proceedings

Proceedings Paper

Adsorption of rare earth elements from aqueous solutions using geopolymers †

Željka Fiket[1,*], Ana Galović[2], Gordana Medunić[3], Martina Furdek Turk[1], Maja Ivanić[1], Matej Dolenec[4], Ivica Biljan[2], Goran Kniewald[1]

[1] Ruđer Bošković Institute, Division for Marine and Environmental Research, Bijenička 54, 10000 Zagreb, Croatia; zeljka.fiket@irb.hr, mfurdek@irb.hr, mivanic@irb.hr, kniewald@irb.hr
[2] University of Zagreb, Faculty of Science, Department of Biology, Rooseveltov trg 6, 10000 Zagreb, Croatia; anagalovic1303@hotmail.com, ibiljan@stud.biol.pmf.hr
[3] University of Zagreb, Faculty of Science, Department of Geology, Horvatovac 95, 10000 Zagreb, Croatia; gordana.medunic@gfz.hr
[4] University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Geology, Aškerčeva c. 12, 1000 Ljubljana, Slovenia, matej.dolenec@geo.ntf.uni-lj.si
* Correspondence: zeljka.fiket@irb.hr; Tel.: +385-1-456-1036
† Presented at the 1st International Electronic Conference on Geosciences; 15/06/2018 - 30/06/2018.

Received: date; Accepted: date; Published: date

Abstract: Rare earth elements, i.e. lanthanides, are important components of many latest technology applications and their increasing use in the industrial sector, medicine and agriculture over the last few decades provided them with a title of "new pollutants". Different methods are nowadays applied for removal of various pollutants from wastewaters, whereby the emphasis is placed on the adsorption due to its simplicity, high efficiency and low cost. In the present study, geopolymers prepared from coal ash were examined regarding their capacity for adsorption of lanthanides from model solutions. The obtained results indicate efficient removal of lanthanides by prepared geopolymers, depicting them as effective adsorbents for this group of elements.

Keywords: rare earth elements; geopolymers; adsorption

1. Introduction

Rare earth elements (REEs), also known as lanthanides, are important components of many latest technology applications and are widely used in the industrial sector, medicine and agriculture. Although lanthanides are ubiquitous in the environment, their increasing use in aforementioned sectors over the last few decades provided them with a title of "new pollutants".

Consequently, an increase in the concentration of lanthanides, especially gadolinium (Gd), in natural water systems was observed over the last two decades [1-4]. The elevated concentrations of gadolinium, up to two orders of magnitude higher than their natural levels, are primarily attributed to the discharge of wastewater, i.e. application of Gd in the form of very stable organic complexes for magnetic resonance [2-4].

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 [5], while zeolites and geopolymers are extensively studied as the most common adsorbents [6-10].

Geopolymers can be synthesized from any material with high silicon and aluminium content, regardless of its origin, e.g. natural raw materials such as clay or byproducts of various industrial plants such as ash [6-9]. Activation of fly ash with alkaline solution produces porous alumosilicates, i.e. geopolymers, characterized by an increased specific surface, high pore volume, and possibility of adsorption of chemical species that even zeolites cannot remove [6].

The previous studies on the adsorption and stabilization of metals using geopolymers were mainly oriented to heavy metals (Cd, Cr, Cu, Ni, Pb, Zn) [6-9, 11, 12], while the group of lanthanides was not significantly investigated. Sporadic studies mainly dealt with the adsorption of lanthanide on biological materials [13], zeolites [14], clay [15] and less on geopolymers [16]; focusing only on certain lanthanides, and rarely on the whole group.

Given the fact that lanthanides 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.

2. Materials and methods

2.1. Geopolymer preparation

The geopolymers were prepared using the Raša coal ash (Istria, Croatia) as starting material. The Raša coal characteristics, summarized by Medunić et al. [17], are as follows: total moisture 5.80-19.1 wt%, ash content 10.3-23.9 wt%, carbon 58.3-67.5 wt%, hydrogen 4.10-5.00 wt%, sulfur (org.) 7.90-10.6 wt%, oxygen 5.90-12.9 wt%, nitrogen 1.00-1.80 wt%, and an average content of rare earth elements 81.1 mg kg^{-1} [18].

