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Some examples of interactions between certain rare earth elements and soil

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Abstract: The rare earth elements represent an increasingly more important industrial resource. The increased use may result in waste generation, and their impact upon the environment quality has not been studied sufficiently. Their interaction with soil has been studied in this paper. Freundlich adsorption isotherm has been determined for lanthanum, erbium and gadolinium at three different soil types (humus, clay and sand type), whereas sequential extraction at these soil types has been applied for lanthanum and neodymium. The interaction of certain rare earth elements with soil components has been tested as well as the quantity in which these elements are bound to soil and later on extracted in solutions. The objective was to determine the soil capacity for disposal, first of all, of the electronic waste that contains these elements and to assume their fate in the environment.

Keywords: Freundlich adsorption isotherm; sequential extraction, metallic ions, ICP-OES

INTRODUCTION

The demand in rare earth elements (REE) has been increasingly greater year in year out, as their application in military, pharmaceutical and nuclear industry, metallurgy, electronics, medicine, chemical engineering[1], agriculture[2] and others has been on the upscale. The reason of their widespread use in important fields are their different chemical, electrical, magnetic, metallurgical, optical and catalyst properties.[1, 3] In nature they crop up in the lithophyile part of the earth's crust[4,5] and are widely prevalent in small quantities, with the average concentration in the

earth's crust between 130- 240 μg g^{-1}.[6] There are significant reserves also in the oceans for which it has been assumed to be in greater quantities than in the earth's crust and that are more cost effective than the earth's resource.[7, 8] Ionic radiuses of these elements are such that enable an easy replacement with alkaline and alkaline-earth metals, adsorbing at the surface[9] and at the interlayer places of clay mineral. In addition to adsorption being greater, there also comes to more rapid equilibrium establishment.[10,11] The result of their properties is their wide-spread use and as the consequence of the widespread use there is an increased quantity of waste that is disposed and often in the inappropriate manner and ends up in the nature, disrupting the resources such as water and soil. The contamination occurs due to insufficient legal regulations and controls both in mining and also in the processing fields.[12] The effects of contamination, resulting as the consequence of the improper waste disposal are seen very quickly.[13]

In this paper the equilibrium between the liquid and solid phase has been studied and which can contribute to elimination of these elements from the contaminated soil. To describe the affinity of the rare earth elements to soil the Freundlich adsorption isotherm has been used since it is suitable for working with heterogeneous surfaces, such as in soil and for working with medium and high concentrations.[14] Sequential extraction (SE) was used for desorption of these elements from the soil.

<div align="center">EXPERIMENTAL</div>

Material and method

The soils used for the analysis are: humus, clay and sand type of soils. The soil fractions do not mutually differentiate as per the particles sizes but also as per mineralogical composition and therefore as per physical and chemical properties. The soil preparation comprised cleaning from foreign bodes (twigs, leaves and stones), air drying for 7 days and following that determining the hygroscopic moisture content. Mineralogical soil sample composition was determined by X-ray diffraction method (Rigaku SmartLab, X-ray diffractometer) under the conditions provided in Table I. The humus content has been determined by volumetric method[15] and the clay content by hydrometric method.[16] Sorption capacity for all three soil types has been determined.

Table I. Test conditions for samples on the difractometer.

Operating voltage, kV	40
Current, mA	30
X-ray radiation from the copper (Cu) anticathode, Wavelength, nm	15.4178
Scan range, 2θ / °	2 – 70
Step size, 2θ / °	0.01
Time constant, ° / min	10
Scan range (clay minerals), 2θ / °	2 – 30
Step size (clay minerals), 2θ / °	0.01
Time constant (clay minerals), ° / min	5

As the source of lanthanum, erbium and gadolinium (III)– ions, their nitrate –hexahydrate salts (Sigma-Aldrich, 99.9 % trace metals basis, ≤1500.0 ppm Trace Rare Earth Analysis) were used for determining Freundlich adsorption isotherm, whereas as the source of neodymium and lanthanum (III)- ions, $NdCl_3x6H_2O$ (Merck, 99.9 % trace metals basis) and $La_2(CO_3)_2$ (Sigma-Aldrich, 99.9% trace metals basis, ≤ 1500.0 ppm Trace Rare Earth Analysis) were used for sequential extraction. The concentration of stock solution amounted to 2000 mg L^{-1}, and working solutions used for determining sorption capacity and Freundlich adsorption isotherm were in the range of 500– 1500 mg L^{-1}. All solutions were analyzed by ICP-OES technique (SPECTRO-BLUE TI). The calibration solutions were prepared from the stock solution of all these elements (Certified Reference Material, Sigma– Aldrich, Periodic Table Mix 3 for ICP) and calibration curves were constructed for the stated elements. Imaging of the calibration solutions, extraction solutions and results processing was done as per the created "Rare Earths" method. The limit of detection (LOD) for this method for La amounts to 0.23 μg g^{-1}, and the limit of quantification (LOQ) 0.77 μg g^{-1}, whereas LOD for Nd amounts to 0.52 μg g^{-1}, and LOQ 1.74 μg g^{-1}.[17,18]

