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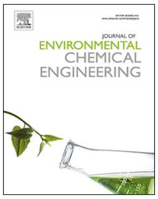

Fabrication of porous adsorbent *via* eco-friendly Pickering-MIPEs polymerization for rapid removal of Rb$^+$ and Cs$^+$

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ABSTRACT

A novel carboxymethylcellulose-*g*-poly(acrylamide)/montmorillonite (CMC-*g*-PAM/MMT) hybrid adsorbent with sufficient interconnected pores was prepared *via* the Pickering medium internal phase emulsions (MIPEs) polymerization using eco-friendly inolenic acid oil (IAO) as the disperse phase and MMT as the stabilized particles. The effects of the dosages of MMT and Pluronic F68 on the pore structures were studied. It was found that the well-defined pore structure was obtained when the amounts of MMT and Pluronic F68 were 2% and 6%, respectively. The FTIR spectra analysis showed that MMT participates in the polymerization reaction. The porous adsorbent can rapidly reach adsorption equilibrium within 30 min, with the maximum adsorption capacities of 177.90 mg/g for Rb$^+$ and 265.93 mg/g for Cs$^+$. The fitting results confirmed that chemisorptions play a crutial role in the adsorption process, and the complexation of COO$^-$ and Rb$^+$ or Cs$^+$ was the main driving force for adsorption. Cyclic adsorption experiment results in static and fixed bed column show that the porous adsorbent can be recycled for the adsorption of Rb$^+$ and Cs$^+$ ions. The new porous adsorbent has the potential for rapid adsorption and removal of metal ions such as radioactive Rb$^+$ and Cs$^+$.

1. Introduction

Emulsion polymerization is a simple, effective and relatively mild method of preparing a variety of porous materials with well controlled pore size, morphology, composition and spatial arrangement [1–3]. Among them, the high internal phase emulsions (HIPEs, the internal phase volume is larger than 74%) has attracted wide attention in recent years [4–6]. The porous materials could be obtained by the polymerization of the monomers in the continuous phase, followed by removing the dispersed phase. The HIPEs polymerization method is advantageous because it facilitates to the formation of uniform porous materials with high permeability and controlled pore size [7,8]. However, it still has some drawbacks, such as the toxic organic phase, the high internal phase ratio, poor mechanical properties, and so on [9,10]. Alternatively, the drawbacks can be effectively solved by reducing the internal phase volume from high to medium or low internal phase emulsion (MIPEs and LIPEs) whose dispersed phase volume fractions are comprised between 74 and 30 vol% and below 30 vol%, respectively [11,12].

But, the porous materials fabricated from MIPEs have closed-pore structure, which have the poor permeability and are unfit for using in the adsorption process [13]. So how to obtain the porous materials with interconnected pore structure *via* MIPEs has become a hot research topic. Luo et al. prepared a porous polymeric monolith with interconnected pore structure *via* miniemulsion template [14]. Compared with the porous materials prepared by conventional emulsion template which has micron-sized pore structure, the pore structure of porous material can be reduced to nanoscale. Manley et al. showed that by tailoring of the porosity and the interconnecting pore throat diameter of the macroporous polymers, the permeability can be adjusted in a wide range [15]. And the research result of Mathieu et al. proved that the surfactant is a vital factor for preparing polyMIPEs with interconnected porous structure [16]. But if using only the surfactant to stabilize the MIPEs, more surfactants are required. Besides, the residual surfactant, which influences the property of porous material, is also difficult to be removed after the polymerization. Compared with the emulsion stabilized by surfactant, the Pickering emulsion has the higher stability and the resulting porous materials can be endowed with novel function [17,18]. But the Pickering MIPEs, which is used to fabricate the porous material with interconnected porous structure, was rarely reported.

In this study, we have successfully prepared a novel porous material of carboxymethylcellulose-*g*-poly(acrylamide)/montmorillonite (CMC-

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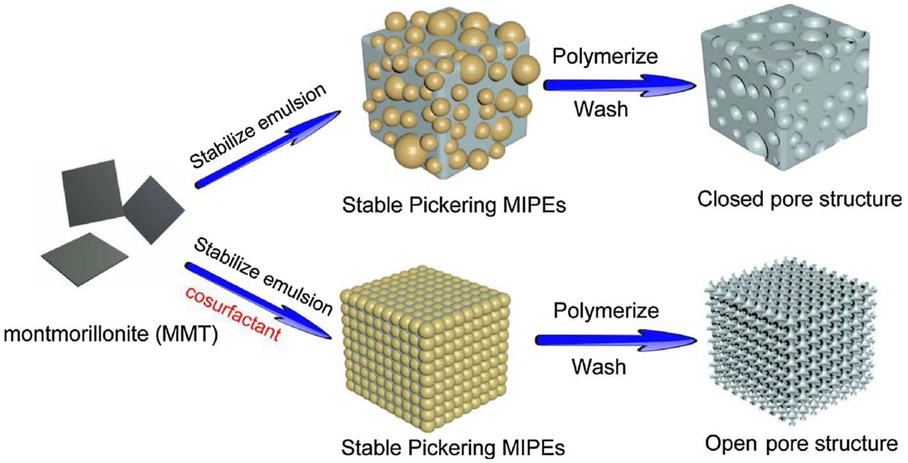

