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Preparation of PolyHIPE beads and the application in bio-degradation of sulfate containing wastewater

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ABSTRACT

Porous polymer support beads modified by a silicone resin with bifunctional groups were prepared by using High Internal Phase Emulsion (HIPE) templated method. Their surface properties and morphological characteristics were investigated. The effect of silicone resin content has been highlighted. When the content of the silicone resin was 30%, the support exhibited a relatively higher hydrophobicity (contact angle was 118.8°) and suitable pore diameter distribution. The Sulfate Reducing Bacteria (SRB) loading biofilm/support and its desulfurization experiments for the sewage with 1000–4000 mg SO_4^{2-}/L have been performed, and the result shows that the polymer bead support has given higher sulfate reducing rates than that of the traditional active carbon (AC) beads and the maximum sulfate reducing rate reached to 84.56% for the wastewater with 1000 mg SO_4^{2-}/L after 12 h.

1. Introduction

Sulfate containing waste water produced by pharmaceutical, mining and chemical industries always have inhibitory problems to methane-producing process [1], therefore, microorganisms such as sulfate reducing bacteria (SRB) have been used for sulfate-containing pollutant degradation [2–34]. To enhance the retention time of the microorganism, various supports have often been used as bio-supports to immobilize biofilms [5, 6]. It is widely accepted that one kind of the bacteria needs to select a specialized support with satisfactory structure and surface properties, and it plays an important role on the loading and stabilization behaviors.

For SRB system, effect of the hydrophobicity and pore structure of the support have been widely studied. For the hydrophobic/hydrophilic issue, several polymers, including polyurethane foam (PU), low-density polyethylene (PE) and polystyrene (PS) have been taken in some papers [7, 8] to investigate the SRB adhesion behaviors thereon. It is concluded that a support with higher hydrophobicity can load larger amount of the microbe cell because of its lower interface energy between SRB and support, which is also closely related to the apparent contact angle. The same conclusion has also been given for SRB on a support from a PDMS porous polymer in another work [9]. Therefore, SRB immobilization performance and loaded amount correlate to the interface energy and hydrophobicity of the support and more amount of the bacteria would be adhered on the support at higher contact angle (θ) with lower interfacial free energy. As to the pore structure issue, it is reported in the literature that macroporous supports with pore diameter 1–5 times larger than the scale of the bacteria can provide a better performance for biomass [10–12]. Conventional supports such as ceramics, natural activated carbon, lava and other synthesis compounds are often of pores in nano scale, therefore, they are only able to enhance the adhesion of microorganism by increasing the roughness on the support surface. While polymers with pores in micro-meter scale can stimulate the proliferation of the bacteria, until the free volume is run off and a high density of bacterial colony could be reached. In other words, macroporosity provides a free volume high enough to strongly enhance bacterial proliferation and concentration [13].

To meet the challenge for a support as above, a HIPE-templated polymer (PolyHIPE) is prepared and used as a support for SRB biofilms in this paper. It is a macroporous material synthesized by polymerizing styrene monomer with a special crosslinking agent in the continuous phase of HIPE. This porous polymer has a tunable and hierarchical pore structure. The large voids are of diameter, ranging from 0.5 to 600 μm and they are connected by small windows with 0.1–300 μm in diameter [14, 15]. Therefore, it provides to the polymer a high porosity, a low diffusion resistance and a low density and thus makes the polymer a promising support in SRB system. Moreover, this kind of polymer has also attracted considerable researches in fields of hydrogen storage

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[16], biocatalysts [17–19], environmental science [20, 21], etc.

Up to now, only few works in the literature have involved the bacterial proliferation performance on such a macroporous polymer as described in this paper. Additionally, the PolyHIPE product is often shaped like monoliths in the preparation procedure. However, it is necessary to be used in a bead-shaped form to meet the requirement in a microbial fluid reactor. In this paper, a novel method to improve the preparation of this product is described. The support is in a bead form and is of high hydrophobicity and well-arranged voids with narrow diameter distribution. This paper also highlights the effect of preparation parameters on the properties of this support. When the SRB biofilm is loaded on the above PolyHIPE polymer support, satisfactory performance is exhibited in sulfate biodegradation of waste water. Comparison with the results by using active carbon granule, which is widely used in biological waste water treatment processes is also given.

2. Experimental

2.1. Materials

3-Methacryloxypropyl trimethoxysilane (MPS, 97%, contains 100 ppm butylated hydroxytoluen), and Hexamethyldisiloxane (MM, 99%) were purchased from Aladdin Industrial Co. Styrene (St, AR), Ethanol (AR), and Tetraethoxysilane (TEOS, AR) were purchased from Shanghai Titan Scientific Co. Ltd. Sodium lactate (60 wt%) and Potassium 2,2′-Azobis (2-methylpropionitrile) (AIBN, 98%) were purchased from Shanghai Maclin Biochemical Co. Ltd. In addition, hydrochloric acid (HCl, 37%) and Span 80 (CP) and Poly (dimethyldiallylammonium chloride) (PDDAC, 35 wt%) were purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. Other chemical materials involved in this paper were all analytical grades. Before used, St and MPS were washed by using 5 wt% NaOH solution to remove the inhibitor and then dried by $CaCl_2$. All the solutions were prepared by using deionized water.

