Interconnected Porous Material Prepared Via High Internal Phase Emulsion Stabilized by Mixture of Fe₃O₄ and Tween85

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Abstract. PolyHIPE monoliths with open-cell structure were prepared using an oil-in-water Pickering high internal phase emulsion (HIPEs) template. Fe_3O_4 nanoparticles and Tween 85 were used to stabilize the HIPE. The effects of surfactant concentration, nanoparticle amount and internal phase fraction on the average void and interconnecting pore diameter and interconnectivity degree were investigated. Efficiency of these PolyHIPEs as catalyst for Fenton reaction to decompose methyl orange was tested. The results showed that the PolyHIPE was an excellent and reusable supporter for Fenton reaction.

1. Introduction

PolyHIPEs are well-defined porous polymers synthesized with high internal phase emulsion (HIPE, ≥74.05 vol% internal phase) as template [1]. These PolyHIPE have been found a variety of applications including catalytic supports [2], chromatographic separation [3,4], scaffolds for tissue engineering [5], etc. Pickering emulsion is stabilized by nanometer- or micrometer-sized particles[6]. Both organic and inorganic nanoparticles have been used to stabilize HIPE like titania and silica nanoparticles, carbon nanotubes, copolymer particles [7,8]. Advantages of using particles as emulsifiers to prepare PolyHIPE include low concentration of particles that are required (generally less than 1 wt%), high stability of the HIPE and functionalizing the surface of the polymer backbone for new applications.

The dyeing wastewater with strong acidity and basicity and large amounts of organic matter or salt is hard to be purified with common physical and bio-chemical method. Fenton reaction is a good method for dye decomposition [9,10]. Hydroxyl radicals from H_2O_2 promote the dye molecular chain scission catalyzed by Fe^{2+}. Traditional homogeneous reaction system have been faced with many problems. Secondary pollution caused by remaining Fe^{2+} massive H_2O_2 requirement restrict its application.

Recently, heterogeneous Fenton system in which catalytic is adsorbed on the surface of inorganic porous materials such as zeolite, activated carbon, etc. to solve those problems

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[11-13]. But this kind of method has shortcoming in low catalyst loading and catalytic efficiency. PolyHIPE functionalized with Fe_3O_4 is supposed to be a good carrier for catalyst.

In this work, interconnected PolyHIPE was successfully prepared using HIPE stabilized by Fe_3O_4 and Tween 85. The effects of surfactant content, amount of Fe_3O_4 nanoparticles and internal phase fraction on the morphology of the PolyHIPE were investigated. Fenton reaction to decompose methyl orange in a Fe_3O_4 loaded PolyHIPE was used as a model of sewage treatment to verify the availability of PolyHIPE in the application of purification or catalyzing.

2.   Materials

Acrylamide (AM), paraffin, N,N,N',N'-tetramethylethylenediamine (TMEDA), hydrochloric acid (37%), hydrogen peroxide (H_2O_2, 38%), cyclohexane (Lingfeng chemical reagents Co. Ltd, Shanghai, China) and Fe_3O_4 nanoparticles (diameter 100~300 nm, Aladdin).N, N'- methylene bisacrylamide (MBAM), Tween 85 and methyl orange (MO) (Sinopharm Chemical Reagent Co., Ltd) were used as received. Ammonium persulfate (APS, Lingfeng chemical reagents Co. Ltd, Shanghai, China) was recrystallized twice before use. Deionized water was used throughout all experiments.

2.1Preparation of Poly-Pickering-HIPE Monolith

4.0 ml of a aqueous solution containing 1.420g monomer AM (20mmol), 0.309g crosslinker MBAM (2mmol) and 0.04g initiator APS as well as appropriate amount of surfactant Tween 85 and Fe_3O_4 nanoparticles was prepared as aqueous phase. The aqueous phase was poured into a 100 ml three-necked, round-bottomed flask equipped with a mechanical stirrer. Then paraffin as oil phase was added drop-wise into this aqueous phase at 25 ºC under stirring at 300 rpm. Once all of the oil phase had been added, 16 μl of TMEDA was injected into the emulsion and kept stirring for 1 minute. The prepared HIPE was transferred into a chromatography column, sealed and polymerized at 30 ºC for 24 h. The chromatography column was then connected to the constant fluid pump and the Poly-HIPE was purified with cyclohexane and deionized water for 24 h separately and then dried under vacuum at 50 ºC to constant weight. The characteristics of the PolyHIPE samples are listed in Table 1.

