A versatile strategy to fabricate dual-imprinted porous adsorbent for efficient treatment co-contamination of λ-cyhalothrin and copper(II)

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ABSTRACT

Smart absorbents with high affinity to specific toxicant, especially with multi-affinity to both metal ions and organic pollutants, are very appealing for the treatment of heavy metal and organic co-contaminated water. A versatile strategy based on Pickering high internal phase emulsions (HIPEs) and controllable pore-filled technique was reported to fabricate molecule and ion dual-imprinted polymer adsorbent (M/I-DIPA). 2-Bromoisobutyryl bromide (BIBB)-modified silica nanoparticles (MSPs) were firstly employed to form Pickering HIPEs template, and then it was used to prepare λ-cyhalothrin (LC)-imprinted polymer foam (MIPA). Secondly, surface-initiated atom transfer radical polymerization (SI-ATRP) was adopted to controllably produce Cu(II)-imprinted adsorbent onto the MSPs which firmly "locked" in the MIPA shell. As-prepared M/I-DIPA effectively avoids the burying of recognition sites in a secondary imprinting process, and possesses highly permeable macroporous morphology. In batch mode experiments, M/I-DIPA exhibits fast binding kinetics (i.e. 60 min), and the maximum monolayer adsorption amount from Langmuir model for LC and Cu(II) are 120.8 $\mu mol\,g^{-1}$ and 101.7 $\mu mol\,g^{-1}$ at 35 °C, respectively, indicating this strategy makes the defined imprinted cavities well protected in twice imprinting steps. Moreover, LC and Cu(II) have both higher imprinting factor α (about two times) than the other structural analogues, and the excellent selectivity coefficient β in multi solute system also demonstrates the preferential affinity to templates (i.e. LC and Cu(II)) due to a good imprinting effect. The loss in adsorption amounts of M/I-DIPA for LC and Cu(II) at 120 min after four regeneration cycles are 7.295% and 13.05%, respectively, illustrating good retention of the activity of M/I-DIPA.

1. Introduction

In aquatic system, the co-contamination of heavy metals (e.g., Cu (II), Pb(II) and Cd(II), from industrial activities) and organic pollutants (e.g., pesticides, from traditional agriculture) has always been a threat to the environment and human health due to their co-toxicity and persistence in nature [1–3]. Various methods, including chemical precipitation, ion exchange, reverse osmosis and extraction, have been developed to remove the two kinds of pollutants before discharging them into the environment [4–7]. However, such conventional techniques can only apply to removing either metal ions or organic pollutants. Combination of the above methods can realize sequential removal but still suffer from many disadvantages, such as complicated process, high cost, underutilization and possible secondary pollution [8,9]. From the view of environment and economy, simultaneous removal of heavy metal and organic pollutants from co-contaminated wastewater shows great promise in the field of water treatment. However, it is still a challenge if only relying on the above-mentioned separation techniques.

Adsorption of metal ions or organic pollutants by means of specific materials has been considered as one of the effective methods for wastewater treatment due to the flexibility in material design, the simplicity of operations, and reusability [10–12]. To date, many absorbent materials, including graphene oxide (GO) [13], mesoporous carbon [14], ferrihydrite [15] and chitosan [16], have been designed to remove pollutants but still limited by their low recognition, slow binding kinetics, and in particular, the monotonous removal ability towards either metal ions or organic pollutants. Therefore, smart absorbent materials with high affinity to specific toxicant, especially with multi-affinity to both metal ions and organic pollutants, are very appealing for the treatment of heavy metal and organic co-contaminated water [17,18].

