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STUDY OF SIMULTANEOUS RADIONUCLIDE SORPTION BY MIXTURE DESIGN

METHODOLOGY

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2
3 ABSTRACT
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5 The problem of simultaneous removal of Co^{2+} , Sr^{2+} and Cs^+ ions from aqueous solutions was
6 addressed using oxide, phosphate and aluminosilicate materials from economical and abundant
7 sources. Competition between cations was analyzed by following approaches: (i) addition of
8 each sorbent separately to variously concentrated cation mixtures (using simplex lattice
9 experimental design methodology), (ii) application of mixture sorbents (using extreme vertices
10 experimental design), and (iii) consecutive addition of sorbents in varying order. Investigated
11 materials exhibited different selectivity for Co^{2+} , Sr^{2+} and Cs^+ in the mixture, thus combination
12 of materials in one-step sorption, or successive addition of sorbents in multi-step process, lead to
13 better removal efficiency. Regression equations obtained by statistical analysis satisfactorily
14 predicted sorbed amounts of cations as a function of both the composition of mixed waste and
15 the composition of mixed sorbent. Mixture designs should be considered as useful tools for
16 getting better insight into the complex sorption processes.
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40 **Keywords:** Mixture design; Liquid radioactive waste; Competitive sorption; Mixed sorbents;
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INTRODUCTION

Liquid radioactive wastes (LRW) from nuclear reactors, test probes and various branches of industry and medicine exhibit a complex and variable composition¹⁻³. In addition to inorganic salts, complexing agents, organic matter, etc., different radionuclides are simultaneously present. Consequently, several physicochemical processes, or purification stages, are frequently required in order to achieve an adequate degree of purity^{1,4,5}.

Activity of LRW decreases exponentially during the time, and 20 to 30 years after the closure of a nuclear reactor among dominant carriers of radioactivity are ¹³⁷Cs, ⁶⁰Co and ⁹⁰Sr³. ⁶⁰Co (half-life 5.27 y) is the major activation product, which occurs from reactor made ferritic materials and alloys, while ¹³⁷Cs and ⁹⁰Sr are fission products with half-lives of 30 and 28.7 y, respectively. Therefore, mixture of Co²⁺, Sr²⁺ and Cs⁺ is a combination of chemically different elements, which is particularly interesting and challenging from the aspect of LRW treatment.

One of the methods for purification of LRW is based on the utilization of inorganic sorbents/ion-exchangers, with high capacity, high chemical and radiological stability and low cost^{1,4-8}. In this regard, numerous studies dealt with applicability of abundant natural minerals or waste derived materials⁹⁻¹¹. Despite the fact that LRW contain different isotopes in varying concentrations, sorbents were commonly tested using single metal solutions and two-component mixtures⁵. The effect of competition between Co²⁺, Sr²⁺ and Cs⁺ was reported in a few studies. Based on the Langmuir isotherm data, competitive Co²⁺, Sr²⁺ and Cs⁺ sorption was tested using Ca-montmorillonite as a sorbent¹². It was found that Co²⁺ and Sr²⁺ ions behave in a different manner when compared to Cs⁺, due to their affinity for particular sorption sites. The same authors reported results of Co²⁺, Sr²⁺ and Cs⁺ sorption by clayey soil, starting from binary and

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3 ternary mixtures¹³. Presence of Co^{2+} and Cs^+ ions highly influenced the sorption of Sr^{2+} , while
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5 Co^{2+} and Cs^+ did not seem to compete for the same sorption sites. Similar conclusions were
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7 derived based on the investigation of Co^{2+} , Sr^{2+} and Cs^+ from single and bi-solute solutions onto
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9 phosphate-modified montmorillonite¹⁴ and ammonium molybdophosphate–polyacrylonitrile
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11 (AMP–PAN)¹⁵. Furthermore, Sr^{2+} ions did not affect the removal of coexisting Co^{2+} ions by
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13 activated carbon felts¹⁶, while the experiments with equimolar ternary mixture of Co^{2+} , Sr^{2+} and
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15 Cs^+ showed decreased selectivity of zeolite in the order $\text{Cs}^+ \gg \text{Sr}^{2+} > \text{Co}^{2+}$ ¹⁷. Generally, the
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17 presence of other cations in the solution, with similar dimensions or valence may influence the
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19 sorption process to the greater extent¹⁸. According to the literature data, there is still a strong
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21 need to study the behavior of potential sorbents in multicomponent solutions. Furthermore, it is
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23 evident that capacities and selectivity of sorbents to Co^{2+} , Sr^{2+} and Cs^+ ions are different; thus, it
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25 is difficult to achieve purification of wastewater containing their mixture using only one sorbent.
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32 In this study, the problem of simultaneous Co^{2+} , Sr^{2+} and Cs^+ sorption from liquid wastes was
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34 addressed using oxide, phosphate and aluminosilicate based materials, chosen based on their
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36 effectiveness for cation immobilization^{8,19-23}. The process is far more economical if sorbents are
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38 derived from abundant sources and with little pretreatment. Therefore, bauxite residue from
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40 alumina industry (red mud) was utilized as an oxide composite, phosphate representative was
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42 bio-apatite material recovered from animal bones, while mineral zeolite was used in its raw form.
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44 The influence of following parameters on the removal efficiency was studied: mole fractions of
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46 cations in the simulated waste solutions; the type of sorbent used in one stage sorption process;
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48 the ratio of selected materials in the sorbent mixtures using one-stage sorption protocol and the
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50 order of different sorbents addition in multistage sorption processes.
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3 In order to consider a wide range of components ratios in the mixture, and to explore and
4 compare the effects of individual and mixed sorbents in one stage and multistage sorption
5 protocols, the design of experiments (DOE) methodology was chosen for experiment planning.
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8 The influence of different experimental conditions onto system response can be investigated by
9 statistical designs such as full factorial design, Box-Benken design, response surface, Taguchi
10 design, etc.²⁴ When the objectives of investigation are multicomponent systems, whose
11 properties are dependent on composition, the mixture design can be used. The exploitation of
12 mixture design gives the following important outputs: a) the empirical models for prediction of
13 system responses at any ratio of the components, and b) the effects of each component
14 individually (or in the combination with other components), on the system responses.
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27 The main aim of the study was a better insight into the competitive sorption of Co^{2+} , Sr^{2+}
28 and comparison of different protocols for treatment of mixed wastes.
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34 1. MATERIALS AND METHODS