Procedure for determining Freundlich adsorption isotherm

Approximately 5 g of soil was measured and 50 mL of metallic ion solution added. The pH of the solution wasn't adjusted. The solutions were mixed at the shaker at the speed of 80 rpm for two hours, and then they were filtered through "blue band" filter paper (pores size < 2 μm) into the 100 mL volumetric flasks. The sediments were rinsed three times with 10 mL distilled water each and filled up with distilled water up to the line. The solutions prior to mixing and the solutions after the mixing were analyzed by ICP-OES. The values have been presented in Table II.[17]

The values obtained were graph presented as the dependence of the metallic ion adsorbed mass per mass of adsorbent on the equilibrium concentration of that ion in the solution-Freundlich adsorption isotherm. Parameters for adsorption intensity (*n*) and Freundlich isotherm constant (*k*f) are determined in the equation of the line, according to the equation (3).

Also, the sorption capacity or elimination efficiency was determined as well and which represents the ability of soil to bind to itself a certain quantity of metallic ion until there comes to its saturation. Sorption capacity is represented by equation (1):

$$q = (c_0 - c_1 /m)V \qquad (1)$$

where *q* is sorption capacity (mg g^{-1}), c_0 initial metallic ions solution concentration (mg L^{-1}), c_1 equilibrium concentration (mg L^{-1}), *m* adsorbent mass (g) and *V* the solution volume (L).[19]

Preparation of soil samples for sequential extraction

Dry samples of soil (sand, humus and clay type of soil, about 10 g) had previously been saturated separately with 100 ml of lanthanum (III)- ion solution concentration of 50 mg L^{-1} and neodymium (III)- ion solution concentration of 50 mg L^{-1} so that their concentration would amount to 500 μg of element per gram of soil. The soil samples and solutions for the saturation were placed in glass bottles and were agitated for 12 h at a rotational shaker for the soils to be saturated with the ions from the solutions. After the saturation process, the suspensions were filtered and the soil samples were dried for the extraction. The same solutions used for soil saturation were analyzed by ICP-OES before and after the saturation for determining their real concentrations. The total quantities of lanthanum and neodymium ions in the soil were determined from calculating the difference of what was introduced and what remained in the solutions. The soils had previously been digested by microwave digestion[20] and analyzed by ICP-OES for verification and assurance that lanthanum and neodymium were not present in the soil. These elements were below the detection limits.[16]

Sequential extraction was performed in five phases.[21]

Phase I: saturated soils were extracted in glass bottles at rotational shaker with 100 mL of 1 mol L^{-1} ammonia-acetate solution each. The pH value of obtained suspensions amounted to about 7. The control test was formed of 100 mL extraction agent. Extraction at rotational shaker lasted for two hours. Upon extraction the samples were left to age for 12 hours for as better separation of phases. The liquid phases were filtered into 250 mL volumetric flask and were filled up to the line. The sediment was rinsed with bidistilled water up to negative reaction to ammonia ion and returned to the initial bottles.

Phase II: in each bottle containing soils from phase I was added 100 mL of 0.2 mol L^{-1} hydroxylamine hydrochloride and 0.02 mol L^{-1} hydrochloric acid solutions. The pH value was adjusted by adding 0.6 mol L^{-1} hydrochloric acid up to the value of about 4. Extraction at rotational shaker lasted for twelve hours. Upon extraction, the suspensions were filtered immediately, and sediment rinsing was performed by bidistilled water as far as the absence of reaction to chlorides. The filtrates obtained were transferred to the 250 mL volumetric flasks and were filled up to the line as well as blank test. The sediments were transferred to the initial bottles.

