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Rinsed and thermally treated red mud sorbents for aqueous Ni^{2+} ions

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ABSTRACT

Red mud, an abundant industrial waste from alumina industry, represents a rich source of various metal oxides, mainly of Fe_2O_3, Al_2O_3 and SiO_2. In this study, the rinsed Bosnian red mud (RBRM) was evaluated as an economical, composite sorbent for aqueous Ni^{2+} ions. The process was investigated as a function of pH, contact time and initial metal concentration. The investigated mineral mixture exhibited a high acid neutralising capacity, and its most important role in cation immobilization was observed in the initial pH range 2–8. The initial metal ion concentration strongly influenced the sorption kinetics and equilibrium times. Addition of 5 g/L of RBRM caused 100% removal from the solutions of 10^{-4} to 5×10^{-4} mol/L, whereas with the further increase of Ni^{2+} concentration to 8×10^{-3} mol/L, the removal efficiency decreased to 26%. The maximum sorption capacity of 0.372 mmol/g, at initial pH 5, was determined using Langmuir theoretical model. The possibility of sorption efficiency improvement by annealing RBRM powder was investigated in the range 200–900 °C and the relationships between temperature, red mud physicochemical and sorption properties were established. The optimum heating temperature was found to be 600 °C, due to water exclusion from gibbsite and bayerite phases, leading to improved porosity and surface area, as well as increased pH value and sorption efficiency. The stability of the sorbed cation was assessed by leaching experiments in distilled water and acidic TCLP2 solution.

1. Introduction

Given that heavy metal ions are harmful to a variety of living species, issues of significant importance are their transport and distribution through the environment as well as their removal from contaminated water, soil and sediments. Industrial wastewaters that contain high levels of heavy metal cations are treated by different physicochemical processes, with the focus on chemical precipitation, coagulation–flocculation, flotation, ion-exchange, membrane filtration and sorption [1]. A survey of recent patents for water and wastewater treatments [2] showed that significant amount of patents related to sorption technologies still include only carbon based materials which are relatively expensive, act in a non-selective manner and exhibit unsatisfactory efficiency in the removal of inorganic contaminants. For that reason, there is an increasing trend in searching for new heavy metal sorbents among commercially available materials such as by-products of various industries. Recent comparison of composite sorbents which are accessible, inexpensive and effective for treating a variety of contaminants have emphasized the outstanding metal removal capabilities of materials originating from agricultural and industrial by-products [3]. The examples of stabilized industrial solid wastes that were evaluated as composite sorbents are red mud, fly ach, waste from electroplating industry and blast furnace slag [4–7]. One of the most promising sorbent was found to be red mud, a waste sludge obtained after processing the bauxite ore following Bayer's process. Iron in bauxite ores occurs in various minerals forming the principal component of the red mud waste. In addition, red mud usually contains Al-bearing phases boehmite (AlOOH) or gibbsite ($Al(OH)_3$), titania (TiO_2), quartz (SiO_2), sodalite ($Na_4Al_3Si_3O_{12}Cl$), and many residual minerals such as cancrinite-type sodium aluminum silicate (CAN), gypsum ($CaSO_4{\cdot}2H_2O$), calcite ($CaCO_3$), whewellite ($CaC_2O_4{\cdot}H_2O$), etc [8].

In nature, oxides of iron are important components of soils and sediments and represent the most important sink for toxic metal ions, released into the environment from a variety of anthropogenic sources [9]. Taking into account the main mineralogical phases of red mud, it is not surprising that samples from different parts of the world have revealed high removal efficiency for numerous heavy metal cations [8]. In addition, red mud was studied as an effective immobilization agent for various other pollutants such as fluoride [10,11], boron [12], phenol [13], dyes [14,15], etc. In the available scientific literature, temperature, acid and combined acid-heat activation procedures of red mud [13–18], were investigated. Temperature effect was thoroughly analyzed using phosphate [16,17] and arsenate anions as sorbates [18], but there it is hard to find a

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similar comprehensive study of the effect of annealing temperature on red mud removal properties in respect to heavy metals cations.

In this study, red mud supplied from the "Birač" Alumina Factory (Zvornik, eastern Bosnia), was evaluated in terms of heavy metal immobilization. At this location, rinsed red mud suspension, of a density between 1.2 and 1.3 g/mL and dry matter concentration 250–350 g/L is disposed as a waste in an open field – a natural dump area. The liquid phase of the suspension still contains about 7 g/L of Na_2O, therefore red mud waste is highly alkaline. As a heavy metal representative Ni^{2+} was selected, the cation most commonly found in wastewaters originated in metal plating operations and acid mine drainage. The results reported on Ni^{2+} removal by a sample from central Greece, indicated that heavy metal cations were efficiently removed from dilute solutions by red mud acting simultaneously as an alkalinity regulator, as an adsorbent of the formed nickel hydroxide and as a flocculant of the resulting fine particulate matter [19].

The objective of this work was: (i) to examine the physicochemical characteristics of rinsed red mud from Bosnia and influence of various experimental conditions on its sorption properties towards Ni^{2+} cations; (ii) to evaluate the effect of thermal treatment on red mud composition, pH and sorption properties, and to select optimal conditions for sorbent pretreatment.

