THE APPLICATION OF EXPERIMENTAL DESIGN METHODOLOGY FOR THE INVESTIGATION OF LIQUID RADIOACTIVE WASTE TREATMENT

by

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The sorption properties of waste facade, brick, and asphalt sample towards Sr(II), Co(II), and Ni(II) ions from single and multicomponent solutions were investigated. The highest sorption capacity was found for Ni(II) ions, while the most effective sorbent was facade. Simplex Centroid Mixture Design was used in order to investigate the sorption processes of ions from solutions with different composition as well as the competition between the cations. Based on the statistical analysis results, the equations for data modeling were proposed. According to the observations, the investigated solid matrices can be effectively used for the liquid radioactive waste treatment. Furthermore, the applied methodology turned out to be an easy and operational way for the investigations of multicomponent sorption processes.

Key words: liquid radioactive waste, mixture design, sorption

INTRODUCTION

The liquid radioactive waste (LRW), produced as a result of the operation, repair and disposal of nuclear energy installations, represents a mixture of different radionuclides whose composition varies during the time due to the radioactive decay [1]. Concerning the radiation and toxic effect, the most hazardous pollutant and common constituents identified in LRW of low and intermediate level are ^{60}Co and ^{90}Sr. Furthermore, ^{63}Ni is produced by neutron reactions and mainly exists in steel and other reactor materials such as graphite, concrete, lead, and Al alloy. From this point of view, the mixtures of Co(II), Sr(II), and Ni(II) ions are interesting for considerations as a simplified model of LRW for the purposes of treatment and disposal.

The treatment is an important phase in the management of LRW. It aims to reduce the volume of generated waste to enhance the safety and/or reduce the costs of further management. The treatment technologies employed in nuclear industry include the chemical precipitation, ion exchange, evaporation, membrane processes, solvent extraction and biotechnology. The most commonly used are evaporation as a financially demanding process, while the ion-exchange and sorption present a low-cost alternative. In this paper, sorption phenomena will be considered onto widespread, easy available and low-cost construction/demolition waste materials. The extremely high amounts of generated construction/demolition waste are deposited on the landfills covering large areas, therefore it is essential to develop technologies for fine fraction utilization and minimization of disposed quantities. Generally, the variety of waste materials showed relative high affinities towards radioactive ions, indicating the promising utilization tool for LRW treatment and also the possibility of recycling and minimization [2-4].

Consequently, the summarized investigation of sorption properties results for three construction/ demolition waste components – concrete facade, brick and asphalt sample – was presented. The study was completed via one, two and three-component solutions containing Sr(II), Co(II), and Ni(II) ions. The main aim was to define the sorption data description mathematical models for the selected sorbent/sorbate system.

EXPERIMENTAL PART

Experimental design

The experimental design is a useful method, applicable in all disciplines of science and engineering,

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able to investigate relations between the cause and the effect. The main characteristic of this approach is simultaneous variation of input independent variables. This is a good way to minimize the total number of experimental trials, in regard to the classic approach (one factor at the time). Depending on the problem type and the purpose of the investigation, different full or fractional factorial design, surface methodology, block designs and others can be utilized. These methodologies are especially useful for the investigation of the experimental conditions changing effects. Otherwise, the influence of mixture composition variation onto system response can be investigated using a mixture design as a type of surface response methodology. Three mixture designs are available: Simplex Lattice, Simplex Centroid, and Extreme Vertices Design [5]. In this work, Simplex Centroid design was used to investigate the effects of the solution composition onto sorbed amounts of each investigated cation. The minimal number of experimental runs is 7 for the three component mixture, which include considerations of the behavior of three single solutions, three equimolar binary mixtures and one equimolar ternary mixture. The number of experimental trials can be enlarged by the addition of three ternary mixtures containing 2/3 of one component and 1/6 per other two components.

The experimental design matrix generation, as well as the analysis of obtained results was done using Minitab Release 13.0 software.