35 2.1. Applied sorbents

36 Rinsed red mud (RBRM) from “Alumina” factory deposit (Bosnia and Herzegovina), bovine
37 bones annealed at 400°C (B400) and mineral zeolite (NZ) from Vranjska Banja (Serbia) were
38 used as sorbents. RBRM was obtained by repeated rinsing of alkaline bauxite residue as
39 described in detail previously²⁵. From the mineralogical point of view, its main components
40 were hematite (Fe_2O_3), gibbsite and bayerite ($\text{Al}(\text{OH})_3$), sodalite ($\text{Na}_8\text{Si}_6\text{Al}_6\text{O}_{24}\text{Cl}_2$), calcite
41 (CaCO_3), quartz (SiO_2) and TiO_2 ²⁵. Biogenic apatite B400 was produced by annealing the
42 bovine femur bones at 400°C²⁶. The chemical and mineralogical studies showed that B400
43 consisted principally of non-stoichiometric nano-sized bio-apatite, with the traces of degraded
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3 organic bone fraction²⁶. NZ was mesoporous material, mostly clinoptilolite, with small amounts
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5 of quartz and albite²⁷. The determined points of zero charge (pH_{PZC}) were 6.83 for B400²⁶ and
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7 7.5 for both RBRM²⁵ and NZ²⁷. Furthermore, the specific surface area (SSA) of the sorbent
8
9 plays an important role in the overall process²⁸. Previous analysis of investigated sorbents
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11 revealed that RBRM particles were non-porous, with SSA of 17 m²/g²⁹, while NZ and B400
12
13 were mesoporous with SSA of 23 m²/g²⁷ and 85 m²/g²⁶, respectively. All sorbents were dried at
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15 80°C, and after grinding and sieving, the fractions of particles smaller than 45µm were collected
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20 for the sorption experiments.
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24 2.2. One-stage sorption experiments with individual sorbents

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29 Concentrations of investigated cations in simulated waste solutions were determined by
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31 experimental design. The mixture simplex lattice design for q=3 components and with m=3
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33 degrees of lattice was used for experimental point's designation. The number of experimental
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35 points was:
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$$38 \quad (q+m-1)!/(m!(q-1)!)=(3+3-1)!/(3!(3-1)!)=10$$

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40 which were augmented with axial points. According to the matrix of mixture design (Table 1),
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42 13 solutions were prepared in total (one component, two- components and three-components). In
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44 order to investigate the performances of applied sorbents and to define maximum sorption
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46 capacities, total concentration of each solution was 4.5×10⁻³ mol/L.
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3 Nitrate salts of selected metals ($\text{Co}(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and CsNO_3 , p.a, Merck) were used
4
5 for the preparation of simulated wastes. After the dissolution of adequate masses to obtain target
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7 concentrations, original pH values were in the range 5.3 to 5.9. Given that the investigated
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9 sorbents showed strong buffering properties in the range of initial pH between 4-10²⁵⁻²⁷, no
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11 further adjustment of solution pH was performed.
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15 Removal of Co^{2+} , Sr^{2+} and Cs^+ from solutions defined by Table 1 was investigated by application
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17 of each sorbent separately. 20 mL of each solution was equilibrated with 0.1 g of sorbent, at
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19 room temperature ($21 \pm 1^\circ\text{C}$). Experiments were conducted on the rotary shaker (10 rpm) for 24 h,
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21 in order to achieve equilibrium.
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24 25 26 27 2.3. One-stage sorption experiments with mixed sorbents 28 29 30 31

32 In order to investigate the effect of sorbent mixtures composition onto sorption from equimolar
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34 Co^{2+} , Sr^{2+} and Cs^+ solution (total concentration 4.5×10^{-3} mol/L), the DOE was applied. The
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36 proportions of each sorbent in the mixtures were determined using extreme vertices design
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38 (Table 2). The extreme vertices design is a type of mixture design that covers only a part within
39
40 the whole simplex. This sub-simplex has to be defined using constraints bonds. The adopted
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42 design degree was 2, while linear constraints were set with lower bond at 0.2 and with upper
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44 bond at 0.6. The experimental conditions were the same as those used in one-stage sorption
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46 experiments (total amount of used sorbent materials was 0.1g, solution volume 20 mL, shaking
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48 speed 10 rpm, shaking time 24 h at ambient temperature).
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2.4. Three-stage sorption experiments

Multistage sorption experiments were conducted according to the scheme presented in Figure 1, in order to keep the constant solid to solution ratio. 1, 2 and 3 are denotations of the sorbents used in each iteration. As the number of iterations was three, six permutations of sorbents addition orders were obtained. All experiments were performed at room temperature, using constant solid-liquid ratio (1:200), agitation speed (10 rpm) and contact time (24 h). As a simulated liquid waste, equimolar ternary mixture of Co^{2+} , Sr^{2+} , Cs^+ was applied at total concentration of 4.5×10^{-3} mol/L.

FIGURE 1

After specified time intervals, the suspensions were centrifuged at 7000 rpm for 10 minutes, to separate solid and liquid phase. The metal concentrations in filtrates and pH values were measured.

2.5. Metal concentration measurements

Determination of the exact initial and final Co^{2+} , Sr^{2+} and Cs^+ concentrations was performed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), using Thermo Scientific iCAP 6500 Duo ICP (Thermo Fisher Scientific, Cambridge, United Kingdom) spectrometer equipped with RACID86 Charge Injector Device (CID) detector, concentric nebulizer, quartz torch, and alumina injector. The quantification of elements in the solutions was measured at the

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3 emission wavelengths: Co^{2+} 237.862 nm, Sr^{2+} 215.284 nm and Cs^+ 455.531 nm. Instrumental
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5 operating conditions for ICP-OES measurements are given in Table S1.
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8 The differences between the initial and the final metal concentrations were used for calculation
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10 of the sorbed amounts.
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19 Sorption experiments were conducted in duplicate and the average results are presented. Two
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21 plasma standard solutions, multi-element plasma standard solution 4 (Specpure®, 1000 $\mu\text{g}/\text{ml}$)
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23 and cesium plasma standard solution (Specpure®, Cs 1000 $\mu\text{g}/\text{ml}$) certified by Alfa Aesar GmbH
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25 & Co KG, Germany were used to prepare calibration solutions for ICP-OES measurements. The
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27 instrument was recalibrated after each 20 samples. The reliability of measurements was approved
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29 by relative standard deviation lower than 5%.
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40 Mean values of measured parameters were used as system responses for data interpretation and
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42 statistical analysis. Experimental points designation, analysis of variance (ANOVA), fitting of
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44 regression polynomial models and graphical presentations (ternary plots) were performed using
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46 the statistical software MINITAB Release 13.2. The statistical analysis was done at the
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48 confidence level $\alpha=95\%$.
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53 54 55 2. RESULTS AND DISCUSSION 56 57

3.1. One-stage sorption experiments

After the reaction of each sorbent with the solutions prepared according to the experimental design, equilibrium pH values were measured (Table 1). It is evident that final pH values depended on both the sorbent and the solution. pH values ranged between 5.62 and 6.88 when B400 was used, 6.3 - 7.61 range was characteristic for RBRM, while 4.94 - 5.63 for NZ. For multicomponent solutions a common decreasing trend was observed: $\text{pH}(\text{RBRM}) > \text{pH}(\text{B400}) > \text{pH}(\text{NZ})$. The exceptions were solutions 7 (single-component solution of Sr^{2+}) and 9 (di-component solution of Sr and Cs in the molar ratio 2:1), where pH decreased in the order: $\text{pH}(\text{B400}) > \text{pH}(\text{RBRM}) > \text{pH}(\text{NZ})$. As precipitating of $\text{Co}(\text{OH})_2$ occurs at $\text{pH} > 8$, it can be assumed that all investigated sorbates were in ionic form under given conditions. All equilibrium pH values were lower than determined pH_{PZC} values of used sorbents, suggesting that specific cation sorption was a common operating mechanism.