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 (Table 1). A technical-grade sodium silicate solution (BDH Prolabo) with SiO_2/Na_2O = 3.2-3.4 (Na_2O = 7.5-8.5%, SiO_2 = 25.6-27.6% and H_2O = 67.75%, with density 1.45 g cm^{-3}) was used as the alkaline activator. Sodium hydroxide solution (10 M NaOH) was prepared by dissolution of NaOH pellets (Fluka, Steinheim, Switzerland) in deionized water. 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.

Table 1. Mixture composition for geopolymer preparation.

	Geopolymer A	Geopolymer B
m_{ash}(g)	50	50
$m_{Na\text{-}silicate}$ (mL)	7.5	15
SiO_2/Na_2O	0.7-0.8	1.1-1.3

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.

2.2. 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 aliquots (50 mL) of prepared REEs solution were placed into 2 plastic bottles (A and B) containing accurately weight amounts of the sorbents, i.e. geopolymer A (m = 0.5003 g) and geopolymer B (m = 0.5200 g). The prepared suspensions were shaken using the mechanical shaker at 320 rpm. After the certain contact time (5, 15, 30, 60 and 120 min) 5 mL of suspension was taken by a syringe from each bottle and filtered through 0.45 μm filter. Prior to analysis, obtained solutions were diluted ten times, acidified with 2% (v/v) HNO_3 (65%, supra pur, Fluka, Steinheim, Switzerland) and In (1 μg L^{-1}) as an internal standard was added.

2.3. 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). External calibration was used for the quantification. Standards for multielement analysis were prepared by appropriate dilution of a multielement reference standard (Analytika, Prague, Czech Republic) containing Ce, La, Nd and Pr (100 ± 0,2 mg L^{-1}), and Dy, Er, Eu, Gd, Ho, Lu, Sc, Sm, Tb, Tm and Yb (20 ± 0,4 mg L^{-1}). All samples were analyzed for total concentration of the rare earth elements.

3. Result and discussion

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). 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. Later, concentrations decreased continuously with time and at the end of the experiment (120 min) up to 99% and 96% of the total REEs were adsorbed onto the geopolymer A and B, respectively. The presented data therefore strongly suggest that both geopolymers are efficient sorbents for REEs and could be efficiently used for their removal from the solution, whereas geopolymer A that has lower SiO_2/Na_2O ratios (SiO_2/Na_2O=0.7-0.8) has better performance compared to geopolymer B (SiO_2/Na_2O=1.1-1.3). At the end of the experiment, the lowest concentration in both solutions was measured for Gd, La and Tm (< 3% of the initial concentration), while Yb and Ho were somewhat less adsorbed compared to other elements (up to 7% of the initial concentration remained in the solution).