Sorption experiments

Sorption experiments were done in duplicate. Stock solutions were prepared by dissolving the adequate masses of nitrate salts (Merck, p. a.) in deionized water. Stable isotopes of investigated cations were used. Initial pH values of prepared solutions were in the pH range 5-5.6, and they were used without further pH adjustment. The total concentrations of solutions were set at constant value, while the proportions of each metal were varied according to the matrix obtained using the statistical software (tab. 1).

Waste materials-concrete facade, brick and asphalt – were utilized as sorbents. Samples were collected from the ruins of buildings and roads built in 1970´s. These materials were crushed and sieved at the particle size between 0.3 nm and 0.6 mm.

Batch sorption experiments were conducted in plastic flasks by mixing metal solutions and selected sorbent material for 48 h at rotary shaker (10 rpm). Process temperature was 20 °C 1, while solid/liquid ratio was 1/200.

After 48 h, suspensions were centrifuged (10 min, 9000 rpm) and the concentrations of cations in the liquid phase were measured. Moreover, the exact concentrations of the solutions before the sorption process were determined. The cations' concentrations were defined using absorption atomic spectrometry (Perkin Elmer 3100 AAS). Furthermore, pH values after sorption were measured using WTW InoLab pH-meter. The combined measurement uncertainty of the experimental procedure was lower than 5 % [6, 7].

Table 1. The composition of stock solutions in each experimental run

Experimental run	Sr(II) [molL^{-1}]	Co(II) [molL^{-1}]	Ni(II) [molL^{-1}]
1	0.002	0.0005	0.0005
2	0	0.0015	0.0015
3	0.001	0.001	0.001
4	0	0.003	0
5	0.015	0	0.0015
6	0.0015	0.0015	0
7	0.0005	0.0005	0.002
8	0	0	0.003
9	0.003	0	0
10	0.0005	0.002	0.0005

RESULTS AND DISCUSSION

Sorption experiments

Investigated sorbents are materials which are subject to aging due to the environmental conditions which provoke the changes in their compositions and properties. Thus, EDS analysis of aged facade showed that Si, Ca, and O are major constituents [8] as well as for the aged concrete samples. Generally, recently prepared samples contain calcium-silicate-hydrate (C-S-H) gel, calcium hydroxide and Fe compounds degraded with time into silica oxides, carbonates, *etc*. [9]. On the other side, bricks are produced by burning clay mixtures. Depending on the process temperature, the final product contains transformed clay minerals or only SiO_2, for the temperatures higher than 1100 °C [10]. Asphalt is a bitumen based material which besides natural minerals contains organic compounds, especially hydrocarbons [11].

Different stock solutions (denoted with numbers from 1-10) were equilibrated with selected waste materials. After suspensions' centrifugation, filtrate pH values were measured. These final pH values were higher in respect to the initial ones (fig. 1), indicating sorbents buffering properties. Final pH values after sorption onto facade were the highest in respect to other two samples. This was expectable due to the fact that the facade contain cement is highly alkaline. Furthermore, the pH values measured in the neutral region were very close for brick and asphalt sample.

Sorption capacities of investigated materials from one, two and three component solutions were defined according to the experimental design matrix and they are presented in fig. 2.

The investigation of sorbed amounts from one component solution showed that the affinities of investigated matrices toward Sr(II) and Ni(II) ions de-

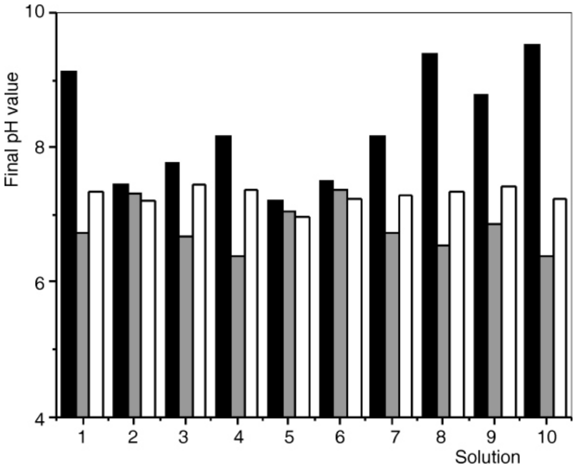


Figure 1. Final pH values measured after sorption of different solutions onto facade (black bars), brick (gray bars), and asphalt (white bars) samples