2. Experimental

2.1. Preparation of red mud samples

Preliminary experimental results have shown that the original sample collected from the "Birač" Alumina Factory have pH around 10.5, and significant Ni^{2+} removal efficiency due to precipitation of insoluble $Ni(OH)_2$. Furthermore, thermal treatment had limited effect on Ni^{2+} removal by original red mud, because the effect of excess base covered other effects induced by annealing of the sample. In order to investigate the sorption properties of red mud mineral constituents, and produce environmentally benign sorbents, it was necessary to remove excess base by repeated washing. The sample was thoroughly washed with distilled water in the following way: in a 10 L plastic container, a 2.5 L of original red mud was mixed with approximately 6 L of distilled water; the suspension was stirred intensively by hand for a couple of minutes and then allowed to equilibrate and settle overnight. After decanting, a small solution aliquot was centrifuged and used for pH measurement. The fresh distilled water was then added to the red mad sample, and the whole procedure was repeated during the period of 2 weeks, i.e. until no further changes in pH were detected. The solution was decanted once more, the residual red mud was transferred to shallow pots, dried in an oven at 105 °C and, finally, powdered using mortar and pestle. Additional activation of the sample, denoted as RBRM, was carried out by annealing the 15 g portions in an electrical furnace, at 200 °C, 400 °C, 600 °C, 800 °C and 900 °C for 3 h. These samples were denoted as RBRM200–RBRM900.

2.2. Characterization of red mud samples

The chemical composition of RBRM sample was determined in the central laboratory of the "Birač" Alumina Factory. Additionally, the mineralogical composition of RBRM, as well as of temperature treated samples, was studied by X-ray diffraction (XRD) analyses using a Philips PW 1050 diffractometer, with Cu $K\alpha_{1,2}$ radiation and a step/time scan mode of 0.05°/1 s.

The pH value of RBRM was measured following the EPA 9045D method for soil and waste pH [20]. According to this method, waste is continuously stirred with reagent water for 5 min, and after settling for another 15 min, aqueous phase used for pH measurement is separated from the suspension by filtration or centrifugation. The 1:1 solid to solution ratio is preferred, but the method allows additional dilutions, if working with hygroscopic or other problematic matrices. Since investigated RBRM powder tends to absorb water and form dense mud, different solid/solution ratios in the range 1:200 to 1:1 (5–1000 g/L) were investigated. For the comparison, the pH values of thermally treated samples were determined at selected 1:2.5 solid/solution ratio.

The point of zero charge (pH_{PZC}) of RBRM was determined by batch equilibration technique [21]. The sample was agitated for 24 h with the electrolyte solution of known initial pH, at solid/solution ratio of 1:200. As an electrolyte 0.1 mol/L, 0.01 mol/L and 0.001 mol/L NaCl solutions were applied. Initial pH values were adjusted in a wide pH range (from ~1 to ~11) by adding minimum quantities of variously concentrated HCl and NaOH solutions. Final pH values were plotted against initial pH and the pH_{PZC} was determined from the plateau of the graph.

2.3. Ni^{2+} sorption/desorption tests

In general, sorption tests were carried out in closed PVC bottles by agitating suspensions containing 0.1 g of a sorbent and 20 mL of $NiCl_2$ solution. Experiments were conducted on a horizontal laboratory shaker for 24 h at room temperature (20 ± 1 °C). Variously concentrated NaOH and HCl solutions were used for the adjustments of initial pH values. After equilibration, the solid residues were separated from the liquid phase by both centrifugation and filtration, and the remaining metal concentrations were determined by a flame Atomic Absorption Spectrometer (Philips Pye Unicam SP9) at 232.0 nm. The detection limit for Ni^{2+} ions was 0.059 mg/L. The amounts of Ni^{2+} removed from the solution were calculated as difference between initial and final metal concentrations. The initial and final solution pH values were measured by InoLab WTW pH-meter.

The effect of pH on Ni^{2+} uptake by RBRM was screened using solution with initial cation concentration of 10^{-3} mol/L and adjusting the initial pH values in the range from ~1 to ~12.

The effect of contact time on the amount of heavy metal cations removed was determined by equilibrating the RBRM powder with 10^{-4} mol/L and 8×10^{-3} mol/L $NiCl_2$ solutions, at initial pH 5. For each system, nine identical batches containing sorbent and appropriate $NiCl_2$ solution were prepared and placed on the shaker. At different time intervals (from 5 min to 48 h) one of the batches was taken for solid/liquid separation. Along with the determination of residual Ni^{2+} concentrations, solution pH changes were monitored.

The effect of initial cation concentration was analyzed using initial Ni^{2+} concentrations in the range 10^{-4} to 8×10^{-3} mol/L. pH values of all solution were adjusted to five prior to addition of sorbent, whereas equilibrium pH values were recorded.

The desorption of Ni^{2+} ions, previously sorbed from differently concentrated solutions, was examined in acidic conditions, by equilibrating dried solid residues with 20 mL of solution. Leaching solution was prepared from acetic acid, following Toxicity Characteristic Leaching Procedure (TCLP) [22] for more aggressive extraction media (TCLP2, pH 2.88 ± 0.05).

In order to evaluate and compare sorption properties of RBRM and products obtained at different annealing temperatures, Ni^{2+} solutions of 2×10^{-3} mol/L was applied, whereas initial pH values were adjusted in the range 2–5. For the assessment of final pH changes sorbents were additionally equilibrated for 24 h with distilled water, at 1:200 solid/solution ratio.

The stability of obtained Ni-loaded products was also estimated. The red mud residues loaded with Ni^{2+} at initial pH 2, 3 and 4 were dried at 105 °C overnight, resuspended in 20 mL of distilled water and shaken for another 24 h. For the estimation of leaching characteristics in acidic media, sorption products obtained at initial pH

Table 1
Chemical composition of rinsed red mud.

