Preparation of Macroporous Adsorbent Based on Montmorillonite Stabilized Pickering Medium Internal Phase Emulsions

F. Wang^{1,2}, Y. Zhu¹, W. Wang¹, and A. Wang¹(✉)

¹ Key Laboratory of Clay Mineral Applied Research of Gansu Province,
Center of Eco-Material and Green Chemistry,
Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences,
Lanzhou, People's Republic of China
aqwang@licp.cas.cn

² College of Petroleum and Chemical Engineering, Qinzhou University,
Qinzhou, People's Republic of China

Abstract. A macroporous material was prepared using oil-in-water Pickering medium internal phase emulsions (Pickering MIPEs) as template. The obtained macroporous materials with interconnected pore structure exhibited good adsorption capacities to Ce (III) and Gd (III) in water. The adsorption process could be achieved in 30 min, and the maximum adsorption capacities reached 230.64 mg/g for Ce (III) and 240.49 mg/g for Gd (III). Furthermore, the macroporous monolith exhibited excellent reuseability after consecutive adsorption-desorption cycles.

Keywords: Pickering emulsion · Medium internal phase emulsions · Rare metal · Adsorption · Porous material

1 Introduction

Compared with the conventional emulsion, Pickering emulsions exhibit peculiar long-term stability against droplet coalescence, in which the solid particles adsorbed at the oil-water interface act as a mechanical barrier to protect the dispersion phase liquid drops from the coalescence with the continuous phase (Tajik et al. 2017). Due to the unique properties, Pickering emulsions have been used as template to prepare porous polymer monoliths (Briggs et al. 2015). However, the dispersion phase of oil/water Pickering high internal phase emulsions mostly need a large amount of organic solvent, and thus it is indispensable to develop Pickering MIPEs by replacing poisonous organic solvent with low-cost and eco-friendly plant oil and reducing the internal phase volume.

Herein, monolithic macroporous materials were fabricated for adsorption of Ce (III) and Gd (III) based on Pickering MIPEs template, which was composed of the stabilizer of montmorillonite (Mt) and Tween-20 and the continuous phase of flaxseed oil. The effects of adsorption parameters including initial concentration and contact time on the adsorption properties were investigated, and the reusable performance of the adsorbent was also evaluated.

2 Methods and Approaches

Typically, macroporous carboxymethyl cellulose-g-poly(acrylamide)/montmorillonite (CMC-g-PAM/MMT) monolith was prepared based on Pickering MIPEs, which stabilized with 5% of Mt and 4% of Tween-20 (Wang et al. 2017). The obtained monolithic polymers were washed with acetone for 12 h and then immersed into 0.5 M NaOH aqueous alcohol solution ($V_{\text{water}}/V_{\text{alcohol}} = 3/7$) for 24 h to transfer the amide group to carboxyl.

The effect of the adsorption time and the initial concentration on the adsorption capacities were conducted according to the following procedure: 20 mg porous adsorbents were added into 25 mL Ce (III) and Gd (III) solution and shocked in a thermostatic shaker at 120 rpm and 30 °C for a given time. After the adsorption, the adsorbents were separated and the concentrations of the Ce (III) and Gd (III) were determined via UV-vis spectrophotometer using the chlorophosphonazo and azo arsine as the complexing agents, respectively. The adsorption capacities q_e (mg/g) of the porous monolithic adsorbents were calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e were the initial and equilibrium concentrations of Ce (III) and Gd (III) (mg/L), V (L) was the volume of the Ce(III) and Gd(III) solution.

The reusability studies were performed as follows: The adsorbents were desorbed by immersing 30 mL hydrochloric acid solution (0.5 M) for 2 h after adsorption, and then regenerated with 0.5 M NaOH solution. Finally, the adsorbents were filtered and washed to reach neutral using distilled water before next adsorption process. The adsorption-desorption cycle was repeated five times.