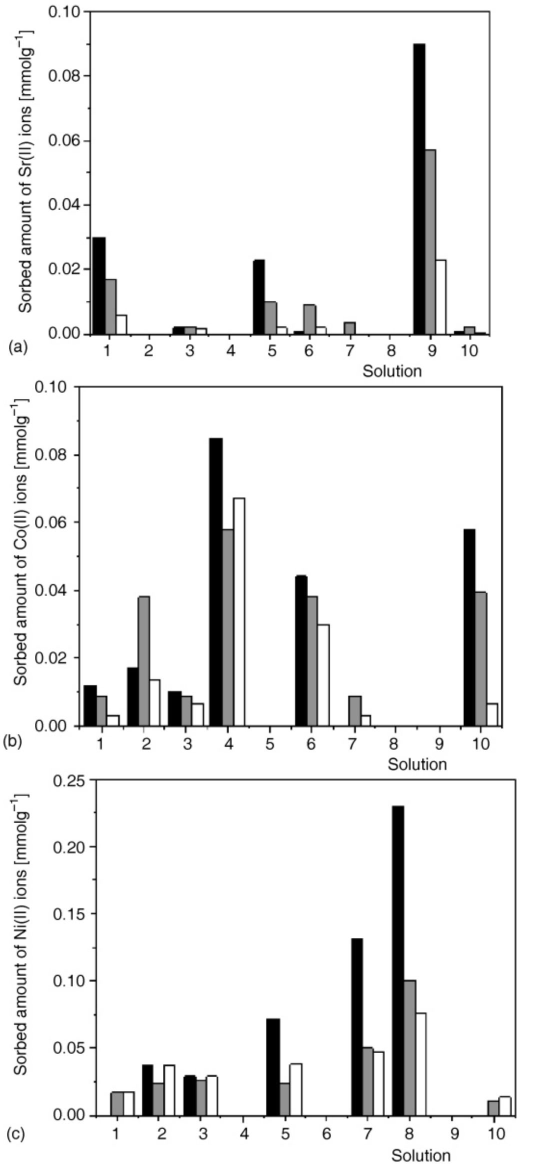


Figure 2. Sorbed amounts of the investigated cations from different solutions onto facade (black bars), brick (gray bars), and asphalt (white bars) samples

creased in the sequence facade > brick > asphalt, while for Co^{2+} bonding tendencies of solid matrices decreased as facade > asphalt > brick. The highest sorption capacity was observed using facade probably due to the high final pH values which might provoke Co and Ni precipitation as hydroxides even at pH > 8 [12, 13]. For this sample, the precipitation of Sr(II) ions as carbonate was also possible.

Sorbed amounts from binary equimolar solutions were reliant on applied sorbent and coexisting cation. Thus, sorption capacity of facade toward Ni(II) ions was lower in the occurrence of Co(II) ions than Sr(II) ions, suggesting a stronger competition between Ni(II) and Co(II) ions. Also, Sr(II) sorption onto facade was more suppressed with the coexisting of Co(II) than Ni(II) ions. The influence of coexisting ions onto Ni(II) and Sr(II) sorption for brick and asphalt sample was similar provoking close values of defined sorption capacities.

Already reported investigations about the competition between cations onto other matrices can be found in the available literature. The existence of Ni(II) ions suppressed the sorption of Sr(II) and Co(II) ions onto felts [14] and enhanced Co (II) sorption onto sugarcane fiber waste [15]. Furthermore, the bonding of Sr(II) ions was inhibited in the coexistence of Co(II) ions onto red mud and annealed animal bones [1].

