

THE EFFECT OF KH570 CONTENT ON THE PREPARATION OF MOLECULAR IMPRINTED MATERIALS

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Introduction

Molecularly imprinted polymers (MIPs) can be prepared by copolymerizing a mixture of monomers and cross-linkers in the presence of a template molecule. After removing the template, cavities are left in the polymeric matrix with the shape complementary to the template. These recognition sites enable the polymer to rebind the imprinting species from a mixture of closely related compounds by specific selectivity. MIPs are very attractive because of their unique pre-determinative characteristics, and their specific and practical abilities for template molecule recognition. The first molecularly imprinted sorbent assay was reported in 1993 [1]. Nowadays, MIPs have been used in a variety of applications such as chromatographic stationary phases [2], immunoassay-type analyses [1] and sensor development [3]. In the present work, we used a surface imprinting technique to obtain the MIP-PAMPS/CMSs for selectively combining dibenzothiophene (DBT), which is very hard to remove in deep desulfurization. The effect of KH-570 content on the preparation was mainly investigated.

Experimental

The process for preparation of MIP-PAMPS/CMSs is shown in Fig.1. CMSs were synthesized by chemical vapor deposition (CVD) [4] (C_2H_2 as carbon sources, Ar as carrier gas), then dispersed in mixed acids (96 wt% H_2SO_4 and 65 wt% HNO_3 in volume ratio 3:1) at $70^\circ C$ under ultrasonication for 1 h. The products were diluted in water, filtered until the pH value approached to neutrality, and then dried. The oxidized CMSs were modified by silanisation with KH570, which supplies double bonds for CMSs. Different amount of KH570 (1ml, 2ml, 3ml) was added to 0.3g of oxidized CMSs separately and stirred for 2h at $65^\circ C$ for silanization. The products were filtered, washed with ethanol, then dried at $50^\circ C$ overnight.

AMPS(2-acryloylamino-2-methyl-1-propanesulfonic acid) was grafted as the functional monomer to the surface of silanized CMSs by initiating with $(NH_4)_2S_2O_8$ in water under N_2 atmosphere at $70^\circ C$ for 12h. The particles were extracted with water to remove the polymers physically attached to the particles, then dried to obtain PAMPS/CMSs.

MIP-PAMPS/CMSs were prepared by crosslinking reaction. DBT as template and PAMPS/CMSs were added to a flask. After ultrasonication for a while, EDMA (ethylene dimethacrylate) was added at $50^\circ C$ for 12h. A mixture of methanol and acetic acid (volume ratio 9:1) was used to remove DBT from the cross-linked network.

An aliquot of 0.06 g of MIP was added in a 50 ml centrifugal tube, containing 25 ml of 1 mmol/L DBT in normal hexane. After vibrating the tube for 5 h, the concentration of DBT in filtered liquor was measured.

Fourier transform infrared (FTIR) spectrometry and scanning emission microscopy (SEM) were used to characterize the changes in chemical structure and surface morphology of the CMSs after each step. UV-Vis spectrophotometry was used to examine the concentration of DBT. The absorbance (Q , mg/g) of MIP-PAMPS/CMSs towards DBT was calculated according to

$$Q = 184.26 \times \frac{V(C_0 - C)}{m} \quad (1)$$

Where 184.26 is the molecular weight of DBT; C_0 (mmol/l) is the initial concentration of DBT and C is the DBT concentration after adsorption; V (l) is the volume of the DBT solution; m (g) is the mass of the MIP-PAMPS/CMSs;

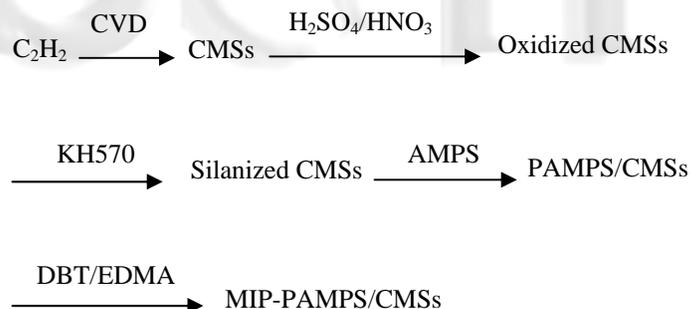


Fig. 1 The process for preparation of MIP-PAMPS/CMSs

Results and Discussion

Fig.2 shows the SEM images of the CMSs at different processing steps. The oxidized CMSs (Fig.2a) after the treatment of mixed acid showed good dispersion with few agglomerates. When 1 ml of KH570 was added, the presence of Si was proved by the EDS spectra on upper right corner of Fig. 2b, indicating that KH570 was grafted on the surface of CMSs. With the increase of the content of KH570, silanized CMSs showed more agglomeration (Fig.2c and Fig.2d). Fig.2e shows the image of PAMPS/CMSs particles, and Fig.2f shows

MIP-PAMPS/CMSs particles with significant agglomeration because of crosslinking reaction.