Component	Mass fraction (%)
SiO_2	12.37
Fe_2O_3	44.35
Al_2O_3	18.33
TiO_2	4.70
CaO	3.01
Na_2O	7.76
Loss of ignition	7.03

5 were dried and subsequently equilibrated for 24 h with TCLP2 leaching solution.

3. Results and discussion

3.1. *Physicochemical characteristics of red mud sorbents*

3.1.1. *Chemical composition*

The chemical composition of rinsed sample is presented in Table 1. The major component was iron oxide, followed by alumina and silica. The red mud composition is strongly dependent on the characteristics of precursor bauxite ore, as well as on applied technological process, and consequently fluctuates strongly between samples generated in different parts of the world. The quantity of each major constituent of investigated sample falls into ranges mentioned in the literature [8].

3.1.2. *XR-diffraction analysis*

The mineralogical composition of RBRM sample was investigated by XRD analysis (Fig. 1). The main crystalline phase present was found to be hematite (Fe_2O_3), whereas gibbsite and bayerite ($Al(OH)_3$) were identified as Al-bearing minerals. In addition, the peaks originated from sodalite ($Na_8Si_6Al_6O_{24}Cl_2$), calcite ($CaCO_3$) and quartz (SiO_2) were present, as well as of TiO_2 in the forms of both anatase and rutile. The main mineralogical components are in a good agreement with the chemical composition of investigated samples (Table 1).

The large effect of temperature on mineralogical composition of red mud was demonstrated in Fig. 2. The increase of temperature to 200 °C (Fig. 2a) caused decrease of intensity of XR-diffraction peaks characteristic for gibbsite and bayerite, whereas the complete loss of these peaks was observed in the specimens heated at ≥400 °C. These observations are consistent with the dehydration process of gibbsite [23,24] as well as of bayerite phase [25], and they can be expressed by the reaction:

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

The intensity of sodalite peaks started to drop at 600 °C, and disappeared at higher heating temperatures, as a result of the structure destruction and a creation of amorphous aluminosilicate phase. Temperature increase to 800 °C (Fig. 2d) was followed by the formation of a new crystal phase low-carnegieite ($NaAlSiO_4$), according to the reaction:

$$Na_4Al_3Si_3O_{12}Cl \xrightarrow{-NaCl} 3NaAlSiO_4$$

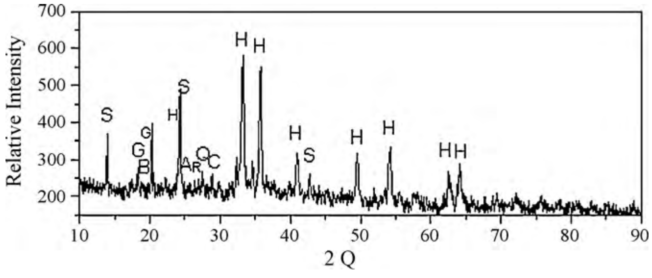

Fig. 1. XRD patterns of RBRM sample (H – hematite, S – sodalite, G – gibbsite, B – bayetite, C – calcite, Q – quartz, A – anatase, R – rutile).

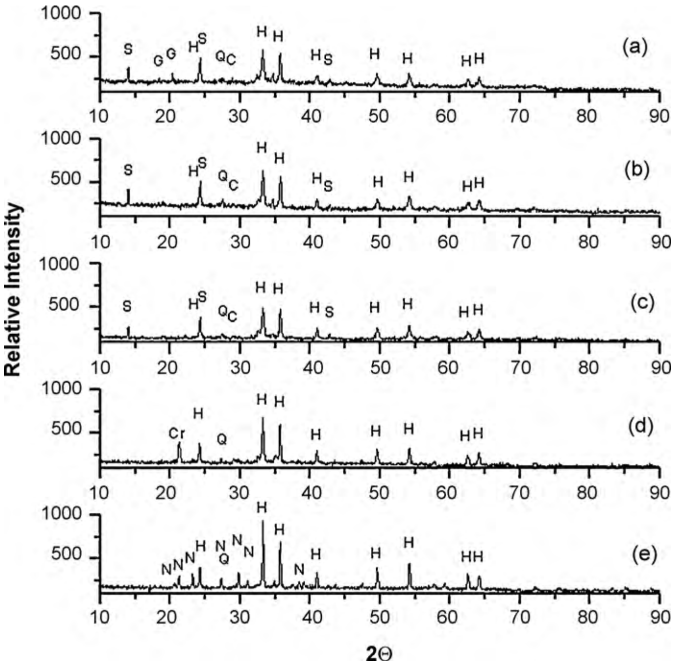

Fig. 2. XRD patterns of: a) RBRM200, b) RBRM400, c) RBRM600, d) RBRM800 and e) RBRM900 (H – hematite, S – sodalite, G – gibbsite, B – bayetite, C – calcite, Q – quartz, Cr – low-carnegieite, N – nepheline).

At 900 °C (Fig. 2e), transformation of low-carnegieite into a different polymorphic form – nepheline, was detected. This important mineral can be found in nature in a variety of alkaline igneous rocks, and it was found to be stable up to 1270 °C [26].

In the investigated temperature range quartz, hematite and rutile were not affected by the heating process, however, the improved hematite crystallinity with temperature increase above 600 °C, was clearly observed.

3.1.3. *pH values of red mud wastes*

In order to determine the influence of solid/solution ratio on the waste pH, different quantities of red mud samples were suspended in the same amount of reagent water. Fig. 3a shows that the pH increased significantly, from 7.56 to 9.77, with the increase of solid/solution ratio in the investigated range.