3.1.1. Capacity and selectivity of B400

Sorption effectiveness of selected sorbents toward Co^{2+} , Sr^{2+} and Cs^+ ions, from solutions of the same total concentration, but different metal ratios, is given in Fig. 2. Removal efficiency of B400 was affected by cation type and solution chemistry. Sorbed amounts of Co^{2+} ions were the highest and ranged between 0.14 mmol/g and 0.46 mmol/g. Sr^{2+} ions were sorbed moderately by B400 (0.07-0.31 mmol/g), while detected tendency for Cs^+ sorption was very poor (0-0.03 mmol/g).

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3 Considering multicomponent solutions, similar amounts of Co^{2+} ions were sorbed in the presence
4 of Sr^{2+} and Cs^+ ions. In opposition to Co^{2+} , removal of Sr^{2+} by B400 was more suppressed in the
5 presence of Co^{2+} , than Cs^+ ions. Finally, due to a very low affinity of B400 toward Cs^+ ions the
6 estimation of the influence of coexisting cations is impractical. Capacities of B400 surface
7 towards Co^{2+} and Sr^{2+} ions from single solutions were already reported^{26,30} and were
8 comparable to the values obtained in this study.
9

10 Accordingly, sorption capacities of B400 decreased in the order $\text{Co}^{2+} > \text{Sr}^{2+} > \text{Cs}^+$, which is in
11 accordance with the literature data. The main recognized mechanisms by which apatites bond
12 cations from the solution are: ion-exchange and specific cation sorption³¹⁻³⁶. Ion exchange
13 occurs between cations from the solution and cations (mainly Ca^{2+}) from apatite surface. High
14 sorption efficiency of B400 for Co^{2+} and Sr^{2+} ions, observed in Fig. 2, can be attributed to the
15 same ionic charge and similar crystal radii to that of Ca^{2+} ion (1.13 Å for Sr^{2+} , 0.73 Å for Co^{2+} and
16 0.99 Å for Ca^{2+} ion³⁷). Comparing sorption capacities of various divalent cations by apatites, it
17 can be observed that alkaline-earth elements were sorbed in lower quantities in respect to various
18 divalent heavy metals such as Pb^{2+} , Cd^{2+} , Zn^{2+} .^{21,31} The investigation of the sorption properties
19 of biogenic apatite (Apatite II) toward radionuclides showed that Cs^+ ions were not sorbed^{38,39}.
20 This was explained by the fact that crystal radii of Cs^+ ion (1.69 Å) is too large to fit in the
21 apatite crystal lattice. Furthermore, comparing Sr^{2+} and Cs^+ sorption by natural apatite, a few
22 times higher distribution coefficients were determined for Sr^{2+} ⁴⁰. Selectivity sequence was also
23 directly proportional to the values of the first ionization energy of investigated elements (376
24 kJ/mol, 549 kJ/mol and 760 kJ/mol for Cs^+ , Sr^{2+} and Co^{2+} respectively⁴¹).
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FIGURE 2

3.1.2. Capacity and selectivity of RBRM

Sorbed amounts of Co^{2+} ions onto RBRM (0.16 mmol/g - 0.44 mmol/g) were comparable to the values obtained for B400. Considering the quantities sorbed from multicomponent solutions of the same initial concentrations, it can be observed that about 0.40 mmol/g was sorbed from the solution of higher Co^{2+} concentration (3×10^{-3} mol/L), while from the solutions of lower initial Co^{2+} concentration (1.5×10^{-3} mol/L) approximately 0.28 mmol/g was sorbed, regardless of the solution composition. This suggested that Co^{2+} sorption was undisturbed by the coexisting cations.

Experimentally defined sorption capacities of Sr^{2+} ions onto RBRM ranged from 0.029 mmol/g to 0.19 mmol/g. The highest sorption was attained from a single-component Sr^{2+} solution, which exhibited the highest initial Sr^{2+} concentration. The lowest sorption of Sr^{2+} was detected from a three-component solution containing high amounts of Co^{2+} ions. Strontium sorption from multicomponent solutions was significantly higher in the presence of Cs^+ ions than in the presence of Co^{2+} ions. Previously reported values of Co^{2+} and Sr^{2+} sorption from single metal solutions using raw (unwashed) red mud were 0.52 mmol Co^{2+} /g and 0.31 mmol Sr^{2+} /g⁷. In comparison to RBRM, enhanced cation removal obtained using the raw sample can be attributed to its higher alkalinity¹⁰.

Cs^+ sorption onto RBRM was generally very low (maximum 0.017 mmol/g). Measurable sorption occurred only when Cs^+ ions were mixed with Sr^{2+} , which is an interesting fact. In the mixtures with Co^{2+} , Cs^+ sorption occurred only when Co^{2+} concentration was significantly lower in respect to the content of Cs^+ and Sr^{2+} ions.

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3 The results are in line with the available literature. Considering sorption and desorption of
4 radiocesium and radiostrontium onto water-washed red mud, Apak et al.¹¹ also found much
5 lower sorption of Cs⁺ (5.1×10^{-3} mmol/g) than Sr²⁺ (10.6 mmol/g). Acid and heat treatments of
6 red mud led to increased Cs⁺ sorption but were unfavorable for Sr²⁺ removal¹¹, which indicates
7 that these ions do not compete for the same sorption sites. The authors presumed that Cs⁺ ions
8 were predominantly sorbed by irreversible fixation and, in part, by ion exchange.
9

10 Bonding of selected cations onto RBRM surface obviously occurred via different mechanisms.

11 Co²⁺ sorption by RBRM, which was found to be independent on Sr²⁺ and Cs⁺ presence and
12 content, suggested formation of specific surface complexes of the inner-sphere type and/or the
13 surface precipitates. Sr²⁺ sorption by red mud was previously characterized as specific, with the
14 contribution of ion exchange¹¹. Affinity of red mud surface was found to be in correlation with
15 the electronegativity and ionic potential of sorbing cations¹⁰. The electronegativity of
16 investigated ions decreased in the order Co²⁺(1.8) > Sr²⁺ (1.0) > Cs⁺ (3.29), as does the ionic
17 potential (Co²⁺ (4.55) > Sr²⁺ (3.03) > Cs⁺ (0.59)).
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39 3.1.3. Capacity and selectivity of NZ

