SUPPLEMENTARY MATERIAL

Synthesis, characterization and application of a novel mercapto- and new kind of polyaminophenol-bifunctionalized MCM-41 for dispersive micro solid phase extraction of Ni(II) prior to inductively coupled plasma-optical emission spectrometry (DMSPE-ICP-OES)

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1S. The FT-IR spectrum of Ni(II) complex

Fig.1S. FT-IR spectra of Ni(II)-EP4NP complex.

2S. The N₂ adsorption-desorption isotherms

The nitrogen adsorption-desorption isotherms for mesoporous silicas are shown in Fig 2S. They all displayed type IV isotherms with a capillary condensation step as a major feature of the mesoporous structure, according to the classification of the International Union of Pure and Applied Chemistry. The volume adsorbed for all isotherms increased sharply at a relative pressure (P/P_0) of approximately 0.3, which represents capillary condensation of nitrogen within the uniform mesopore structure. The volume of nitrogen adsorbed decreased with functionalization, which is indicative of a reduction in pore size. The specific surface area of mesoporous silicas MCM-41 was calculated by employing the Brunauer-Emmet-Teller (BET) method in the range of relative pressure from 0.1 to 0.4. The porosity of the MCM-41 samples was evaluated using N₂ adsorption isotherms. The pore volume and average pore diameters of mesoporous silicas were calculated using the Barrett-Joyner-Halenda (BJH) model of the adsorption branch. The specific BET surface area, average pore diameters and pore volume of the MCM-41 materials are presented in Table 1. The obtained results indicate that the BET surface area and total pore volume decreased after chemical modification and incorporation. That is because the mercaptopropyle chains were grafted to the surface of hexagonal channels and then aided the stable and strong incorporation of the EP4NP via SH-NH interactions. It was observed that in the absence of MPTMS, the incorporation of EP4NP is not so stable and can be leached by HCl 1 mol L⁻¹. However, the resulting issue of the chemical modification and incorporation steps is the occupation of the interior space of hexagonal pores.

Fig 2S. Nitrogen adsorption-desorption isotherm of calcined-MCM-41(a), MPTMS MCM-41 (b) and EP4NP-MPTMS-MCM- 41(c).

3S. The FT-IR investigation of silicas mesoporous materials

The FT-IR patterns of surfactant-containing MCM-41, calcined-MCM-41, MPTMS-MCM-41 and EP4NP-MPTMS-MCM-41 are shown in Fig 3S. The main characteristic of the MCM-41 spectra include a large broad peak between 3400 and 3200 cm^{-1} , which is attributed to O-H stretching of the surface silanol groups and the remaining adsorbed water molecules. The broad and strong peak centered at 1100 cm^{-1} is related to siloxane groups (-Si-O-Si-). The stretching band of Si-O bond of silanol groups appeared at approximately 900 cm^{-1} . The absorption band at approximately 1650 cm^{-1} is due to deformation vibrations of adsorbed water molecules [40]. The surfactant-containing MCM-41 showed two strong bands at 2851 and 2920 cm^{-1} due to C-H vibrations of the surfactant CTAB. Therefore, major characteristics of the surfactant disappeared after calcinations of surfactant-containing MCM-41 at 550 °C (see Fig 3S. b). The MPTMS-MCM-41 and EP4NP-MPTMS-MCM-41 hybrid materials showed characteristic bands for C-H stretching vibrations at around 3000-2800 cm^{-1} that confirmed grafting and incorporation of MPTMS and EP4NP into calcined MCM-41. However, in the case of EP4NP-MPTMS-MCM-41, the band of C=C of EP4NP may be overlapped with the broad vibration of Si-O-Si. Therefore, the observation of C-H vibrations in modified materials in FT-IR patterns and MPTMS-MCM-41 color change from white to brown EP4NP-MPTMS-MCM-41 (Fig 3S, inset), confirmed the presence of two modifiers in ordered structure of MCM-41.

Based on all of the obtained results and data, it can be concluded that the ordered calcined MCM-41 was successfully functionalized and incorporated by MPTMS and EP4NP, respectively.

Fig. 3S. FT-IR spectra of surfactant-containing MCM-41 (a) calcined-MCM-41 (b), MPTMS-MCM-41 (c) and EP4NP-MPTMS-MCM-41 (d).