Molecule or ion imprinting technique is well known as an efficient approach to creating tailor-made recognition sites in cross-linked polymer matrices with high affinity towards targeted molecule or ion [19–21]. Due to the reversible nature of recognition sites in

noncovalent molecular imprinting, such molecule or ion imprinted polymers have showed great promise as reusable adsorbents for recognition and separation of organic molecules (e.g., pesticides and antibiotics, etc.) [22–24] and metal ions (e.g., Cu(II), Pb(II) and Sr(II), etc.) [25–27] from water samples. However, molecule and ion dual-imprinted adsorbents that could simultaneously remove both heavy metal and organic pollutants from co-contaminated water remain a hard nut to crack, probably due to the complexity to fabricate dual-recognition sites (e.g., the burying of recognition sites in a secondary imprinting process).

Herein, we reported a twice imprinting strategy to fabricate molecule and ion dual-imprinted polymer adsorbent by the combination of Pickering high internal phase emulsions (HIPEs) and controllable pore-filled technique [28]. To demonstrate the proof-of-principle of our strategy for subsequent treatment of heavy metal and organic co-contaminated water, a pyrethroid pesticide (λ-cyhalothrin, LC) and a toxic metal ion (Cu(II)) were chosen as the template molecule and ion, respectively. In our design, 2-bromoisobutyryl bromide (BIBB)-modified silica nanoparticles (MSPs) were employed to form the Pickering HIPEs template. Thereby, a LC-imprinted polymer foam with hierarchical porous was firstly prepared via Pickering HIPEs polymerization. Through the BIBB on the inner porous surface, a Cu(II)-imprinted polymer layer was then grafted into the pore via a surface "living"/ controlled radical polymerization, i.e., controllable pore-filled strategy [29]. In contrast to previous dual-imprinting, the combination of Pickering HIPEs and controllable pore-filled strategy could not only obtain porous adsorbent with dual-recognition sites but also efficiently reduce the burying of recognition sites during a secondary imprinting. Therefore, this study will provide an efficient approach to fabricating molecule and ion dual-imprinted adsorbents that could simultaneously remove heavy metal and organic pollutants in co-contaminated water.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS), 3-aminopropyltriethoxysilane (APTES), tetrahydrofuran (THF), N,N′,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA), 4-vinyl pyridine (4-VP), triethylamine (TEA, ≥99%), 2-bromoisobutyryl bromide (BIBB), divinylbenzene (DVB), styrene (St), acrylamide (AM), cyclohexanone (CYC) and diethyl phthalate (DP) were supplied by Aladdin Industrial Corporation (Shanghai, China). Methylacrylic acid (MAA), rhodamine B, α,α′-azoisobutyronitrile (AIBN), λ-cyhalothrin (LC), fenvalerate (FEN), HPLC-grade methanol, $CuBr_2$, CuBr, $CaCl_2$, $NiCl_2·6H_2O$, $Ce(NO_3)_3·6H_2O$, and $Cd(NO_3)_2·4H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Hypermer 2296 were kindly supplied by Foshan Excel Chemical Co., Ltd. (Fujian, China).

2.2. Characterization

The morphology and structures of different as-prepared adsorbents was examined by scanning electron microscopy (SEM, S-4800), and elemental analysis of imprinted and porous adsorbents was measured by Energy Dispersive Spectrometer (EDS) and SEM mapping. Fourier transform infrared spectra (4000–400 cm^{-1}) for various samples were recorded on a Nicolet Nexus 470 FTIR apparatus (U.S.A.), and the samples were prepared by mixing the products with KBr and pressing into a compact slice. X-ray photoelectron spectroscopy (XPS) was performed to investigate the surface chemical composition of various synthesized materials. The static water contact angle was measured by using a KSV CM200 contact angle instrument (Finland). The metal ions were determined by TAS-986 flame atomic adsorption spectrometer (FAAS) (Beijing, China), and LC was tested by UV–vis spectrophotometer at the detection wavelength of 278 nm.

