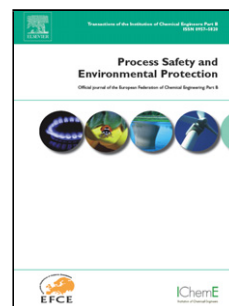


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UTILIZATION OF WASTE CERAMICS AND ROOF TILES FOR RADIONUCLIDE SORPTION

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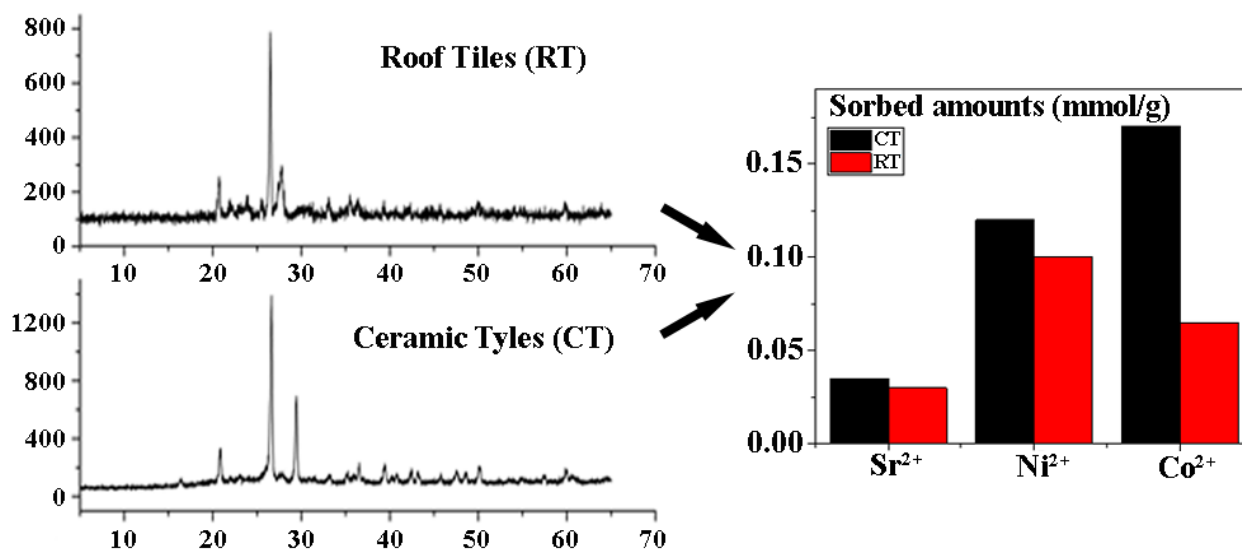
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Graphical abstract



Highlights

- The reduction of liquid radioactive waste using construction waste was explored.
- Sr^{2+} , Co^{2+} and Ni^{2+} were sorbed onto waste ceramic (CT) and roof tiles (RT).
- The XRD, FT-IR and radiological analysis of CT and RT was performed.
- Sorption isotherms were defined and modeled.
- Simplex centroid design was used for the investigation of cation competition.

ABSTRACT

The possible utilization of waste ceramic (CT) and roof tiles (RT), as sorbents for liquid radioactive waste (LRW) treatment, was investigated. Following the European directives on waste and politics of saving natural raw materials, it is reasonable and desirable to explore potential applicability of such construction wastes. These materials are low-cost and locally available in high quantities, yet, their sorption characteristics were not evaluated to this point.

In the present study, detailed physicochemical characterization of waste CT and RT included determination of mineral composition, surface functional groups, radioactivity, as well as the stability in aqueous media. The batch sorption study of Sr^{2+} , Co^{2+} and Ni^{2+} ions from single- and multi-component solutions was performed, as their radioactive isotopes are common constituents in LRW. Sorption equilibrium was best described by Freundlich isotherm model, regardless of the sorbent and the sorbate type. Sorption capacities of CT, defined in single element solutions, increased in the order $0.035 \text{ mmolSr/g} < 0.12 \text{ mmolNi/g} < 0.17 \text{ mmolCo/g}$, while the affinity of RT was generally lower ($0.030 \text{ mmolSr/g} < 0.065 \text{ mmolCo/g} < 0.10 \text{ mmolNi/g}$). The study of competitive cation sorption was performed following a simplex centroid experimental design matrix. The equations for the prediction of metal sorption capacities from multi-component solution were derived. Utilization of CT and RT might be an efficient way for waste water purification, with simultaneous reduction in construction waste amount on municipal landfills.

Keywords: radionuclides, waste tiles, sorption, recycling, water treatment.

1. Introduction

Civil engineering generates construction and demolition debris, representing nearly 75% of waste worldwide (Mymrin et al. 2015, Zimbili et al. 2014). Although this waste falls into the category of nonhazardous solid waste, it consumes the capacities of municipal landfills. Large amounts of diverse materials such as concrete, ceramic (bricks and roof tiles), asphalt, wood, steel and other metal products, plastic, etc., are being disposed. The problem of accumulation of non-recyclable construction waste has exhibited global

proportions, and since it continues to increase rapidly, it is necessary to develop innovative and efficient strategies for its reduction and valorization (Mymrin et al. 2015). Ceramic materials contribute approximately 54% to construction and demolition wastes, and associated recycling and reuse rates are not available in the EU due to an absence of a systematic European reporting system (European Commission, 2011). One of potentially prosperous fields in ceramic waste utilization is exploitation of its sorption properties. During the last decade, interest in waste materials and by-products utilization as sorbents for purifying contaminated water was markedly increased (Ahmaruzzaman, 2011).

Thanks to their chemical composition and compatibility with solid matrixes (such as cement) used for the disposal of radioactive waste, ceramic materials are prospective sorbents for immobilization of radionuclides present in aqueous solutions. Radioactive waste is generated due to the activity of nuclear power plants, nuclear weapon testing, industrial applications, research institutions, medical uses, etc. (IAEA, 1998), and consequently, liquid radioactive waste (LRW) streams of different origin exhibit variable chemical composition. In LRW streams associated with the operation of nuclear reactors, isotopes of ^{60}Co , ^{63}Ni , ^{90}Sr are recognized as abundant and important even many years after the reactor shutdown (IAEA, 1998). ^{60}Co and ^{63}Ni originate from reactor made ferritic materials, while ^{90}Sr is a fission product. The sorption of such radionuclides using different low-cost materials was already investigated (Milenković, et al. 2014, Galamboš et al. 2011, 2012, Jiménez-Reyes and Solache-Ríos, 2016, Šljivić-Ivanović et al. 2015, Ofomaja et al. 2015), however, there are no available literature data on the utilization of waste tiles.

The main objective of this study was to evaluate waste ceramic and roof tiles as sorbent materials for the treatment of LRW containing Co^{2+} , Sr^{2+} and Ni^{2+} . For the first time, physicochemical and sorption properties of waste tiles were analyzed to better

comprehend the potential hazards and prospects for cation immobilization. The sorption kinetics and the capacities towards Co^{2+} , Sr^{2+} and Ni^{2+} ions were determined using single-component solutions, whereas competitive cation removal was explored using three-component solutions with different metal proportions, according to simplex centroid experimental design matrix.

2. Experimental Part

2.1. Collection, preparation and characterization of waste tiles

Samples of roof tiles (RT) and ceramic tiles (CT) were collected from different locations in Belgrade (Serbia). About 2-3 kg of the tile pieces were taken from 5 different building ruins. The tiles were crushed, milled and then sieved. After homogenization, obtained powders were spread over the area of around 1 m^2 , and 50 g were sampled from five randomly found points. Fraction with particle size between 0.3 and 0.6 mm was collected for further experiments, rinsed with deionized water and dried at 100°C .

CT and RT powders were characterized in terms of mineral composition, surface functional groups, content of radioactive elements, pH, and stability in aqueous media. Mineral phases were identified by X-ray diffraction analysis (XRD) using Ultima IV Rigaku diffractometer, equipped with $\text{Cu K}\alpha_{1,2}$ radiation, at generator voltage of 40.0 kV and current of 40.0 mA . The range of 4 to $65^\circ 2\theta$ was used for analysis in a continuous scan mode with a scanning step size of 0.02° and at a scan rate of $5^\circ/\text{min}$. For phase identification, the obtained XRD patterns were compared with the ICDD data base (ICDD, 2010).

Fourier transform infrared spectroscopy (FT-IR) analysis was performed to identify the major functional groups at the surface of the materials. The spectra were recorded at ambient

conditions in the mid-IR region (400 – 4000 cm^{-1}) using Nicolet IS 50 FTIR Spectrometer operating in the ATR mode (resolution of 4 cm^{-1} with 32 scans).

The spectrometry of γ -emitters was conducted for 3000 s in plastic beakers of 250 cm^3 . HPGe p-type detector with relative efficiencies of 18 % and one n-type detector with relative efficiency of 20 % were used. Calibration of detectors was performed using silicone resin matrix spiked with a series of radionuclides (^{241}Am , ^{109}Cd , ^{139}Ce , ^{57}Co , ^{60}Co , ^{203}Hg , ^{88}Y , ^{113}Sn , ^{85}Sr and ^{137}Cs) with total activity of 41.48 kBq on the day of the thirty first of August 2012 (Czech Metrological Institute, Praha, 9031-OL-420/12, type CBSS 2). The background spectrum was recorded before and after sample counting. The spectra were analyzed using GENIE 2000 program, and the results are given at 95% level of significance.