3 Results and Discussion

The representative images of macroporous monolith prepared by Pickering-MIPEs with 5% Mt and 4% Tween-20 as the stabilizer were shown in Fig. 1. The emulsions didn't flow in the inverted plastic centrifuge tube (Fig. 1a), indicating that the oil droplets were closely packed and the formed emulsion was a typical gel emulsion. The macroporous polymer monoliths of CMC-g-PAM/MMT were synthesized by free radical polymerization using APS as the initiator. The prepared wet monoliths were cut into pieces and Soxhlet extracted using acetone to remove the oil phase and surfactant, and then immersed into NaOH alcohol solution to complete hydrolysis of amide groups. Finally, the white monoliths of CMC-g-PAM/MMT were obtained after the dehydrated with acetone and dried in oven at 40 °C (Fig. 1b). The surface morphology of CMC-g-PAM/MMT was shown in Fig. 1c, and it presented a hierarchical pore structure with high connectivity. According to the statistical result of Image-Pro Plus 6.0 software, the average pore size of the macropore and the pore throat were 1.43 μm and 0.39 μm , respectively. Furthermore, the as-prepared porous materials exhibited narrow macropores and pore throats size distribution (Fig. 1d).

Fig. 1. Digital photographs of (a) the as-prepared Pickering MIPEs, (b) CMC-g-PAM/MMT monolith, (c) SEM image of porous CMC-g-PAM/MMT monolith and (d) pore size distribution of porous CMC-g-PAM/MMT

CMC-g-PAM/MMT monoliths were employed to remove of Ce (III) and Gd (III) from water. As shown in Fig. 2a and b, the adsorption capacities increased with the increase in the initial metal ions concentrations until the adsorption saturation was reached. The maximum adsorption capacities of the macroporous monoliths were 230.64 mg/g for Ce (III) and 240.39 mg/g for Gd (III). The higher adsorption capacity might be due to the sufficient functional groups and the highly interconnected pore structure. The effect of contact time of on the adsorption behavior was depicted in Fig. 2c and d. It was obvious that the porous monolithic adsorbent showed fast adsorption rate for Ce (III) and Gd (III), and the adsorption equilibrium could be reached within 30 min and 25 min Ce (III) and Gd (III), respectively. The macro-pores allowed fast and efficient mass transport, as well as provided sufficient contact between active groups and adsorbents, while the pore throats contributed to a high specific surface area.

Fig. 2. Effect of the initial concentration of (a) Ce (III) and (b) Gd (III) on the adsorption capacity of porous monolith. Adsorption kinetic curves of the porous monolith for (c) Ce (III) and (d) Gd (III).

4 Conclusions

Macroporous polymer monoliths of CMC-g-PAM/MMT were successfully synthesized by free radical polymerization based on based on Pickering MIPEs stabilized with 5% of Mt and 4% of Tween-20. The as-prepared macroporous polymer monoliths possessed a hierarchical pore structure and highly interconnection, which favored enhancing the adsorption properties to Ce (III) and Gd (III), such as high adsorption capacity, quick adsorption rate, and good reusability.

Acknowledgements. The authors are grateful for financial support of the Major Projects of the National Natural Science Foundation of Gansu, China (18JR4RA001) and the National Natural Science Foundation of China (21706267).

References

- Tajik S, Nasernejad B (2017) Surface modification of silica-graphene nanohybrid as a novel stabilizer for oil-water emulsion. *Korean J Chem Eng* 34:2488–2497
- Briggs NM, Weston JS, Li B, Venkataramani D, Aichele CP, Harwell JH, Crossley SP (2015) Multiwalled carbon nanotubes at the interface of Pickering emulsions. *Langmuir* 31:13077–13084
- Wang F, Zhu YF, Wang WB, Zong L, Lu TT, Wang AQ (2017) Fabrication of CMC-g-PAM/Pal superporous polymer monoliths via eco-friendly Pickering-MIPEs for superior adsorption of methyl violet and methylene blue. *Front Chem* 5:33

Open Access This chapter is licensed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license and indicate if changes were made.

The images or other third party material in this chapter are included in the chapter's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the chapter's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.