2.3. Synthesis of BIBB-modified silica nanoparticles (MSPs)

The SiO_2 particles with the average diameter of 200 nm were prepared by base-catalyzed hydrolysis and condensation of the TEOS according to the Stöber method [30]. In brief, TEOS was added into a solution of deionized water (10 mL), ethanol (90 mL) and ammonia (3.14 mL) in a 250 mL round flask, and then the mixture was stirred at 30 °C for 1.0 h. By centrifugation at 8000 rpm for 6.0 min, the collected SiO_2 particles were washed with ethanol and water, and the resulting product was dispersed in 60 mL of ethanol. Secondly, the grafting of APTES onto SiO_2 particles surface was carried out via the method described by Simon [31]. Ethanol (30 mL) and ammonia (15 mL) was added into 30 mL of the colloidal dispersion in a 100 mL round flask, and the mixture was heated to 40 °C and stirred at 100 rpm for 2.0 h. 20 mL of APTES solution (10 mL) in ethanol was added dropwise into the reaction mixture, and the turbid suspension was allowed to react for 12 h at 40 °C with stirring. After centrifuging and washing with deionized water, ethanol and THF, SiO_2-NH_2 were dispersed in 60 mL of THF by ultrasonication. Subsequently, the products (i.e. SiO_2-NH_2) were used to synthesize the MSPs in the presence of BIBB·THF (10 mL) and TEA (12.5 mL) were added into 30 mL of SiO_2-NH_2 dispersion, and the mixture was treated by ultrasonication for 10 min and then kept at 0 °C. After 2.0 h, a pre-mixed solution of BIBB (1.0 mL) in 10 mL of THF was added dropwise. After a further 10 min, this reaction was stirred under continuous N_2 presence for 24 h at 25 °C. The mixture was repeatedly washed with THF, ethanol and water, respectively. Finally, the product (MSPs) was placed in a vacuum oven at 60 °C for 24 h.

2.4. Preparation of molecularly imprinted porous adsorbent (MIPA)

MIPA was prepared by water in oil (W/O) Pickering HIPEs template stabilized by MSPs (Scheme 1), which followed a literature method with slight modifications [32,33]. Briefly, AM (40 mg), MAA (400 μL), LC (60 mg), St (2.5 mL) and DVB (2.0 mL) were firstly added into a 100 mL flask, and then the formed mixture was ultrasonicated for 30 min in an ice-water bath. After that, this mixture was stored in the dark at room temperature under nitrogen atmosphere overnight for the self-assemble between template molecule LC and functional monomer. Then, Hypermer 2296 (1.0 mL) and AIBN (60 mg), as the assistant emulsifier and initiator, respectively, were added into the mixture of monomers and LC to form the organic phase (external phase). Subsequently, 0.25 g of MSPs as the main emulsion stabilizer was dispersed in 0.27 M $CaCl_2·2H_2O$ aqueous solution (25 mL) ultrasonic bath, and the obtained mixture was considered as the water phase (internal phase). Under vigorous stirring at 600 rpm in an ice-water bath, the water phase was injected into the organic phase dropwise, and the W/O Pickering HIPEs were formed due to the mechanical stirring. Eventually, the formed emulsion templates were transferred into a thick-walled glass tube and polymerized at 70 °C for 24 h. The resulting MIPA was washed with acetone in soxhlet extraction to remove residual monomers and surfactant. After that, the template molecule LC was removed by the mixture of methanol/acetic acid (9:1, V/V) until no LC was tested by UV–vis spectrophotometer in the eluent. Finally, the purified MIPA was dried at 60 °C for 24 h. As compared, non-imprinted porous adsorbent (NIPA) were also synthesized in parallel but without the addition of LC. In addition, a portion of MIPA was dipped into HF solution (10 wt%) for 30 min, and then the product (MIPA-HF) was washed and dried.

2.5. Preparation of molecule/ion dual-imprinted porous adsorbent (M/I-DIPA)

In the surface-initiated atom transfer radical polymerization (ATRP) for molecular imprinting, BIBB bound-silica nanoparticles (i.e. MSPs), which were located on the surface of MIPA or NIPA were the macro-initiator [34]. The catalyst system was composed of CuBr and PMDETA,