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43 NZ affinity toward Co²⁺ ions was very low and the sorption capacities ranged between 0.013 and
44 0.056 mmol/g, depending on the solution composition. Amounts of Co²⁺ sorbed from mixed
45 solutions were comparable, but lower in respect to the value reported for single-metal Co²⁺
46 solution¹⁷. Therefore, unlike the sorption on B400 and RBRM, Co²⁺ removal by NZ was
47 suppressed in the presence of other ions in binary and ternary solutions.
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3 NZ was found to be the least selective toward Sr^{2+} ions, whose sorbed amounts varied between
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5 0.049 mmol/g and 0.14 mmol/g. The lowest Sr^{2+} sorption was determined using three-component
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7 mixtures containing very high amounts of Co^{2+} or Cs^+ ions. Sorption efficiency from two-
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9 component and three-component solutions was comparable and independent on coexisting cation
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11 type, pointing out that Sr^{2+} sorption was affected by coexisting Co^{2+} and Cs^+ ions in the same
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13 manner.
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17 On the other hand, NZ was by far the best sorbent for Cs^+ ions, with the sorption capacities
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19 between 0.14 and 0.68 mmol/g measured in the single component Cs^+ solution. Sorption of Cs^+
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21 from binary solutions was equivalent regardless of a competing cation type and content, i.e. it
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23 depended solely on the initial Cs^+ concentration (0.30 mmol/g and 0.5 mmol/g was sorbed, from
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25 mixtures with lower and higher Cs^+ concentration, respectively). Sorption capacities and
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27 selectivity of zeolite towards Cs^+ , Co^{2+} and Sr^{2+} was in good correlation with previous studies¹⁷.
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29 Due to specific crystal structure, zeolites exhibit particularly high affinity towards Cs^+ ions^{17, 42}.
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31 Removal of cations by zeolite involves ion-exchange and specific surface sorption as a dominant
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33 sorption mechanism¹⁷. Therefore, its capacity depends on hydrated ionic radii which increase in
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35 the order Cs^+ (3.29 Å) > Sr^{2+} (4.12 Å) > Co^{2+} (4.23 Å)³⁷. Due to small dimensions, diffusion of
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37 monovalent Cs^+ ions into the pores of zeolite material is easier compared to larger divalent Co^{2+}
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39 and Sr^{2+} ¹⁷. Preferred sorption of Cs^+ ions in respect to Co^{2+} was also observed using Lewatite
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41 S100 ion-exchanger⁴³ and zirconium silicate⁴⁴. Besides the size of ions, electrostatics forces are
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43 more intensive in the case of multivalent cations, reducing their mobility inside the particles of
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45 ion-exchange resin. Calculation of effective diffusion coefficients has revealed higher values for
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47 Cs^+ ions than for Co^{2+} ⁴⁴, which was in agreement with the selectivity of ion-exchangers. The
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intensity of cation sorption by zeolites was also found to be inversely proportional to their ionization potentials ⁹.

3.1.4. Statistical analysis of simplex lattice mixture design

Results presented in Fig. 2 were statistically analyzed and the prediction of sorbed amounts was predicted using regression models. Concentrations of each metal in the solution and interactions between the cations were selected as variables, while sorbed amounts of Co^{2+} , Sr^{2+} and Cs^+ onto each sorbent were selected as system responses. Using quadratic mixture regression fitting model, regression coefficients were estimated. Concerning only statistically significant terms, the following equations were obtained for the prediction of sorbed amounts:

$$\text{Co-B400} = 0.009471 \times \text{Sr} + 0.456388 \times \text{Co} + 0.006016 \times \text{Cs} + 0.528273 \times \text{SrCo} + 0.607720 \times \text{CoCs}$$

(1)

$$\text{Sr-B400} = 0.29368 \times \text{Sr} + 0.00362 \times \text{Co} + 0.005380 \times \text{Cs} + 0.226640 \times \text{SrCs}$$

(2)

$$\text{Co-RBRM} = 0.005502 \times \text{Sr} + 0.428546 \times \text{Co} + 0.005039 \times \text{Cs} + 0.554924 \times \text{SrCo} + 0.59184 \times \text{CoCs}$$

(3)

$$\text{Sr-RBRM} = 0.1796 \times \text{Sr} + 0.0073 \times \text{Co} - 0.0029 \times \text{Cs} - 0.2129 \times \text{SrCo} + 0.2488 \times \text{SrCs}$$

(4)

$$\text{Sr-NZ} = 0.133839 \times \text{Sr} + 0.002442 \times \text{Co} + 0.002665 \times \text{Cs} + 0.1237 \times \text{SrCo} + 0.12333 \times \text{SrCs}$$

(5)

$$C_s-NZ=0.00774 \times Sr+0.00013 \times Co+ 0.6684 \times Cs+0.253 \times SrCs+0.255 \times CoCs$$

(6)

Furthermore, in Fig. 3, the ternary contour plots are presented, which indicate the influence of the proportion of ionic species on their sorbed amounts. In general, these plots are graphical interpretation of Eq. 1-6.

FIGURE 3

The values of coefficients in Eq. 1 show that sorbed amounts of Co^{2+} by B400 depended mainly on the Co^{2+} content in the solution, but also on Co-Sr and Co-Cs interactions. Similar coefficients obtained for interaction terms showed comparable Co^{2+} removal in the presence of Sr^{2+} and Cs^+ ions. Almost the same equation was obtained for Co^{2+} sorption by RBRM (Eq. 3) suggesting the similar performance of both sorbents towards aqueous Co^{2+} .

Sorption of Sr^{2+} by B400 can be described using Eq. 2, with the highest positive coefficients for the initial Sr^{2+} content and Sr-Cs interaction, indicating that Sr^{2+} sorption was higher in the presence of Cs^+ than in the presence of Co^{2+} . Eq. 4 showed that sorbed amounts of Sr^{2+} onto RBRM were positively influenced by Sr^{2+} content and Sr-Cs interaction, but negatively by Co-Sr interaction. This confirmed the antagonistic effect of Co^{2+} ions onto Sr^{2+} removal by RBRM.

Finally, Cs^+ immobilization using zeolite was influenced dominantly by the initial content of Cs^+ in the solution.

The results of ANOVA tests are given in Table S2, as R^2 , R^2_{pred} and F and p values for regression and for linear and quadratic terms. R^2 values describes the variation of the observed

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3 responses explained by the model, R^2_{pred} reflects the goodness of fit in the wider range of
4 experimental conditions, whereas F and p are Fisher's and probability test values.
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8 Calculated R^2 values were higher than 95% for Co^+ and Sr^{2+} sorption onto B400, RBRM, as well
9 as for Sr^{2+} and Cs^+ sorption onto zeolite. High R^2_{pred} values approved the applicability of
10 proposed equations in the wider data range. High F-values and $p < 0.05$ supported statistical
11 significance of regression models and linear and quadratic terms included.
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16 Concerning the data of the regression analysis for Co^{2+} sorption by NZ and for Cs^+ sorption by
17 B400 and RBRM, the significant terms were not found (F-value were very low, $p > 0.05$). These
18 processes cannot be described properly by proposed equations because calculated R^2 values were
19 lower than 50% and data prediction was disabled (R^2_{pred} tends to 0).
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25 The proposed Eq. 1-6 have predicted system responses with high accuracy in the investigated
26 range, as indicated by good correlations presented in Fig 4.
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FIGURE 4

3.2. One-stage application of mixture sorbents to mixture waste

3.2.1. The results of sorption experiments

Given that investigated sorbents exhibited different selectivity towards Cs^+ , Sr^{2+} and Co^{2+} , their mixtures were applied to equimolar three-component simulated liquid waste. Sorbed amounts of each cation and equilibrium pH values are given in Table 2. Depending on the proportion of different materials, 1 g of mixed sorbent sorbed 0.13-0.21 mmol of Co^{2+} , 0.069-0.10 mmol of Sr^{2+} and 0.11-0.22 mmol of Cs^+ from equimolar solution. Final pH values ranged from 6.18 to 6.53; therefore, precipitation of $\text{Co}(\text{OH})_2$ was excluded.

