SIMULTANEOUS SOL GEL AND IONIC IMPRINTING PROCESS IN THE SYNTHESIS OF ORGANO-SILICA HYBRID FOR SELECTIVE ADSORBENT OF TRANSITION METALS

ABSTRACT

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Synthesis of an organo-silica hybrid imprinted with Cd(II) and Cu(II) ions using 3-aminopropyltrimethoxysilane (3-APTMS) and 3-mercaptopropyltrimethoxysilane (3-MPTMS) compounds with precursor of tetraethyl orthosilicate (TEOS) as the silica source and metal ion solutions as the imprinting ions was carried out through simultaneous sol gel and ionic imprinting process. Several variables including sol-gel media, metal ion concentrations, and metal ion elution were evaluated. The characterizations of the ionic imprinted materials were performed through identification of functional groups, surface morphologies and elemental compositions, specific surface area, as well as metal concentrations. Adsorption properties studied on ionic imprinted amino-silica hybrid of Cd(II) (*i*-Cd-HAS) and Cu(II) (*i*-Cu-HAS) as well as ionic imprinted mercapto-silica hybrid of Cd(II) (*i*-Cd-HMS) material include medium optimum acidity, rate and adsorption mechanism, capacity and adsorption energy, selectivity, chemical stability, reusability, adsorption mechanism, characteristics of multi-metal adsorption-desorption, and preconcentration of trace level of metal ions.

The synthesis of the organo-silica hybrid material used water-ethanol media in a volume ratio of 1 : 1 resulting a bonding and a releasing an optimum template ion by using an eluent of 0.1 M Na_2EDTA-0.5 M HCl. The interaction contribution of the metal ions (templates) in the ionic imprinted HAS and HMS material was dominated by a covalent and an electrostatic interaction, with the value of 43.06 ± 0.42 and 50.91 ± 0.25 % on Cd-HAS, 40.96 ± 0.21 and 54.87 ± 0.20 % on Cu-HAS, and 35.24 ± 0.33 and 61.57 ± 0.09 % on Cd-HMS, respectively.

The adsorption of Cd(II) ion on *i*-Cd-HAS was optimum at pH 5, those of Cu(II) ion on *i*-Cu-HAS and Cd(II) ion on *i*-Cd-HMS were optimum at pH 6. The adsorption kinetics of Cd(II) ion on *i*-Cd-HAS and Cu(II) ion on *i*-Cu-HAS followed the first order kinetic up to equilibrium, as well as Cd(II) ion on *i*-Cd-HMS followed the pseudo second order kinetic model. The adsorption isotherm of Cd(II) ion on *i*-Cd-HAS, Cu(II) ion on *i*-Cu-HAS, and Cd(II) ion on *i*-Cd-HMS followed Langmuir adsorption isotherm model with the adsorption capacities of 43.40 - 62.10, 50.84 - 71.40, and 65.74 - 83.89 mg g^{-1}, respectively, and these were higher than the adsorption capacities of HAS and HMS without ionic imprinting. Materials of *i*-Cd-HAS, *i*-Cu-HAS, and *i*-Cd-HMS were stable in an acid condition because of protonation and lack of stability in a base condition. The data of adsorption selectivity showed that the ionic imprinted material was more selective than HAS and HMS materials and it can be reused for 4–5 times. The adsorption mechanism of Cd(II) ion on *i*-Cd-HAS, Cu(II) ion on *i*-Cu-HAS, and Cd(II) ion on *i*-Cd-HMS were dominated by the formation of hydrogen bonding. The ionic imprinted material has the metal ion adsorption recovery of 94.50 ± 1.32; 99.86 ± 0.14; 99.90 ± 0.10% for *i*-Cd-HAS, *i*-Cu-HAS and *i*-Cd-HMS respectively, with the metal ion initial concentrations of 10.0 μg L^{-1}.

Key word : ionic imprinted, organo-silica hybrid, sol-gel, selective adsorbent