Stability of investigated materials was explored in the solutions with different initial pH. The pH values of deionized water were preset at 2, 6 and 8, by adding minimum amounts of 0.01 mol/L HNO_3 or NaOH . The suspensions having solid/liquid ratio of 1:200 were shaken in PP bottles on laboratory shaker, at 120 rpm, for 24 h. The suspensions were filtered afterwards, and pH values of clear filtrates were measured, as well as concentrations of released Ca^{2+} ions.

Modified US EPA 9045D method for determination of soil and waste pH (US EPA, 2002) was applied in this study. The pH values of CT and RT were determined for different mass ratios of the powders in deionized water, namely 1:1, 1:10, 1:20, 1:100 and 1:200. Suspensions were shaken, at 120 rpm for 5 minutes, than centrifuged (5500 – 6000 rpm for 15 – 20 min) and filtered. The measurements of pH values were conducted in both the suspensions and the filtrates using WTW InoLab pH-meter. Furthermore, electrical conductivities of filtrates were measured by WTW InoLab Cond 7110.

2.2. Sorption Experiments

Cation sorption was investigated in the batch system. The amount of 0.1 g of each sorbent was shaken with 20 mL of appropriate Sr^{2+} , Co^{2+} and Ni^{2+} solutions, on a rotary shaker at 10 rpm, at room temperature. The solutions were prepared using nitrate salts of investigated cations (Merck, p.a.). Initial pH values of the solutions were in the range 5-5.6, and they were applied without further pH adjustments. Aforementioned conditions were constant in all sorption experiments.

Process kinetics was investigated to define contact time between the sorbents and the solutions, required for attaining sorption equilibrium. As the equilibrium time generally increases with the increase of initial metal concentration, experiments were conducted taking into account the highest concentration of cations used in further work ($\sim 8 \cdot 10^{-3}$ mol/L). In that manner, sufficient contact was ensured for the entire investigated concentration range. Contact time varied between 15 minutes and 72 hours.

The effect of initial cation concentration on the amounts sorbed at equilibrium from single-component solutions was determined in the range from $\sim 10^{-4}$ to $\sim 8 \cdot 10^{-3}$ mol/L. Based on kinetics experiments, contact time was set at 48 h.

Competitive sorption of Sr^{2+} , Co^{2+} and Ni^{2+} ions was explored using mixture simplex centroid experimental design methodology. This methodology was selected in order to fit the experimental data with appropriate mathematical models and express response variables as functions of components' proportions. Analysis of Mixture Experiment enables the modelling of blending surface, so that the prediction of the response for any mixture component, (individually or in combination) can be made empirically. Thus, the proportions of components in the mixtures were set by Simplex centroid design with 10 runs (Table 1), while the total metal concentration was fixed at $3 \cdot 10^{-3}$ mol/L.

After equilibration, the suspensions were filtered and pH values of filtrates were measured as well as residual metal concentrations. All sorption experiments were run in duplicate.

TABLE 1

2.3 Measurements of cation concentrations

The concentrations of Sr^{2+} , Co^{2+} , Ni^{2+} and Ca^{2+} ions in material stability and sorption experiments were determined using Perkin Elmer 3100 Atomic Absorption Spectrometer (AAS). For the instrument calibration, single element Perkin Elmer standard solutions (1000 mg/L) were used. The calibration was re-checked after each 10 samples. In order to diminish interfering effects of coexisting cations, matrix matched standard solutions were prepared for multi-component solutions. The exact initial concentrations of Sr^{2+} , Co^{2+} and Ni^{2+} in starting solutions were measured, as well as the concentrations after sorption experiments. Sorbed amounts of cations were calculated as the differences between the initial and the residual concentrations.

2.4 Statistical Analysis

The results of sorption experiments presented in this study are given as the mean values of duplicates with the corresponding error. Furthermore, interpretation and analysis of the results obtained in experimental design were performed using Minitab Release 13.2 software.

3. Results and Discussion

3.1 Samples Characterization

3.1.1 XRD Analysis

X-ray diffraction patterns of investigated powders (Figure 1) have revealed their main crystal phases. RT sample contained quartz and albite, while quartz and calcite were detected in CT. Furthermore, peaks originated from silver-chromium-tin-selenide-sulfide phase were also detected in CT spectrogram. The presence of such phase can be explained by utilization of silver and tin based dyes, as well as by utilization of chromium and tin based additives as opacifiers (Peterson and Peterson 2012).

Depending on applied technology for tiles production, the XRD analysis of various samples showed quite different results. The minerals like quartz, gypsum, goethite, sepiolite, muscovite, hematite, etc., were detected in tile mineral composition (Jordá, et al., 2015). Another investigation, which considered ceramic tiles from different time periods (XVI - XX century), has shown that tiles produced in XX century contained quartz as the single crystal phase (Carvalho et al., 2006). This phenomenon was attributed to the advances in ceramic processing, like higher firing temperatures. Furthermore, it is important to mention that detection limits for various components in tiles and ceramic mixtures varied in the wide range, aggravating the detection of crystal phases present in low percentages (Jordá, et al., 2015).

FIGURE 1

3.1.2 FTIR analysis

The FT-IR spectrograms of waste tiles (Figure 2) showed presence of Si-O groups at 1023, 770, 690 and 525 cm^{-1} , and Si-O-Si and O-Si-O groups at 460 cm^{-1} . At wave numbers 680, 640, 570, 540, 450 and 420 cm^{-1} characteristic absorbance bands of AlO_6 -groups were found.

Additionally, bands characteristic for carbonates (at 870, 1420 and 1793 cm^{-1}) were found in the FT-IR spectrogram of CT, as well as the peak at 700 cm^{-1} which can be attributed to C-S stretching bands.

The results obtained by FT-IR analysis are in a good agreement with mineral composition detected by XRD. However, the existence of sulphates or phosphate groups cannot be discarded, because their peaks largely overlap with silica bands (Jordá, et al., 2015).

FIGURE 2.

3.1.3. Gamma-spectrometric analysis

The activity of ^{226}Ra and ^{232}Th was determined by their decay products: ^{214}Bi (609, 1120 and 1764 keV), ^{214}Pb (295 and 352 keV) and ^{228}Ac (338 and 911 keV), respectively. The activities of ^{40}K and ^{137}Cs were determined from their 1460 and 661 keV γ -energy, respectively.

Measured activities of gamma emitters in investigated samples are shown in Table 2. In general, the most abundant radionuclides in both samples were ^{40}K and ^{226}Ra . Activities of ^{40}K were 790 ± 80 and 860 ± 80 Bq/kg, for RT and CT, indicating that ^{40}K isotope was the largest contributor to the total activity for both studied samples. Furthermore, the existence of uranium isotopes was detected in sample CT, while RT contained ^{137}Cs and ^{210}Pb .

Concerning alpha radiation due to inhalation of radon from building materials, both samples contained less than 200 Bq/kg which is the limit for ^{226}Ra concentration in building materials (Estokova and Palascakova, 2013). Radium equivalent activity was calculated using the following equation:

$$Ra_{eq} = C_{Ra} + 1,43 \cdot C_{Th} + 0,077 \cdot C_K \quad (1)$$

Calculated Ra_{eq} values were 192.3 and 242.0 Bq/kg for RT and CT, respectively. Both values were < 370 Bq/kg, which is the maximum permissible activity of Ra_{eq} in raw building materials and products, to keep the external dose below 1,5 mSv/y for safe use (Beretka and Mathew, 1985, UNSCEAR, 2000). As the average worldwide exposure due to natural sources is 2.4 mSv/y (UNSCEAR, 2000), storage and utilization of investigated CT and RT don't pose a potential radiological risk.

Measured and calculated values obtained using gamma spectrometry of CT and RT are in accordance with the radiological measurements already reported. For example, the investigation of 97 different tile samples showed average activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K were 47.4 ± 3.3 , 42.84 ± 2.8 and 313.6 ± 34.3 Bq/kg respectively, with similar values obtained for roof and wall tiles (Uosif, 2015). Also, the highest contribution of ^{40}K in the overall measured radioactivity and similar values of specific radionuclide activities were obtained investigating tile samples around the world (Senthilkumar et al. 2014, Turhan et al. 2008, Krstić, et al. 2007).

TABLE 2.

3.1.4 Material Stability at Different pH Values

Stability of investigated materials was explored in aqueous solutions having initial pH values of 2, 6 and 8, using solid/liquid ratio of 1:200. Amounts of leached Ca^{2+} ions and final pH values were strongly dependent on material type, as well as on initial pH (Figure 3).

