Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2023.29774

306 (2023) 151–158
September

Degradation of trichloromethane by immobilized microspheres of modified red brick

Shuying Song, Haiyan Sun*, Xue Zhang, Ting He, Yuying Wang, Qian Mo, Chengrui Zhuo

School of Ecological Technology and Engineering, Shanghai Institute of Technology, Shanghai, China, Tel.: +8617785074870; email: sj-shy@163.com (H. Sun), Tel.: +86021-64941200; email: songshuying95@163.com (S. Song), Tel.: +8615692166927; email: 752146768@qq.com (X. Zhang), Tel.: +8618512169875; email: Valentina0726@163.com (T. He), Tel.: +8618751970806; email: 13920455681@139.com (Y. Wang), Tel.: +8613920455681; email: a120271824@163.com (Q. Mo), Tel.: +8618816701176; email: 1933734446@qq.com (C. Zhuo)

Received 20 March 2023; Accepted 9 July 2023

ABSTRACT

In this study, a combination of adsorption–embedding and cross-linking methods was employed to prepare immobilized pellets using modified red brick as the carrier and *Bacillus subtilis* as the target bacterium for the removal of trichloromethane (TCM). The optimal preparation technology for the immobilized pellets was also optimized. Results demonstrated that when the adsorption time of modified red brick to *Bacillus subtilis* was 24 h, the temperature was 37°C, the rotation speed was 160 rpm, the concentration of the embedding agent sodium alginate was 1.5%, the concentration of calcium chloride was 3%, and the cross-linking time was 6 h, the composite immobilized agent showed a TCM removal percentage of 75%. This was significantly higher than the pure modified red brick with free bacteria and unfixed microorganisms.

Keywords: Trichloromethane; Modified red brick; Immobilization technology; Biodegradation; Sodium alginate

1. Introduction

Trichloromethane (TCM) is an organic compound that appears as a colorless and transparent liquid. It is slightly soluble in water and highly sensitive to light. Due to its excellent solubility, powerful cleaning effect, and high thermal stability, it has been widely applied in various fields, including industry and daily life. However, improper handling during production, usage, and storage could lead to TCM volatilization, leakage, and discharge into the environment, including the atmosphere, soil, and water, leading to severe pollution [1]. In October 2017, the World Health Organization listed it as a Group 2B carcinogen. In 2019, trichloromethane was included in the first batch of toxic and harmful water pollutants [2]. As a type of volatile organochlorine hydrocarbon, TCM not only poses a severe threat to the water environment but also has a negative impact on human health. Its release into the environment can cause extensive pollution and contamination, leading to adverse effects on the ecosystem and biodiversity. In addition, human exposure to TCM can result in a range of health problems, such as respiratory issues, liver and kidney damage, and even an increased risk of cancer. Therefore, it is crucial to develop effective methods for TCM removal and remediation to minimize its adverse impacts on both the environment and human health [3]. TCM treatment technology mainly includes the treatment of surfactant-modified materials [4], zero valent iron site recovery [5] and in situ bioremediation [6]. Microbial immobilization technology is a type of bioremediation that involves the physical or chemical fixation of free microorganisms in

* Corresponding author.

an embedding agent to maintain their activity over a longer period and allow for their repeated use. The main physical remediation methods include gas diffusion, adsorption, membrane separation, and gas volatilization [7]. Physical remediation methods can have several limitations and drawbacks, including incomplete removal, low efficiency, high costs, and the potential for significant secondary pollution. It requires significant human resources, materials, and financial investments [8]. The chemical remediation techniques have been extensively employed over a prolonged period, and their technical application is well-established. These methods involve the disruption of the internal structure of pollutants, leading to their conversion into alternative substances. Nevertheless, it should be recognized that the intermediate by-products formed during the reaction process may possess higher toxicity compared to the original contaminants. Additionally, the introduction of chemical agents may pose potential risks of detrimental effects on the water body. Compared to traditional remediation methods, microbial immobilization technology offers several advantages, including safety, no secondary pollution, and low economic cost. This approach eliminates the need for additional chemicals and reduces the release of pollutants into the environment, making it a sustainable and environmentally-friendly solution for the removal of contaminants, such as TCM, from various matrices [9].

