties of the modified cellulose matrix in the slow-release material and its mechanism of action in targeted recognition of pollutants were studied, and the law of the surface modification process and targeted recognition of pollutants was characterized. The dissolution mechanism and law of typical pollutants in petrochemical contaminated sites were studied to elucidate the release mechanism of targeted recognition slow-release materials for pollutants, and to establish a quantitative relationship between the slow-release rate, slow-release time, material ratio assembly process, and material ratio, to achieve quantitative control of the slow-release performance of pollutant-targeted recognition slow-release materials.This study has significant implications for the development of effective and sustainable remediation technologies for NAPL pollutants in groundwater at petrochemical contaminated sites, and provides a theoretical basis and technical support for the practical application of pollutant-targeted recognition slow-release materials.

Keywords**:** NAPL pollutants, slow-release, petrochemical contaminated sites, pollutant-targeted recognition

1. Introduction

Although the application of slow-release materials in environmental remediation has gradually been promoted [1, 2], no reports have been found on research related to targeted recognition slow-release oxidants. Addressing the issue of reverse diffusion of LNAPL and DNAPL type pollutants in groundwater at petrochemical contaminated sites [3, 4], combined with advanced oxidants such as potassium permanganate, persulfate, and persulfate based on nZVI activation as active remediation agents, this study aims to develop pollutant-targeted recognition slow-release materials based on safe and non-toxic modified cellulose as the matrix. Establishing an assembly method for the oxidant/matrix core-shell structured slow-release materials, constructing an organic phase separation assembly system for the solvent's complete recovery and reuse, aiming to significantly reduce the production cost of pollutant-targeted recognition slow-release materials. Investigate the surface properties of the modified cellulose matrix in the slow-release materials and their interaction mechanism with pollutant-targeted recognition, characterizing the relationship between the matrix surface modification process and the interaction of pollutant-targeted recognition. Study the dissolution mechanism and rules of typical petrochemical site pollutants on the matrix, clarifying the release mechanism of pollutant-targeted recognition slow-release materials, establishing the quantitative relationship between release rate, release time, material ratio assembly process, and material ratio, realizing the quantitative controllability of the slow-release performance of pollutant-targeted recognition slow-release materials.

This research aims to significantly enhance the targeted removal effect of conventional active remediation agents on organic compound pollutants, improve the material's synergistic pollutant removal capability, break through the large-scale production technology of new materials, achieve long-term release of remediation agents in the underground environment, attain long-lasting pollutant plume remediation, and overcome rebound and tailing issues.

2. Methods

2.1. Preparation of Targeted Recognition Slow-release Materials:

Selecting cost-effective, highly active composite oxides as the encapsulated active components, and using safe, non-toxic, and low-cost modified cellulose as the embedding matrix, the encapsulation of peroxides is achieved through the organic phase separation method. By inducing the aggregation of modified cellulose in the matrix solution through changes in experimental conditions such as temperature variation and the addition of non-solvents, the resulting powder product is named p-TRSRM.

2.2. Morphological Characterization:

The surface and internal structure of the prepared p-TRSRM are scanned and observed using a Scanning Electron Microscope (SEM, Merlin) to obtain the morphological characteristics of the product.

2.3. Simulated Pollutant Indoor Batch Experiments:

In a 100 mL graduated cylinder, 100 mL of distilled water and 10 mL of toluene solution are added separately. After allowing the solution to stand for 1 hour to form the LNAPL phase, different dosages of active components (SP) and p-TRSRM are added. The removal effect on organic pollutants is semi-quantitatively assessed by detecting the mass quantification of the removal system caused by the mineralization of organic matter decomposition.

3. Result and Discussion

3.1. The Morphological features of p-TRSRM

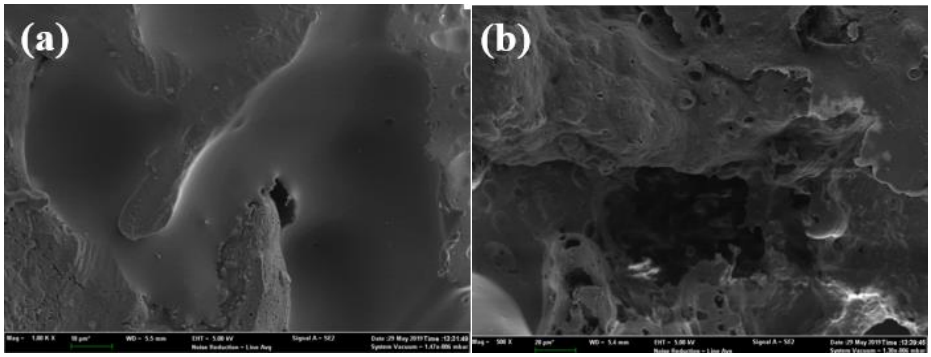

Fig. 1: The appearance of p-TRSRM encapsulation matrix before (a) and after (b) contact with organic pollutants.