Due to hygroscopic nature of dried red mud, the solid to solution ratio of 1:2.5 was chosen for further comparison of thermally treated samples. The increase of heating temperature in the range 200–600 °C caused the increase of pH from 9.51 to 10.20 (Fig. 3b) whereas with further temperature increase up to 900 °C, the solution pH decreased to 9.57. The pH values of temperature treated samples varied according to the transformation occurring in them. The observed increase of pH between 200 °C and 600 °C was probably due to the dehydroxylation process confirmed by the XRD analysis. The pH values of samples heated at higher temperatures decreased, since less soluble and more crystalline phases occurred at temperatures above 600 °C. The results are consistent with the study reported for dissolution of thermally treated red mud [27], where the maximum total dissolution was obtained for specimen heated at 600 °C due to loss of the major quantity of releasable constituents and the highest specific surface area. In another study, the red mud density was found to increase for $T > 600$ °C, due to the progressive formation of crystalline phases with higher densities [28].

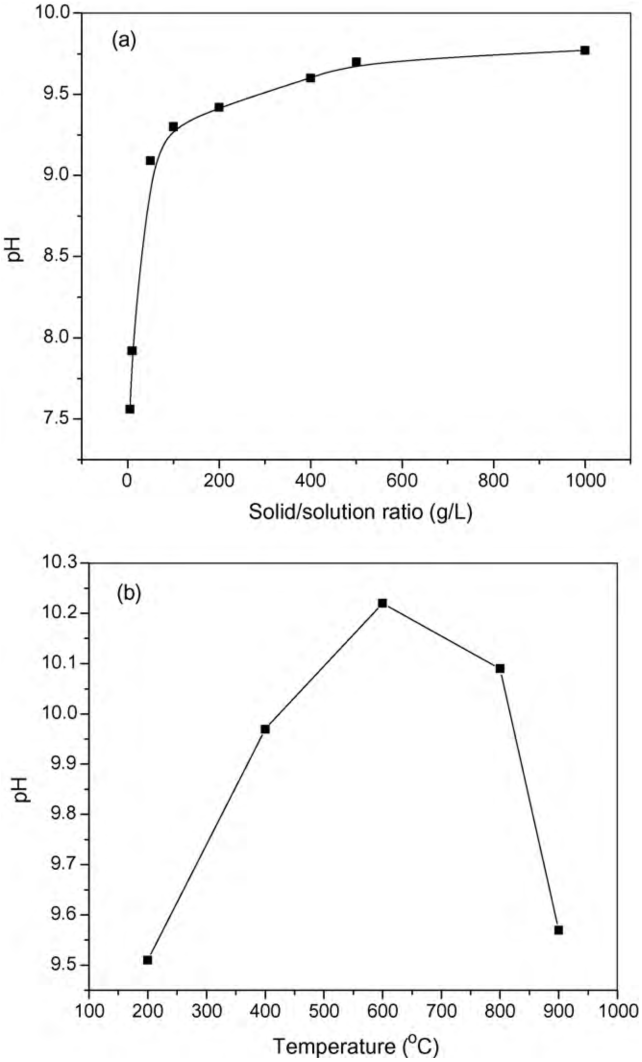

Fig. 3. (a) pH values of RBRM sample as a function of solid to solution ratio; (b) the relationship between RBRM heating temperature and solution pH at solid/solution ratio of 1:2.5.

It is important to notice that the elevated pH of red mud wastes generally represents a major obstacle for its further reuse. According to EPA regulatory levels, red mud is not classified as a hazardous waste [29]. However, any waste is classified as corrosive if exhibits aqueous $pH < 2$ or $pH > 12.5$. It can be concluded that samples investigated in this study had pH values in the appreciated range, regardless of the solid/solution ratio and heating temperature.

3.1.4. pH$_{PZC}$ value of RBRM sample

The point of zero charge, defined as the pH at which the net charge on the surface is zero, is useful for the determination of the surface charge properties of sorbent materials. Fig. 4, presents a relationship between the initial pH values of variously concentrated NaCl solutions and the final pH obtained after equilibration with RBRM sample. Buffering section, occurring as nearly horizontal section of the curves, was found to be a result of hydroxyls on the surfaces of iron oxide and sodalite and calcite dissolution [30]. The position of the plateaus was not a function of NaCl concentration, suggesting that this electrolyte is inert in respect to RBRM surface. For the applied solid/solution ratio, the pH$_{PZC}$ value of 7.5 ± 0.2 was estimated. In the literature, both lower (6.5 [31]) and higher (8.3 [32] and 8.5 [33]) pH$_{PZC}$ values were reported for different red mud samples.

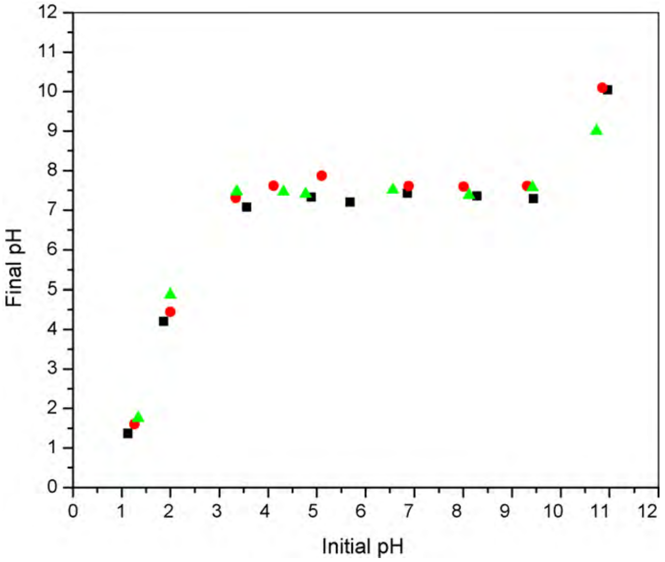

Fig. 4. Determination of the pH$_{PZC}$ value of RBRM sample. Inert electrolyte (NaCl) concentrations: 0.1 mol/L (■), 0.01 mol/L (●) and 0.001 mol/L (▲).