Construction waste refers to the waste generated during the construction and demolition of buildings, which typically contains various materials such as plaster, cement, red brick, tile, wood, and glass. In most cases, construction waste is disposed of in an unorganized manner, leading to significant environmental pollution and the depletion of soil resources. To address these issues, many scholars and experts worldwide have conducted research on the resource utilization of construction waste. By promoting recycling and the re-use of construction waste, we can reduce environmental pollution and conserve valuable resources. This approach also helps to minimize the generation of waste and supports the sustainable development of the construction industry. Yang et al. [10] believed that the quality and particle size of recycled materials can be improved by using a vertical impact crusher to break garbage, and construction waste can be used as pavement. Raju et al. [11] pointed out by others that brick waste can be used as an alternative material in the production of concrete, and that cement can be partially replaced by brick ash obtained by crushing brick particles. The surface of red brick mainly comprises inorganic silicate, which has limited adsorption capability for organic matter. To improve its adsorption effectiveness, researchers typically modify the red brick material. Common modification methods include acid–base modification [12], microwave modification [13], CO_2 modification [14], and magnetic material modification [15]. Upon modification, the specific surface area and morphological characteristics of the red brick material are altered, resulting in an improved capacity for adsorption. The modified red brick material can thus be used as an efficient adsorbent material for the removal of pollutants from environmental matrices. Furthermore, the utilization of waste materials as immobilized carriers has been explored, offering a practical solution for the problem of urban garbage accumulation and environmental pollution. By converting waste materials into functional immobilized carriers, we can not only reduce the environmental burden of waste disposal but also create a sustainable solution for pollutant removal. This approach promotes the concept of circular economy and supports the development of a greener and more sustainable society.

Thus, in this study, the focus was on utilizing isolated and purified TCM-degrading bacteria as the target microorganisms and modified red brick as the immobilization carrier to develop an efficient TCM removal system. The adsorption–embedding–cross-linking method was employed to investigate the effects of adsorption time, temperature, and speed on the amount of bacterial liquid adsorbed on the carrier. Additionally, the study evaluated the impact of embedding agent concentration, cross-linking agent concentration, and cross-linking time on the removal efficiency of TCM from the immobilized pellets. The aim of this research was to provide experimental reference for the sustainable utilization of construction waste and the biological treatment of TCM, promoting a more environmentally friendly approach to waste management and pollutant removal.

2. Materials and methods

2.1. Experimental material

2.1.1. Strain

The strain used in this experiment is *Bacillus subtilis*, which can degrade TCM, purchased from Shanghai Conservation Biotechnology Center, (China).

2.1.2. Medium

LB (Luria-Bertani) medium was used for bacterial culture: peptone 10.0 g, yeast powder 5.0 g, sodium chloride 10.0 g, pH = 7.0, autoclaved at 121°C for 15 min.

To prepare the bacterial suspension, the bacterial culture was incubated for 24 h at 37°C in a liquid medium. The resulting bacterial solution was then subjected to centrifugation at 1,000 rpm for 10 min, and the wet bacteria were collected and washed three times with sterile normal saline. The wet bacteria were mixed with sterile normal saline to adjust the bacterial concentration to $OD_{600} = 1$, and the resulting bacterial suspension was stored at 4°C until further use.

2.1.3. Immobilized reagents

Sodium alginate, sodium hydroxide, and calcium chloride were all analytically pure, and purchased from Shanghai Titan Technology Co., Ltd., (Shanghai, China). Powder red brick, particle size 0~1 mm.

2.2. Experimental methods

2.2.1. Preparation of modified red brick

In order to modify the red brick material, a pre-experimental treatment was carried out, where red bricks with a particle size of 0~1 mm were soaked in a 1.5 mol/L NaOH solution for 24 h. Afterward, they were washed with distilled water until a neutral pH was achieved and then dried.

The modified red brick was denoted as NHZ, while the unmodified red brick was denoted as HZ.

2.2.2. Immobilization rate of modified red brick immobilization agent

To immobilize the bacterial suspension, the modified red brick was mixed with the suspension and agitated at 160 rpm and 37°C. The resulting mixture was then transferred to a centrifuge tube and centrifuged at 1,000 rpm for 10 min. This process was repeated three times, and the OD_{600} value of the supernatant was measured to indirectly determine the number of bacteria in the suspension. The amount of immobilized bacterial agent was obtained by calculating the difference between the initial amount of bacteria in the suspension and the amount remaining in the supernatant. The immobilization rate of the modified red brick carrier was calculated using Eq. (1).

$$\text{Fixation rate of immobilized microorganism in red brick}\left(\%\right) = \frac{\left(P_0 - P_1\right)}{P_0} \times 100\%$$

where P_0, initial bacterial suspension OD_{600} value and P_1, OD_{600} value of supernatant.

2.2.3. Preparation of immobilized pellets

To activate the preserved *Bacillus subtilis* strains, they were added to LB medium and incubated for 24 h. Then, 10 mL of the bacterial solution was added to 250 mL of sterilized LB medium, along with 5 g of modified red brick. The mixture was shaken at a constant temperature of 37°C and 160 rpm for 24 h. After shaking, the mixture was centrifuged at 4°C and 1,000 rpm for 10 min, and the collected modified red brick mixed bacterial liquid was stored for later use.