FIGURE 3

The most intensive leaching of Ca^{2+} ions was observed at initial pH 2 (0.805 mmol/g for CT and 0.365 mmol/g for RT). Lower and almost equivalent amounts of Ca^{2+} were released in solutions having initial pH 6 and 8 (approximately 0.03 mmol/g for both materials). Quite the opposite, the trend of final pH increase with the increase of initial pH values was observed.

Both examined parameters are related to the dissolution of CT and RT components. Namely, in acidic media, the calcite contained in CT and albite in RT, are unstable. Albite solubility in near neutral pH range was found to be very slow, but increased rapidly at $\text{pH} < 4.5$ (Chen and Brantley, 1997). Furthermore, solubility of calcite logarithmically increases with decreasing pH (Goss et al. 2007). As Ca^{2+} content in albite is much lower than in calcite, higher amounts of these cations were released from CT. Carbonate dissolution is also responsible for higher buffering capacity of CT, i.e., regardless of initial pH, final pH values were positioned in the near neutral pH region (Fig. 3b). Relatively high amounts of Ca^{2+} ions leached from RT imply that albite dissolution process might be accompanied by dissolution of some Ca^{2+} containing amorphous or crystalline phases which have remained unidentified due to detection limitations of XRD.

3.1.5 Determination of waste tiles pH and conductivity

Different quantities of CT and RT powders were mixed with deionized water, to achieve solid/solution ratios from 1:1 to 1:200. The pH values were measured firstly in the suspension (Fig. 4,a) and then in the clear supernatants (Fig. 4,b). With the increase of solid/solution ratio from 5g/L to 1000 g/L, pH of CT suspensions decreased (9.6-8.1), whereas it increased in the case of RT (7.2-8.3). Different impact of CT and RT content on the suspension pH is a result of their different composition. In previous investigations, pH values of suspensions

containing different quantities of calcite were found to increase with dilution, approaching a constant value at higher dilutions (Buehrer and Williams, 1936). This was attributed to hydrolysis of the surface layer of molecules, forming a less soluble basic carbonate, like $\text{CaCO}_3\text{Ca}(\text{OH})_2\text{xH}_2\text{O}$. The degree of hydrolysis, and consequently the pH, increased as the volume of water increased and finally became constant with further dilution. Such a trend fully corresponds to the behavior of CT, in which composition calcite was identified. On the other hand, mineral components of RT exhibit negatively charged surface sites at near neutral pH, as well as exchangeable (Na^+) sites, thus with the increase of their mass, more H^+ ions will be attached to the surface, leading to higher suspension pH. The trend was also observed in suspensions with increasing albite content (Deer et al., 2001.)

According to the US EPA classification, waste is classified as corrosive if suspension pH in water is lower than 2 or higher than 12.5 (US EPA, 2002). Therefore, investigated construction waste materials are not corrosive, regardless of solid content.

Furthermore, after solid/liquid separation, the final pH values and the conductivities of the filtrates were measured (Figure 4. b,c). Small pH variations were detected, i.e., for investigated solid concentration range, the average pH value for CT was 8.3 ± 0.5 , while 7.7 ± 0.4 for RT. Measured conductivities increased with the increase of solid content due to higher amounts of dissolved minerals under investigated conditions. The increase was slight in solid/liquid ratio range 1:200-1:10, whereas the increase was drastic for 1:1 ratio.

FIGURE 4

3.2 Sorption characteristics of CT and RT

3.2.1 Sorption kinetics

The results of contact time influence on sorbed amounts of cations (Q_t) are given in Figure 5. Sorption curves commonly exhibited continuous increase until the equilibrium was achieved, while equilibrium times were dependent on both the sorbent and the sorbate type. Namely, 6

h of contact was required for equilibrating the system containing Ni^{2+} and CT, while 24 h was sufficient for equilibrium sorption of Sr^{2+} ions onto CT and Co^{2+} onto RT. In other investigated systems, 48 h was required to achieve equilibrium. These results are in accordance with equilibrium times (few hours to few days), reported for Sr^{2+} , Co^{2+} and Ni^{2+} sorption onto clay minerals (Bilgin et al., 2001; Lu and Mason, 2001; Yavuz et al., 2003), and silica (Negrea et al., 2013).

During cation removal process, final pH values were monitored. In respect to the initial pH, the increase of solution pH occurred immediately after contact with CT and RT. Moreover, final pH values have remained high, during the entire period of equilibration. This phenomenon can be attributed to buffering properties of CT and RT constituents, especially calcite contained in CT, provoking higher pH values in respect to RT.

Experimental data were modeled using pseudo- first (Lagergren, 1898) and pseudo-second order kinetic model given in the following linear form (Ho and McKay, 1999):

$$\ln \frac{q_e - q_t}{q_e} = -k_1 \times t \quad (2)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 \times Q_e^2} + \frac{t}{Q_e} \quad (3)$$

Where Q_t and Q_e are sorbed amounts at time t and at equilibrium, t is contact time and k_1 and k_2 are pseudo-first and pseudo-second order constant. The product $k_2 \cdot Q_e^2$ denotes initial sorption rate h .

Calculated kinetic parameters are listed in Table 3. Based on correlation coefficients, better data description was obtained using pseudo- second order kinetic model than pseudo-first, with an exception of Ni^{2+} sorption onto RT and Co^{2+} sorption onto CT. Calculated k_1 values were in the range 0.731×10^{-3} to 7.48×10^{-3} 1/min, while calculated k_2 values were found to be between 5.88×10^{-3} and 1.58 g/mmol min. Furthermore, Q_e values predicted by the pseudo-second order kinetic model are in good agreement with the values obtained experimentally.

Calculated k_1 , k_2 and h values correspond with experimentally determined equilibrium times (i.e. the higher the k_1 , k_2 and h values – the shorter the equilibrium time). Finally, it is important to notice that good agreement with tested models is not the evidence of a certain sorption mechanism (Simonin, 2016). For example, processes that comply with pseudo-second-order kinetic model were found to be governed by different sorption mechanisms such as diffusion, ion-exchange, dissolution/precipitation, etc.

FIGURE 5

TABLE 3.

3.2.2 Sorption isotherms from single-component Sr^{2+} , Co^{2+} and Ni^{2+} solutions

Sorption affinities of chosen materials toward Sr^{2+} , Co^{2+} and Ni^{2+} ions from single-component solutions were investigated under equilibrium conditions. The results are given as a relationship between amounts of cations sorbed per unit mass of sorbents (Q_e) and their equilibrium concentrations in solution (C_e) (Figures 6-8).

FIGURE 6

FIGURE 7

FIGURE 8

For Sr^{2+} ions, the shape of sorption isotherm was strongly dependent on waste tile type (Fig. 6). In contact with water, CT releases huge amounts of Ca^{2+} ions, which act as strong competitors to Sr^{2+} ions. Consequently, the sorption of Sr^{2+} onto CT was negligible in the lower concentration range, and started to increase only after initial Sr^{2+} concentration increased over $2 \cdot 10^{-3}$ mol/L. Further increase of initial Sr^{2+} concentration provoked the increase of sorption efficiency, and the maximum sorbed amount was 0.035 mmol/g. On the other hand, isotherm obtained for Sr^{2+} onto RT showed measurable sorption for each initial

metal concentration, with maximum sorption capacities similar to those obtained for CT (approximately 0.030 mmol/g).

Sorption isotherms of Co^{2+} ions onto CT and RT (Fig. 7) exhibited similar shape, however, CT had higher sorption capacity. Experimentally obtained maximum sorption capacities for CT and RT were 0.17 mmol/g and 0.065 mmol/g, respectively. The absence of the plateau part on sorption isotherms can be explained by high quartz content in investigated tiles, for which Co^{2+} sorption does not show a simple plateau - monolayer behavior (James and Healy, 1972).

Finally, CT and RT showed similar affinities to Ni^{2+} ions (Fig.8). The sorption capacities of CT and RT towards Ni^{2+} ions were 0.12 mmol/g and 0.10 mmol/g..

In each experiment, pH values measured after attaining the equilibrium are presented in Fig. 6 - 8. Equilibrium pH values were dependent on the sorbate and the sorbent type, but they were generally higher than initial pH of metal solutions (approximately 5.5), due to dissolution of the components unstable under applied conditions. Equilibrium pH values were almost independent on initial Ni^{2+} concentrations, while in the experiments considering sorption of Sr^{2+} and Co^{2+} , pH decreased with the increase of sorbed amounts. This trend can be attributed to specific cation sorption mechanism, involving the binding of metal cations by hydroxyl surface groups with simultaneous release of H^+ ions (Šljivić-Ivanović et al. 2015). The pH decrease associated with cation sorption was more pronounced using CT. Furthermore, final pH values of metal containing solutions were slightly higher after contact with CT. According to Ni and Co speciation diagrams against solution pH (Smiljanić et al. 2010, Park et al. 2012), formation of insoluble $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ starts at pH 8. Therefore, based on final pH values of CT, which were close to precipitation threshold for both Co^{2+} and Ni^{2+} , the participation of such mechanism cannot be ruled out. Higher

contribution of specific cation sorption and possible precipitation of Co- and Ni-hydroxides using CT, is consistent with its higher metal sorption capacity in respect to RT.