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3 Percentages of removed cations as a function of sorbent composition are given in Fig. 5. In
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5 general, low sorption of Sr^{2+} (20-30%), moderate removal of Co^{2+} (39-60%) and efficient Cs^+
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7 sorption (42-80%) was detected. Total percentage of removal was in the range 38-50%,
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9 depending on proportions of each sorbent. The mixture of 20% RBRM, 20% B400 and 60% of
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11 zeolite was found as the most efficient.
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15 In comparison to the performance of individual sorbents in equimolar mixture (Fig. 2, solution
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17 no. 12), application of their combinations led to a more uniform removal of all ions present. A
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19 synergetic effect was insignificant and therefore, selectivity of sorbents in combination with their
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21 share in the mixture was the most important factor influencing efficiency of cations removal.
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27 FIGURE 5

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32 The literature on the applicability of mixed sorbents is very limited, especially for
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34 multicomponent wastes. Li and coworkers³⁹ investigated sorption of ^{99}Tc , ^{129}I and ^{137}Cs from
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36 simulated groundwater solution onto 14 different sorbents, including Apatite II, raw and
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38 modified zeolite. At first, sorbents were applied separately, and subsequently, binary mixtures of
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40 some best performing sorbents in 1:1 ratio were explored for radionuclides immobilization. The
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42 authors concluded that K_d values obtained for mixtures of sorbents were equal or lower than K_d
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44 values of the most efficient sorbents for either ^{99}Tc or ^{129}I . On the contrary, the synergetic effect
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46 was detected for some sorbents mixtures, resulting in higher sorption of ^{137}Cs compared to
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48 individual components. Binary and ternary mixtures of hydroxyapatite, goethite, natural zeolite
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50 and two waste-derived sorbent were studied for remediation of sediments contaminated by heavy
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52 metals⁴⁵. Application of all mixtures led to compliance of the regulatory limits, therefore they
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3 have been characterized as suitable for *in-situ* remediation. It has to be noted that composite
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5 sorbents obtained by physical mixing (without chemical treatments) can be very efficient and
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7 economical, at the same time. For example, the sorbent prepared from tea waste and dolomite
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9 was found to be equally efficient but more cost-effective for the removal of Cu^{2+} and methylene
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11 blue, than some other composites ⁴⁶.
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17 3.2.2. Statistical analysis of extreme vertices design

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22 The results of sorption experiments were subjected to quadratic regression analysis, which gave
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24 the following outputs:
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$$26 \text{Co} = 0.3491 \text{ B400} + 0.3383 \text{ RBRM} - 0.0138 \text{ NZ} \quad (7)$$

$$28 \text{Sr} = 0.12125 \text{ B400} + 0.03455 \text{ RBRM} + 0.09270 \text{ NZ} + 0.12856 \text{ B400 RBRM} \quad (8)$$

$$30 \text{Cs} = -0.1361 \text{ B400} - 0.1284 \text{ RBRM} + 0.4084 \text{ NZ} + 1.2835 \text{ RBRM B400} \quad (9)$$

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33 The Eq. (7-9) and the graphical representations of the results shown in Fig. 6. indicated that the
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35 presence of B400 and RBRM in the sorbents mixture positively affected sorption of Co^{2+} and
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37 Sr^{2+} ions, while negatively Cs^+ sorption. This can be explained by very low sorption affinities of
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39 the mentioned materials toward Cs^+ ions. The accordance between models and experimental
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41 results was very high ($R^2 > 91\%$), but data prediction in a wider range was defined as excellent for
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43 Sr^{2+} ions ($R^2_{\text{pred}} > 90\%$), satisfactory for Co^{2+} ions ($R^2_{\text{pred}} > 60\%$), but very poor for Cs^+ (R^2_{pred}
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45 9%). Beside R^2 and R^2_{pred} , p and F values are given in Table S3, for terms obtained from
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51 ANOVA analysis.
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FIGURE 6

3.3. Multistage sorption from mixture solution

Considering different selectivity of the sorbents, multistage sorption was considered by using individual sorbents in each step and varying their addition order. The application of multistage sorption onto equimolar ternary mixture containing 1.5×10^{-3} mol/L of each cation approved high removal efficiency of the utilized technology (Fig. 7). Co^{2+} removal was about 98-99% and was not significantly influenced by sorbents order addition. Similar results were obtained for Cs^+ sorption (94-95%). Sr^{2+} sorbed amounts were in the range from 59% (B400-NZ-RBRM) to 65% (RBRM-B400-NZ). Thus, addition of sorbents in the order RBRM-B400-NZ, can be characterized as the most efficient. These differences can be explained by a high sorption affinity of RBRM and B400 towards Co^{2+} , which is a strong competitor for Sr^{2+} ions.

FIGURE 7

Similar studies were not found in the available literature. The results can be of importance because they imply that multistage processes with different sorbents can be very effective and that, beside the type of an added sorbent, the order of sorbents addition has to be considered.

CONCLUSION

The extensive investigation on simultaneous Co^{2+} , Sr^{2+} and Cs^+ sorption was presented in this study, using low-cost and abundant sorbent materials: rinsed bauxite residue (RBRM), calcinated

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3 bovine bones (B400) and mineral zeolite (NZ). The major aims were to evaluate the capacities
4 and selectivity of sorbents and their mixtures, the competition between the cations and the
5 effectiveness of different sorption protocols. The effect of solution composition on metal
6 sorption by individual sorbents was firstly examined using mixture simplex lattice design. The
7 results showed the same selectivity of RBRM and B400 from single metal solutions, which
8 decreased in the order $\text{Co}^{2+} > \text{Sr}^{2+} > \text{Cs}^+$, while the selectivity of NZ was inverse: $\text{Cs}^+ > \text{Sr}^{2+} >$
9 Co^{2+} . As major interaction between the cations, reduced Sr^{2+} sorption in the presence of
10 coexisting Co^{2+} was detected. This inhibition was more pronounced using RBRM than B400,
11 implying higher selectivity of apatite towards Sr^{2+} . Co^{2+} sorption by RBRM and B400, as well as
12 the removal of Cs^+ by NZ, were superior, and unaffected by the presence of other cations in the
13 mixture. As the investigated materials exhibited different selectivity towards Cs^+ , Sr^{2+} and Co^{2+} ,
14 it was assumed that the sorption efficiency could be improved by using sorbents mixtures. In
15 this sense, purification of equimolar three-component solution was tested by: (i) utilization of
16 mixture sorbents and (ii) utilization of individual sorbents in consecutive steps. In the sorbents
17 mixture, mass proportion of each component was varied between 0.2 and 0.6 according to the
18 matrix of the extreme vertices mixture design. The influence of individual sorbent selectivity was
19 dominant, and the highest total sorption was obtained for the composite composed of 20%
20 RBRM, 20% B400 and 60% NZ. Finally, the three-step sorption was considered, using different
21 sorbents in each step and varying the order of addition. This methodology was found to be
22 particularly effective for mixed waste, and it revealed that the order of sorbents addition was an
23 important variable. The percentages of sorbed Co^{2+} and Cs^+ ions were high and relatively
24 independent on the order of sorbent addition; however, Sr^{2+} removal was the most efficient when
25 RBRM was used in the first, B400 in the second and NZ in the last step. The presented results
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3 also signify the applicability of mixture design methodology for the investigations of sorption
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5 from multi component systems, as well as for the prediction of system responses in the range of
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7 experimental conditions.
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FIGURE CAPTIONS

Figure 1. The example of multistage sorption protocol

Figure 2. Sorbed amounts (mmol/g) of a) Co^{2+} , b) Sr^{2+} and c) Cs^+ ions from investigated single, two- and three-component solutions onto different sorbents (gray bars-B400, black bars-RBRM, white bars - NZ). Numbers on x-axis represent the solution compositions defined in Table 1.