To prepare the cross-linked immobilized bacterial agent, a 1.5% solution of sodium alginate (SA) was dissolved in deionized water and stirred until completely dissolved. Then, the modified red brick mixed bacteria solution collected in the previous step was added to the SA solution and mixed thoroughly. The resulting mixture was slowly dropped into a 3% solution of $CaCl_2$ using a peristaltic pump. The solution was left to cross-link at room temperature for 6 h. After this time, the solution was removed and washed on normal saline solution. The resulting immobilized bacterial agent was dried on filter paper and stored in a refrigerator at 4°C for later use.

2.2.4. TCM detection method

The TCM content was determined by gas chromatography (GC) analysis (Agilent Technologies GC7890, Santa Clara, California). To determine the amount of TCM residue, the prepared immobilized pellets were added to a 10 mg/L trichloromethane methanol solution in a conical bottle. The constant temperature shaking bed was set to rotate at 160 rpm and a temperature of 37°C. A DB624 (123–1,334) column was used with a column flow rate of 2 mL/min. The inlet temperature was set to 200°C, and the heating procedure was as follows: The initial temperature was set to 35°C and kept for 6 min. The heating rate was set to 6°C/min until it reached 80°C and kept for 1 min. Then, the temperature was further heated to 100°C at a rate of 10°C/min and kept for 3 min. The temperature was then raised to 200°C at a rate of 10°C/min and kept for 5 min. The detector temperature was set to 250°C. Nitrogen was used as the tail blowing gas, with a flow rate of 30 mL/min [16].

2.2.5. Physico-chemical properties of immobilized pellets

(1) ***Sphericity***: Observe whether the immobilized ball can be restored to its original form and its ability to recover quickly when it is pressed by an external force.
(2) ***Mechanical strength***: Immobilized pellets of the same size and quantity were placed in conical bottles. After 50 mL water was added to each, the pellets were shaken for 24 h (160 rpm, 37°C) to observe the damage of the pellets.
(3) ***Chemical stability***: After soaking in 1 mol/L HCl solution (pH = 4) and 1 mol/L NaOH solution (pH = 14) for 24 h, the solution of immobilized particles was observed.
(4) ***Mass transfer***: The experiment involved placing the same amount and size of immobilized particles in a 2% methylene blue solution, which was then shaken for 24 h. After that, the supernatant was collected and the absorbance at 665 nm was measured. The change in absorbance value indicated the mass transfer of the immobilized particles.

3. Results and discussion

3.1. Analysis and characterization of modified red brick

3.1.1. Scanning electron microscopy (SEM) characterization

Fig. 1 shows the SEM images of 1,000 times amplification at HZ and NHZ. Based on the findings presented in Fig. 1, it can be concluded that the pore structure of the modified red brick particles has changed, resulting in the appearance of more fine particles. As a result, the specific surface area of NHZ is larger than that of unmodified red brick particles (HZ). This conclusion can be further confirmed by using a specific surface area analyzer to measure the specific surface area of the two types of particles.

Fig. 2 shows the X-ray diffraction (XRD) patterns of two kinds of red bricks before and after modification. The XRD pattern of NHZ shown in Fig. 2 indicates that the crystal structure of the red brick is not significantly affected by sodium hydroxide modification. The peak shape and position of the characteristic peak of SiO_2 in NHZ are similar to those of HZ, and there is no significant change in the diffraction angle near 2θ = 26° [17]. Therefore, it can be concluded that the modified red brick particles still maintain an amorphous structure.

3.1.2. Fourier-transform infrared spectroscopy

Fig. 3 shows Fourier-transform infrared spectra of two kinds of red bricks before and after modification. As can be seen from Fig. 3, the characteristic peaks of red bricks

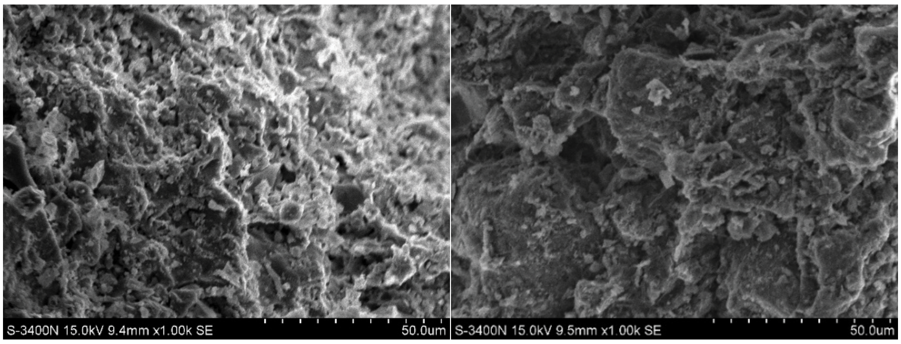

Fig. 1. Scanning electron microscopy images of unmodified and modified red brick.

