Adsorption of rare earth elements from aqueous solutions using geopolymers

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Introduction

Nowadays, various processes are used to remove heavy metals from wastewater, e.g. chemical coagulation, ion exchange, extraction or adsorption. Recently, the emphasis is on adsorption due to the simplicity of the procedure, its high efficiency and low price [1], while geopolymers are extensively studied as one of the most common adsorbents [2-4].

Geopolymers can be synthesized from any material with high silicon and aluminium content by activation with alkaline solution. Previous studies on the adsorption and stabilization of metals using geopolymers were mainly oriented to heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) [2-4], while the group of lanthanides was not significantly investigated.

Given the fact that lanthanides, i.e. rare earth elements, are not significantly studied in this regard, our aim was to investigate the ability of geopolymer matrices, prepared from coal ash, to remove lanthanides from model aqueous solutions.

Materials and methods

Geopolymer preparation

The geopolymers A and B were prepared using the Raša coal ash (Istria, Croatia) as starting material. The Raša coal ash, previously sieved through 2 mm sieve, was activated with a sodium silicate and 10 M sodium hydroxide solutions to prepare paste specimens.

Addition of 10 mL of prepared NaOH solution modified molar ratio SiO_2/Na_2O to 0.7-0.8 and 1.1-1.3 in geopolymer A and B, respectively. The fresh pastes were exposed to heat curing in a laboratory oven at 75°C for 24 h. After two weeks of ageing at room temperature, subsamples of prepared geopolymers A and B were used for adsorption experiments.

Adsorption experiment

Aqueous solutions containing 1 mg L^{-1} of rare earth elements were prepared from multielement reference standard (Analytika, Prague, Czech Republic) containing Ce, La, Nd and Pm (100 ± 0,2 mg L^{-1}) and Dy, Er, Eu, Gd, Ho, Lu, Sc, Sm, Tb, Tm, Y and Yb (20 ± 0,4 mg L^{-1}). The efficiency of tested geopolymers as adsorbents for lanthanides was evaluated by determining the concentration of REEs in solution after the specific contact time with geopolymer (0, 5, 15, 30, 60 and 120 min).

Rare earth elements analysis

Multielemental analysis of prepared solutions was performed by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS) using an Element 2 instrument (Thermo, Bremen, Germany). All samples were analyzed for total concentration of the rare earth elements, including Y.

Literature:

1. Bhattacharyya, K.G.; Gupta, S.S. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. Adv. Colloid Interface Sci. 2008, 140, 114-131.
2. Wang, S.; Li, L.; Zhu, Z.H. Solid-state conversion of fly ash to effective adsorbents for Cu removal from wastewater. J. Hazard. Mat. 2007, 139(2), 254–259.
3. Muzek, M.N.; Svilovic, S.; Zelic, J. Fly ash-based geopolymeric adsorbent for copper ion removal from wastewater. Desalin. Water Treat. 2014, 52, 2519–2526.
4. Al-Zboon, K.; Al-Harahsheh, M.S.; Hani, F.B. Fly ash-based geopolymer for Pb removal from aqueous solution. J. Hazard. Mater. 2011, 188, 414–421.

Results and discussion

The results presented in Fig. 1 demonstrate the decrease of REEs concentration in both solutions (A and B). The adsorption onto geopolymers occurred rather fast in the initial phase of the experiment and already in the first five minutes the REEs concentration decreased to 7-13% and 23-35% of the initial concentration in solution A and B, respectively.