Figure 3. Ternary contour plots for: a) Co^{2+} , b) Sr^{2+} sorption by B400, c) Co^{2+} , d) Sr^{2+} sorption by RBRM, e) Sr^{2+} and f) Cs^+ sorption by NZ.

Figure 4. Predicted vs. experimental sorbed amounts a) Co-B400, b) Sr-B400, c) Co-RBRM, d) Sr-RBRM, e) Sr-NZ and f) Cs-NZ.

Figure 5. Sorbed amounts of Co^{2+} (white bars), Sr^{2+} (black bars) and Cs^+ (gray bars) ions and total sorbed amounts obtained for 10 different mixtures of B400, RBRM and NZ. Numbers on x-axis indicate the sorbents mass proportions given in Table 2.

Figure 6. Ternary contour plots for sorbed amounts (mmol/g) of: a) Co^{2+} , b) Sr^{2+} and c) Cs^+ ions onto mixed sorbents

Figure 7. The removal of Co^{2+} , Sr^{2+} and Cs^+ by varying the order of sorbent addition in the multistage process. NZ-white bars, RBRM- black bars and B400- gray bars.

Table 1. Experimental design matrix and equilibrium pH values

Solution	Molar ratios of metals in simulated liquid wastes			Equilibrium pH values		
	Sr ²⁺	Co ²⁺	Cs ⁺	B400	RBRM	NZ
1	0.333	0	0.667	6.27±0.07	7.11±0.08	5.26±0.01
2	0.167	0.666	0.167	5.67±0.04	6.83±0.11	5.02±0.02
3	0.333	0.667	0	5.62±0.04	6.74±0.05	4.97±0.01
4	0	1	0	5.83±0.03	6.84±0.05	4.94±0.06
5	0.167	0.167	0.666	6.20±0.10	7.08±0.03	5.23±0.07
6	0	0.667	0.333	5.81±0.05	6.90±0.04	5.02±0.06
7	1	0	0	6.70±0.06	6.35±0.03	5.63±0.03
8	0	0.333	0.667	5.95±0.01	6.88±0.06	5.11±0.04
9	0.667	0	0.333	6.88±0.02	6.73±0.10	5.63±0.11
10	0.667	0.333	0	5.80±0.03	6.92±0.09	4.98±0.01
11	0	0	1	6.56±0.03	7.61±0.03	5.52±0.05
12	0.333	0.333	0.334	5.67±0.03	6.96±0.03	5.03±0.03
13	0.666	0.167	0.167	5.85±0.03	6.96±0.03	5.17±0.03

Table 2. Experimental design matrix for preparation of mixed sorbents and sorbed amounts of Co^{2+} , Sr^{2+} and Cs^+ as system responses

Sorbent mixture	Mass ratio of sorbents			System response			
	B400 (A)	RBRM (B)	NZ (C)	Sorbed Co (mmol/g)	Sorbed Sr (mmol/g)	Sorbed Cs (mmol/g)	Equilibrium pH
1	0.20	0.40	0.40	0.16	0.073	0.17	6.25±0.03
2	0.40	0.20	0.40	0.17	0.090	0.18	6.18±0.05
3	0.33	0.33	0.34	0.17	0.082	0.16	6.35±0.05
4	0.20	0.60	0.20	0.20	0.069	0.11	6.53±0.06
5	0.60	0.20	0.20	0.20	0.10	0.12	6.40±0.02
6	0.27	0.46	0.27	0.19	0.079	0.14	6.40±0.05
7	0.46	0.27	0.27	0.19	0.095	0.14	6.32±0.03
8	0.40	0.40	0.20	0.17	0.093	0.18	6.18±0.04
9	0.20	0.20	0.60	0.13	0.078	0.22	6.30±0.05
10	0.27	0.27	0.46	0.15	0.078	0.19	6.30±0.05