The morphology of foam obtained was detected by a Hitachi S-4800 SEM. The interconnectivity degree (I) of the foam was calculated by

$$I(\%) = 25 \times n \times (d/D)^2$$

(1)

Where n was the average number of interconnecting pores per void, d was the average interconnecting pore diameter, D was the average void diameter and all calculated from SEM images with formula

$$D = 2/\sqrt{3} \ D'$$

(2)

Where D is the actual diameter and D′ is the diameter of voids or interconnecting pores measured from the SEM image [14]. At least 50 voids were calculated for each sample.

2.2Characterization of the Decomposition of Methyl Orange

Fenton reaction was detected through the concentration measurement of MO in water by an ultraviolet-visible spectrophotometer UV-2550PC. PolyHIPE with internal phase 80%, Tween 85 3.0 wt% and Fe_3O_4 concentration 1.0, 2.0, 4.0 wt% (Samples PC-1, PC-2 and PC-4) were selected to estimate the efficiency of material. 15 ml of aqueous solution (pH=2 adjusted with HCl) containing 20 ppm MO and 0.2 ml H_2O_2 (38%) was circulating in the column driven by a constant flow pump HL-2B at 30 rpm. Absorption intensity at wavelength of 505 nm was measured every 1 h during the reaction. PolyHIPE was washed with deionized water driven by the constant flow pump for 24 h and dried under vacuum at 50 ºC for 24 for next batch reaction.

3.   Result and Discussion

TABLE 1 COMPOSITION OF PICKERING HIPES TEMPLATES AND THE PROPERTIES OF THE RESULTING POLYHIPES.

[a] Surfactant and particle concentration with respect to the aqueous phase.
[b] Internal phase volume ratio.
[c] Average void and interconnecting pore diameter.
[d] Interconnectivity of the PolyHIPEs.
[e] Average large void diameter and average small void diameter in Sample 9 respectively.

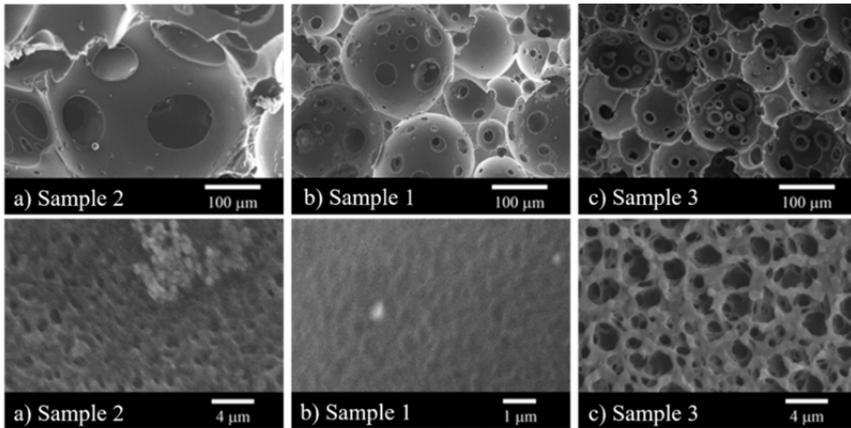| Sample ID	Surf. [a] [wt%]	Particle [a] [wt%]	$R_{internal}$ [b] [%]	D [c] [μm]	d [c] [μm]	I [d] [%]
1	3.0	2.0	80	153.4	44.7	12.7
2	1.0	2.0	80	286.5	97.1	11.4
3	5.0	2.0	80	105.8	35.1	16.5
4	3.0	0	80	92.5	15.1	3.3
5	3.0	1.0	80	175.0	45.8	6.8
6	3.0	4.0	80	169.2	46.9	13.4
7	3.0	2.0	75	134.4	31.4	4.7
8	3.0	2.0	85	198.9/68.5 [e]	38.4	19.6
9	3.0	2.0	90	55.8	15.2	14.8

3.1Effect of Surfactant Amount

Fig. 1 SEM images of PolyHIPE with different surfactant concentration a) 1.0 wt%, b) 3.0 wt%, c)