Phase III: to each soil from Phase II, 50 mL of 0.4 mol L^{-1} oxalic acid and 0.4 mol L^{-1} ammonia oxalate was added. The control test was made up of the extraction solutions. At rotational shaker the extraction lasted for nine hours, following which the suspensions were left to age for minimum twelve hours for better phases separation. The samples were filtered, and sediments rinsing was performed with bidistilled water as far as the negative reaction to oxalates. The filtrates obtained were transferred each to 250 mL volumetric flasks and filled up to the line. The sediments from the funnels were quantitatively transferred each to 250 mL glasses by rinsing with 40 mL of 0.02 mol L^{-1} nitric acid and 60 mL bidistilled water.

Phase IV: in each glass with suspension from Phase III, 10 mL of 30 % hydrogen peroxide was added, which was acidified by concentrated nitric acid up to pH 2. The control test was represented only by the acid solution of hydrogen peroxide. The glasses were covered by watch glass and were heated for two hours at water bath at 85 °C. Thereafter another 6 mL of acidified hydroxide peroxide solution was added to each glass, and heated for another three hours with occasional stirring. Suspensions were then left to cool. After being transferred to the initial bottles, to each suspension was added 100 mL of 3.2 mol L^{-1} ammonia acetate and filled up with bidistilled water up to 500 mL. Suspensions were mixed at the rotational shaker for thirty minutes and then the bottles were left to age overnight. Decanting was done same as in all phases, and the sediment was rinsed up to the negative reaction to ammonia ion. The filtrates obtained were concentrated to about 200 mL and then cooled and diluted in 250 mL volumetric flasks.

Phase V: for Phase V about 0.5 g of each dried up soil from the preceding phase was taken for microwave digestion. In each vessel containing soil 9 mL of concentrated nitric acid (MERCK), 3 mL concentrated hydrochloric acid (MERCK) and 2 mL of concentrated hydrofluoric acid (MERCK) were added. The samples were digested by microwave digestion (CEM Microwave Digestion System) 2×15 min with cooling between two digestions for 15 minutes. Control blank was formed of the acids added. Upon digestion and cooling the solutions were filtered into 50 mL volumetric flasks and diluted up to the line.

RESULTS AND DISCUSSION

Freundlich adsorption isotherms

Adsorption isotherm is unit defined as the diagram of the relationship between the quantity of the adsorbate adsorbed per mass of adsorbent and the

quantity of adsorbate remaining in the equilibrium solution following adsorption, whereby the distribution between the liquid and solid phase of adsorption solution for different concentrations is presented. Most often by adsorption isotherms the information on adsorption intensity, adsorbed quantity as well as on maximum adsorption capacity of the adsorbent is obtained.[22, 23]

One of the most frequently used adsorption isotherms is the Freundlich (H. Freundlich) isotherm. Freundlich isotherm is used for describing the physical adsorption, being the consequence of the Van der Waals forces impact, it is reversible and there may come to adsorption of adsorbents in a number of layers.[14, 24] The equation of Freundlich adsorption isotherm is (2):

$$q = k_f c_1^{1/n} \tag{2}$$

where q represents the quantity of adsorbed metallic ion per unit of mass (mg g^{-1}), k_f is the Freundlich isotherm constant, c_1 represents the solution equilibrium concentration (mg L^{-1}) and $1/n$ Freundlich constant that describes the adsorption intensity.[25]

Table II. Calculated values for x_0 - initial mass of metallic ion and x_1- adsorbed mass of metallic ion in the soil sample.

Sample	La		Er		Gd	
	x_0 / mg g^{-1}	x_1 / mg g^{-1}	x_0 / mg g^{-1}	x_1 / mg g^{-1}	x_0 / mg g^{-1}	x_1 / mg g^{-1}
Humus	8.64	8.64	10.89	10.89	9.51	9.51
	14.27	14.27	17.23	17.23	14.65	14.66
	17.83	17.77	21.76	21.76	17.69	17.69
	21.26	21.03	25.51	25.51	20.67	20.54
	27.07	25.81	31.21	31.21	23.44	22.56
Clay	8.76	8.74	10.88	10.88	9.51	9.51
	14.27	13.90	17.22	17.22	14.81	14.41
	17.69	16.55	21.88	20.74	18.16	16.64
	21.34	19.05	25.89	22.94	20.33	17.48
	27.96	23.77	30.11	23.92	23.53	18.18
Sand	8.74	6.50	10.78	7.52	9.49	6.35
	14.15	9.93	17.27	10.49	14.85	8.96
	17.65	11.68	21.48	12.36	17.73	10.24
	21.28	13.30	25.16	13.90	20.89	11.73
	26.42	15.55	31.12	15.70	23.58	11.62