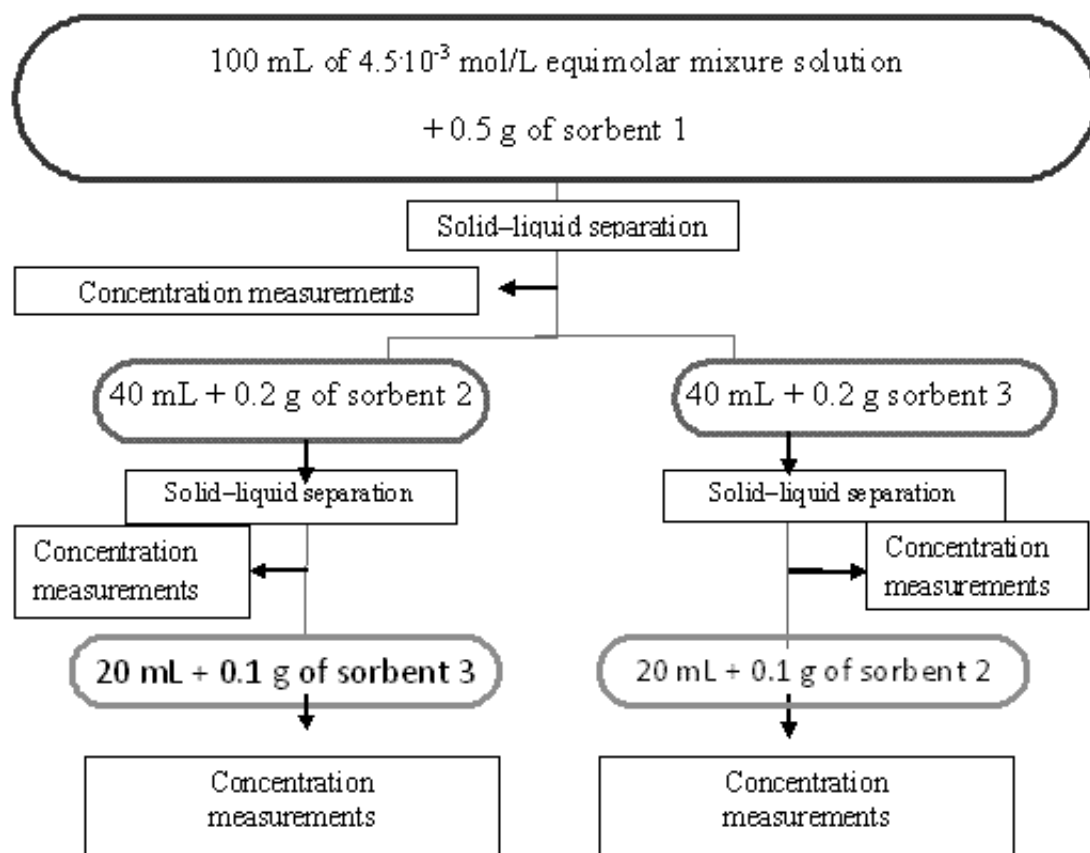


Figure 1

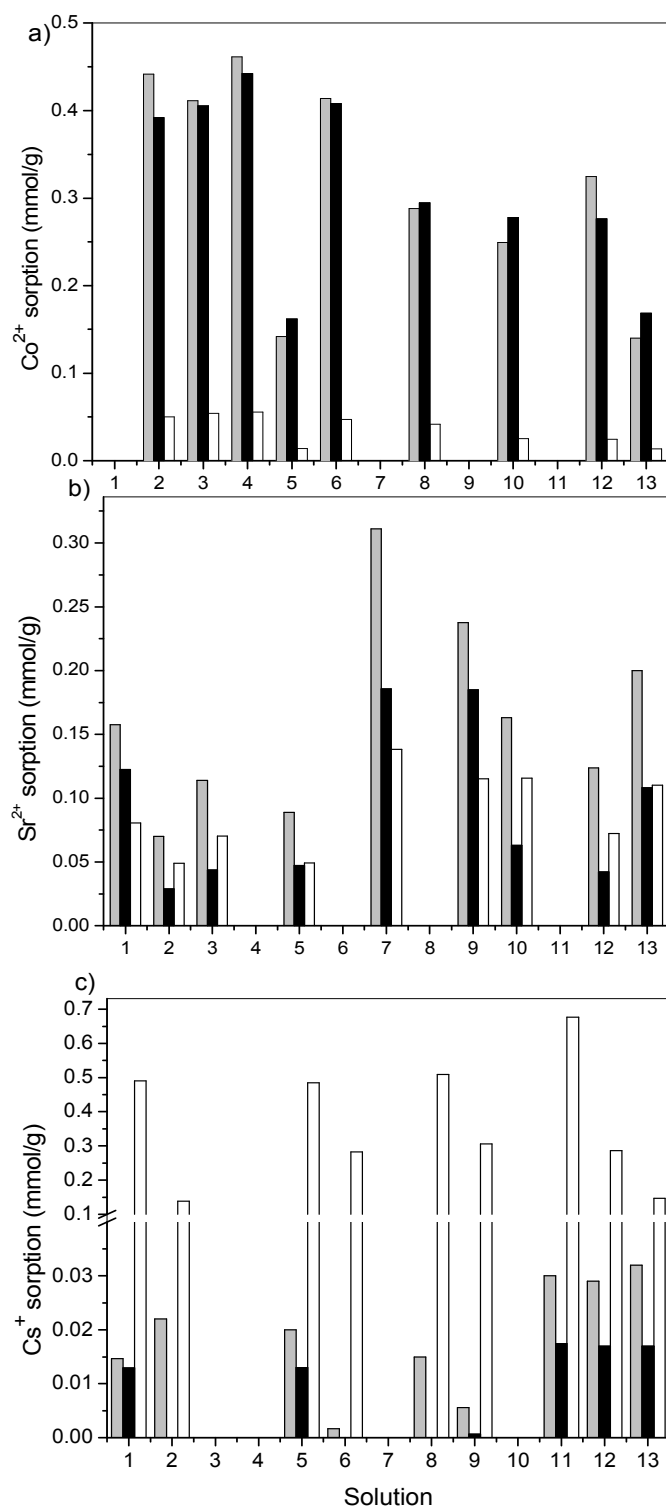


Figure 2.