5.0 wt%

Surfactant plays a major role in the stabilization of the HIPE. When the Fe_3O_4 nanoparticle concentration is 2 wt% and Tween 85 concentration got increasing from 1.0 and 3.0 to 5.0 wt% (Samples 1, 2 and 3 in table 1 and Fig. 1), the D decreased gradually from 286.5μm to 105.8μm and interconnectivity degree increased from 11.4% to 16.5%. Firstly, more Tween 85 in the aqueous phase may get adsorbed on the oil/water interface can reduce the interfacial tension, stabilize the HIPE and inhibit coalescence between droplets, which leads to a decrease in D as a result. Moreover, the surfactant also adsorbs at the particle surface and helps them well dispersed in water. This reduced viscosity leads to the sedimentation of the less concentrated emulsions and results in thinner droplet films, which results in higher interconnectivity [15]. By the way, when Tween 85 was increased to 5%, hierarchical porous structure was found (Sample 3). Excess Tween 85 may give rise to much smaller size of droplets around a droplet, which lead to the formation of small cavity on the surface of the backbone.
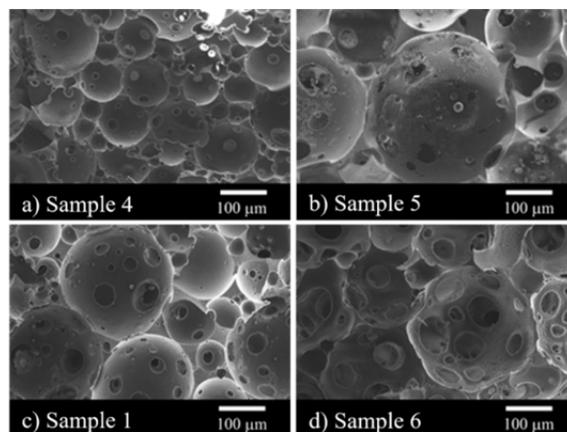

Fig. 2 SEM images of PolyHIPE with different Fe3O4 nanoparticle amount: a) 0%, b) 1%, c)2%,

d)4%

3.2Effect of the Fe3O4 Nanoparticle Amount

Effect of Fe_3O_4 nanoparticle amount on the morphology is shown in fig. 2. A significant increase had been found in void size after Fe_3O_4 nanoparticles were added and slight decrease when the Fe_3O_4 nanoparticle amount was increased from 1.0 to 4.0 wt%. This may be attributed to the fact that the particles act as the primary stabilizer of Pickering emulsions in the presence of this surfactant, so the droplet size is larger than particle free emulsion. Increasing the nanoparticle amount adsorbed on the interface can reduce the interfacial tension thus decreasing the droplet size of emulsion and void size of PolyHIPE.
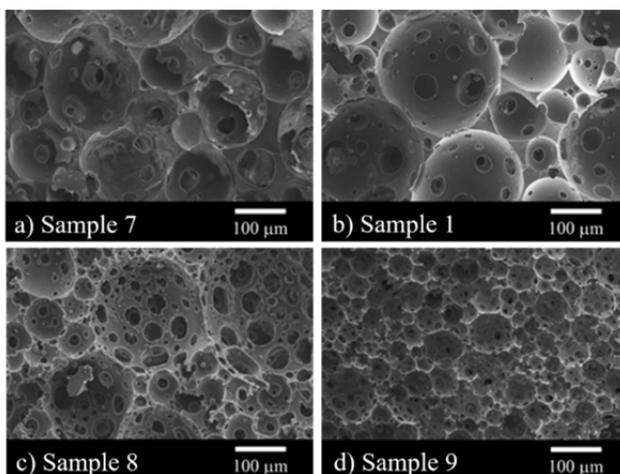
3.3Effect of the Internal Phase Fraction

Fig. 3 SEM images of PolyHIPE with different inter phase fraction: a) 75%, b) 80%, c)85%, d)90%

When the paraffin fraction was increased from 75% to 85% while surfactant and nanoparticle remain constant (Tween 85 and Fe_3O_4 of 3.0 wt% and 2.0 wt%, respectively), the D enlarged from 134.4 μm to 198.9 μm and I increased from 4.7 % to 19.6 % (Fig. 3). As the internal phase increased while surfactant and nanoparticle concentration remain unchanged, the surfactant and nanoparticles were less able to effectively stabilize the HIPE. Some of the droplets coalescence and translates to the increase in void diameter. Bimodal distribution of void diameter was found at the same time when oil phase fraction was 85%. Meanwhile, the thickness of the polymer membranes of continuous phase decreased, which helps the formation of interconnecting pores during polymerization [16]. However, when the internal phase increased to 90%, average D decreased substantially to 55.8 μm and interconnectivity degree decreases to 14.8 %. This may be attributed to the fact that the high viscosity limit the translation of droplets thus reducing the coalescence and Ostwald ripening.

