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KINETIC STUDY OF COMPETITIVE Co^{2+} AND Sr^{2+} SORPTION BY BAUXITE RESIDUE

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ABSTRACT

Multi-component sorption studies are essential to identify the applicability of red mud as a low-cost sorbent for the simultaneous removal of metal ions from wastewaters. Sorption kinetics of Co^{2+} and Sr^{2+} ions was studied, at their different molar ratios in the mixture. The pseudo-second-order rate model best described the kinetics of metal sorption from binary metal systems. The increase of initial concentration of each cation in the mixture provoked its increased sorption capacity, but decreased sorption rate. Co^{2+} sorption was superior in terms of both the rate and the capacity, therefore exerted strong inhibitory effect on Sr^{2+} sorption.

INTRODUCTION

Due to high efficacy and low-cost, sorption processes can be applied for the decontamination of liquid radioactive wastes [1]. Nowadays, wastes and by-products from various industries are studied as potential sorbents [2]. Red mud, an alkaline by-product of alumina industrial production from bauxite ore, is an example of heterogeneous mineral material interesting for environmental applications [3].

In the previous study, alkaline red mud from "Birač" Alumina Factory (Bosnia and Herzegovina) was found to be a promising sorbent for ^{60}Co and ^{90}Sr ions [4]. These two radioactive isotopes go hand in hand as products of nuclear reactor operations: ^{60}Co is a corrosion product, while ^{90}Sr occurs by fission of uranium and plutonium. Therefore, multi-component sorption studies are required to identify the capabilities and limitations of red mud as a low-cost sorbent for the simultaneous removal of these metal ions from wastewater.

In this paper, time dependant sorption of ^{60}Co and ^{90}Sr was examined using mixtures with different molar ratios of selected cations.

EXPERIMENTAL

After settling, the liquid phase above red mud particles was decanted, whereas the solid residue was dried at 105°C and homogenized in the mortar. Stock solutions of Co²⁺ and Sr²⁺ ions (2·10⁻³ mol/dm³) were prepared by dissolving Co(NO₃)₂·6H₂O and Sr(NO₃)₂ salts, in deionized water. Simulated liquid wastes with different molar ratios of two cations (Co²⁺: Sr²⁺ = 1:2, 1:1 and 2:1) were prepared from stock solutions, keeping the overall cation concentration constant (2·10⁻³ mol/dm³). The initial pH of each mixture was adjusted to 5, with a few drops of 0.01 mol/dm³ HNO₃. The effect of contact time on the amount of cations removed was determined by equilibrating 0.1000 g of red mud with 20.00 cm³ of mixture solutions, on the laboratory shaker. At different time intervals ranging from 15 min to 48 h, one of the batches was taken for solid/liquid separation. Sorbed cation concentrations were determined by Perkin Elmer 3100 Atomic Absorption Spectrometer, as differences between initial and final concentrations.

RESULTS AND DISCUSSION

The amounts of Co²⁺ and Sr²⁺ sorbed at various time intervals from the mixed solutions are presented in the Fig. 1. It can be observed that the sorption onto red mud was generally fast during first hours of contact, followed by a slower reaction step. With the increase of initial concentration of each cation, equilibration time increased as well. Equilibrium times for Co²⁺ sorption were 6 h for 1:2 molar ratio to Sr²⁺, and 24 h for the ratios 1:1 and 1:2. Sorption of Sr²⁺ reached equilibrium in 6 h and 30 h, for Co²⁺: Sr²⁺ molar ratios 2:1 and 1:1, respectively, whereas for the ratio 1:2 sorbed amounts of Sr²⁺ slightly increased during the second day of equilibration.

Applicability of several kinetic models for the interpretation of experimental results was tested. Highest correlation coefficients (R²) between the model and the experimental results were obtained using the pseudo-second-order kinetic equation [5]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (1)$$

where k₂ (g/(mmol min)) is the pseudo-second-order rate constant, q_e (mmol/g) the amount of cations sorbed at equilibrium, and q_t is the amount of cations sorbed at any time t. Calculated kinetic parameters are presented in Table 1. Calculated sorption capacities increased along with the initial concentration of a particular cation, whereas the rate constants decreased.

From binary solutions, Co²⁺ was sorbed more selectively on red mud surface, showing higher q_e and k₂ values. Considering equimolar mixture, Co²⁺ sorption capacity was almost twice the amount of Sr²⁺ sorbed (0.203 mmol/g

and 0.117 mmol/g, respectively). The equilibrium sorbed amounts from single metal solutions (initial cation concentration 10^{-3} mol/dm^3) were found to be 0.206 mmol/g for Co^{2+} and 0.197 mmol/g Sr^{2+} [4].

