

Immobilization of 5-amino-1,3,4-thiadiazole-thiol onto kanemite for thorium(IV) removal: Thermodynamics and equilibrium study

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Abstract – The compound 5-amino-1,3,4-thiadiazole-thiol (ATT) was anchored onto Amazon kanemite surface (K) by homogeneous and heterogeneous routes. The ability of these materials to remove thorium(IV) from aqueous solution was followed by a series of adsorption isotherms adjusted to a Sips equation at room temperature and pH 4.0. The maximum number of moles adsorbed was determined to be 7.48×10^{-3} , 9.82×10^{-3} and 12.94×10^{-3} mmol g⁻¹ for K, K_{CTT} and K_{ATT}, respectively. The energetic effects ($\Delta_{\text{int}}H^\circ$, $\Delta_{\text{int}}G^\circ$ and $\Delta_{\text{int}}S^\circ$) caused by metal cations adsorption were determined through calorimetric titrations.

This investigation reports the use of original (K) and modified kanemite (K_{CTT} and K_{ATT}) as alternative absorbents for extraction of toxic metal, which are commonly present in waters from a variety of sources and industrial effluents. For this propose, the adsorption isotherms of Th(IV) 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. The chemical modification process was developed with functionalization of Amazon kanemite with 5-amino-1,3,4-thiadiazole-thiol (ATT) using homogeneous and heterogeneous routes. The performance in adsorbing thorium cation from natural water under dynamic flow (column) conditions was also studied and the results confirmed the batch experiments. From calorimetric determinations the quantitative thermal effects for all these cation/basic center interactions gave exothermic enthalpy, negative Gibbs free energy and positive entropy [1].

X-ray powder diffraction of K, K_{CTT} and K_{ATT} showed significant changes. In Figure 1 an increase in the interlayer distance is observed after the intercalation process, by changing d_{001} from 1.232 to 2.208 nm (K_{CTT}) and 2.217 nm (K_{ATT}) for the modified kanemite samples. This is attributed to the presence of ATT molecules that were intercalated in the phyllosilicate structure through of the interaction with reactive centers anchored in the interlayer spacing of natural kanemite, such as the silanol groups.

In order to evaluate natural and modified kanemite samples as absorbents for wastewater treatment of Th(IV) containing effluents, breakthrough curves of this metallic ion using K, K_{CTT} and K_{ATT} as absorbents were obtained (Figure 2). As can be seen, the lower breakthrough points (BP₁), determined when the metallic ion effluents from column attained the concentration 0.010 mg dm⁻³. The BP₁ value is relative with the capacity of the absorbents in retaining thorium(IV) ion from aqueous media. The higher breakpoints (BP₂) are related with the complete saturation of the kanemite samples with the Th(IV) ion. The values of BP₁ indicates that the natural and modified kanemite samples are efficient absorbents for decontaminating radionuclide Th(IV) from industrial effluents, using a dynamic system, since one volume of the adsorbent is able to remove completely at least 100 volumes of contaminant thorium(IV) ion from aqueous media [2].

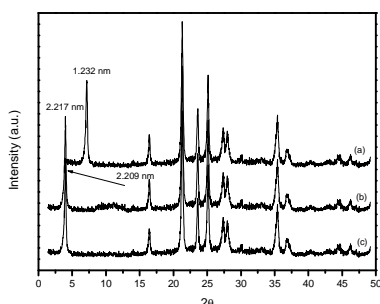


Figure 1: X-ray diffraction patterns of natural and modified kanemite: K (a), K_{CTT} (b) and K_{ATT} (c).

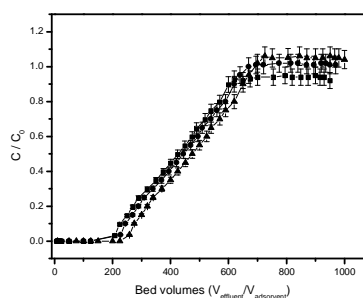


Figure 2: Breakthrough curves for 2.00×10^{-2} mmol dm⁻³ of thorium(IV) (K ■, K_{CTT} ● and K_{ATT} ▲) (kanemite 1.0 g dm⁻³, pH 4.0, time 360 min and controlled temperature in 298 ± 1 K).

References

- [1] F. A. Pavan, I. S. Lima, E. C. Lima, C. Airoldi, Y. Gushikem, J. Harzard. Mater. 137 (2006) 527.
[2] D. L. Guerra, C. Airoldi, R. R. Viana, Inorg. Chem. Commun. 11 (2008) 20.