Obtained sorption data were further analyzed using statistical methods with intention to find out the effect of each cation occurrence and the interaction effects onto accurate sorption capacity.

Statistical analysis

The results of the experimental design were analyzed using multiple regression models. The special cubic mathematical model can be used for the description and modeling of the results obtained utilizing Simplex Centroid Experimental Design. When three components are considered, this model can be expressed with following eq. [5]

$$\begin{aligned} &Y \quad \beta_1 A \quad \beta_2 B \quad \beta_3 C \quad \beta_{12} AB \\ &\beta_{13} AC \quad \beta_{23} BC \quad \beta_{123} \quad ABC \quad \varepsilon \end{aligned} \tag{1}$$

where Y is chosen system response, sorbed amounts of each metal ion [mmolg^{-1}], A, B, and C denotes initial concentrations of Sr(II), Co(II), and Ni(II) ions, respectively, in solutions before sorption process, AB, BC, AC, and ABC denotes interactions between input variables representing quadratic and ternary interaction terms, $\beta_i, \beta_{i,j}, \beta_{ijk}$ are coefficients related to linear, quadratic and ternary terms, respectively, ε-residual.

By solving eq. 1 for each experimental point, the unknown coefficients β can be obtained. The application of analysis of variance (ANOVA) test can give the information about statistically significant terms. Furthermore, the F-values (Fisher test) and p-values

Table 2. ANOVA analysis

Waste components	R^2	Model		Linear terms		Quadratic terms		Ternary terms	
		F	p	F	p	F	p	F	p
Sr									
Facade	0.994	189.65	<0.0001	358.19	<0.0001	95.25	<0.0001	–	–
Brick	0.985	82.93	<0.0001	162.4	<0.0001	35.52	0.001	–	–
Asphalt	0.980	61.04	<0.0001	116.33	<0.0001	33.98	0.001	–	–
Co									
Facade	0.977	83.97	<0.0001	125.22	<0.0001	127.8	0.006	–	–
Brick	0.996	218.95	<0.0001	386.4	<0.0001	13.76	0.016	62.73	0.001
Asphalt	0.715	8.78	0.012	8.78	0.012	–	–	–	–
Ni									
Facade	0.984	75.42	<0.0001	149.22	<0.0001	15.39	0.007	–	–
Brick	0.995	173.40	<0.0001	431.68	<0.0001	43.87	0.002	25.63	0.007
Asphalt	0.992	457.42	<0.0001	457.42	<0.0001	–	–	–	–

(probability test) were calculated for the regression and for the terms (tab. 2). The chosen confidence level was $\alpha = 95\ \%$, implying that calculated $p < 0.05$ suggested that corresponding term is statistically significant. Consequently, involving only statistically significant terms, following models were obtained for:

– Sr(II) sorption onto

$$\text{facade} = 0.0891\text{Sr} + 0.0021\text{Co} - 0.0001\text{Ni} - 0.1701\text{Sr-Co} - 0.0872\text{Sr-Ni} \quad (2)$$

$$\text{brick} = 0.05560\text{Sr} + 0.00112\text{Co} - 0.00144\text{Ni} - 0.07746\text{Sr-Co} - 0.07366\text{Sr-Ni} \quad (3)$$

$$\text{asphalt} = 0.02211\text{Sr} + 0.00053\text{Co} + 0.00047\text{Ni} - 0.03469\text{Sr-Co} - 0.03482\text{Sr-Ni} \quad (4)$$