Freundlich adsorption isotherm is linearized by logarithmic computation for easier determination of parameters n and k_f, and thus the equation is obtained (3):

$$\log q = \log k_f + 1/n \log c_1, \tag{3}$$

where $\log k_f$ in the diagram represents the intercept at y axis, and $1/n$ the line inclination.[26]

Table II presents the values of the initial mass of the metallic ion (x_0) - the mass of ions in solutions divided by the mass of the sorbent and adsorbed mass of the metallic ion in the soil sample following agitation (x_1).

The values obtained for determining humus and clay content, hygroscopic moisture content, pH value and soil sorption capacity have been presented in Table III.

Table III. Display of hygroscopic moisture, humus, clay and sand content, soil sorption capacity and pH.

Soil type	Content, %				q / mg g^{-1}			pH
	Moisture	Humus	Clay	Sand	La	Er	Gd	
Humus	2.97	4.43	≤ 0.5	≤ 0.5	17.77	n.a.*	20.54	7.45
Clay	2.66	≤ 0.5	12.59	≤ 0.5	8.74	20.74	14.41	6.64
Sand	1.02	≤ 0.5	≤ 0.5	91.02	6.5	7.52	6.35	5.53

*not achieved

The diffractogram presentation on the determined mineralogical content of sand, clay and humus soil has been shown in Fig. 1.
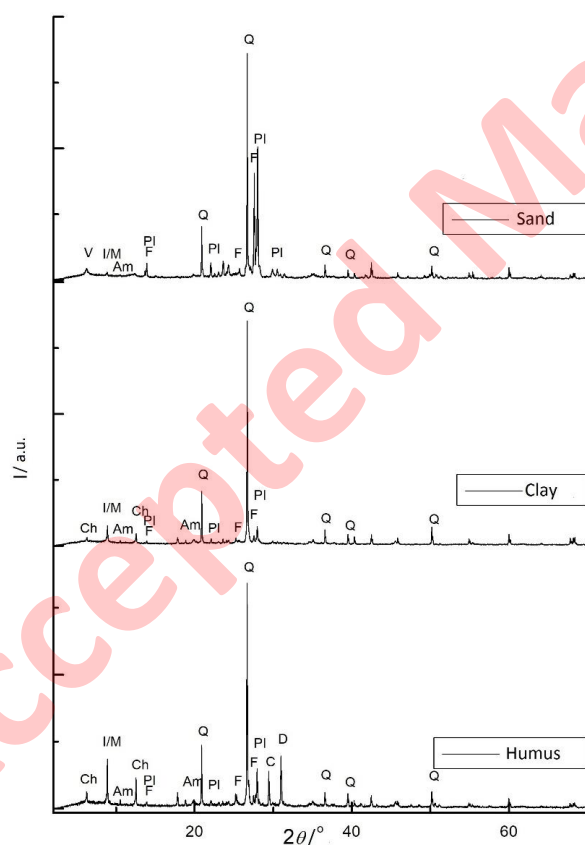

Fig. 1. X-ray diffractograms of powdered samples of sand, clay and humus type of soil

Table IV shows the mineral phases of the samples and their presence in the tested samples as well as the phase designations used on the diffractograms.

Table IV. Mineral phases and their presence in tested samples.

Type of soil	Humus	Clay	Sand
Quartz (Q)	+	+	+
Plagioclase (Pl)	+	+	+
Feldspar (F)	+	+	+
Amphibole (Am)	+	+	+
Calcite (C)	+		
Dolomite (D)	+		
Illite / Mica (I/M)	+	+	+
Chlorite (Ch)	+	+	
Vermiculite (V)			+