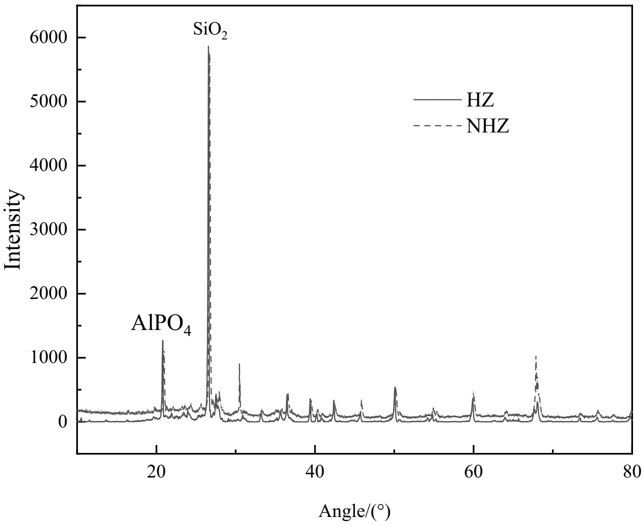

Fig. 2. X-ray diffraction patterns of unmodified and modified red brick.

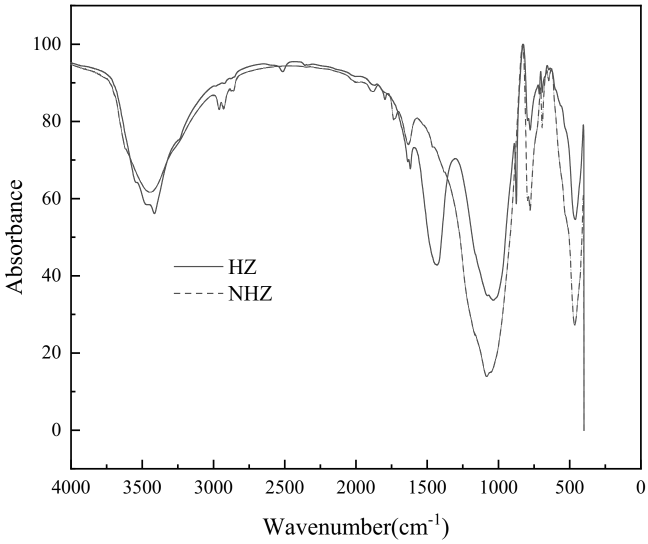

Fig. 3. Fourier-transform infrared spectra of unmodified and modified red brick.

Table 1
Specific surface area and pore volume of unmodified and modified red brick

Sample	Specific surface area ($m^2 \cdot g^{-1}$)		Pore volume ($cm^3 \cdot g^{-1}$)		Mean aperture /nm
	Brunauer–Emmett–Teller	Micropore	Total pore	Mesoporous	
HZ	1.8275	1.2554	0.007202	0.000635	15.7632
NHZ	11.3743	8.0891	0.017001	0.003621	5.9786

modified with sodium hydroxide are the same as those before modification, but most of the characteristic peaks are like O–Si–O bond at 1,200–950 cm^{-1} [18] and the Si–O–Si bond at 460 cm^{-1} [19] have been reduced. This may be due to the destruction of the functional groups of these characteristic peaks in the process of NaOH impregnation modification, which leads to the reduction of these functional groups. It can be clearly seen from the figure that the characteristic peak of SiO_2 at 460 cm^{-1} decreases. The main reason is that NaOH reacts with SiO_2 to produce soluble SiO_3^{2-}, which leads to the decrease of SiO_2 on the surface of red brick [20].

3.1.3. Specific surface area and pore volume

The specific surface area and pore volume of red brick before and after modification are shown in Table 1. Table 1 shows that the specific surface area of NHZ is significantly larger than that of unmodified red brick, with an increase of 6.22 times. The total pore volume and micropore area and volume are also significantly increased, by 2.36 and 6.47 times, respectively. The average adsorption pore size is smaller, indicating that more micropores are generated after modification. The increase in specific surface area is likely due to the interaction between NaOH and red brick, which increases porosity and creates more micropores [21].

The initial micropore volume was only 1.2554 m^2/g, whereas after modification with sodium hydroxide, the micropore volume increased significantly to 8.0891 m^2/g which was much higher compared to the unmodified state. Therefore, NaOH modification improves the surface roughness and pore structure of red brick, resulting in a significant increase in specific surface area and pore volume.