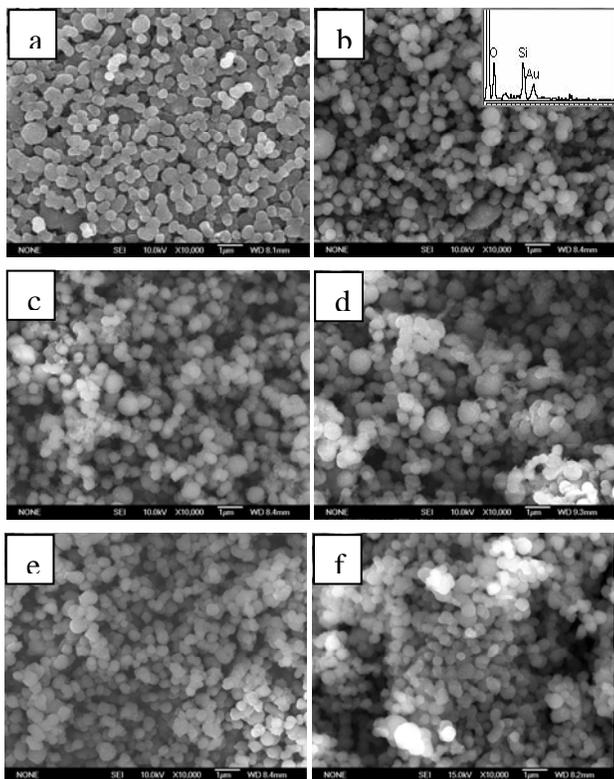


Fig. 2 SEM images of oxidized CMSs (a), 0.3 g of silanized CMSs with 1 ml of KH570 (b) (EDS spectra on the upper right corner), 2 ml of KH570 (c), and 3 ml of KH570 (d), PAMPS/CMSs (e) and MIP-PAMPS/CMSs (f)

Fig.3 shows the FTIR spectra of the CMSs obtained at different processing steps. For the oxidized CMSs (Fig.3a), the band at 3450 cm^{-1} was attributed to the presence of hydroxyl groups (-OH) on the surface of the CMSs, another band at 1622 cm^{-1} was assigned to the C=O stretching vibrations. In the silanized CMSs (Fig.3b), the band at 3440 cm^{-1} became weaker as a result of the reactions between -OH groups on the surface of CMSs and Si-OH of the KH570 molecules. In Fig.3c, with the grafting of AMPS, bands at 1039 and 1221 cm^{-1} were attributed to aliphatic S-O stretching vibrations of -SO₃H groups in PAMPS units, and the characteristic absorption of carbonyl groups at 1650 cm^{-1} was overlapped and enhanced by the bending vibration of amide groups (1650 cm^{-1}) originated from PAMPS.

The concentration of DBT as measured by UV-Vis spectrophotometry was 0.86 mmol/l after absorption for 5 h. According to Eq. (1), the adsorbance (Q , mg/g) of MIP-PAMPS/CMSs was 10.7 mg/g .

Conclusion

CMSs were synthesized by CVD, and oxidized by mixture acids. Different amount of KH570 were added separately to silanize the CMSs. The addition of 1 ml of

KH570 gave the CMSs with good dispersion and little agglomeration. MIPs on the surface of CMSs were synthesized with DBT as template molecule, AMPS as functional monomer, EDMA as cross-linker and (NH₄)₂S₂O₈ as initiator. The MIP-PAMPS/CMSs showed a good capacity for DBT.

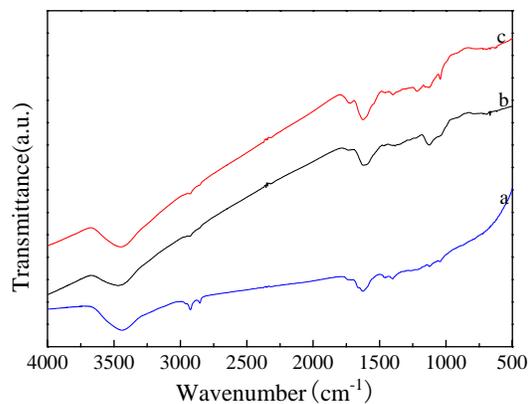


Fig. 3 FTIR spectra of the oxidized (a), silanized CMSs (b) and PAMPS/CMSs(c)

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