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Effect of the homoionic form of clinoptilolite on Ni2+ adsorption isotherms: A thermodynamic study

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2012-07-06
http://hdl.handle.net/10539/11630

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ABSTRACT

This study investigates the effect of zeolite modification on Ni^{2+} removal from synthetic wastewaters. In this study sorptive removal of nickel ions from solutions containing 1-100mg/L using natural and pretreated clinoptilolite (Na^{+}, K^{+}, and Ca^{2+} homoionic forms) was investigated. The natural clinoptilolite (from Kwa-Zulu Natal, South Africa) was pretreated with 2M metal chlorides for 24 hrs to yield near homoionic Na, K, and Ca-forms. Experiments were carried out as a function of solute concentration and different zeolite masses. The equilibrium distribution was determined by contacting tared amounts of clinoptilolite (2g batches to 100mL of solution) with a known concentration of Ni^{2+} until equilibrium was reached. The natural and pretreated clinoptilolite samples were structurally studied using X-ray fluorescence (XRF), X-ray diffraction (XRD), BET, FTIR and scanning electron microscopy (FIB/SEM). The cation exchange capacity of this zeolite was determined to be 2.45×10-3 eq/g from XRF major elemental analysis. The equilibrium concentration of the solution was analysed for Ni^{2+} using Atomic Absorption Spectroscopy and results presented by plotting ion exchange isotherms. A comparison of the isotherms for the Na^{+}-Ni^{2+}, K^{+}-Ni^{2+}, Ca^{2+}-Ni^{2+} and natural-Ni^{2+} systems gave us insight into how the displaced ion affects the selectivity of the clinoptilolite for Ni^{2+}.The Na, K and natural forms presented highly selective convex isotherms whereas the Ca-form has a concave graph suggesting that the selectivity series is Ca^{2+}> Ni^{2+}> (Na^{+}, K^{+},

Natural). Fitting of the Langmuir and Freundlich isotherms to experimental data gave good fits, R^2 values ranging from 0.9 – 0.99. Thermodynamic parameters revealed that the Ni^{2+} sorption capacity increases as the values of K_{eq} and $\Delta G°$ increase with increasing temperature from 25 to 75°C. The $\Delta G°$ values were all negative except for calcium exchanged clinoptilolite at 25 and 35°C, where the $\Delta G°$ values were positive 3.098kJ/mol and 0.527kJ/mol respectively. $\Delta H°$ was positive for all forms of clinoptilolite and ranged from 18.72 to 42.05 kJ/mol, this provides an indication that the sorption reaction is endothermic for Ni(II). The values of $\Delta S°$ for Ni^{2+} sorption were positive and ranged from 0.08 to 0.14 kJ/mol.K. These positive values indicate increased randomness at the solid-solution interface during the adsorption of Ni^{2+} on clinoptilolite. As expected from theory, the enthalpy obtained from the Van't Hoff plot is dependent not only on the metal ion being adsorbed, but also on the ion being displaced