3.2. Evaluation of Ni^{2+} removal by red mud

3.2.1. Effect of pH on Ni^{2+} removal

Using appropriate Ni^{2+} and Cl$^-$ concentrations, the Visual MINEQ software was applied for the calculation of Ni-species distribution vs. solution pH (Fig. 5a). In the absence of sorbent material, Ni^{2+} cations are prevalent up to pH 8. At $pH > 8$, the hydrolysis of Ni^{2+} cations starts, reaching the maximum concentration of insoluble $Ni(OH)_2$ at pH 10. With further pH increase, the dissolution of nickel-hydroxide and formation of negatively charged $Ni(OH)_3{}^-$ species occur.

As shown in Fig. 5b, Ni^{2+} sorption by investigated powders was the most strongly pH dependent in the initial pH range 1–3, where the sharp increase of final pH values was observed indicating high acid neutralising capacity of investigated mineral mixture. In the same initial pH range, Ni^{2+} removal increased sharply as well, from 3.5% up to 87%. The lower metal uptake in acidic media can be connected with progressive dissolution of soluble sorbent components, as well as by H$^+$ cations competition with Ni^{2+} for RBRM sorption sites, which both caused increase of pH. The region of initial pH 4–7, was characterized by stabile final pH values (~6.5) and relatively stabile Ni^{2+} sorption (90–95%). Comparing the data from Figs. 4 and 5b, it is obvious that the final pH values at the plateaus were lower in Ni^{2+} solutions, than in the inert electrolyte. The release of H$^+$ ions into the solution signifies the specific Ni^{2+} sorption on the RBRM surface. Further initial pH increase from 8 to 12 was followed by increase in final pH, while heavy metal removal was completed. pH increase resulted in greater metal removal from the solution due to the following reasons: (i) at $pH > pH_{PZC}$ sorbent surface became negatively charged and attracted more positively charged sorbate particles Ni^{2+} as well as NiOH$^+$, and (ii) precipitation of $Ni(OH)_2$ started at $pH > 8$, and reached maximum concentration at pH ~10. By evaluation of the data presented in Fig. 5a and b, it can be concluded that in the overall process of investigated heavy metal removal, presence of RBRM sorbent exhibited largest significance in the initial pH range 2–8. According to the red mud dissolution studies [30], at pH values 4~5 to 8, considerable amounts of Na, Ca and Si can be leached due to dissolution of sodalite and calcite. Below pH 4 or 5, in addition to congruent sodalite dissolution, Fe-oxides start to dissolve increasing the amounts of dissolved Fe and Al. Therefore, in our further study of

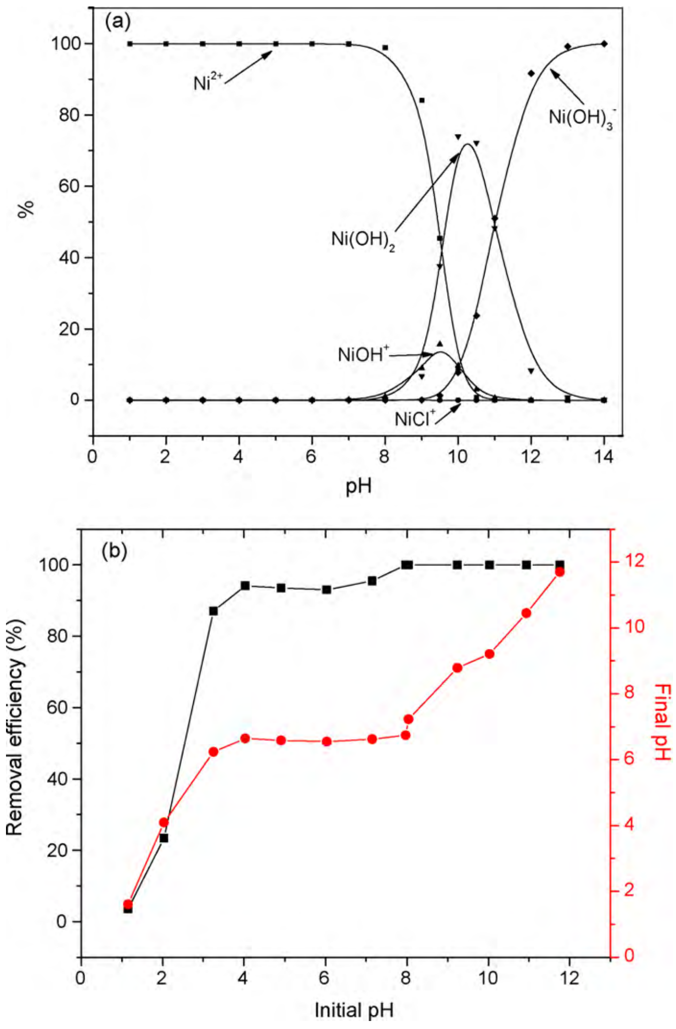

Fig. 5. (a) Ni-species distribution vs. solution pH; (b) The Ni^{2+} removal efficiency from the solution (■) and variations of final pH values (●) with the changes of initial pH.

the effect of contact time and initial cation concentration onto Ni^{2+} removal by RBRM, the initial pH 5 was selected.