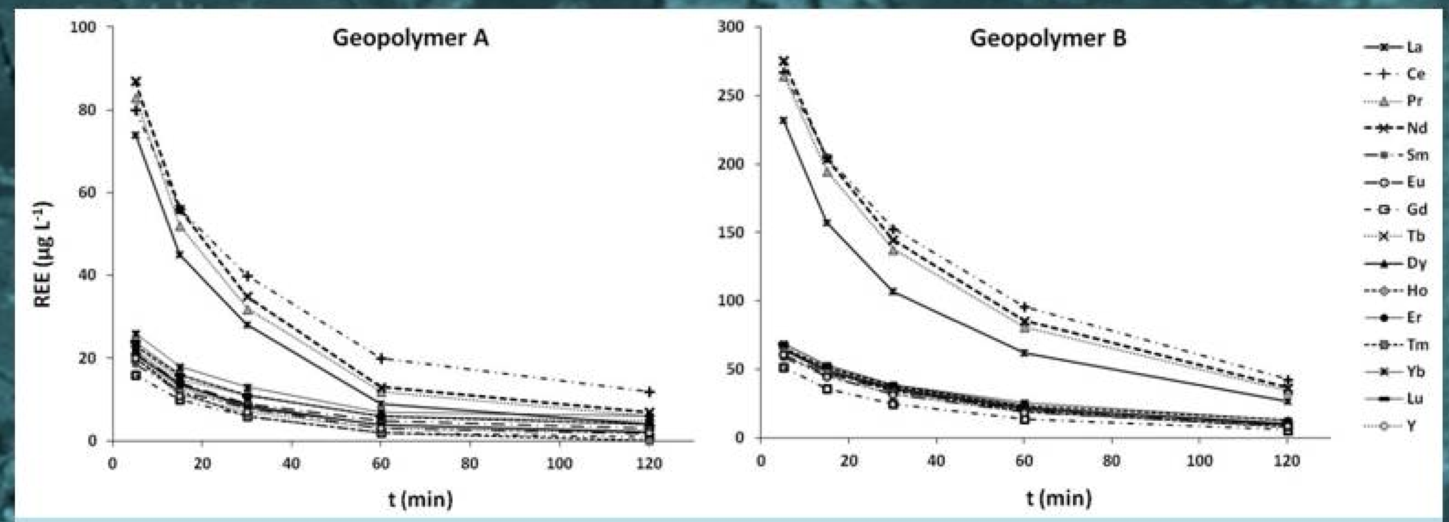

Fig. 1 The concentration of REEs in solutions (μg L^{-1}) after certain contact time (t) with geopolymers A and B.

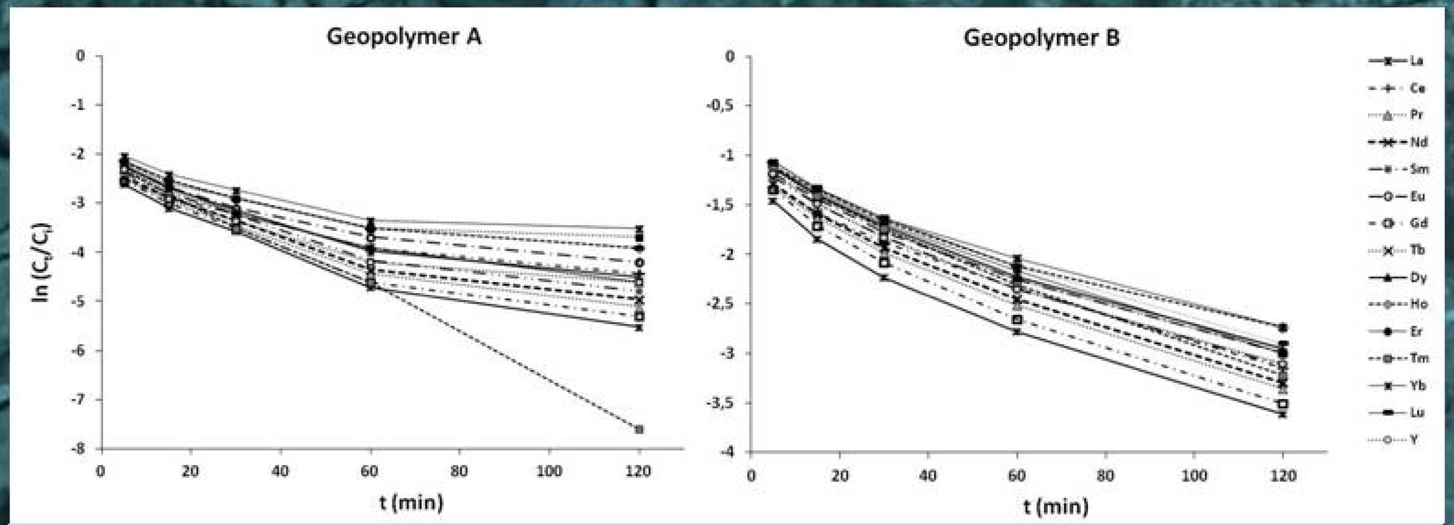

Fig. 2 First order kinetic fit of REEs adsorption data on geopolymer A (a) and geopolymer B (b).