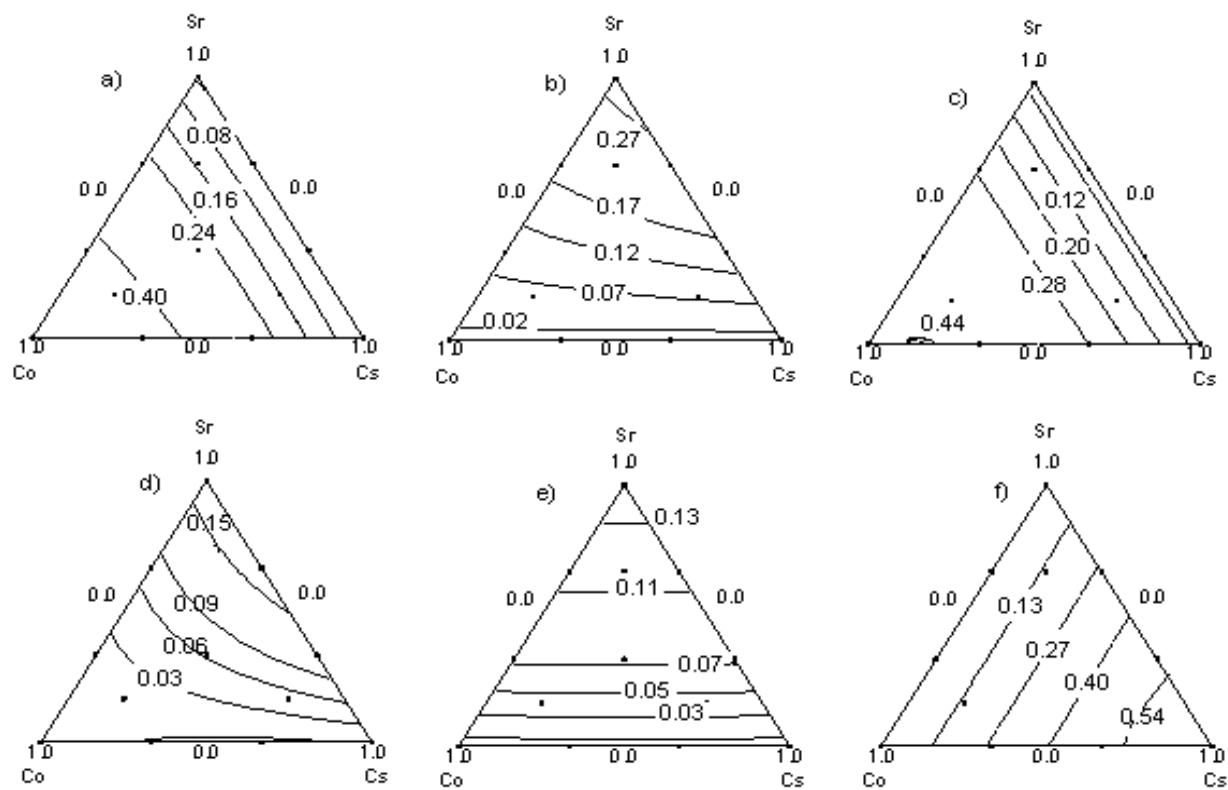


Figure 3

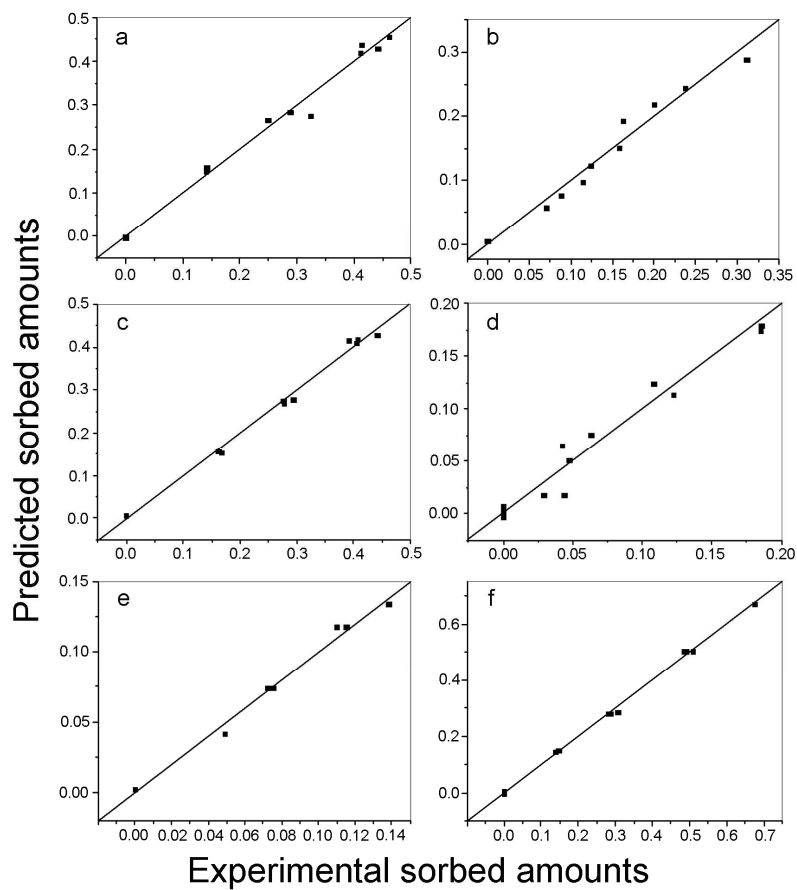


Figure 4

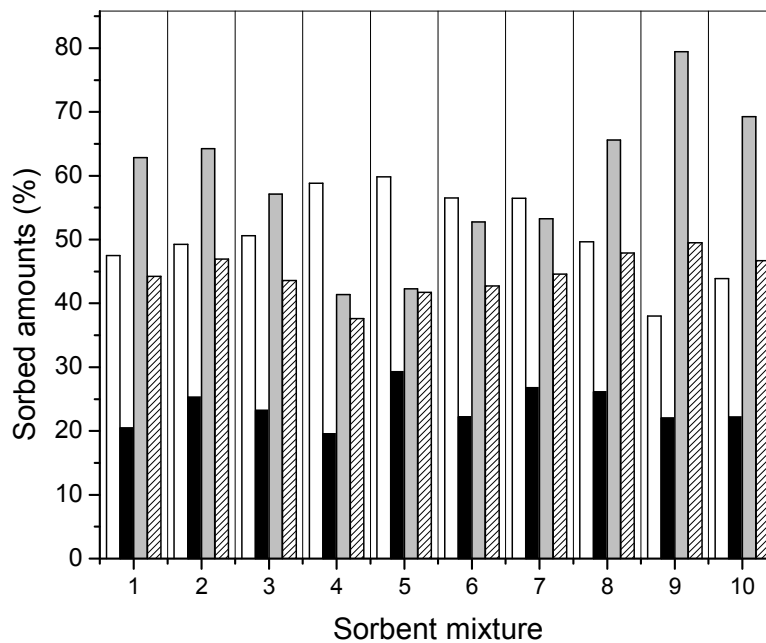


Figure 5.

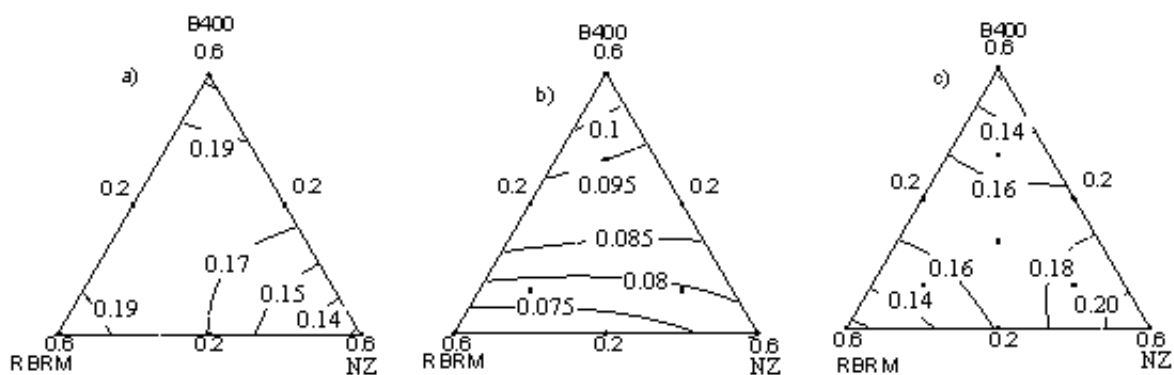


Figure 6

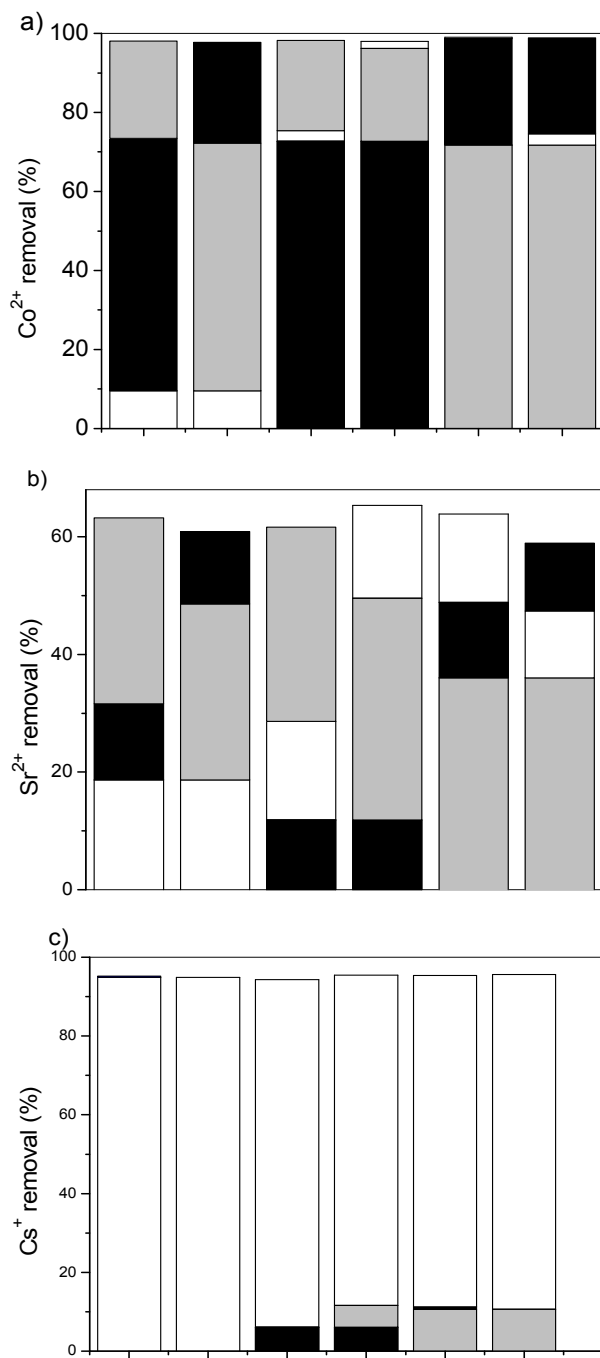


Figure 7.

For Table of Contents Only