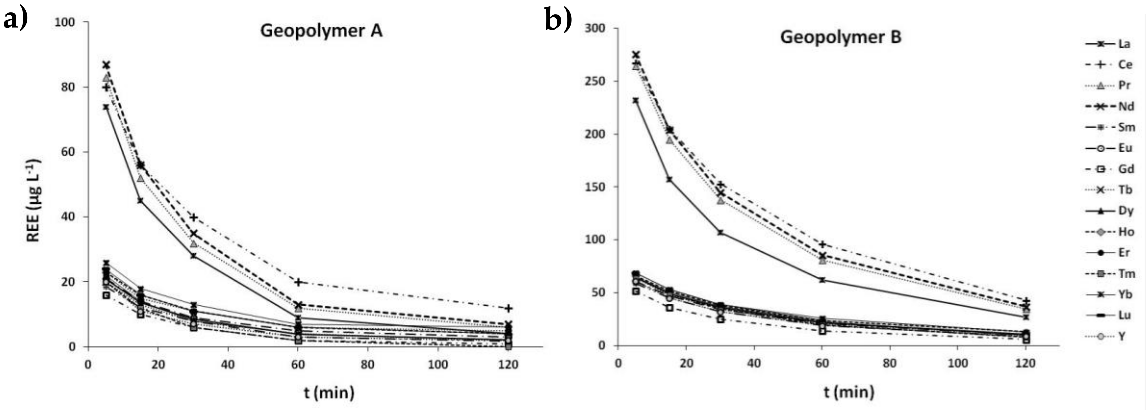

Figure 1. The concentration of REEs in solutions (µg L^{-1}) after certain contact time (t) with geopolymers A (a) and B (b).

3.1. Adsorption rate constants

The adsorption kinetics could be described by first order kinetic model given in equation 1;

$$c_t = c_i e^{-kt} \quad (1)$$

where c_i and c_t represent the initial (t=0) concentration and concentration of REE after the specific time t, whereas k and t represent adsorption rate constant and time, respectively. The obtained kinetic curves are presented in Fig. 2. As can be noticed, they are not equal for both geopolymers; while the sorption of REEs on geopolymer A has two phases, an initial rapid phase followed by slower adsorption that occurred after 60 min, the rates of adsorption on geopolymer B did not vary significantly through the whole experiment. Although the slower adsorption rate that was observed in the second phase (60-120 min) could be attributed to the different properties and microstructure of geopolymer A, the most probable explanation is lower elements concentrations that remained in the solution.

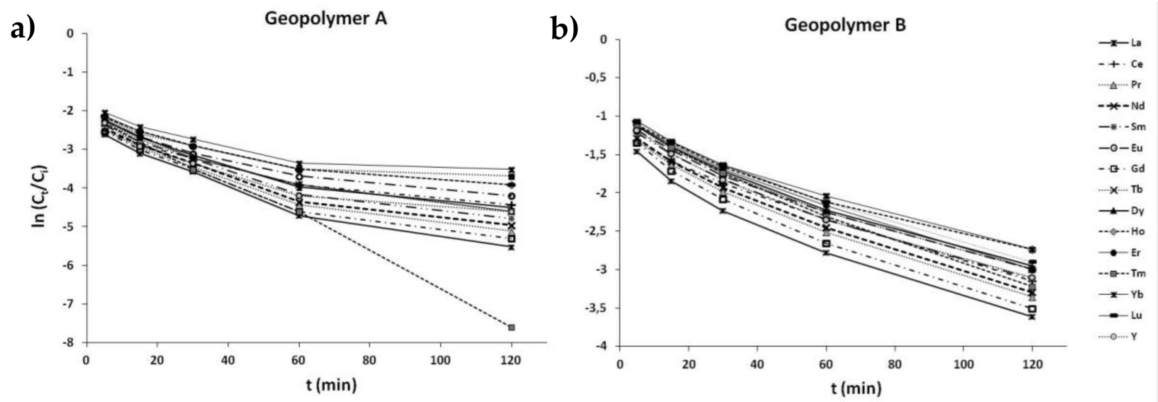

Figure 2. First order kinetic fit of REEs adsorption data on geopolymer A (a) and geopolymer B (b).

The adsorption rate constants (k) are calculated using the equation 1 and summarized in Table 2. The values range 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. Comparing these two geopolymers, it could be observed that adsorption of REEs on geopolymer A is faster (up to 2 times) at the beginning of the experiments. After first 60 minutes, the rate of adsorption decreased for both geopolymers, although much less for geopolymer B (up to 2 times for geopolymer B, and 3-9 times for geopolymer A).