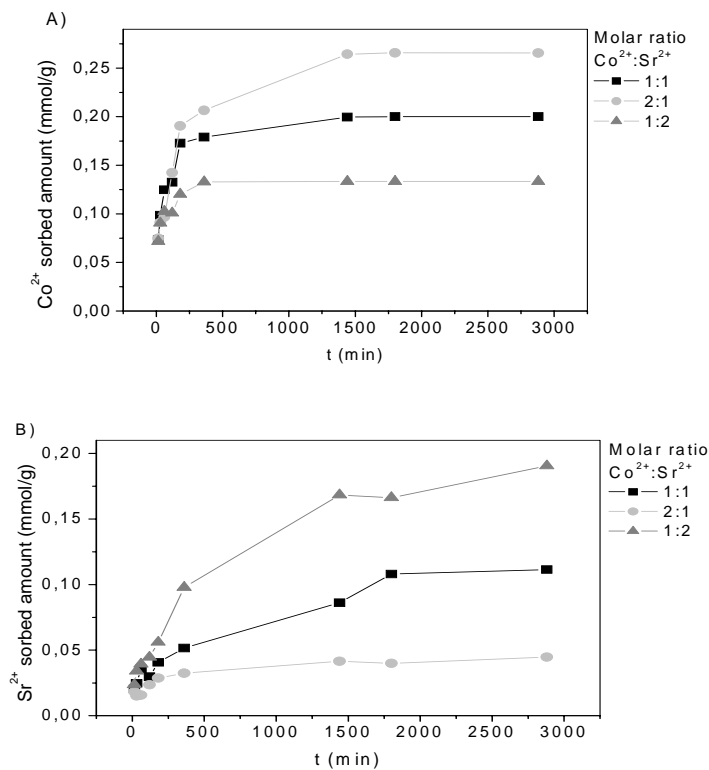


Figure 1. Effect of contact time on competitive Co^{2+} (A) and Sr^{2+} (B) sorption by red mud.

Table 1. The parameters of pseudo-second-order kinetic model for competitive Co^{2+} and Sr^{2+} sorption onto red mud

Molar ratio Co: Sr	Co^{2+}			Sr^{2+}		
	q_e mmol/g	k_2 g/(mmolmin)	R^2	q_e mmol/g	k_2 g/(mmolmin)	R^2
1:2	0.134	0.412	0.99	0.205	0.015	0.98
1:1	0.203	0.128	0.99	0.117	0.033	0.98
2:1	0.275	0.043	0.99	0.045	0.227	0.99

For each binary system, total sorption capacity remained relatively constant ($\Sigma q_e = 0.326 \pm 0.006 \text{ mmol/g}$). Individual and overall sorbed amounts are

presented in Fig. 2. The results demonstrate that the presence of Sr^{2+} ions in the mixture did not interfere with Co^{2+} sorption. Conversely, Co^{2+} inhibited removal of Sr^{2+} .

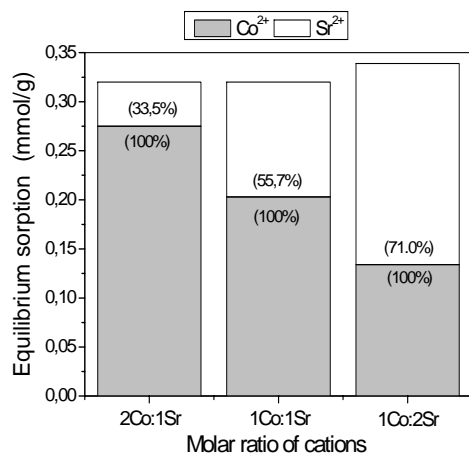


Figure 2. Individual and overall amounts of Co^{2+} and Sr^{2+} sorbed by red mud from binary mixtures.

CONCLUSION

With the increase of the initial concentration of a particular cation in the mixture, its sorption capacity increased, whereas the corresponding pseudo-second-order rate constant decreased. Considering experimental conditions applied in this study, red mud can be utilized for simultaneous removal of Co^{2+} and Sr^{2+} cations. However, coexisting Sr^{2+} ions did not affect Co^{2+} sorption capacity, while Co^{2+} exerted strong inhibitory effect on Sr^{2+} removal.

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