3.2. Microbial adsorption fixation rate of modified red brick

Fig. 4 presents the results of the exploratory experiment conducted to investigate the effects of adsorption time, temperature, and rotational speed on the microbial adsorption capacity of the modified red brick. The experiment revealed that the adsorption capacity of the modified red brick increased with an increase in the adsorption time, temperature, and rotational speed. The maximum adsorption capacity was achieved after 12 h of adsorption at 37°C and 160 rpm. Beyond this time, the adsorption capacity tended to remain constant, suggesting that the saturation point had been reached. Similarly, at higher temperatures and rotational speeds, the adsorption capacity increased significantly, indicating that these parameters can be optimized to enhance the microbial adsorption capacity of modified red brick.

Based on the results shown in Fig. 4, it can be concluded that the microbial adsorption capacity of modified red brick is influenced by various factors, including adsorption time, temperature, and rotational speed. The fixation of modified red brick to microorganisms first increases and then decreases with the gradual increase of time, reaching the maximum of 60% at 24 h due to the saturation of the adsorption sites. Similarly, the immobilization rate of bacteria by NHZ demonstrates a biphasic response to temperature, characterized by an initial augmentation and subsequent attenuation. This phenomenon can be attributed to the diminished metabolic activity of microorganisms under low temperature conditions, rendering them less mobile. Conversely, at elevated temperatures, the heightened thermal stress adversely affects the viability and functionality of bacteria, resulting in a decline in immobilization rate. When the rotational speed is 160 r/min, the fixed rate of the modified red brick reaches a high value of 65%. Thus, considering the previous experimental studies, the optimal parameters for NHZ adsorption of microbial agents were determined as follows: adsorption time of 24 h, temperature controlled at 37°C, and rotational speed set at 160 rpm.

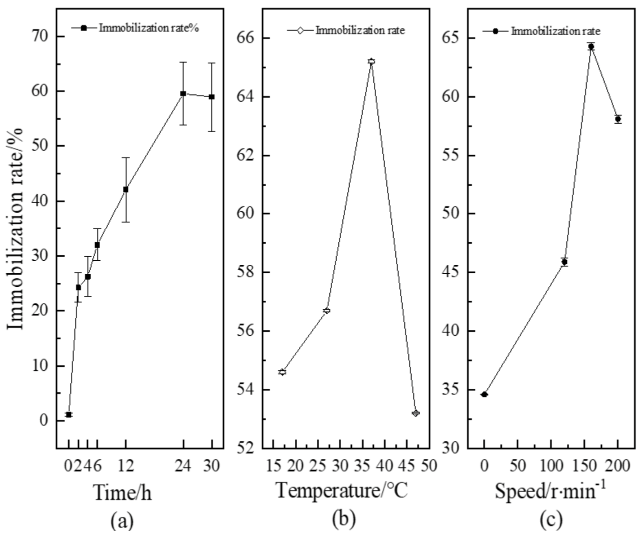

Fig. 4. Effect of adsorption time, temperature, and rotation speed on immobilization rate.

3.3. Selection of embedding and cross-linking conditions

To optimize the immobilization effect of trichloromethane degradation, a three-factor and three-level orthogonal design was conducted to investigate the influence of embedding agent SA concentration, $CaCl_2$ concentration, and cross-linking time on the physical and chemical characteristics of the immobilized pellets and the degradation rate of trichloromethane. Table 2 displays the experimental factors and levels of the immobilized embedding and cross-linking orthogonal design, while Table 3 presents the analysis of the orthogonal experiment results. Additionally, Table 4 shows the physical and chemical characteristics of the immobilized microbial agent, and Fig. 5 depicts the pellet formation characteristics of embedding and cross-linking solidified pellets under the orthogonal parameters.

According to the range analysis results in Table 3, the primary influencing factors in descending order are cross-linking time, sodium alginate concentration, and calcium chloride concentration. The concentration of calcium chloride primarily affects the mechanical strength and formation of the immobilized carriers during the preparation process. Considering the mechanical strength in Table 4 and the spherical characteristics in Fig. 5, the influence of the calcium chloride concentration on the sphere formation of the immobilized microbial agents is not significant. Consequently, experiments were conducted using 1%, 3%, and 5% $CaCl_2$ as cross-linking agents. The results showed that when 1% $CaCl_2$ was used, the pellets were soft and weak in strength, while using 5% $CaCl_2$ resulted in trailing phenomenon during pellet formation. Therefore, it was determined that 3% $CaCl_2$ is the optimal cross-linking agent concentration, as it resulted in the best pellet formation and moderate strength.

Based on the orthogonal experimental results and the physico-chemical properties of the formed spheres, the

Table 2
Factors and levels of immobilized embedding–cross-linking experiments[a]

Level	Factor		
	A	*B*	*C*
	SA (%)	$CaCl_2$ (%)	Time (h)
1	1	1	2
2	1.5	3	4
3	2	5	6

[a]Percentage in the table is the mass fraction.