At the highest initial cation concentration applied in this study, the affinity of CT increased in the order $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Sr}^{2+}$, whereas RT exhibited different selectivity order: $\text{Ni}^{2+} > \text{Co}^{2+} > \text{Sr}^{2+}$. Considerably lower sorption of Sr^{2+} ions was partially a result of coexisting Ca^{2+} ions in the solution (Fig. 3). As both cations belong to the alkaline earth group, Sr^{2+} and Ca^{2+} have similar chemical behavior and reactivity, thus selectivity of sorbent materials towards Sr^{2+} is generally low in the presence of Ca^{2+} ions. Previous investigations on cation sorption by calcite have revealed that Ba and Sr (cations with larger ionic radii than Ca) were weakly sorbed, while smaller cations (Cd, Mn, Zn, Co, and Ni) were sorbed more strongly (Park et al. 2012). It was also suggested that Co and Ni form surface complexes that remain hydrated until the ions are incorporated into the calcite structure by re-crystallization (Zachara et al. 1991). Moreover, point of zero charge determined for quartz was found to be about 2 (Brown and Parks, 2001), indicating that under the conditions applied in these experiments, SiO_2 surface was negatively charged, with the high tendency to sorb cations by electrostatic attraction forces. Consequently, the affinity of SiO_2 toward Co^{2+} was found to be higher (Vydra and Galba, 1969) or similar (Taniguchi et al. 1970) to affinity toward Ni^{2+} ions.

Sorption isotherms were fitted using the most utilized models, Langmuir and Freundlich. One of the most used linear forms of Langmuir model is:

$$\frac{C_e}{Q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (4)$$

While, the linearization of Freundlich model gives:

$$\ln Q_e = \ln K + n \times \ln C_e \quad (5)$$

where Q_e (mmol/g) and C_e (mmol/L) denotes the equilibrium concentrations of cations in the solid and the liquid phase, respectively, q_m (mmol/g) is the maximum sorption capacity, and K_L (L/g) is the Langmuir constant related to the energy of adsorption, n and K_F are Freundlich isotherm parameters. Linear fitting of functions C_e/Q_e vs. C_e , and $\ln Q_e$ vs. $\ln C_e$ gave the parameters of Langmuir and Freundlich models, respectively (Table 4). Predicted maximum sorption capacities were higher than experimentally obtained ones. In general, better data description was obtained using Freundlich than Langmuir isotherm, especially for the sorption of Sr^{2+} onto CT for which Langmuir model was not applicable. The lowest values for K_F were obtained for Sr^{2+} , which is in the agreement with its low sorption capacities, whereas higher sorption affinity of CT toward Co^{2+} and Ni^{2+} ions was supported by higher K_F values.

TABLE 4.

Reported sorption capacities of some industrial waste materials toward ions investigated in this study, are presented in the Table 5. At first sight, the majority of listed waste materials exhibited higher sorption potential than CT and RT. However, it must be taken into account that sorption capacity is strongly associated, not only with material properties, but also with a number of process parameters such as solid/liquid ratio, pH, sorbent particle size, ionic strength of the solution, etc. In this sense, the literature data are not straightforwardly comparable. Particles with smaller size have more developed specific surface area and, thus, higher sorption capacity. Red mud (treated or untreated) is generally a fine grained material with particle size $< 28 \mu m$ (Agatzini-Leonardou et al., 2008). Furthermore, the investigation of animal bones (Dimović et al., 2009; Smičiklas et al. 2010) was conducted using particles in the range 45-200 μm . Given that CT and RT were of much larger particle size (0.3 - 0.6 mm), it is reasonable to expect that their specific surface area and sorption efficiency could

be enhanced by further reduction of particle size. Similarly, optimization of solid/liquid ratio and solution pH is a way to increase the sorption capacities of CT and RT.

What corroborates the potential of CT and RT is, also, a minimal pretreatment (mechanical), whereas preparation of sorbents by thermal (Kobyas et al. 2005, Smiljanić et al. 2010, Dimović et al., 2009; Smičiklas et al. 2010) and chemical modification of waste materials (Smičiklas et al. 2014; Zhai et al. 2004) implies consumption of energy and chemical reagents. Finally, CT and RT are highly compatible with solidification mixtures used for permanent radioactive waste disposal.

TABLE 5.

3.2.3 Competitive sorption – Experimental design methodology

The wastewaters are often multi-component solutions with a wide range of components' proportions. In order to investigate sorption process under more realistic conditions, the experiments with multi-component solutions were performed. The competition between chosen cations was examined using experimental design methodology. The results of the sorption experiments set by the Simplex centroid design (Table 1), are presented in Fig. 9.

FIGURE 9

The sorption of Sr^{2+} from three-component solution which contained excessive amounts of Sr^{2+} and from Sr-Ni or Sr-Co equimolar two-component solutions, was slightly more pronounced onto RT than on the CT. Quite the opposite, CT was more efficient considering experiments where Sr^{2+} ions were present in much smaller amounts. Additionally, the

sorption of Co^{2+} and Ni^{2+} from multi-component solutions was slightly higher using CT than RT, regardless of the solution composition.

The results of experimental design were analyzed using mixture regression model fitting method. The results of ANOVA tests are given in Table 6, as R^2 values and F and p values, calculated for the overall regression and for linear and quadratic terms. R^2 values are statistical measure of how close the data are to fitted regression line, while F and p represent Fisher's and probability test values.

The linear, quadratic, full and special cubic and quadratic terms involved in the model were tested. For the results of Sr^{2+} sorption by RT, and Ni^{2+} sorption by CT from multi-component solutions, the adequate model with statistically significant terms was not found. On the other hand, Sr^{2+} sorption on CT was well described ($R^2 > 97\%$) by special cubic model with statistically significant linear and quadratic terms. Taking into account statistically significant parameters, Eq. 6 was obtained, according to which sorption process was the most affected by Sr^{2+} concentration (positively) and by Sr-Co and Sr-Ni interactions. Based on the negative signs in front of the interaction terms, it can be concluded that coexisting Co^{2+} and Ni^{2+} diminished sorption of Sr^{2+} . Co^{2+} sorption onto CT was the best described using only linear terms at 95% confidence level ($p < 0.05$) (Eq. 7). The order of magnitude of coefficients presented in this equation implies that sorption efficiency was majorly dependent on Co^{2+} concentration in the solution.

TABLE 6.

$$\text{SrCT} = 0.03812\text{Sr} + 0.000134\text{Co} - 0.00053\text{Ni} - 0.07748\text{SrCo} - 0.08122\text{SrNi} \quad (6)$$

$$\text{CoCT} = 0.002457\text{Sr} + 0.0596\text{Co} - 0.001492\text{Ni} \quad (7)$$

$$\text{NiRT} = 0.002409\text{Sr} - 0.000997\text{Co} + 0.054013\text{Ni} \quad (8)$$

$$\text{CoRT} = -0.0003\text{Sr} + 0.0679\text{Co} + 0.0074\text{Ni} \quad (9)$$

Furthermore, sorption of Co^{2+} and Ni^{2+} onto RT can be explained by quadratic and linear model, presented by Eq. 9 and 8, respectively, with coefficients significant at 90 % confidence level ($p < 0.1$). Generally, removal rate of Co^{2+} and Ni^{2+} was highly independent of the presence and concentration of coexisting cations.

Sorption from multi-component solutions with different proportions of sorbates is relatively rarely investigated. Literature survey showed that coexisting cation may cause both the antagonistic and the synergetic effects on the overall sorption process, depending on the solution composition, as well as on the type of applied sorbent. The removal of Sr^{2+} , from Sr^{2+} , Co^{2+} and Cs^+ multi-component solutions using thermally treated bovine bones and red mud, was suppressed by the coexisting Co^{2+} ions (Šljivić-Ivanović et al. 2015). The same study also showed that Co^{2+} ions binding by rinsed red mud sample, as well as Cs^+ binding by zeolite, were unaffected by the occurrence of other cations in the solutions, which makes such processes very selective. On the other hand, using activated carbon felts, Sr^{2+} ions did not affect the sorption of Co^{2+} and Ni^{2+} , but the sorption of Sr^{2+} and Co^{2+} was inhibited by coexisting Ni^{2+} ions (Ferreira Esmi et al. 2014). Quite the contrary, the presence of Ni^{2+} ions supported Co^{2+} sorption onto carboxylated sugarcane bagasse (Ramos et al. 2015).

Obtained empirical Equations 6-9 allow the prediction of investigated cations sorption onto CT and RT from the solutions containing other combinations of cation proportions. Graphical interpretations of obtained regression equations are given in the Fig. 10, as a ternary contour plots.

FIGURE 10

The utilization of wastes for water purification purpose is a promising tool, however, further modifications of sorbents and optimization of experimental conditions are essential for the improvement of process efficiencies.