– Co(II) sorption onto

$$\text{facade} = -0.0003\text{Sr} + 0.0888\text{Co} - 0.0017\text{Ni} - 0.1039\text{Co-Ni} \quad (5)$$

$$\text{brick} = 0.0005\text{Sr} + 0.058\text{Co} + 0.0006\text{Ni} + 0.0364\text{Sr-Co} + 0.0365\text{Co-Ni} - 0.4448\text{Sr-Co-Ni} \quad (6)$$

$$\text{asphalt} = -0.001978\text{Sr} + 0.048478\text{Co} - 0.007452\text{Ni} \quad (7)$$

– Ni(II) sorption onto

$$\text{facade} = -0.0047\text{Sr} - 0.0016\text{Co} + 0.2365\text{Ni} - 0.1544\text{Sr-Ni} - 0.2844\ \text{Co-Ni} \quad (8)$$

$$\text{brick} = 0.0018\text{Sr} - 0.0001\text{Co} + 0.0993\text{Ni} - 0.1027\text{Sr-Co} - 0.1084\text{Co-Ni} + 0.4610\text{Sr-Co-Ni} \quad (9)$$

$$\text{asphalt} = 0.001936\text{Sr} + 0.000629\ \text{Co} + 0.074566\text{Ni} \quad (10)$$

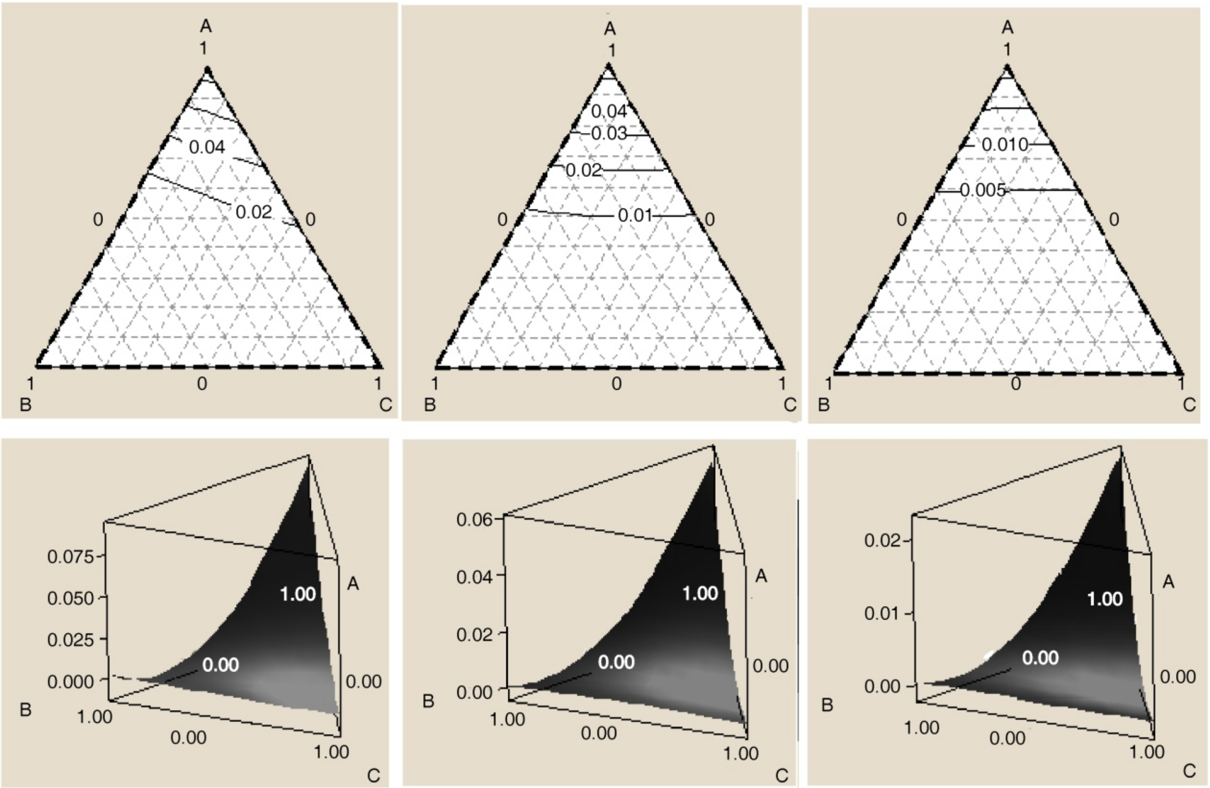
Certain conclusions can be proven by summarizing values of regression coefficients and ANOVA test results. For example, stronger negative influence of Co(II) in respect to Ni(II) ions onto Sr(II) bonding by facade sample was confirmed by high negative coefficient corresponding to the Sr-Co interaction term. Since this coefficient had the highest vales in the eq. 2, the Sr-Co term had dominant effect onto response function. Furthermore, the coefficients related to the linear terms Co and Ni and onto interaction terms Sr-Co and Sr-Ni were very close indicating a similar effect of coexisting Co(II) and Ni(II) ions onto Sr(II) sorption onto brick and asphalt.