The adsorption kinetics could be described by first order kinetic model (Fig. 2) given in equation:

$$c_t = c_i e^{-kt}$$

The adsorption rate constants (k), calculated using this equation ranged from 0.007 min^{-1} to 0.050 min^{-1} for geopolymer A, and from 0.010 min^{-1} to 0.023 min^{-1} for geopolymer B.

The evaluation of data revealed that the adsorption of REEs fit to Langmuir adsorption isotherm (Fig. 3) described by the following equation:

$$\frac{c}{c_a} = \frac{1}{b\, c_m} + \frac{c}{c_m}$$

The slopes of the isotherms for La, Ce, Pr and Nd are very similar and are around 5 times lower than those for other REEs, considering both geopolymers.

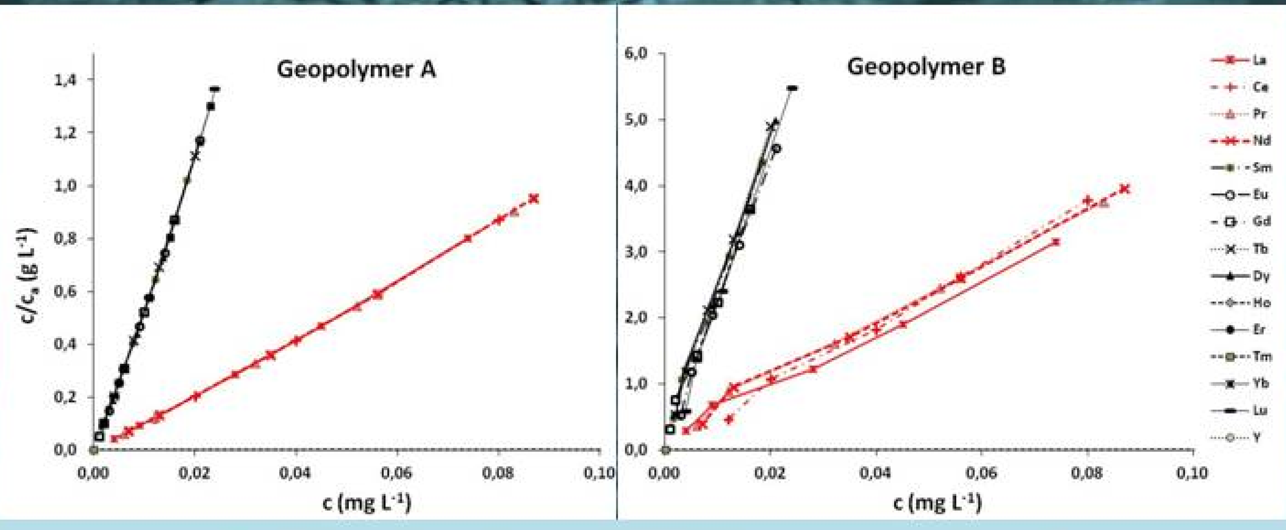

Fig. 3 Adsorption isotherms of REEs for geopolymers A and B.

Conclusion

The obtained results indicate an efficient removal of lanthanides from solution by prepared geopolymers.
The observed differences between prepared geopolymers indicate the importance of preparation procedure, i.e. the composition of the geopolymer and the activators used, in ensuring the optimal adsorption conditions.

In general, the adsorption of REEs on tested geopolymers can be described by Langmuir adsorption isotherm, whereas REEs initially present in higher concentration (La, Pr and Nd), as well as those with lower atomic number (Y, La, Gd, Pr, Nd, Y, Sm) displayed higher adsorption rates.