The encapsulation matrix of the p-TRSRM material prepared by organic phase separation exhibits hydrophobicity, making it easy for p-TRSRM to come into contact with organic substances and allowing organic pollutants to easily spread on the surface of the p-TRSRM product. The SEM scans of the p-TRSRM encapsulation matrix before and after contact with organic pollutants revealed the following:

Before contact with pollutants (Figure 1(a)), the matrix surface is smooth with very few pore channels, and the dense encapsulation matrix's structural features effectively prevent agent loss.

After contact with pollutants (Figure 1(b)), the matrix surface is rough and filled with numerous pore channels. The loose and porous structure is conducive to the release of remediation agents.

Therefore, based on the apparent morphological changes in the p-TRSRM encapsulation matrix before and after contact with organic pollutants, the feasibility of releasing agents through matrix dissolution and pore formation after the contact of pollutants with the targeted recognition slow-release material has been verified.

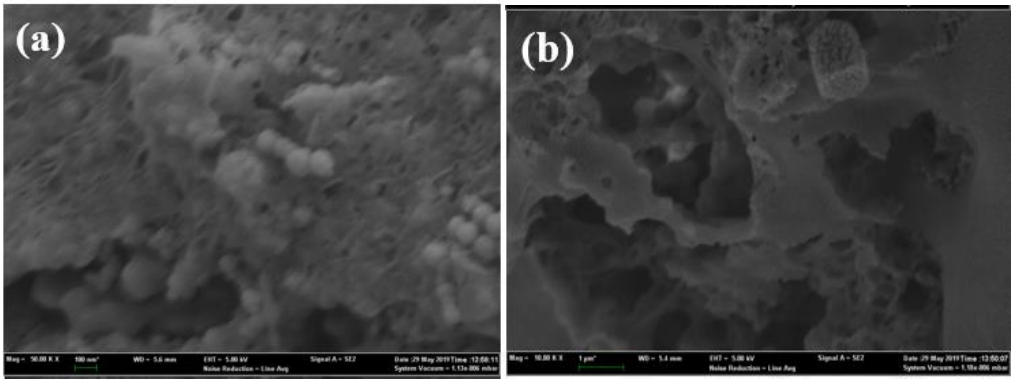

Fig. 2: SEM images of p-TRSRM material before (a) and after (b) contact with organic pollutants for removal

The SEM scans of the prepared p-TRSRM material (Figure 2(a)) revealed that particulate remediation agents and nanoscale spherical activators (nZVI) are embedded within the matrix. However, after the p-TRSRM participated in the remediation experiments of organic pollutants, the embedded particles completely disappeared, leaving only the loose and porous encapsulation matrix (Figure 2(b)). The aforementioned SEM scanning results verified the release behavior of the active agent particles within the p-TRSRM matrix.

3.2. p-TRSRM target recognition ability

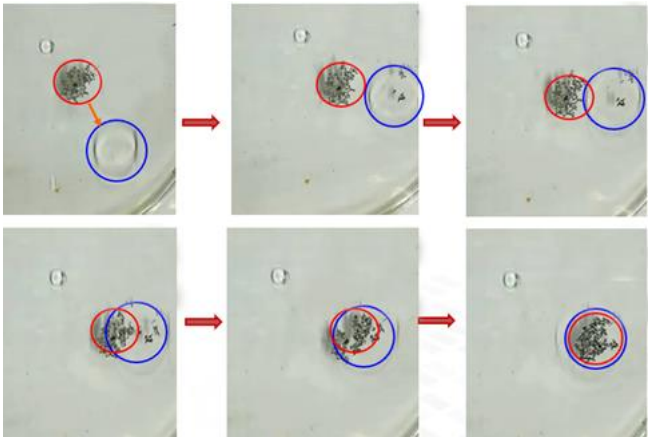
Fig. 3: p-TRSRM and toluene position change scenario on the water surface

Observation of the relative positions of p-TRSRM and toluene droplets on the static water surface (Figure 3) reveals that the toluene droplets gradually approach p-TRSRM until they eventually merge completely. Due to the hydrophobic encapsulation of the base material, p-TRSRM exhibits strong hydrophobicity. The p-TRSRM has a strong affinity for toluene, causing them to be drawn closer together. As a result, p-TRSRM demonstrates target recognition capability for toluene droplets.

