

# THE STUDY OF KINETICS, EQUILIBRIUM, AND MECHANISM OF HEAVY METAL CATION ADSORPTION ONTO CALIX[4]ARENE POLYHYDROXY

Ratnaningsih E. Sardjono\*, Fitri Khoerunnisa, Soja S. Fatimah

Chemistry Department, Indonesia University of Education

\*ratnaeksa@yahoo.com

## Summary

Heavy metal adsorption was a common and effective process to reduce its concentration in effluent. The using of polyhydroxy calix[4]resorcinarene as heavy metal cation adsorbent was a new activity, and theoretical studies to know the adsorption kinetics, equilibrium (isotherm), and mechanism of heavy metal cation (soft, borderline and hard acid) onto four of polyhydroxy calix[4]resorcinarene can explained the adsorption phenomenon clearly. There were four adsorbent of polyhydroxy calix[4]resorcinarene, i.e. C-methyl calix[4]resorcinarene (CMKR), C-4-hydroxyphenyl calix[4]resorcinarene (CHFKR), C-4-methoxyphenyl calix[4]resorcinarene (CMFKR), and C-4-hydroxy-3-methoxyphenyl calix[4]resorcinarene (CHMFKR), and six heavy metal cations, i.e. Cr(III), Cu(II), Pb(II), Cd(II), Hg(II), dan Ag(I). The effects of pH, time, and adsorbent weight on the uptake of metal ions have been studied. Kinetics studies was investigated at different interaction time, the equilibrium (isotherm) was studied at variation of adsorbent weight, and the mechanism was studied by sequential adsorption. The optimum pH was found to be 4 - 5.5. Different kinetics models have been applied to fit the experimental kinetics data. Kinetics studies of Lagergren pseudo first order and Ho pseudo second order kinetic models showed that all of the studied adsorptions followed pseudo second order model kinetics. The highest rate constant was showed by the adsorption of Ag(I) onto CHFKR. It was possibly due to the best size suitability and the characteristic of the adsorbent which had abundant hydroxyl groups. The equilibrium (isotherm) data of the adsorption studied were analyzed by using Langmuir, Freundlich, and D-R (Dubinin-Radushkevich) isotherms. The experimental data were found to fit well on Freundlich and D-R isotherm models. The highest value of  $X_m$  (maximum adsorption capacity) calculated by D-R isotherm equation was given by the adsorption of Cr(III) onto CHMFKR. Among all of the studied adsorbate and adsorbent, Cr(III) had characteristic as the hardest acid, and CHMFKR as the hardest base. The sequential desorption was conducted by using aquades and 1M HCl solution to recover the column. Generally, aquades leached Pb(II) poorly, whereas 1 M HCl solution leached Pb(II) completely, except for Pb(II) desorption from CHFKR. Based on the desorption test, adsorptions of Pb(II) onto CMFKR, CHFKR, CHMFKR and CMKR were dominated by chemisorptions (about 90%), both via ion exchange and hydrogen bond mechanism. On the contrary, physisorptions ruled adsorption in little portions (less than 10%). Especially for Pb(II) adsorption onto CHFKR, there was 30% of adsorption mechanism estimated via unknown mechanism (possible chelate formation). The parameter of adsorption equilibrium result, i.e. adsorption capacity, was determined by the suitability of hard-soft acid-base character. On the contrary, the parameters of kinetics adsorption process, such as adsorption rate, and adsorption mechanism, were affected by the suitability of size between adsorbent and adsorbate, and the existence of hydroxyl group, which was strong electron donating (strong base).