Table 3
Results of orthogonal experiment

Number	Factor			Removal percentage (%)
	A-SA (%)	*B*-$CaCl_2$ (%)	*C*-Time (h)	
1	1	1	2	45.9
2	1	3	4	56.6
3	1	5	6	60.4
4	1.5	1	4	73.4
5	1.5	3	6	75.0
6	1.5	5	2	54.3
7	2	1	6	59.8
8	2	3	2	51.6
9	2	5	4	56.2
K_1	162.9	179.1	151.8	
K_2	202.7	183.2	186.2	
K_3	167.6	170.9	195.2	
R	13.27	4.10	14.47	

K_1: represents the sum of experimental results corresponding to any factor (or treatment) at level 1 in orthogonal experimental design;
K_2: represents the sum of experimental results corresponding to any factor (or treatment) at level 2 in orthogonal experimental design;
K_3: represents the sum of experimental results corresponding to any factor (or treatment) at level 3 in orthogonal experimental design;
R: R typically represents the range, which is obtained by subtracting the minimum K-value from the maximum K-value.

optimal conditions for preparing immobilized microbial spheres for trichloromethane degradation are determined to be a sodium alginate (SA) concentration of 1.5%, a calcium chloride ($CaCl_2$) concentration of 3%, and a cross-linking time of 6 h.

3.4. Comparative degradation of TCM by immobilized and unfixed bacteria in modified red brick

Fig. 6 illustrates the comparison of TCM removal between modified red brick immobilized microbial agent and unfixed microbial agent treated with 10 mg/L trichloromethane solution. The results showed that the TCM removal of the immobilized microbial agent was significantly higher than that of the unfixed microbial agent, and the removal reached 92.86% after 24 h of reaction. The immobilized microbial agent has a certain degree of stability and reusability. It can maintain a removal of 86.63% after 4 consecutive reaction cycles, indicating that it has a good practical application prospect in the treatment of trichloromethane wastewater.

The results in Fig. 6 demonstrate that the trichloromethane removal percentage of the modified red brick immobilized microbial agent was markedly higher than that of the free bacteria and unfixed modified red brick, with a gradual increase over time. This is primarily due to the modified red brick, serving as an immobilized carrier, providing protection to the microbial agent, thereby promoting

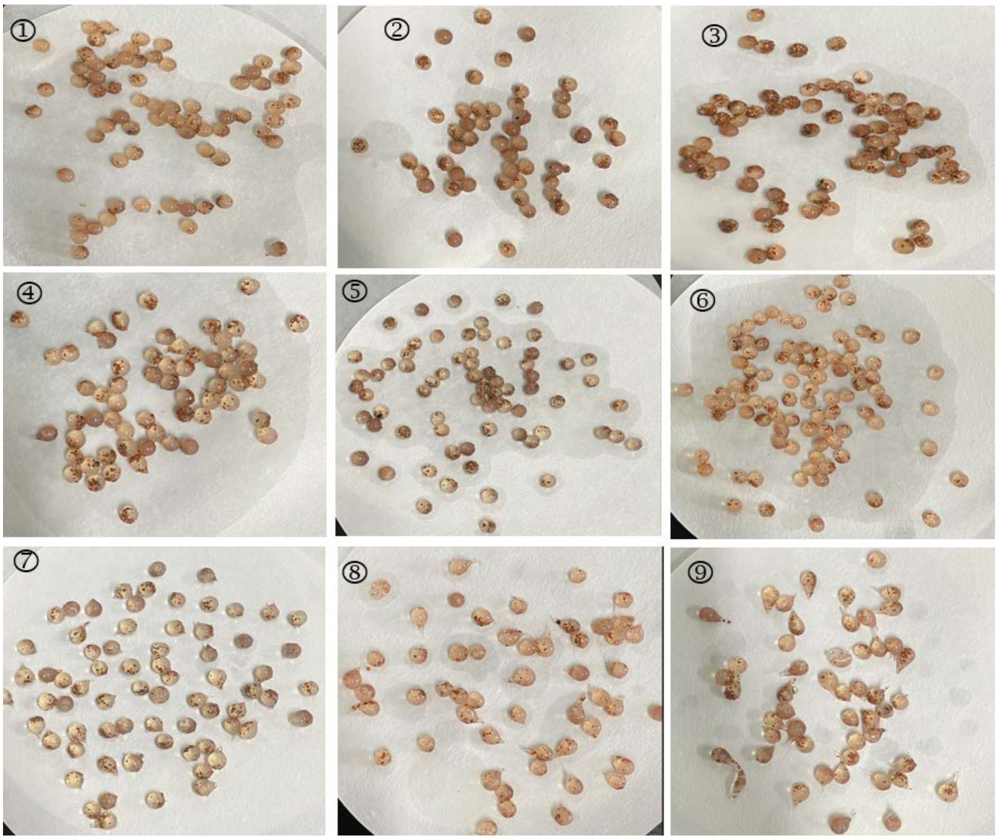

Fig. 5. Characteristics of embedded-cross-linked solidified pellets under orthogonal parameters.