Scheme 1. Synthesis of the porous CMC-*g*-PAM/MMT *via* the Pickering MIPEs.

g-PAM/MMT) with interconnected porous structure by grafting AM onto CMC *via* O/W Pickering-MIPEs, and using MMT and inolenic acid oil (IAO) as the stabilizer and disperse phase, respectively (Scheme 1). The morphology of the porous material with or without the surfactant were characterized carefully and the adsorptive properties for the radioactive Rb^+ and Cs^+, which are the most hazardous and problematic for the environment as well as human health [19,20], were also evaluated. The effects of the adsorption capacity on the contact time, initial concentration, and initial pH were all studied intensively. Breakthrough studies were also carried out to evaluate the effect of process parameters, such as flow rate, adsorbent bed height and initial adsorbate concentration on the shape of breakthrough curves of the sorption of both ions onto prepared material.

2. Materials and methods

2.1. Materials

Sodium carboxymethylcellulose (CMC, chemically pure, the viscosity was 300–800 mpa·s) was purchased from J&K Scientific Ltd. (Beijing, China). Acrylamide (AM, chemically pure), *N, N'*-methylene-bis-acrylamide (MBA, chemically pure), ammonium persulphate (APS, analytically pure), RbCl (analytically pure) and CsCl (analytically pure) were all purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Inolenic acid oil (IAO, food grade) was purchased from Shanghai Drum Biotechnology Co., Ltd. (Shanghai, China). Pluronic F68 (biochemical reagent) was provided by Kangbaotai Fine-Chemical Co., Ltd. (Wuhan, China). Na-montmorillonite (MMT) with a cation exchange capacity (CEC) of 90 meq/100 g, specific surface area of 374 m^2/g was obtained from Zhejiang Fenghong New Material Co., Ltd. (Huzhou, China). Other reagents were all analytical grade and all solutions were prepared with distilled water.

2.2. Preparation of the CMC-g-PAM/MMT porous adsorbent via Pickering MIPEs

The O/W Pickering MIPEs was prepared by using IAO as the organic phase, the solution containing CMC, AM and MBA as the disperse phase, and MMT as the stabilized particles. Typically, 0.1 g of CMC, 0.5 g of MMT, 3.6 g of AM and a small amount of Pluronic F68 were added into 20 mL of distilled water in a beaker, and then 20 mL of IAO was added. The mixture was dispersed by a high-speed shearing homogenizer at the speed of 6000 rpm for 5 min to form thick MIPEs. After that, 100 mg of APS was added into the Pickering MIPEs under stirring at 20 rpm for 3 min. Then the Pickering MIPEs was transferred into the PE pipe, sealed, and kept at 60 °C for 12 h. The resultant product was washed with acetone *via* the Soxhlet extraction for 24 h to remove the residual surfactant and monomers. After that, the porous CMC-*g*-PAM/MMT was cut into slices and immersed into the solution of NaOH in ethanol/water ($V_{ethanol}/V_{water}$ = 7/3) to convert the amide group to carboxyl groups. The obtained porous adsorbent was dehydrated with absolute alcohol in the presence of zeolite 3A, and then dried under vacuum at 60 °C for 12 h.

2.3. Characterization

The surface morphologies of the porous material were observed on a Field Emission Scanning Electron Microscope (FE-SEM, JSM-6701F, JEOL, Japan). FTIR spectra were recorded on a Nicolet NEXUS FTIR spectrometer in the wavenumber region of 4000–400 cm^{-1} using KBr pellets. The pore size distribution was estimated by counting 200 pores using Image Pro Plu software, which provides the number distribution of pores. The hydrolyzing degree of the porous material was determined by elemental analysis.

2.4. Batch adsorption studies

Adsorption experiment was conducted by mixing 20 mg of the porous adsorbent with 25 mL of Rb^+ or Cs^+ solution, and then the mixture was shaken in a thermostatic orbital shaker (SHA-C, Changzhou Guohua Co., Ltd., China) at 120 rpm and 30 °C for a given time. The concentration of Rb^+ or Cs^+ in the solution was detected by using an atomic absorption spectrometry (AAS, TAS-990 Super, Beijing Purkinje General Instrument Co., Ltd. China). The adsorption capacity (Q_e) of the porous adsorbent for Rb^+ or Cs^+ can be calculated according to Eq. (1) based on the change of ion concentrations before (C_0) and after (C_e) adsorption.

$$Q_e = [(C_0\text{-}C_e) \times V]/m \tag{1}$$

Where, m was the amount of adsorbent (20 mg), V was the volume of Rb^+ or Cs^+ solution (25 mL). The effects of contact time, initial concentration, pH values on adsorption capacities were all studied, and the reusability was evaluated by conducting the adsorption-desorption process for five consecutive cycles. The adsorbed Rb^+ or Cs^+ was desorbed using 0.5 mol/L of HCl solution and the adsorbent was regenerated using 0.5 mol/L of NaOH solution.

The fixed bed adsorption experiment was conducted on an adsorption column with the length of 11.5 cm and the internal diameter of 1.70 cm, and the porous adsorbent was packed on a porous sintered glass disk at the bottom. Influent feed flow rate was supplied and maintained throughout the experiment process by the use of variable flow peristaltic pump. The column effluents were collected and the metallic ions content was determined using the AAS method (TAS-990 Super). The reusability of the adsorbent was evaluated by conducting