The Co(II) sorption onto facade was negatively influenced by the existence of Sr(II) and Ni(II) ions, mostly dominant by Co-Ni interaction. On the other hand, sorption onto brick (eq. 6) was positively affected with all involved linear and quadratic significant terms, but negatively with ternary term, whose effect was dominant. The Co(II) sorption onto asphalt can be described by linear model (eq. 7), where the response function was primary affected by initial Co(II) concentration.

Based on eq. 8, the higher coefficient related to Co-Ni than Sr-Ni interaction, indicated that the sorption of Ni(II) ions onto facade was more suppressed by existence of Co(II) than Sr(II) ions. Similar to the Co(II) ions sorption onto brick, Ni(II) sorption was majorly dependent on ternary term. Also, the sorption onto asphalt sample was described by the linear model.

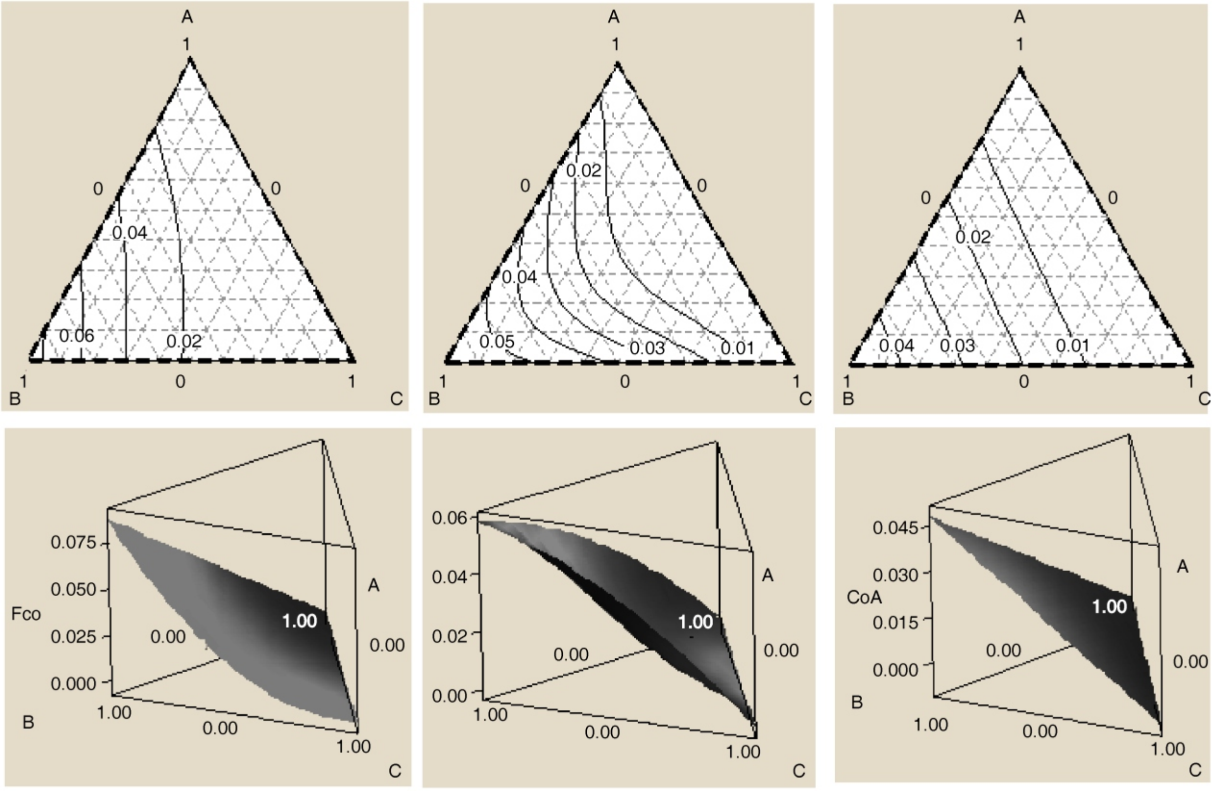
The agreement between the experimental data and the proposed models were excellent with R^2 values higher than 0.97 (tab. 2). Slightly lower R^2 value was obtained for model proposed for Co(II) removal by asphalt sample.