2.2. Preparation of MTQ silicone resin

Preparation equation of MTQ is shown in Fig. 1. It is there seen that intermediate products from hydrolysis of MM, MPS and TEOS, have mono-, tri- and quadri-functional siloxane chains respectively and therefore they are there abbreviated as M, T and Q in order. MTQ silicone resins were prepared by hydrolytic condensation of MPS and TEOS under the presence of MM as end-capping agent. It has specialized three-dimensional structure and Si-O-Si chains that is advantageous to improve the product characteristics, when it is added as a cross-linking agent.

The procedure to prepare MTQ silicone resins is, therefore, as follows [22]: 0.048 mol TEOS, 0.048 mol EtOH, 0.014 mol MM and 0.030 mol MPS were firstly added into the reactor; then the catalyst and 0.9 g HCl solution (HCl 8 wt%), was dropped into it. The whole system was stirred under 75 °C for 2 h. After the reaction, the product was washed by deionized water to neutral nature. A sticky, transparent oil product was thus obtained in this way.

2.3. Synthesis of Poly (St-MTQ) HIPE beads

The scheme to prepare Poly (St-MTQ) HIPE beads has been exhibited in Fig. 2. To prepare these beads, St, MTQ, Span 80 and AIBN were added to the reactor and the mixture was stirred with a magnetic stirrer. Their ratios were listed in Table 1. Then the $CaCl_2$ aqueous phase was dropwise added into the oil phase under constant stirring within 30 min. In our tests, 4 wt% of $CaCl_2$ was solved in the inner phase. It is not only able to maintain the stability of the emulsion and restrain the Ostwald ripening effect but also provide a proper density to the emulsion. After all the aqueous phase had been added, the mixture was stirred for another 10 min, until it became a homogeneous emulsion with a proper viscosity.

For shaping to poly(St-MTQ)HIPE beads, the above emulsion was dropwise added into 1.5 wt% PDDAC solution at 40 °C by using a plastic syringe with a diameter of 0.5 mm and spread them on each of several separated plates for polymerization in the solution. After all the emulsion was squeezed into the outer phase, the temperature was switched to 60 °C and kept unchanged for 10 h. The formed solidified particles were extracted with distilled water and ethanol for 12 h, respectively and then dried in the vacuum drying oven at 80 °C for 24 h. In this way, poly(St-MTQ)HIPE beads were thus obtained.

For simplicity, poly(St-MTQ) HIPE is abbreviated to poly(St-MTQ) in this paper hereafter.

2.4. Biofilm preparation

The SRB were firstly isolated from a sewage pipe on the oil field in Jiangsu, China. They were then cultured in sealed serum bottles under 150 rpm at 38 °C with the Postgate C as enrichment culture medium [23]. The formulation of the latter is composed of KH_2PO_4 0.5 g/L, NH_4Cl 1 g/L, Na_2SO_4 4.5 g/L, $CaCl_2{\cdot}6H_2O$ 0.06 g/L, $MgSO_4{\cdot}7H_2O$ 0.06 g/L, sodium lactate (60%) 6 mL/L, yeast extract 1 g/L, $FeSO_4{\cdot}7H_2O$ 0.004 g/L and ascorbic acid 0.1 g/L at pH of 7.0–7.5. About 5 days after the inoculation, the substrate turned from transparent to dark black color, resulting from the reduction of sulfate ions into sulfur ions by the ascendant of SRB and the formation of dark black FeS precipitate with ferrous ions in the culture medium. The enrichment circle was repeated

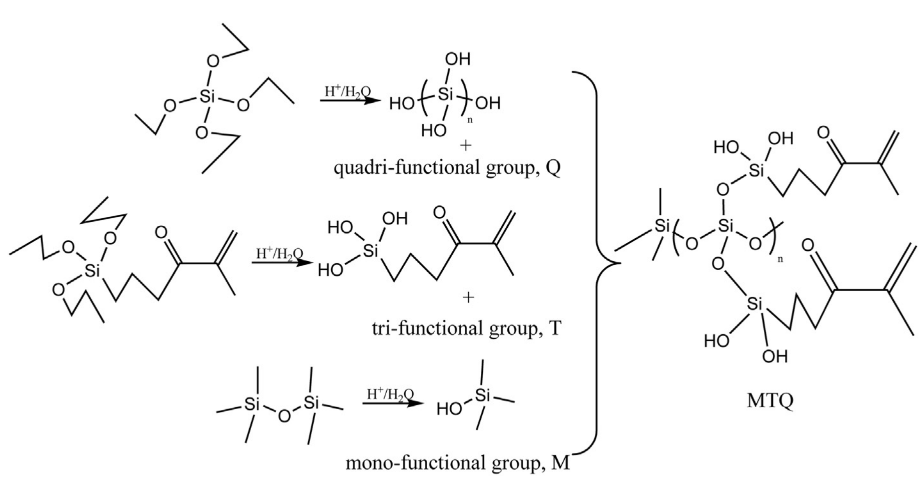

Fig. 1. Preparation equation of MTQ silicone resin.