Based on the values obtained from Table II, it was possible to determine Freundlich adsorption isotherms for lanthanum and gadolinium ions in the clay and sand type of soil and erbium ions in the sand soil (Fig. 2). The values for Freundlich isotherm constant (k_f) and adsorption intensity (n) have been provided in Table V.
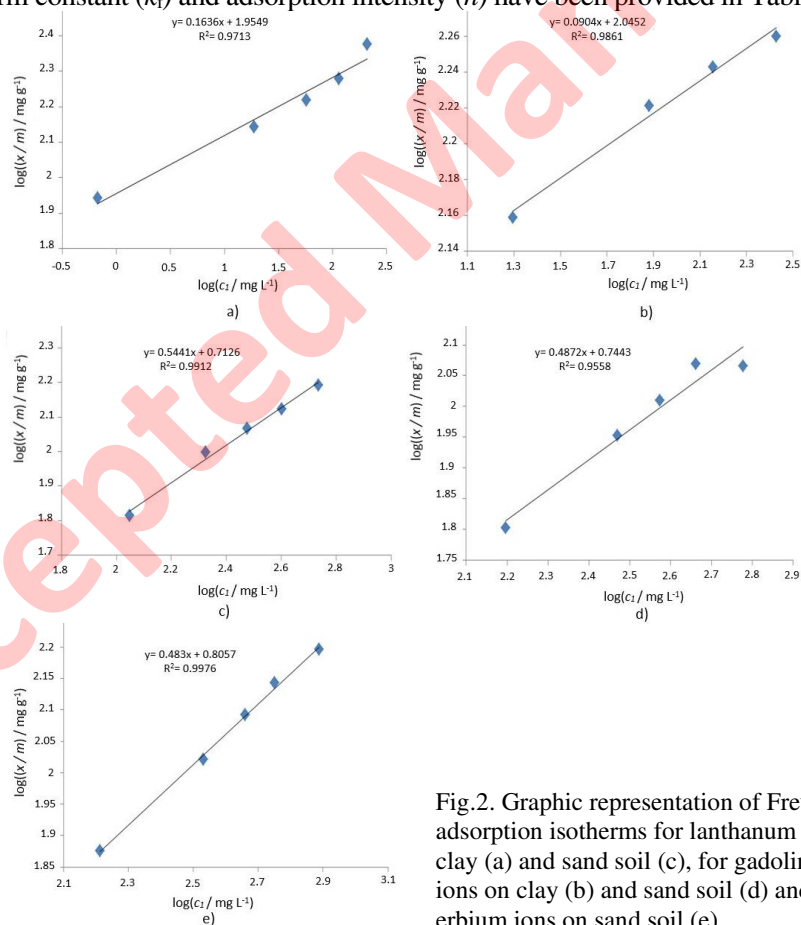

Fig.2. Graphic representation of Freundlich adsorption isotherms for lanthanum ions on clay (a) and sand soil (c), for gadolinium ions on clay (b) and sand soil (d) and for erbium ions on sand soil (e)

Table V. Parameters for Freundlich adsorption isotherms.

Sample name	n	k_f
La- clay soil	6.11	90.14
Gd- clay soil	2.07	6.39
La- sand soil	1.84	5.16
Er- sand soil	2.07	6.39
Gd- sand soil	2.05	5.55

Sorption capacity of the clay soil for all three elements is approximately the same. The greatest sorption capacities are in the clay soil for erbium ions and humus soil for gadolinium ions (Table III). Sorption capacity of humus soil for erbium ions has not been achieved, meaning that it has much greater adsorption capacity than the applied concentration of erbium (III)- ions. Freundlich adsorption isotherms have been achieved in five cases (Fig. 2), whereas for all three ions in humus and erbium in clay soil they have not been achieved due to exceptional soil sorption capacity. The clay type of soil has been demonstrated as the best sorbent for lanthanum (III)- ions. The parameters for other ions in clay and sand type of soils demonstrate that the adsorption rate is approximately the same, and as the adsorbents, these two soils are similar for the given ions. The exception being the sand type of soil for lanthanum (III)- ions, where the adsorption rate is lower and where it has been demonstrated that sand type of soil is poorer adsorbent for this elements (Table V).

The results of sequential extraction for lanthanum and neodymium

Values of the initial concentration of lanthanum and neodymium ions in the soils, results from different phases of extraction and the extracted amount of metal ions from the different types of soil are presented in Table VI. Histogram presentation of extracted lanthanum and neodymium ions through different phases of extraction has been shown in Figs. S-1 and S-2 of the supplementary material of this paper, respectively.