4. Conclusion

Preliminary investigation concerning possible utilization of waste ceramic and roof tiles, as sorbents for liquid radioactive waste decontamination, was performed. RT contained quartz and albite as the major mineral constituents, while ceramic tiles were a mixture of quartz and calcite. According to radiological analysis, and pH determination at various solid/liquid ratios, investigated materials do not represent a potential risk to the environment and human health. Sorption kinetics data were excellent, described by pseudo-second-order kinetic model. Contact time necessary for reaching equilibrium was found to be dependent on applied sorbent and sorbate. The sorption of Sr^{2+} , Co^{2+} and Ni^{2+} ions was investigated by batch experiments, at equilibrium conditions. At the highest investigated concentration levels, the affinity of CT decreased in the following order: $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Sr}^{2+}$, while the affinity of RT followed the trend: $\text{Ni}^{2+} > \text{Co}^{2+} > \text{Sr}^{2+}$. Being sensitive to Ca^{2+} presence and concentration, the shape of the Sr^{2+} sorption isotherms was strongly dependent on material type. Sr^{2+} and Co^{2+} ions showed higher affinity to CT, while both investigated waste tiles were similarly effective towards Ni^{2+} ions. Specific sorption of Sr^{2+} and Co^{2+} ions was anticipated based on solution pH changes. Furthermore, precipitation is a possible mechanism of Co^{2+} and Ni^{2+} removal. Carbonate content and higher equilibrium pH values make the precipitation more likely using CT sorbent. Generally, better description of experimental data was obtained using Freundlich than Langmuir isotherm model. From multi-component solutions, sorption of Sr^{2+} ions was disturbed by coexisting Co^{2+} and Ni^{2+} ions, while sorption of Co^{2+} and Ni^{2+} occurred independently on other cations' existence in multi-component solutions. The utilization of

waste ceramic and roof tiles for water purification purpose is a promising tool, still, sorbent modifications and the optimization of experimental conditions are needed to gain higher sorption capacities.

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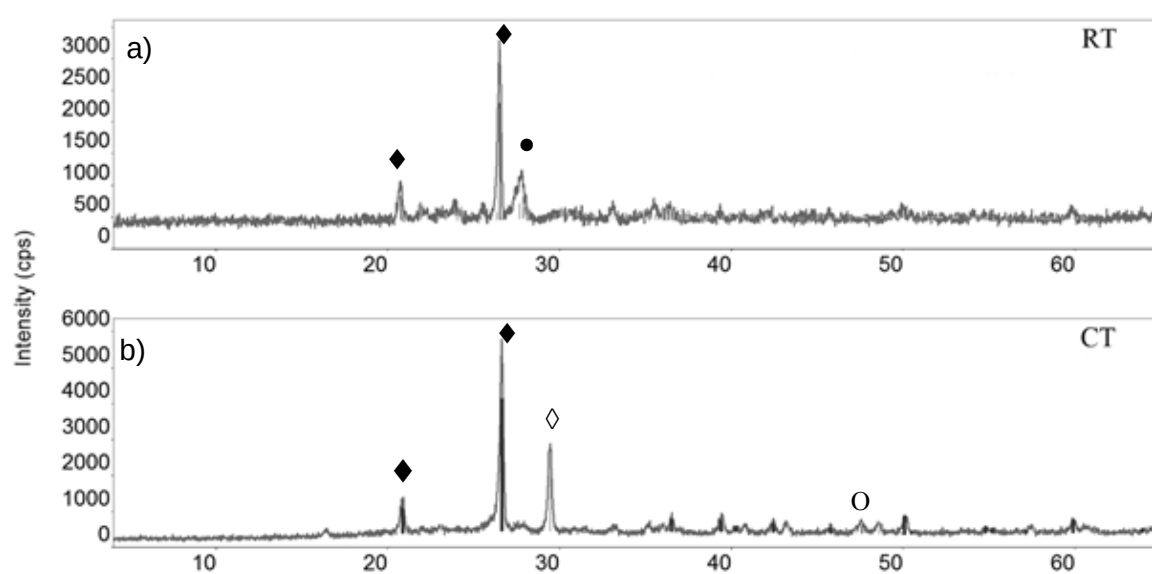


Figure 1. XRD patterns of (a) RT and (b) CT sample. Symbols: quartz (♦), albite (●), calcite (◊) and silver-chromium-tin-selenide-sulfide (○).

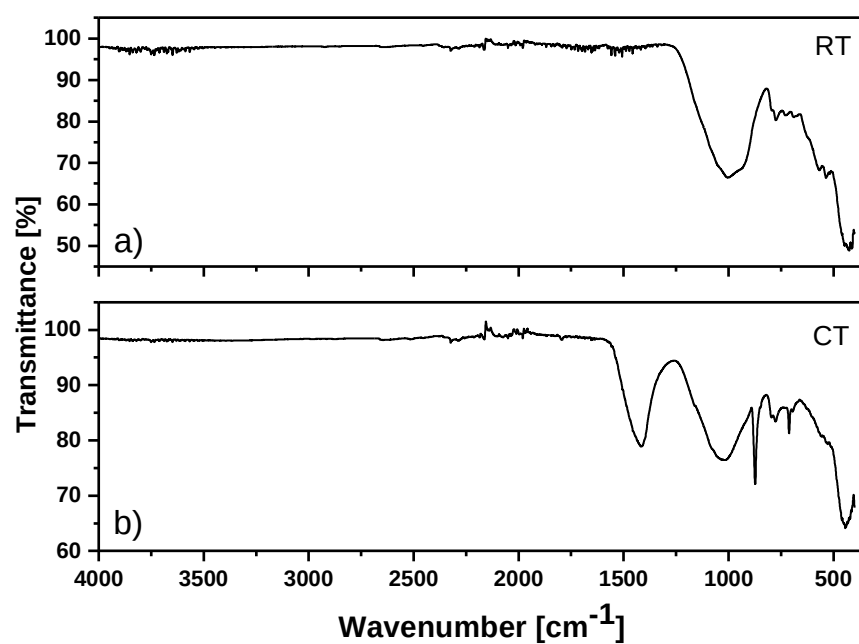


Figure 2. FT-IR spectrums of (a) RT and (b) CT samples.

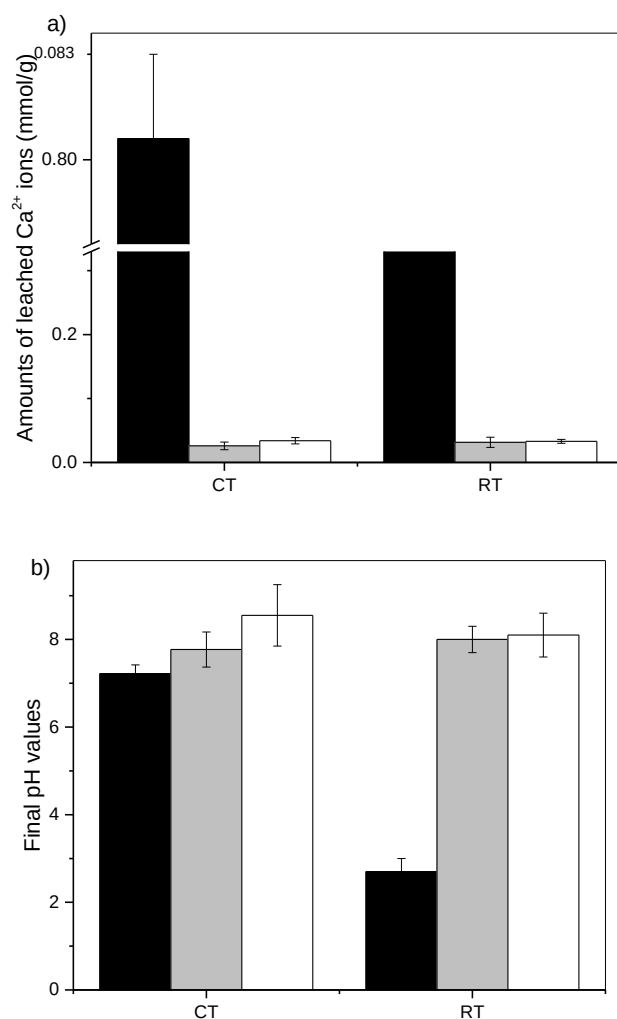


Figure 3. Amounts of leached Ca^{2+} ions (a) and final pH values (b), measured after equilibration of CT and RT with aqueous solutions having initial pH 2 (black bars), pH 6 (grey bars) and pH 8 (white bars).