The graphical presentation of eqs. 2-10 was given as 3-D surfaces or as a 2-D contour plots (figs. 3-5). Contour plots representing linear equations are consisted of straight lines, while the existence of significant quadratic and ternary term provoked curvatures.



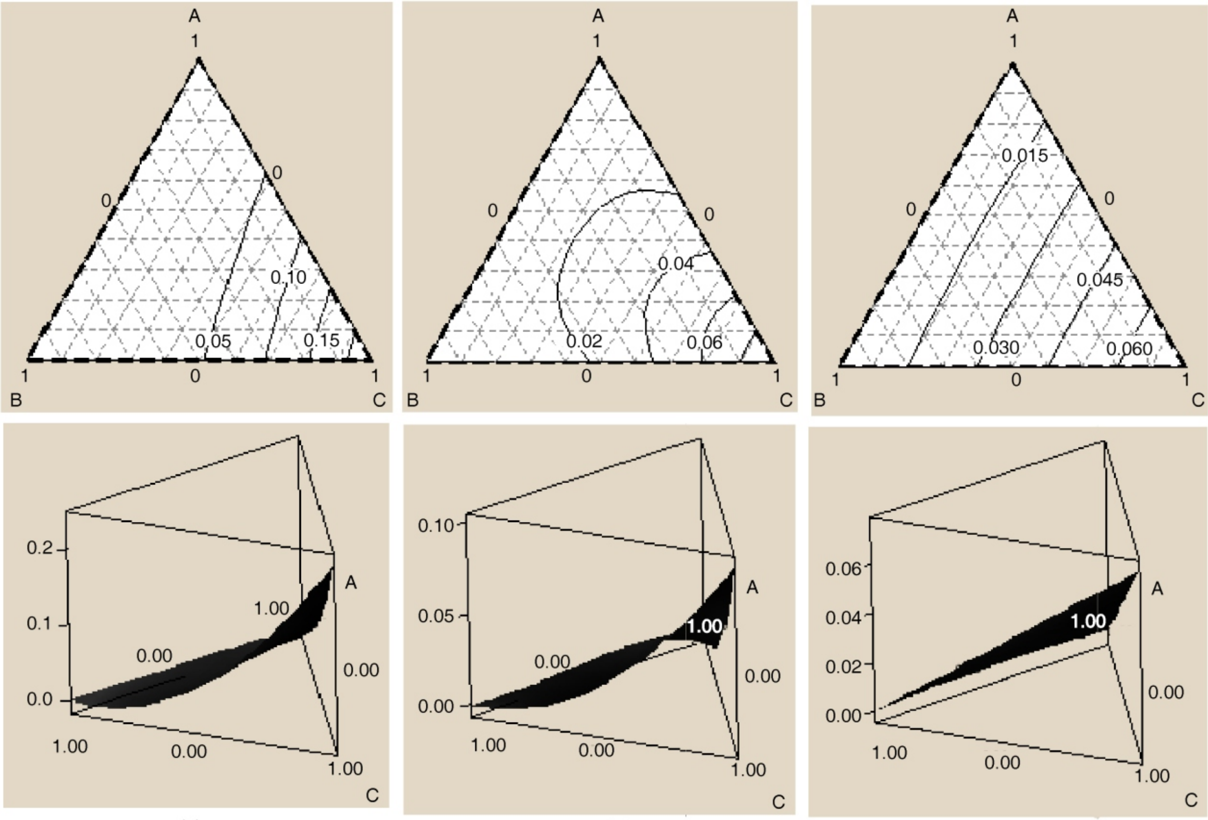
(a) (b) (c)

