SYNTHESIS AND APPLICATION OF CYCLIC TETRAMERS CALIXRESORCINARENES, ALKOXYCALIXARENES, AND ALKENYLCALIXARENES SERIES FOR ADSORPTION OF HEAVY METAL CATIONS

by
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NIM.03/1287/PS

Abstract

This dissertation is an account of the synthesis and characterization of calix[4]resorcinarene, alkoxycalix[4]arene, and alkenylcalix[4]arene series, as well as their application for adsorption of Cr(III), Cu(II), Pb(II), Cd(II), Hg(II), and Ag(I) heavy metals, conducted in batch and fixed bed column systems.

Synthesis of calixarenes in C-alkylcalix[4]resorcinarene series was conducted via 1 or 2 reaction stage(s) of resorcinol and various aldehydes. Synthesis of some calixarenes in calix[4]resorcinaryl acetate series was carried out via acetylation, whereas for aminomethylcalix[4]resorcinarene series, it was conducted via Mannich reaction toward some C-alkylcalix[4]resorcinarenes. Some calixarenes in alkoxycalix[4]arene series were synthesized through alkoxybenzyalcohol route consisted of 2 or 3 reaction stages. Synthesis of 4-allylcalix[4]arene (AKA) was conducted through 4-t-buthylphenol route consisted of 4 reaction stages, whereas polymonoallyloxycalix[4]arene (PMAKA) was synthesized via 6 reaction stages. All the synthesized calixarenes and their precursors were analyzed using IR spectrometer, GC-MS, ^{1}HNMR and/or ^{13}CNMR spectrometer.

In batch system, the adsorption experiments were done in three conditions, i.e. variation of pH, shaking time, and adsorbent dose. In addition to obtain optimum conditions of the adsorptions, the experiments were conducted to study kinetics and equilibrium of the adsorptions. In fixed bed column system, the experiments were conducted to establish breakthrough curve. Based on the breakthrough curve, column efficiency, adsorption capacity, some parameters of mass transfer (H_U, H_{UNB}, and $K_c a$), and adsorption kinetics were then determined. The effect of flow rate difference and initial concentration of the feeding solution was studied as well. Desorption process was done sequentially using water and followed by 1N HCl solution.

There were 6 (CMKR, CMFKR, CHFKR, CHMFKR, CBFKR, and CEKMFKR), 4 (CMKRAS, CMFKRAS, CHFKRAS, and CHMFKRAS), and 5 (TDEACMKR, TDMACMKR, NPOCMKR, TDEACMFKR, and NPOCMFKR) calixarenes that had been synthesized in C-alkylcalix[4]resorcinarene, calix[4]resorcinaryl acetate, and aminomethylcalix[4]resorcinarene series, respectively. In the case of alkoxycalix[4]arene series, 3 calixarenes have been synthesized, namely TEK, TMK, and TBK. Furthermore, AKA has been

synthesized through 4-*t*-buthylphenol route consisted of 4 stages. In the reaction route of PMAKA synthesis, 5 precursor calixarenes have been synthesized. The produced calixarenes varied in yield, from low to high. There were 4 selected calixarenes utilized as adsorbents, i.e. CMKR, CMFKR, CHFKR, and CHMFKR.

The adsorption experiments in batch system figured out that acidity level affected the adsorption significantly, compared with shaking time and adsorbent dose. Generally, adsorptions reached their optimum condition at moderate acidity level (pH = 4-6). The parameter that is related to adsorption equilibrium result in batch and fixed bed column systems, such as adsorption capacity (q and X_m), was determined by the suitability of hard-soft acid-base character. On the contrary, the parameters related to adsorption kinetics process, such as adsorption rate, coefficient of mass transfer, and adsorption mechanism, were affected by the suitability of size between adsorbent and adsorbate, and the existence of hydroxyl group, which was a strong electron donating (strong base). Based on the desorption test, adsorptions were dominated by chemisorptions. The tested adsorbents apparently did not adsorb the heavy metals selectively.