Table 1. The adsorption rate constants (k) for studied geopolymers (A and B).

	k (min^{-1})			
	Geopolymer A		**Geopolymer B**	
	0 - 60 min	60 - 120 min	0 - 60 min	60 - 120 min
La	0.037	0.014	0.023	0.014
Ce	0.025	0.009	0.018	0.013
Pr	0.034	0.012	0.021	0.014
Nd	0.034	0.010	0.021	0.014
Sm	0.032	0.010	0.020	0.013
Eu	0.025	0.009	0.019	0.012
Gd	0.037	0.012	0.023	0.014
Tb	0.029	0.012	0.020	0.012
Dy	0.030	0.009	0.020	0.012
Ho	0.024	0.007	0.018	0.010
Er	0.030	0.012	0.019	0.014
Tm	0.041	0.050	0.021	0.015
Yb	0.023	0.003	0.017	0.012
Lu	0.024	0.007	0.019	0.013

The affinity of REEs for the adsorption on tested geopolymers follows the order;
Geopolymer A Tm > La, Gd > Pr, Nd > Y > Sm > Dy, Er > Tb > Eu, Ce > Lu, Ho > Yb
Geopolymer B La, Gd > Tm, Pr, Nd, Y > Sm, Tb, Dy > Eu, Lu, Er > Ce, Ho > Yb

Both geopolymers showed a similar pattern with the higher adsorption affinity for REEs initially present in higher concentration (La, Pr and Nd).

3.2. Adsorption isotherms

Adsorption isotherms describe the partitioning of REEs between the aqueous solution and the sorbent, i.e. geopolymer. In the present study, the REEs concentrations in geopolymers were determined as the differences between initial concentrations in the solution and concentrations measured in the specific time t. It was considered that all quantity of REEs that is removed from the solution is adsorbed onto the geopolymers. The evaluation of data revealed that the adsorption of REEs fit to Langmuir adsorption isotherm described by equation 2;

$$\frac{c}{c_a} = \frac{1}{b\,c_m} + \frac{c}{c_m} \tag{2}$$

where c represents the REEs concentration in the solution in the time t, c_a is the amount of adsorbed REEs per unit weight of geopolymer, b is the constant of Langmuir isotherm related to the equilibrium constant or binding energy, and c_m is the amount of the maximum REEs adsorbed. Adsorption isotherms shown in Fig. 3 demonstrate the linearity in the investigated concentration range for all REE.

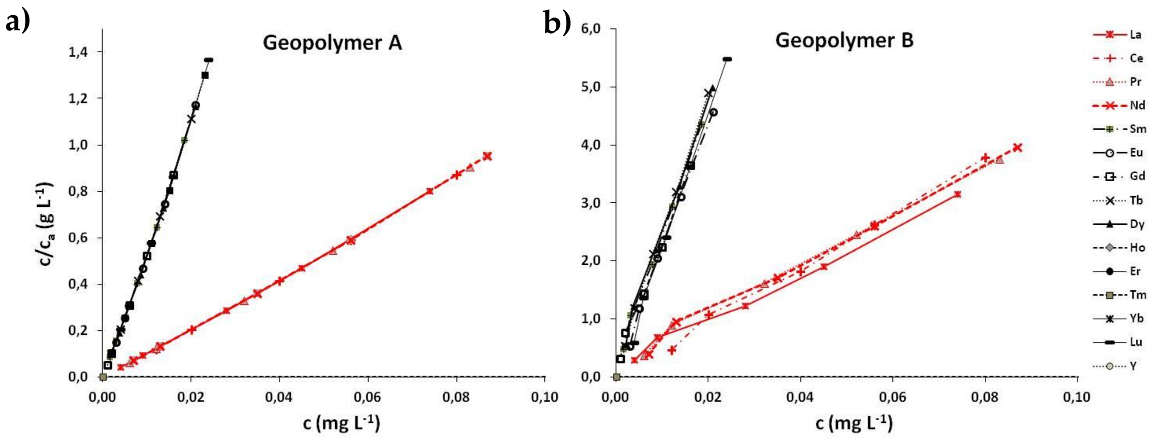

Figure 3. Adsorption isotherms of REEs for geopolymers A (a) and B (b).

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. This implies higher adsorption capacity of both geopolymers for La, Ce, Pr and Nd compared to the other REEs.