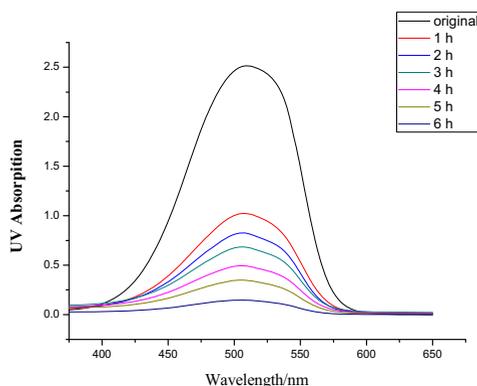## 3.4 Decomposition of Methyl Orange

Fig. 4 UV absorption of MO solution during the reaction

As shown in fig. 5a, the reaction rate in the first hour was the fastest and gradually slow down. Almost 70% of MO had been decomposed after 1 h, according to fig 4. And decomposition rate had been over 95% after 6 h. In contrast, only 6% of MO decomposed in the reaction without Fe_3O_4. Slightly rose of decomposition rate has been found from 93.3%, 98.0% to 99.7% with Fe_3O_4 concentration rise from 1%, and 2% to 4% (Fig. 5a). That may be caused by the difference in number of Fe_3O_4 nanoparticles on the surface of PolyHIPE. When the Fe_3O_4 concentration was low and increased from 1.0 % to 2.0 %, more Fe_3O_4 nanoparticles could be adsorbed on the interface. In comparison, when the concentration was increased to 4%, excess nanoparticles were likely to stay in the aqueous phase and immersed in the PAM backbone after polymerization. So the MO residual amount trended to be stable when Fe_3O_4 nanoparticles were over 2%. 5 batch of methyl orange decomposition reaction were taken place to measure the recyclability of PolyHIPE. The ecomposition rate of MO remained 97.5% even after 4 processes (Fig. 5b), which powerfully demonstrate that Fe_3O_4 loaded PolyHIPE monolith is a reusable and efficient supporter for MO decomposition reaction.
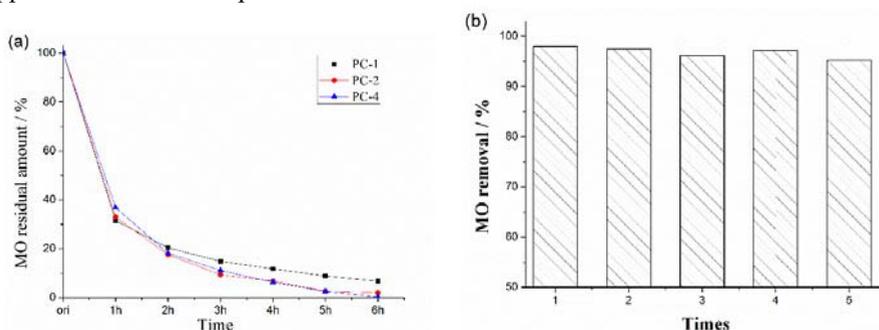

Fig. 5 Residual quantity of MO during the reaction in different PolyHIPE (a)

and MO removal in different batch using PC–2 as supporter (b)

4. Summary

Fe_3O_4 nanoparticles loaded interconnected porous PAM were prepared using HIPE stabilized by the mixture of Fe_3O_4 nanoparticles and Tween85 as templates. The morphology of this porous materials could be adjusted by simply changing Fe_3O_4 nanoparticles content, Tween 85 concentration or internal phase fraction. These porou PolyHIPE was proved to be an excellent supporter for MO decomposition thanks to the

interconnected porous structure and Fe_3O_4 on the surface.

5. Acknowledgements

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