3.2.2. Kinetics of Ni^{2+} removal process

Ni^{2+} removal kinetics was investigated using solutions of initial concentrations 10^{-4} mol/L and 8×10^{-3} mol/L. It can be observed from Fig. 6a, that removal efficiency and equilibrium times strongly depended on metal concentration in the solution. For 10^{-4} mol/L, Ni^{2+} concentration in treated solutions was below detection limit after 5 min of contact. On the other hand, the percentages of Ni^{2+} immobilized from more concentrated solution increased rapidly in the first 5 h, and continued to rise gradually up to 24 h of contact where the maximum of 25% was achieved. Minor differences in removal efficiency were noted at the end of the second day of shaking, consequently a contact time of 24 h was selected for further evaluation experiments. Although sorption kinetics is significantly influenced by variation of experimental parameters, immobilization of various toxic substances by red mud was found to be reasonably fast [11,12,33]. Furthermore, previously published results on phosphorous removal indicated that equilibrium times increased with the increase of the initial sorbates concentration [34], whereas concentration independent equilibrium times were reported for fluoride/red mud system [10].

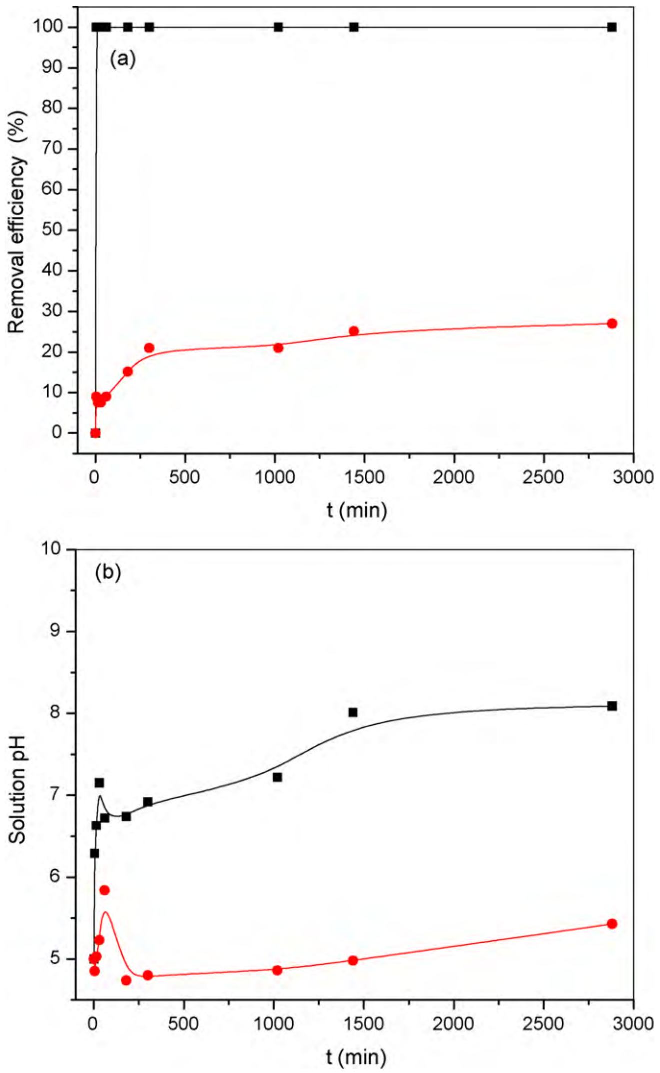

Fig. 6. Effect of contact time on (a) Ni^{2+} sorption efficiency, (b) solution pH value. Initial Ni^{2+} concentrations: 10^{-4} mol/L (■) and 8×10^{-3} mol/L (●).

During the course of the reaction, after solid/liquid separation, solution pH was monitored in order to estimate the role of Ni^{2+} precipitation and/or surface complexation mechanisms (Fig. 6b). In both investigated systems, a rapid pH increase was observed in the first 60 min of shaking. This rise of pH, from initial pH 5, was dependent relative to Ni^{2+} concentration. For low Ni^{2+} concentration, although cation removal process was almost instant, the equilibrium pH value was reached more gradually (in approximately 24 h). These data indicated that in the investigated systems various transport and chemical phenomena i.e. hydrolysis, dissolution, sorption, diffusion etc., took place on the solid/liquid interface, simultaneously. The values of solution pH measured after contact of RBRM with 10^{-4} mol/L solution were <8 at the early process stage where 100% removal was obtained. This implied the significant contribution of sorption mechanisms other than $Ni(OH)_2$ precipitation (such as surface complexation or ion-exchange). Starting from more concentrated solution, initial pH increase was followed by pH decrease to ~5. As the sorbed amount of Ni^{2+} increased with time, resulting pH drop can be a sign of the H^+ substitution from the surface active sites by Ni^{2+} cations, i.e. the sign of inner-sphere complex formation on the surface of investigated sorbent composites.