Figure 3. Contour and surface plots for Sr(II) sorption onto (a) facade, (b) brick, and (c) asphalt sample



(a) (b) (c)

Figure 4. Contour and surface plots for Co(II) sorption onto (a) facade, (b) brick, and (c) asphalt sample



(a) (b) (c)

Figure 5. Contour and surface plots for Ni(II) sorption onto (a) facade, (b) brick, and (c) asphalt sample

CONCLUSION

Experimental design approach was applied on multicomponent sorption with solid components of demolition and construction waste. Concrete facade, bricks and asphalt samples were selected as sorbents, while Sr(II), Co(II), and Ni(II) ions were investigated as sorbates. Sorption experiments in batch system showed that the investigated matrices are suitable for radionuclides removal, and consequently, treatment of radioactive liquid waste. The highest sorption potential was obtained for facade sample, probably due to its high alkalinity which can provoke precipitation of the metal ions. Considering single highly concentrated solutions, the most effectively Ni(II) ions were removed, followed by other two cations. Otherwise, sorption from multicomponent solutions was dependent on coexisting ions for each particular solid matrix. The experimental design methodology was approved as an appropriate way for the investigations of this type. Furthermore, the empirical equations were defined suitable for experimental data description. Moreover, proposed mathematical models can be utilized for Sr(II), Co(II), and Ni(II) ions sorbed amounts prediction from multicomponent solutions with concentrations in the investigated range.

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AUTHORS' CONTRIBUTIONS

On the basis of the literature survey, the experimental procedure was defined by M. Šljivić-Ivanović, while experiments were done by I. Jelić. M. Šljivić-Ivanović and analytical measurements were done by I. Jelić. All authors participated in the analysis and discussion of the results, while paper was written by M. Šljivić-Ivanović and I. Jelić.

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ПРИМЕНА ЕКСПЕРИМЕНТАЛНОГ ДИЗАЈНА У ИСТРАЖИВАЊУ ТРЕТМАНА ТЕЧНОГ РАДИОАКТИВНОГ ОТПАДА

Испитана су сорпциона својства отпадних грађевинских материјала као што су фасада, цигла и асфалт према јонима Sr(II), Co(II) и Ni(II) из једнокомпонентних и вишекомпонентних раствора. Најизраженији афинитет је испољен према јонима Ni(II), док је најефикаснији сорбент фасада. Simplex Centroid дизајн смеше коришћен је да би се испитала сорпција јона из раствора различитог састава као и компетиција међу катјонима. На основу резултата статистичке анализе, предложене су једначине за моделовање добијених података.

Може се закључити да се испитане чврсте матрице могу ефикасно користити за третман течног радиоактивног отпада. Такође, примењена методологија показала се као једноставан и оперативан начин за истраживање сорпционих процеса из мултикомпонентих раствора.

Кључне речи: течни радиоактивни отпад, дизајн смеше, сорпција