

Designed Pendant Chain Covalently Bonded to Analogue of Heulandite for Removal Divalent Toxic Metals from Aqueous Solution: Thermodynamic and Equilibrium Study

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Abstract – An analogue of heulandite was synthesized by using inorganic salts as a source for silicon and aluminum in the hydrothermal synthesis of the material. The resulting solid was modified by organofunctionalization with 1,4-bis(3-aminopropyl)piperazine and subsequent reaction with methylacrylate in a heterogeneous route. The ability of this material to remove nickel(II), cobalt(II) and copper(II) from aqueous solution was followed by a series of adsorption isotherms adjusted to a Sips equation. The energetic effects caused by metal cation adsorption were determined through calorimetric titrations.

This investigation reports the use of original (HEU) and modified analogue of heulandite (HEU_{APPMA}) as alternative absorbents for extraction of toxic metals, which are commonly present in waters from a variety of sources and industrial effluents. For this propose, the analogue of heulandite was chemically modified by 1,4-bis(3-aminopropyl)piperazine and subsequent reaction with methylacrylate using heterogeneous route. The adsorption isotherms of divalent nickel, cobalt and copper from aqueous medium at room temperature were explored, bearing in mind the influence of different parameters such as solution pH, metal concentration and contact time. From calorimetric determinations the quantitative thermal effects for all these cation/basic center interactions gave exothermic enthalpy, negative Gibbs free energy and positive entropy. These thermodynamic data confirmed the energetically favorable condition of such interactions at the solid/liquid interface for all systems.

Typical SEM image of powder original and modified samples of the analogue of heulandite samples in original and modified form are presented in Figure 1a. These micrographs reveal the heterogeneous nature of surface morphology of the analogues of heulandite which also shows that heulandite crystals to possess a needle like morphology. The spectrum related to ¹³CNMR in solid-state is shown in Figure 1b for modified heulandite. These data correlate the important information regarding the immobilization of pendant chains on the inorganic backbone of original heulandite structure. For modified matrix the peaks at 10.5, 17.8 and 22.4 ppm were signed C₁, C₂ and C₃ atoms of the aliphatic propyl chain of the immobilized organochloro compound. The peak centered at 51.1 ppm (C₄) is assigned to the methylene group vibration in the compound. The peaks 54 (C₅) at 58.1 ppm (C₆) denotes the carbon atoms from either unreacted alkoxy groups or structure anchored alkoxy groups [1].

The HEU and HEU_{APPMA} have been used to evaluate the maximum adsorption capacity for uptaking metal ions, such as Co(II), Ni(II) and Cu(II), from aqueous solutions. Such processes occurring at the solid/liquid interface give the isotherms that demonstrate the saturation of the original and modified silicate samples with a definite number of moles of metallic cations, as clearly shown in Figures 2a and 2b respectively, with the highest pronounced adsorption for copper. Based on such ability of the pendant groups attached to the inorganic backbone in coordinating these metallic cations [2], the quantity can be related to N_f^{max}, which presented the values 7.47, 9.83 and 12.93 mmol g⁻¹ for Co(II), Ni(II) and Cu(II), respectively.

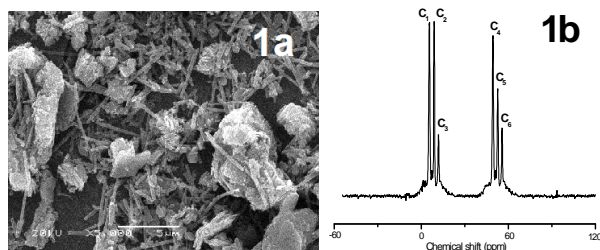


Figure 1: a) SEM image of modified heulandite, b) ¹³C MAS NMR spectrum for modified heulandite.

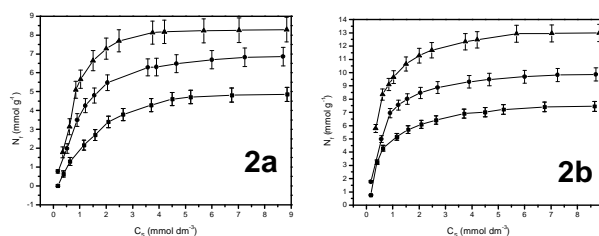


Figure 2: a) Divalent metal adsorption onto original, b) modified heulandite: Co(II) ■, Ni(II) ● and Cu(II) ▲ (matrix 1.0 g dm⁻³, pH 4.0, time 360 min and temperature in 298 ± 1K).

References

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