Table VI. Concentration of rare earth elements (REE) in µg g^{-1} for three types of soil obtained by sequential extraction

Element	Type of soil			Element	Type of soil		
La	Sand	Clay	Humus	Nd	Sand	Clay	Humus
Initial conc.	448.08	447.95	447.97	Initial conc.	527.64	527.44	527.64
Phase I	229.34	3.42	47.52	Phase I	305.21	<1.74	2.32
Phase II	10.69	1.14	<0.77	Phase II	<1.74	<1.74	2.56
Phase III	7.14	12.73	<0.77	Phase III	<1.74	<1.74	<1.74
Phase IV	197.77	430.00	<0.77	Phase IV	118.42	506.09	<1.74
Phase V	<0.77	<0.77	203.69	Phase V	<1.74	<1.74	107.61
Extracted amount, %	99.2	99.8	56	Extracted amount, %	80	96	20

Based on the results from Table VI it can be concluded that there is a difference between the results obtained for lanthanum and neodymium. The experimental results show that significant metallic ions concentration have been extracted, from sand soil 99.2 and 99.8 % from clay soil for lanthanum (Table VI). In humus soil about 56 % of lanthanum has been extracted. Lanthanum mobilization happened in several different phases and the extraction in phases with milder extraction agents had occurred.

In case of neodymium, the nature of soil is important in particular, since only in certain extraction phases there came to ion extraction, and also due to slightly different neodymium properties because of the ionic diameter, where the ions were more tightly "bound" (complexed) to certain organic components characteristic for humus. The extraction was noticed in ion exchange phase (Phase I) and in extraction phases with acids (Phases IV and V).

The results show that in sand soil about 80 % of neodymium ions have been extracted and in the clay type of soil 96 % (Table VI). The extraction from humus soil was about 20 % (Table VI). This is a clear indicator that due to the complexity of interactions of lanthanum and neodymium ions with different soil components, it is not easy to effectively extract them using milder agents. It can be concluded that the extracted quantities depend on soil type, nature of extraction agent and metallic ion characteristics. Neodymium, first of all, due to its ionic diameter reacts differently with soil. For that reason the extraction happened only with solutions of certain extraction agents depending on their nature and ionic forces.

CONCLUSION

The impact between the soil and rare earth elements and the soil capacity to adsorb these elements has been studied. Freundlich adsorption isotherms for the lanthanum, erbium and gadolinium have been presented in two soil types, the clay and sand soils. For humus soil Freundlich adsorption isotherms have not been achieved for the used concentrations of these elements, and thus it has been assumed that humus soil possesses much greater adsorption capacity and the equilibrium between the ions in the solution and at the soil surface is more rapidly established. It can be concluded that soil possesses a certain capacity for binding the rare earth elements, so that physically unprotected soil does not present a suitable surface for disposal of electronic waste. Should such waste be disposed on such soil types, it would be beneficial to protect the soil with polymer or similar non-permeable material.

The method of sequential extraction based on the results presented is suitable for extraction of rare earth elements from sand and clay type of soils. Humus soil has demonstrated more intensive sorption properties, therefore these types of extractions are limited on it, namely this method is not so undemanding. The characteristics (composition) of soil, pH value and extraction solution composition

are particularly important for extraction effects. The suitability of the method presented is reflected in its simplicity, namely the rare earth elements ions can be extracted by this method from a complex matrix. The environment contamination on the occasion of these elements production is evident. Excepting their natural occurrence, the anthropogenic factor is increasingly noticed, waste is accumulating and the concentration of these elements increases rapidly. Developing the methodology of sequential extraction enables better predictions and further understanding of the elements fate as well as their potential hazard to the environment.

SUPPLEMENTARY MATERIAL

Additional data and information is available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/11073, or from the corresponding author on request.

И З В О Д

НЕКИ ПРИМЕРИ ИНТЕРАКЦИЈА ПОЈЕДИНИХ ЕЛЕМЕНАТА РЕТКИХ ЗЕМАЉА И ТЛА

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Елементи ретких земаља представљају све важнији индустријски ресурс. Повећана употреба може довести до стварања отпада, а њихов утицај на квалитет животне средине није довољно проучен. У овом раду је испитивана њихова интеракција са земљиштем. Одређивана је Фројндлихова адсорпциона изотерма за елементе лантана, ербијума и гадолинијума на три различита типа земљишта (хумусном, глиновитом и песковитом), док је секвенцијална екстракција, на овим типовима земљишта, примењена за лантан и неодимијум. Испитивана је интеракција појединих елемената ретких земаља са компонентама земљишта, као и количина у којој се ови метали везују за тло, а касније и екстрахују у растворе. Циљ је био одредити капацитет земљишта за одлагање, превенствено, електронског отпада који садржи ове елементе и претпоставити њихову судбину у животној средини.