Table 4
Physical and chemical characteristics of immobilized microbial agents

Number	Size (mm)	Quantity (g)	Sphericity	Elasticity	Strength	Mass transfer	Chemical stability
1	3.957	0.032	No	Soft	Undamaged	Better	Poor
2	4.05	0.033	No	Medium	Undamaged	Bad	Better
3	3.82	0.041	No	Hard	Undamaged	Better	Optimal
4	3.926	0.042	Little	Medium	Undamaged	Optimal	Better
5	3.678	0.034	No	Hard	Undamaged	Optimal	Optimal
6	3.712	0.033	No	Soft	Undamaged	Bad	Better
7	4.227	0.048	Bad	Hard	Undamaged	Optimal	Optimal
8	4.088	0.044	Bad	Soft	Undamaged	Better	Better
9	4.182	0.048	Bad	Medium	Undamaged	Better	Optimal

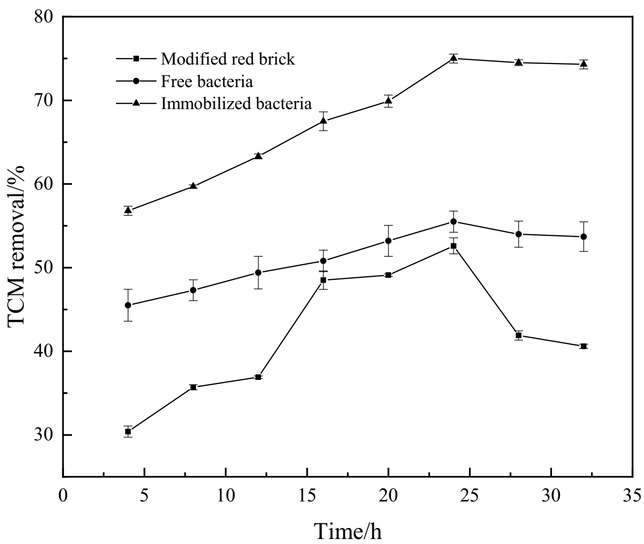

Fig. 6. Comparison of trichloromethane removal.

cell proliferation and forming a protective barrier on the carrier surface. The microorganisms embedded in the carrier can survive for an extended period, enhancing their ability to resist the toxicity of trichloromethane.

4. Conclusions

In the laboratory experiment, modified red brick was used as an immobilized carrier for *Bacillus subtilis* to remove trichloromethane, and promising results were obtained.

(1) The optimal parameters for the adsorption of microorganisms by modified red brick were found to be an adsorption time of 24 h, an oscillation temperature of 37°C, and a rotation speed of 160 rpm.
(2) The optimal conditions for the preparation of immobilized microspheres of modified red brick were determined to be a concentration of 1.5% for the embedding agent SA, a concentration of 3% for $CaCl_2$ as a cross-linking agent, and a cross-linking time of 6 h.
(3) When tested on trichloromethane-contaminated solution with the same concentration, the removal percentage of trichloromethane by the immobilized *Bacillus subtilis* pellets embedded in modified red brick reached 75%, which was significantly higher than that of modified red brick and free bacteria without immobilization.