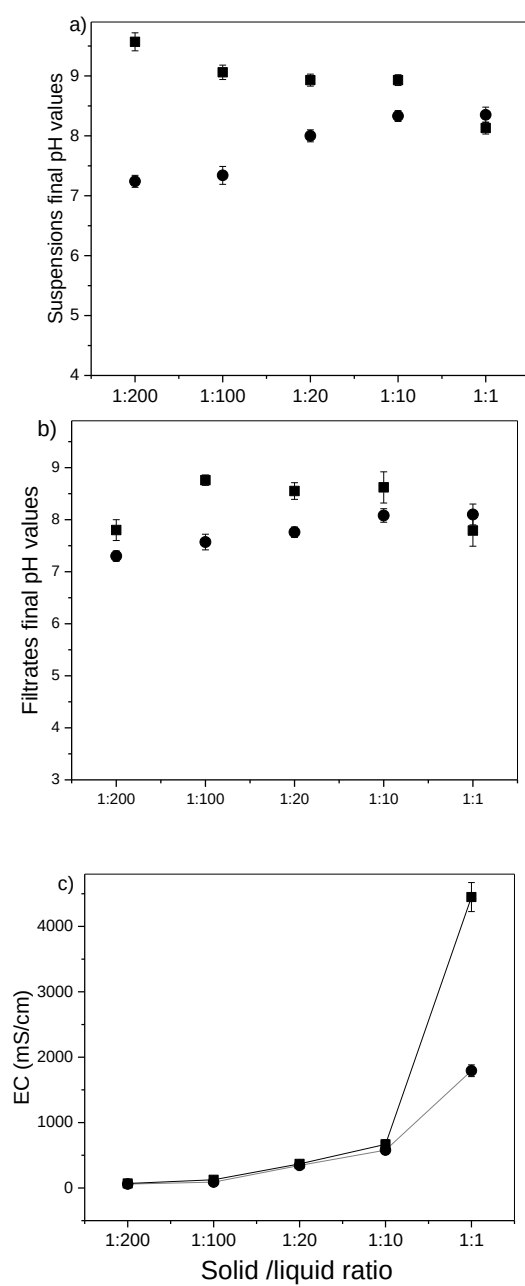


Figure 4. The relationships between solid/liquid ratio of CT (■) and RT (●) containing suspensions and: (a) suspension final pH values, (b) filtrates final pH values and (c) electrical conductivity of filtrates.

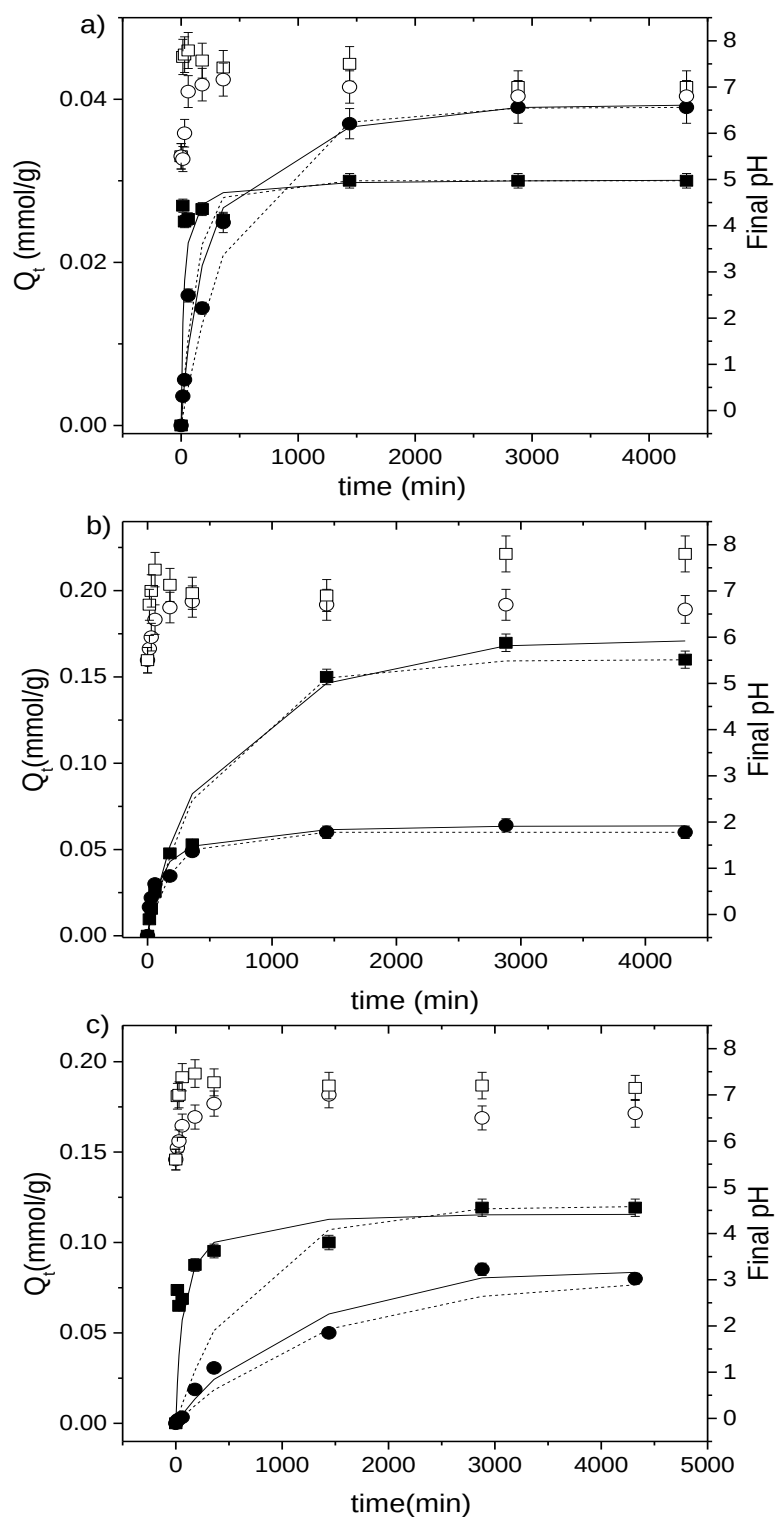


Figure 5. Sorption kinetics curves of a) Sr^{2+} , b) Co^{2+} and c) Ni^{2+} ions onto CT (■) and RT (●). Open symbols represent final pH changes as a function of time, while lines represent pseudo first order (dashed lines) and pseudo-second order kinetic model (solid lines).

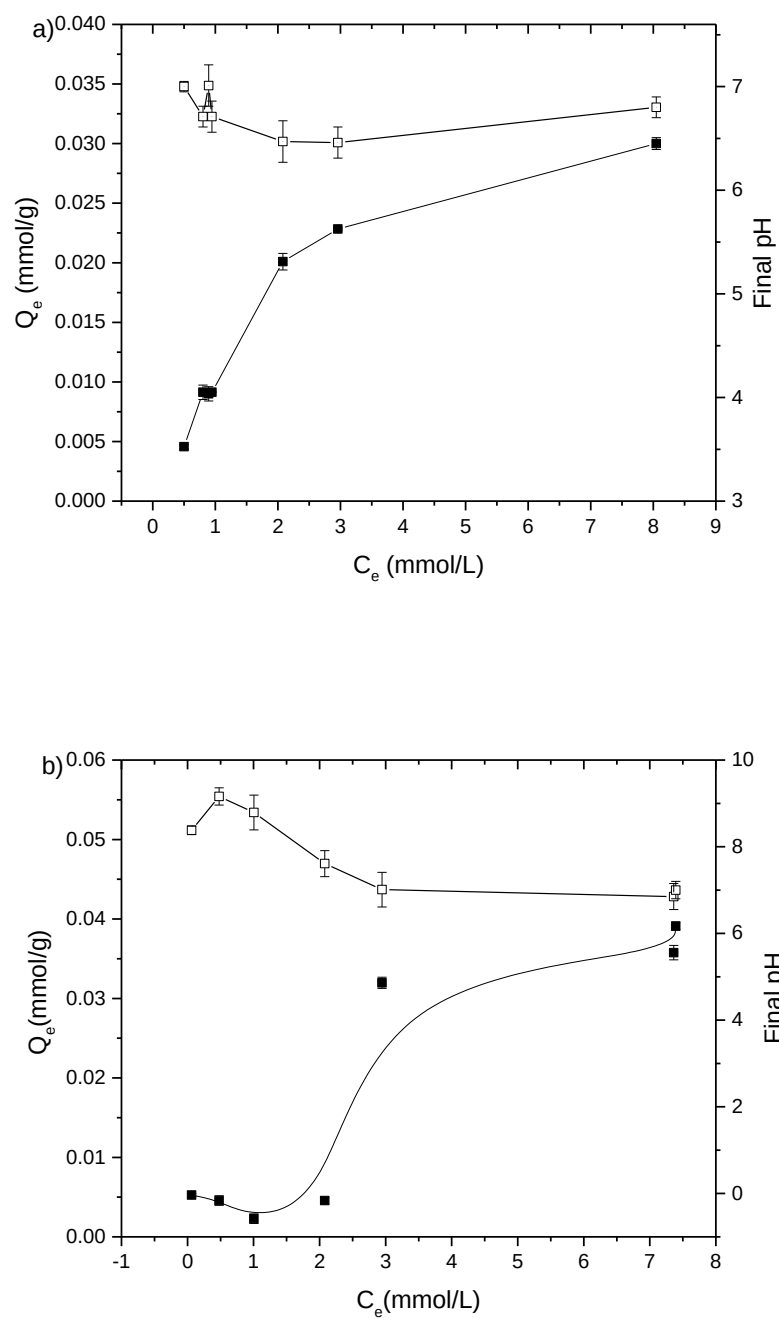


Figure 6. Sorption isotherms (closed symbols) and final pH values (open symbols) for Sr^{2+} ions sorption on (a) RT and (b) CT.