3.2.3. Effect of initial cation concentration

Based on the previous results, the maximum removal capacity of rinsed sorbent RBRM was evaluated at initial pH 5 and contact

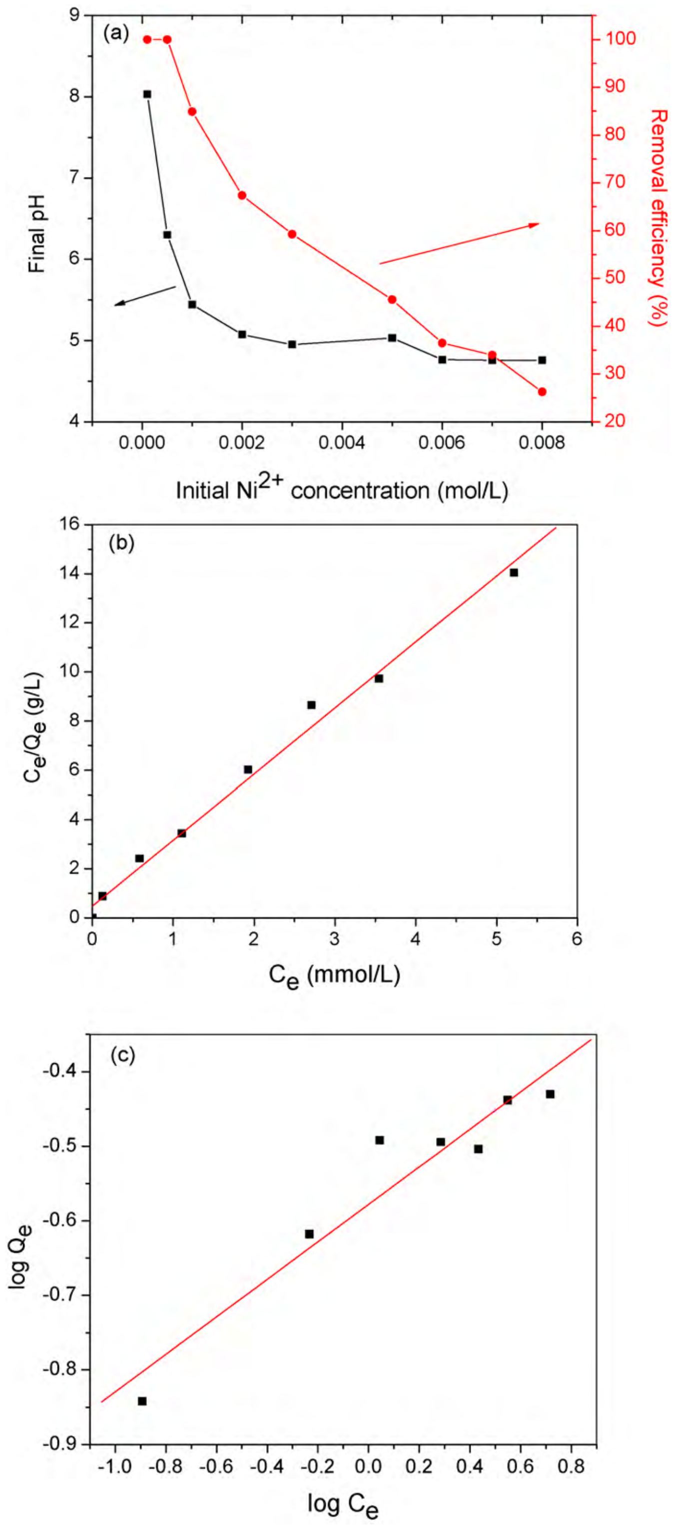

Fig. 7. (a) The relationship between initial cation concentration, Ni^{2+} removal efficiency (●) and equilibrium solution pH (■); equilibrium data fitting using linear Langmuir (b) and Freundlich equation (c).

time of 24 h, using Ni^{2+} solution in wide initial concentration range from 10^{-4} mol/L to 8×10^{-3} mol/L (5.8–465 mg/L).

From the aspect of removal efficiency (Fig. 7a), in the initial cation concentration range 10^{-4} to 5×10^{-4} mol/L, Ni^{2+} concentration in treated solutions was below the detection limit, using RBRM doses of 5 g/L. The overall process efficiency decreased to 26%, with increase of sorbate concentration up to 8×10^{-3} mol/L. However, with the initial concentration increase, absolute amounts of cation removed increased as well reaching the value of 0.371 mmol/g (21.8 mg/g), at the plateau. For the comparison, the value of about 20 mg/g can be estimated from the plot of Greek red mud capacity, at similar solid/solution ratio and initial concentration range [19].

According to Fig. 7a, the precipitation of $Ni(OH)_2$ may represent the predominant cation removal mechanism only for the lowest initial concentrations studied, where equilibrium solution pH values were ~8. Increased removal of Ni^{2+} was followed by significant proton release, confirming the increasing role of specific cation sorption mechanism, at higher metal concentrations.

The obtained equilibrium data were fitted by Langmuir [35] and Freundlich [36] isotherm models. Langmuir equation was used in the following linear form:

$$\frac{C_e}{Q_e} = \frac{1}{X_m K_L} + \frac{C_e}{X_m} \tag{1}$$

where C_e (mmol/L) and Q_e (mmol/g) represent the equilibrium sorbate concentration in solution and in solid phase, respectively; X_m (mmol/g) is the maximum sorption capacity and K_L (L/mmol) represents the Langmuir constant related to sorption affinity.

Freundlich empirical equation has the following linear form:

$$\log\ Q_e = \log K + \frac{1}{n} \times \log C_e \tag{2}$$

where K and $1/n$ represent the Freundlich constants referring to sorption capacity and intensity, respectively. This model does not predict any saturation of the sorbent, and it was proven to be useful for describing sorption processes that exhibits complex interactions and situations in which bound sorbate molecules interact with each other (multi-layer sorption) [37].