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REFERENCES

1. I. Anastopoulos, A. Bhatnagar, E. C. Lima, *J. Mol. Liq.* **221** (2016) 954 (https://doi.org/10.1016/j.molliq.2016.06.076)
2. F. Tommasi, P. J. Thomas, G. Pagano, G. A. Perono, R. Oral, D. M. Lyons, M. Toscanesi, M. Trifuoggi, *J. Arch. Environ. Contam. Toxicol.* **81** (2021) 531 (https://doi.org/10.1007/s00244-020-00773-4)
3. V. Balaram, *J. Geosci. Front.* **10** (2019) 1285
4. V. M. Goldschmidt, *J. Chem. Soc. (Resumed)* (1937) 655 (https://doi.org/10.1039/JR9370000655)
5. M. Bernat, *Cah. ORSTOM Ser. Geol* **7** (1975) 65 (https://core.ac.uk/download/pdf/39881849.pdf)
6. V. Zepf, *Rare Earth Elements: What and where they are. In: Rare Earth Elements,* Springer, Berlin, Heidelberg,, Germany, 2013 pp. 11-39 (https://doi.org/10.1007/978-3-642-35458-8_2)

7. Y. Takaya, K. Yasukawa, T. Kawasaki, K. Fujinaga, J. Ohta, Y. Usui, K. Nakamura, J. Kimura, Q. Chang, M. Hamada, G. Dodbiba, T. Nozaki, K. Iijima, T. Morisawa, T. Kuwahara, Y. Ishida, T. Ichimura, M. Kitazume, T. Fujita, Y. Kato, *Scientific reports* **8** (2018) (https://doi.org/10.1038/s41598-018-23948-5)
8. Y. Kato, K. Fujinaga, K. Nakamura, Y. Takaya, K. Kitamura, J. Ohta, R. Toda, T. Nakashima, H. Iwamori, *Nature Geoscience* **4** (2011) 535 (https://doi.org/10.1038/ngeo1185)
9. Y. Wan, C. Liu, *J. Rare Earths* **23** (2005) 377
10. G. W. Beall, B. H. Ketelle, R. G. Haire, G. D. O'Kelley, *ACS Symposium Series* **100** (1979) 201 (http://dx.doi.org/10.1021/bk-1979-0100.ch012)
11. F. Coppin, G. Berger, A. Bauer, S. Castet, M. Loubet, *Chemical Geology* *182* (2002) 57 (https://doi.org/10.1016/S0009-2541(01)00283-2)
12. IAEA, *Radiation protection and NORM residue management in the production of rare earths from thorium containing minerals*, Safety Reports Series **68** (2011) 259
13. G. Haxel, *US Geological Survey* **87** (2002) (https://pubs.usgs.gov/fs/2002/fs087-02)
14. C. Ng, J. N. Losso, W. E. Marshall, R. M. Rao, *Bioresource technology* **85** (2002) 131 (https://doi.org/10.1016/S0960-8524(02)00093-7)
15. S. McLeod, *Notes on soil techniques* (1973) 73
16. D. P. Gangwar, M. Baskar, *Texture determination of soil by hydrometer method for forensic purpose,* Central Forensic Science Laboratory, Chandigarh (2019) (http://dx.doi.org/10.13140/RG.2.2.16057.60001)
17. J. Isailović, *Freundlich adsorption isotherms for some rare earth elements on different types of soil*, Master's thesis, Faculty of Chemistry, University of Belgrade (2021) (in Serbian)
18. Z. Nikolovski, *Sequential extraction of lanthanum and neodymium from soil*, Master's thesis, Faculty of Chemistry, University of Belgrade (2021) (in Serbian)
19. A. Guša, M. Đolić, B. Lekić, V. Rajaković-Ognjanović, *Water management,* **47** (2015) 67 (http://grafar.grf.bg.ac.rs/handle/123456789/656) (in Serbian)
20. EPA M 3051A: *Microwave assisted acid digestion of sediments, sludges, soils and oils* (2007)
21. B. Stanimirović, J. Otašević, J. Petrović, D. Savić, D. Tonić, A. Šestak, Lj. Miličić, M. Savić, S. Jovanović, *Possibilities of extraction of high-value useful ions and ionic species from ash TPP JP EPS*, Institute MOL d.o.o. Stara Pazova, Institute IMS a.d. Belgrade, Serbia (2016) 33 (in Serbian)
22. D. L. Jensen, A. Ledin, T. H. Christensen, *Water Research* **33** (1999) 2642 (https://doi.org/10.1177%2F0734242X04042146)
23. J. U. Keller, R. Staudt, (2005). *Gas adsorption equilibria: experimental methods and adsorptive isotherms*. Springer Science & Business Media, 1-402 (ISBN 978-0-387-23598-1)
24. A. S. Erses, M. A. Fazal, T. T. Onay, W. H. Craig, *J. Hazard. Mater.* **121** (2005) 223 (https://doi.org/10.1016/j.jhazmat.2005.02.011)
25. S. Veli, B. Alyüz, *J. Hazard. Mater.* **149** (2007) 226 (https://doi.org/10.1016/j.jhazmat.2007.04.109)
26. A. Özer, H. B. Pirincci, *J. Hazard. Mater.* **137** (2006) 849 (https://doi.org/10.1016/j.jhazmat.2006.03.009).