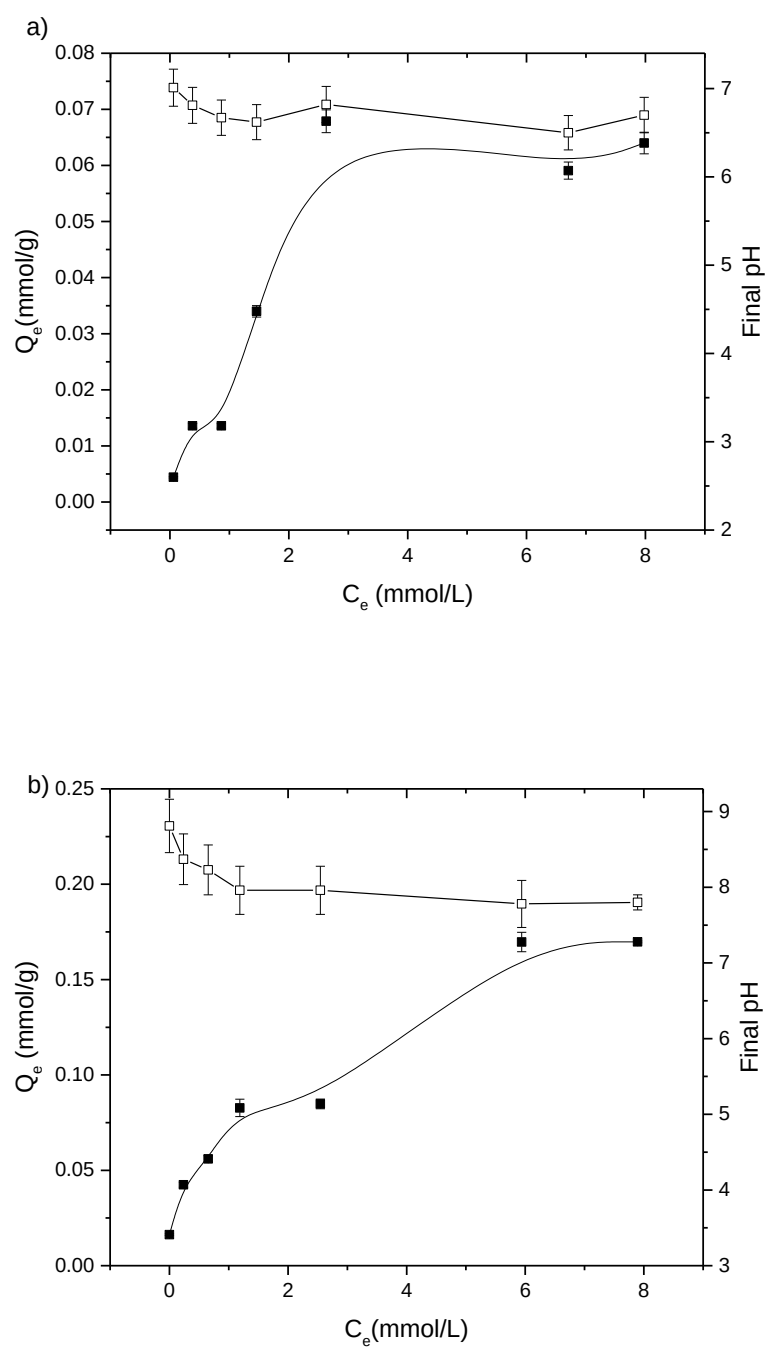


Figure 7. Sorption isotherms (closed symbols) and final pH values (open symbols) for Co^{2+} ions sorption on (a) RT and (b) CT.

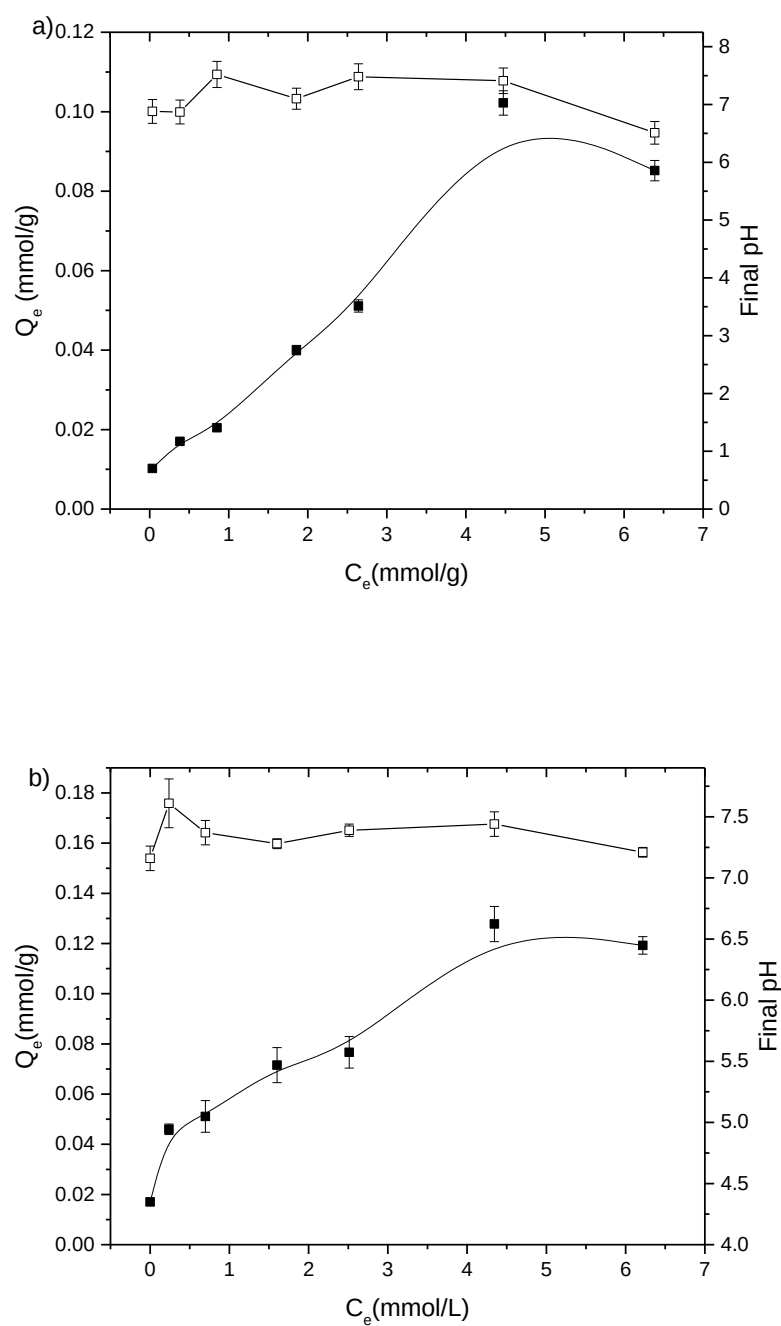


Figure 8. Sorption isotherms (closed symbols) and final pH values (open symbols) for Ni^{2+} ions sorption on (a) RT and (b) CT.

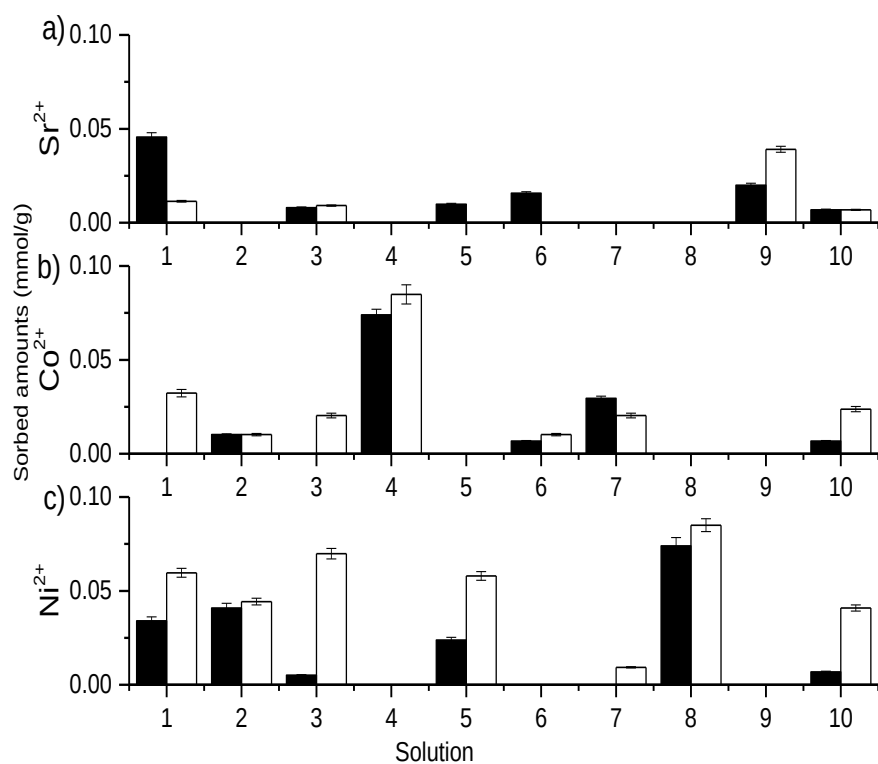


Figure 9. Amounts of Sr^{2+} (a), Co^{2+} (b) and Ni^{2+} (c) ions sorbed from the multi-component solutions by CT (white bars) and RT (black bars). The numbers on the x-axes correspond to the composition of mixture solutions presented in Table 1.