4. Conclusion

The obtained results indicate an efficient removal of lanthanides from solution by prepared geopolymers. Although both geopolymers were efficient sorbents for REEs, geopolymer A displayed slightly better performance compared to geopolymer B. 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.

References

1. Bau, M.; Dulski, P. Anthropogenic origin of positive gadolinium anomalies in river waters. Earth Planet. Sci. Lett. **1996**, *143*, 245–255.
2. Lawrence, M.G. Detection of anthropogenic gadolinium in the Brisbane River plume in Moreton Bay, Queensland, Australia. Mar. Pollut. Bull. **2010**, *60 (7)*, 1113–1116.
3. Kulaksız, S.; Bau, M. Rare earth elements in the Rhine River, Germany: first case of anthropogenic lanthanum as a dissolved microcontaminant in the hydrosphere. Environ. Int. **2011**, *37(5)*, 973–979.
4. Klaver, G.; Verheul, M.; Bakker, I.; Petelet-Giraud, E.; Négrel, P. Anthropogenic rare earth element in rivers: gadolinium and lanthanum. Partitioning between the dissolved and particulate phases in the Rhine River and spatial propagation through the Rhine-Meuse Delta (the Netherlands). Appl. Geochem. **2014**, *47(0)*, 186–197.
5. 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.
6. 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.
7. El-Eswed, B.; Alshaaer, M.; Yousef, R. I.; Hamadneh, I.; Khalili F. Adsorption of Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) onto Kaolin/Zeolite Based- Geopolymers. Adv. Mater. Phys. Chem. **2012**, *2*, 119-125.
8. 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.
9. 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.
10. López, F.J.; Sugita, S.; Tagaya, M.; Kobayashi, T. Metakaolin-based geopolymers for targeted adsorbents to heavy metal ion separation. J. Mater. Sci. Chem. Eng. **2014**, *2*, 16–27.
11. Davidovits, D. Geopolymer, green chemistry and sustainable development: The poly(sialate) terminology: a very usefull and simple model for the promotion and understanding of green chemistry; Proceedings of the world congress Geopolymer 2005; (Ed.:J.Davidovits), Published by Institut Geopolymer, 2005, 9-17.
12. van Jaarsveld, J.G.S.; Van Deventer, J.S.J.; Lorenzeni, L. The Potential Use of Geopolymeric Materials to Immobilise Toxic Metals: Part I. Theoty and Application. Miner. Eng., **1997**, *10(7)*, 659-669.
13. Thomas P. J.; Carpenter, D.; Boutin, C.; Allison, J.E. Rare earth elements (REEs): Effects on germination and growth of selected crop and native plant species. Chemosphere **2014**, *96*, 57–66.
14. Hui, K.S.; Chao, C.Y.H.; Kot, S.C. Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash. J. Hazard. Mat. **2005**, *B127*, 89–101.
15. Coppin, F.; Berger, G.; Bauer, A.; Castet, S.; Loubet, M. Sorption of lanthanides on smectite and kaolinite. Chem. Geol. **2002**, *182*, 57–68.
16. Izquierdo, M.; Querol, X.; Davidovits, J.; Antenucci, D.; Nugteren, H.; Fernández-Pereira, C. Coal fly ash-slag-based geopolymers: Microstructure and metal leaching. J. Hazard. Mat. **2009**, *166*, 561–566.
17. Medunić, G.; Rađenović, A.; Bajramović M.; Švec, M.; Tomac, M. Once grand, now forgotten: what do we know about the superhigh-organic-sulfur Raša coal? Min. Geol. Petrol. Eng. Bull. **2016**, 27-45; doi: 10.17794/rgn.2016.3.3.
18. Fiket, Ž.; Medunić, G.; Kniewald, G. Rare earth element distribution in soil nearby thermal power plant. Environ. Earth Sci. **2016**, *75*, 598, 1-9; doi: 10.1007/s12665-016-5410-2.