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SUPPLEMENTARY MATERIAL TO
Some examples of interactions between certain rare earth elements and soil

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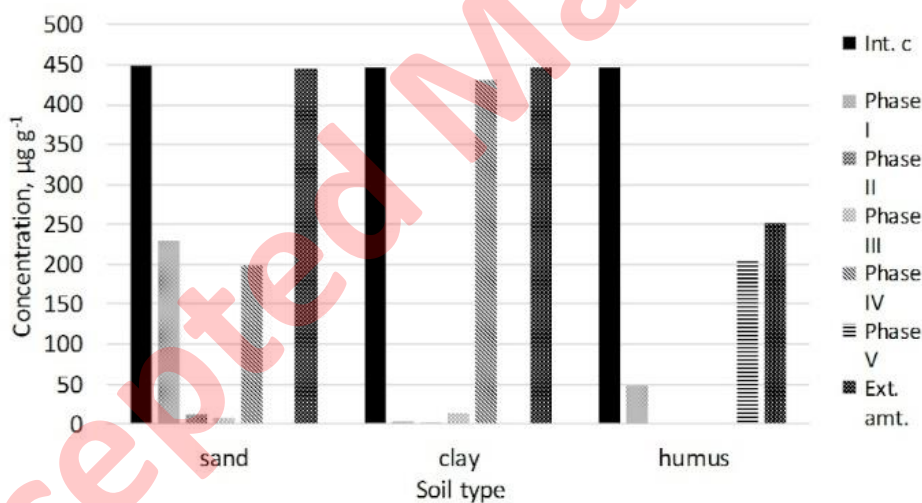
Fig. S-1. Histogram presentation of initial concentrations of lanthanum and extracted ions in different extraction agents.

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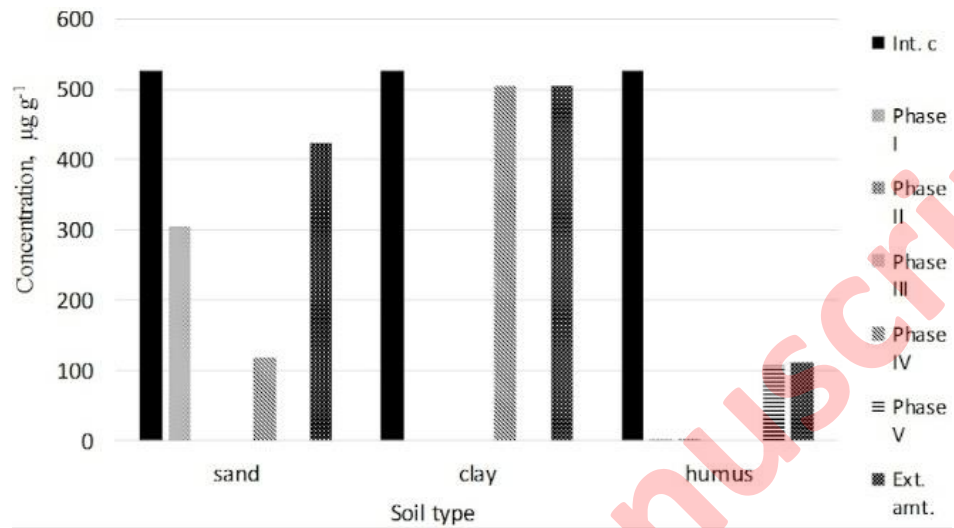#Serbian Chemical Society member

Fig. S-2. Histogram presentation of initial concentrations of neodymium and extracted ions in different extraction agents.