References

[1] G. Pérez-Lucas, M. Martínez-Menchón, N. Vela, S. Navarro, Removal assessment of disinfection by-products (DBPs) from drinking water supplies by solar heterogeneous photocatalysis: a case study of trihalomethanes (THMs), J. Environ. Manage., 321 (2022) 115936, doi: 10.1016/j.jenvman.2022.115936.
[2] M. Porpora, I. Piacenti, S. Scaramuzzino, L. Masciullo, F. Rech, P. Benedetti Panici, Environmental contaminants exposure and preterm birth: a systematic review, Toxics, 7 (2019) 11, doi: 10.3390/j.toxics.2019.7010011.
[3] J. Xiao, X. Xu, F. Wang, J. Ma, M. Liao, Y. Shi, Q. Fang, H. Cao, Analysis of exposure to pesticide residues from Traditional Chinese Medicine, J. Hazard. Mater., 365 (2019) 857–867.
[4] J. Beltrán-Heredia, J. Sánchez-Martín, Municipal wastewater treatment by modified tannin flocculant agent, Desalination, 249 (2009) 353–358.
[5] C. Lei, Y. Sun, E. Khan, S.S. Chen, D.C.W. Tsang, N.J.D. Graham, Y.S. Ok, X. Yang, D. Lin, Y. Feng, X.-D. Li, Removal of chlorinated organic solvents from hydraulic fracturing wastewater by bare and entrapped nanoscale zero-valent iron, Chemosphere, 196 (2018) 9–17.
[6] J. Yang, L. Meng, L. Guo, *In-situ* remediation of chlorinated solvent-contaminated groundwater using ZVI/organic carbon amendment in China: field pilot test and full-scale application, Environ. Sci. Pollut. Res., 25 (2018) 5051–5062.
[7] P. Rajasulochana, V. Preethy, Comparison on efficiency of various techniques in treatment of waste and sewage water – a comprehensive review, Resour.-Effic. Technol., 2 (2016) 175–184.
[8] C. Streche, D.M. Cocârță, I.-A. Istrate, A.A. Badea, Decontamination of petroleum-contaminated soils using the electrochemical technique: remediation degree and energy consumption, Sci. Rep., 8 (2018) 3272, doi: 10.1038/s41598-018-21606-4.
[9] D.L. Freedman, J.M. Gossett, Biological reductive dechlorination of tetrachloroethylene and trichloroethylene to ethylene under methanogenic conditions, Appl. Environ. Microbiol., 55 (1989) 2144–2151.
[10] H. Yang, J. Xia, J.R. Thompson, R.J. Flower, Urban construction and demolition waste and landfill failure in Shenzhen, China, Waste Manage., 63 (2017) 393–396.
[11] J.N.S.S.N. Raju, S.S. Reddy, P. Raju, K. Jagadeep, Red brick dust as a partial substitute to cement in conventional concrete, Int. J. Recent Technol. Eng. (IJRTE), 8 (2019) 5632–5635.
[12] C. Wu, L. Li, H. Zhou, J. Ai, H. Zhang, J. Tao, D. Wang, W. Zhang, Effects of chemical modification on physico-chemical properties and adsorption behavior of sludge-based activated carbon, J. Environ. Sci., 100 (2021) 340–352.

[13] M.R. Cunha, E.C. Lima, N.F.G.M. Cimirro, P.S. Thue, S.L.P. Dias, M.A. Gelesky, G.L. Dotto, G.S. dos Reis, F.A. Pavan, Conversion of *Eragrostis plana* Nees leaves to activated carbon by microwave-assisted pyrolysis for the removal of organic emerging contaminants from aqueous solutions, Environ. Sci. Pollut. Res., 25 (2018) 23315–23327.
[14] H. Abdullah, Md. M.R. Khan, H.R. Ong, Z. Yaakob, Modified TiO_2 photocatalyst for CO_2 photocatalytic reduction: an overview, J. CO_2 Util., 22 (2017) 15–32.
[15] X. Kong, Y. Liu, J. Pi, W. Li, Q. Liao, J. Shang, Low-cost magnetic herbal biochar: characterization and application for antibiotic removal, Environ. Sci. Pollut. Res., 24 (2017) 6679–6687.
[16] T. Huybrechts, J. Dewulf, O. Moerman, H. Van Langenhove, Evaluation of purge-and-trap–high-resolution gas chromatography–mass spectrometry for the determination of 27 volatile organic compounds in marine water at the ng l^{-1} concentration level, J. Chromatogr. A, 893 (2000) 367–382.
[17] K. Sun, K. Ro, M. Guo, J. Novak, H. Mashayekhi, B. Xing, Sorption of bisphenol A, 17α-ethinyl estradiol and phenanthrene on thermally and hydrothermally produced biochars, Bioresour. Technol., 102 (2011) 5757–5763.
[18] R.M. Ali, H.A. Hamad, M.M. Hussein, G.F. Malash, Potential of using green adsorbent of heavy metal removal from aqueous solutions: adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis, Ecol. Eng., 91 (2016) 317–332.
[19] C.C. Perry, X. Li, D.N. Waters, Structural studies of gel phases—IV. An infrared reflectance and Fourier transform Raman study of silica and silica/titania gel glasses, Spectrochim. Acta, Part A, 47 (1991) 1487–1494.
[20] P. Liu, W.-J. Liu, H. Jiang, J.-J. Chen, W.-W. Li, H.-Q. Yu, Modification of biochar derived from fast pyrolysis of biomass and its application in removal of tetracycline from aqueous solution, Bioresour. Technol., 121 (2012) 235–240.
[21] Z. Ding, X. Hu, Y. Wan, S. Wang, B. Gao, Removal of lead, copper, cadmium, zinc, and nickel from aqueous solutions by alkali-modified biochar: batch and column tests, J. Ind. Eng. Chem., 33 (2016) 239–245.