3.3. Morphological Characterization:

Through indoor experiments with SP and p-TRSRM for toluene removal, the experimental phenomena showed that when non-encapsulated SP was added to the pollutant solution, it quickly dissolved in water, but the activator iron powder settled at the bottom of the graduated cylinder, leading to difficulties in effective contact between the oxidant SP and the activator. Simultaneously, only SP molecules near the surface of the water phase came into contact with LNAPL organic pollutant molecules. However, when encapsulated p-TRSRM was added as a remediation agent to the same simulated

pollutant solution, all p-TRSRM particles were distributed at the interface between LNAPL and water. As a result, the slowly released SP formed a localized high concentration at this interface, and the co-encapsulated activator further accelerated the removal rate of pollutants. In the experiment, we also observed the generation of a large number of bubbles, mainly due to the CO_2 produced during the mineralization process of pollutant removal.

Table 1: Long-term removal effect of SP and p-TRSRM on toluene simulated pollutant solution under different dosage concentration conditions.

dosage / Time/h	SP-100 mg/L	SP-500 mg/L	SP-1 000 mg/L	p-TRSRM-100 mg/L	p-TRSRM-500 mg/L	p-TRSRM-1 000m/L
0	0	0	0	0	0	0
1	2.4	3.5	0.6	0.1	1.4	1.7
2	0.4	4.6	--	-1.2	1	1.2
6	1.8	9	--	1	2.9	1.7
9	1.5	9.3	--	1.7	3.8	1.9
12	0.3	5.4	--	2	4.8	2.4
24	--	2.7	--	2.8	9	4
27	--	2.8	--	5.2	10.6	4.8
30	--	1.9	--	6.5	12.9	5.8
33	--	0.9	--	5.5	13.1	5.7
78	--	--	--	16.6	25	15.5
120	--	--	--	25.5	38	19.8
144	--	--	--	32.3	43.9	24
168	--	--	--	35.2	54.4	26.4
288	--	--	--	65	87	48.4
720	--	--	--	163.5	215.4	109.6

The indoor studies of pre-encapsulation, post-encapsulation, and different dosages of removal agents (Table 1) showed that compared with non-encapsulated SP, p-TRSRM had a much better removal effect on organic pollutants at a dosage level of 125 mg/L than SP at 2500 mg/L. This was mainly attributed to the target recognition ability of p-TRSRM for organic pollutants and the localized high concentration during the removal process. Moreover, after 24 hours, the removal rate of SP tended to be flat, while the removal rate of SP/ABS remained at a high level. In a longer time scale removal study, after 30 days, p-TRSRM still demonstrated strong pollutant removal capabilities. Therefore, based on the above results, the removal efficiency of p-TRSRM for organic pollutants increased by more than 200% compared to SP and reduced the dosage of the remediation agent by more than 50%.

4. Conclusion

In this study, the important innovation of the designed targeted release material lies in endowing the material with the ability to recognize pollutants while meeting the basic requirements for the sustained release of the encapsulated active component - the oxidant. This innovation is crucial for the design and development of targeted release materials.

In this study, the organic phase separation method was employed to encapsulate the active components - oxidant and activator, for the removal of organic pollutants. This not only achieved the sustained release of the active components but also endowed the release material with the ability to target pollutants due to the hydrophobic properties of the base material. Ultimately, the continuous and efficient removal of organic pollutants was achieved in the localized high concentrations formed by the released active components and the directionally enriched organic pollutants. Some of the findings in this study are as follows:

(1) The p-TRSRM prepared in this study demonstrated a strong ability to target toluene, enabling directional enrichment of toluene to a certain extent.

(2) Compared with the non-encapsulated oxidant SP, p-TRSRM, through its targeting of pollutants and the integrated enhancement of the activator, increased the removal efficiency of organic pollutants by more than 200% and reduced the dosage of remediation agents by more than 50%.

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