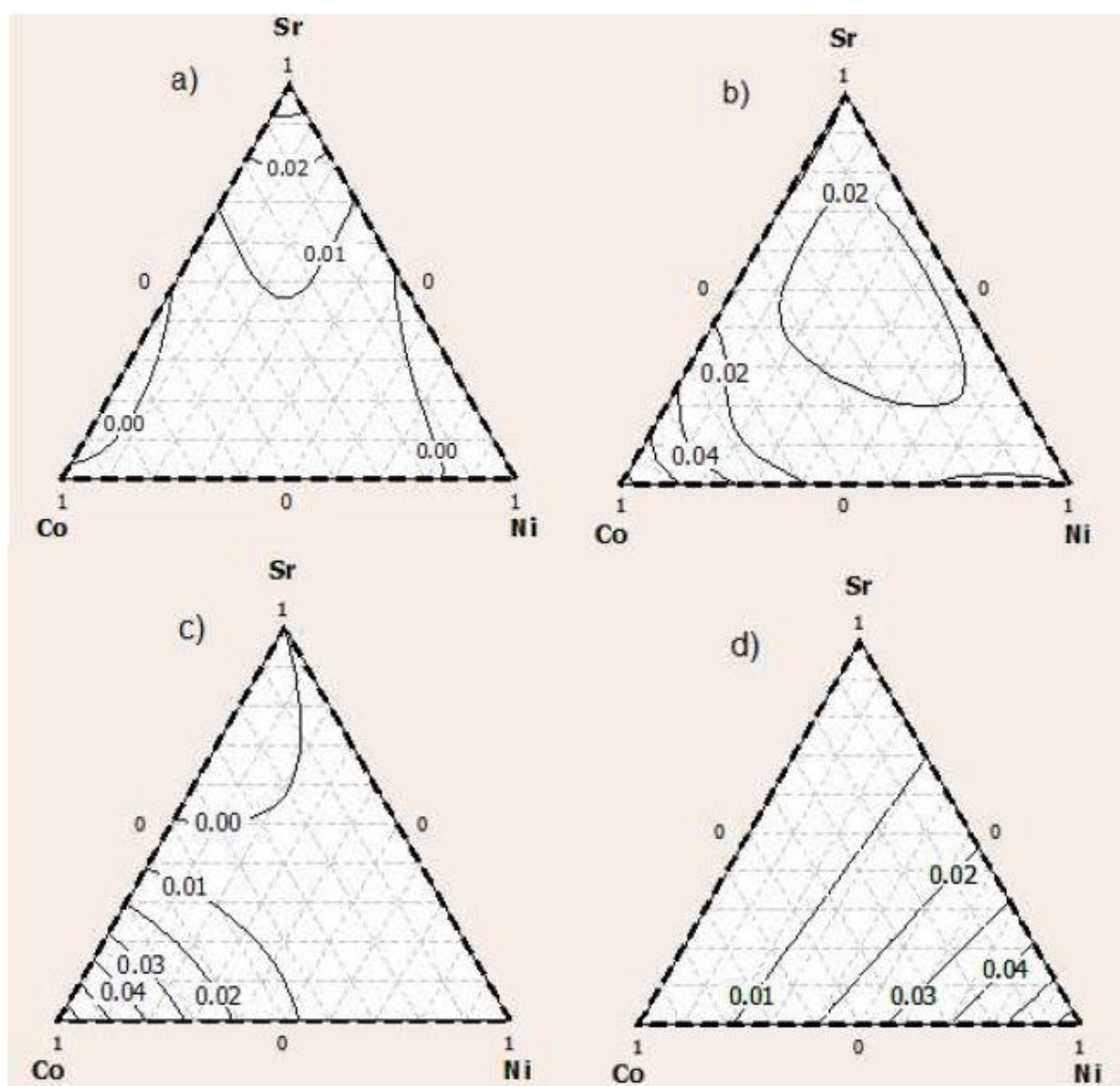


Figure 10. Ternary contour plots of the sorbed amounts (mmol/g) of Sr^{2+} (a) and Co^{2+} (b) ions onto CT, and Co^{2+} (c) and Ni^{2+} (d) ions onto RT.

Table 1. Simplex centroid design matrix for the study of competitive cation sorption

Solution No.	Ratio $\text{Sr}^{2+}:\text{Co}^{2+}:\text{Ni}^{2+}$
1	4:1:1
2	0:1:1
3	1:1:1
4	0:1:0
5	1:0:1
6	1:1:0
7	1:1:4
8	0:0:1
9	1:0:0
10	1:4:1

Table 2. Gamma-spectrometric analysis of waste RT and CT powders

Material	Bq/kg							R _{aeq}
	²²⁶ Ra	²³² Th	⁴⁰ K	²³⁵ U	²³⁸ U	¹³⁷ Cs	²¹⁰ Pb	
RT	60±7	50±10	790±80			23±3	50±20	192.3
CT	90±10	60±10	860±80	2.7±0.6	100±70	<1		242.0

Table 3. Pseudo-first and pseudo-second order kinetic model parameters calculated for Sr^{2+} , Co^{2+} and Ni^{2+} sorption onto RT and CT

Sorbent	Pseudo-first order		Pseudo-second order			
	$k_1 \times 10^3$ (1/min)	R	h (mmol/g min)	q_e (mmol/g)	k_2 (g/mmol min)	R
Sr^{2+}						
RT	2.13	0.987	$2.05 \cdot 10^{-4}$	0.0417	0.118	0.998
CT	7.48	0.685	$1.44 \cdot 10^{-3}$	0.0302	1.58	0.999
Co^{2+}						
RT	4.93	0.962	$6.97 \cdot 10^{-4}$	0.0655	0.162	0.999
CT	1.88	0.994	$3.93 \cdot 10^{-4}$	0.197	0.010	0.978
Ni^{2+}						
RT	0.731	0.971	$8.47 \cdot 10^{-5}$	0.120	$5.88 \cdot 10^{-3}$	0.916
CT	1.55	0.746	$1.85 \cdot 10^{-3}$	0.118	0.133	0.997

Table 4. Cation sorption parameters calculated by Langmuir and Freundlich isotherm models

Sorbent	Freundlich model			Langmuir model		
	n	K_F (mmol ¹⁻ⁿ dm ³ⁿ g ⁻¹)	R	Q_m (mmol g ⁻¹)	K (L mmol ⁻¹)	R
Sr²⁺						
RT	0.668	9.531x10 ⁻³	0.955	0.0437	0.302	0.947
CT	0.480	0.00868	0.679	NA	NA	NA
Co²⁺						
RT	0.579	0.0228	0.956	0.0794	0.511	0.880
CT	0.412	0.0716	0.975	0.191	0.788	0.904
Ni²⁺						
RT	0.447	0.0340	0.934	0.122	0.385	0.842
CT	0.329	0.0650	0.947	0.132	1.271	0.961

NA-not applicable

Table 5. Sorption capacities of some industrial wastes and by-products toward Sr^{2+} , Co^{2+} and Ni^{2+} ions

Sorbent material	Sorption capacity (mmol/g)	Ref.
Sr^{2+}		
Fly ash	1.89	Apak et al 1996
Treated animal bones	0.191-0.384	Smičiklas et al. 2010
Raw red mud	0.31	Milenković et al. 2014
Ceramic tiles	0.035	This study
Roof tiles	0.030	This study
Co^{2+}		
Activated carbon from apricot stone	0.504	Koby et al. 2005
Raw red mud	0.520	Milenković et al. 2014
Treated animal bones	0.078-0.495	Dimović et al. 2009
Ceramic tiles	0.17	This study
Roof tiles	0.065	This study
Ni^{2+}		
Fly ash	0.0068-0.017	Bayat, 2002
Rinsed red mud	0.372	Smiljanić et al 2010
Acid treated red mud	0.014-0.115	Smičiklas et al. 2014
Thermally treated red mud	0.47	Smiljanić et al 2010
Treated sewage sludge	0.155	Zhai et al. 2004
Ceramic tiles	0.12	This study
Roof tiles	0.10	This study

Table 6. ANOVA analysis of regression for Sr^{2+} , Co^{2+} and Ni^{2+} sorption from multicomponent solutions onto CT and RT

Sorbate-sorbent systems	R^2 (%)	Regression analysis		Linear terms		Quadratic terms	
		F	p	F	p	F	p
Sr-CT*	97.49	19.45	0.017	46.44	0.006	14.27	0.028
Co-CT*	60.84	5.44	0.038	5.44	0.038	-	-
Ni-RT**	51.47	3.71	0.08	3.71	0.08	-	-
Co-RT**	77.92%	5.64	0.068	5.64	0.068	1.59	0.325

*significant at 95%, **significant at 90%