The results of linear fitting are presented in Fig. 7b and c. High regression coefficient ($R^2 = 0.990$) suggested good correlation between Langmuir theoretical model and experimental results. The calculated sorption parameters were $X_m = 0.372$ mmol/g and $K_L = 5.63$ L/mmol. Given that X_m characterize the monolayer coverage of sorbent with sorbate, an excellent agreement between calculated and experimentally obtained maximum sorption capacities indicated monolayer cation sorption on the surface of RBRM sorbent.

Using Freundlich model, from the slope and the intercept of the line presented in Fig. 7c, numerical values of $1/n = 0.252$ and $K_F = 0.264$ were obtained. Generally, the numerical value of $1/n < 1$ indicates that the sorption process is favorable and suggests stronger bonds between sorbate and multiple binding sites on the sorbent surface. However, regression coefficient of $R^2 = 0.919$ obtained for Freundlich model indicate that the Langmuir isotherm fits the sorption data better, if overall concentration range is considered.

In comparison with Freundlich, Langmuir isotherm model showed better fit with the experimental data in the case of congo red sorption onto red mad [14], as well as phosphate [17], arsenic [38], and various heavy metal divalent ions such as copper, lead, cadmium, nickel and zinc [34,39]. In all quoted literature, Langmuir modeling has been quite successful in predicting the experimental saturation capacities, indicating monolayer coverage due to strong interactions between red mud surface and investigated sorbates.

The stability of obtained solid residues was studied in acidic leaching solution (TCLP2). The quantity of Ni^{2+} leached from variously loaded products increased with the increase of the previously sorbed amount (Fig. 8a). These quantities were in the range 0.005–0.037 mmol/g. Desorption efficiency, on the other hand, decreased with increased cation loading. At lower utilization of sorption capacities, Ni-RBRM products were generally more labile, whereas at higher loadings desorption percentages were 8–10%.

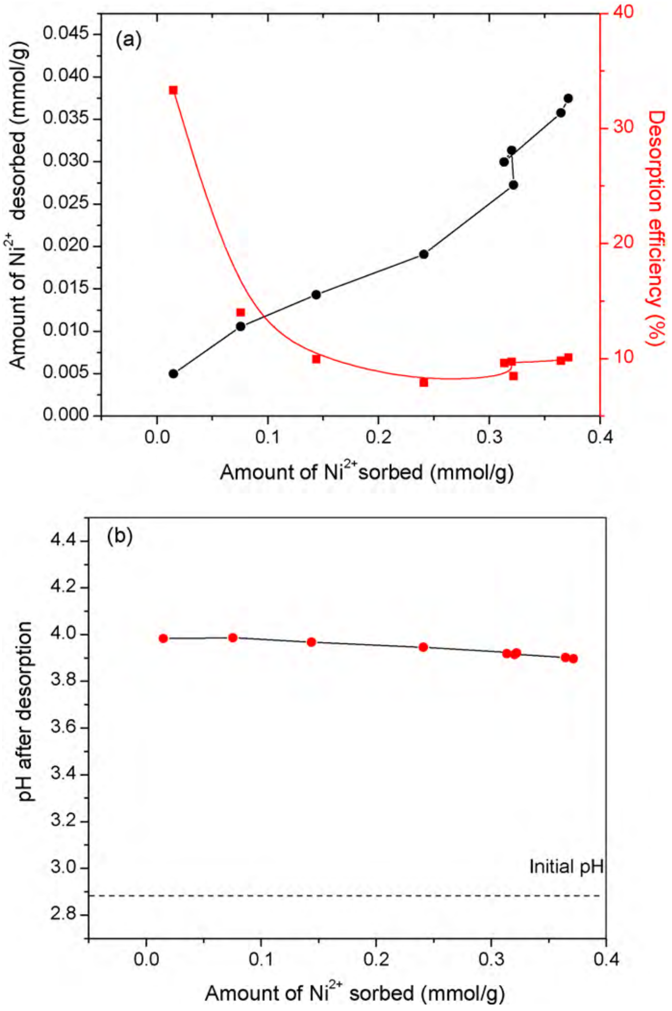

Fig. 8. The relationship between sorbed amount of Ni^{2+} and: (a) desorption efficiency from RBRM surface in TCLP2 leaching solution; (b) solution pH values after leaching experiments.

The most important reason for rather low desortion efficiency was probably the increase of TCLP2 solution pH (from 2.88 to 4.0 ± 0.1) after interaction with spent red mud samples (Fig. 8b).

3.2.4. *Effect of temperature treatment on red mud sorption/desorption properties*

The Ni^{2+} removal efficiency of rinsed and thermally treated RBRM samples, at various initial pH values, was compared in Fig. 9a.

Heavy metal removal from aqueous media was generally the lowest at initial pH 2, rapidly increased between 2 and 3, and became rather pH-independent with further pH increase in the investigated range. The results are consistent with the pH profile of Ni^{2+} sorption by sample RBRM, obtained for lower initial cation concentration (Fig. 3b). In the most acidic media, the percentages of Ni^{2+} sorbed by variously treated samples varied drastically from practically 0–52%, whereas in the initial pH range 4–5 sorption reached maximum values of 40–83%, depending on the sorbent type.

The evaluation of differences in Ni^{2+} removal, induced by annealing, revealed that cation sorption exhibited an increase with the increase of temperature up to 600 °C, following by sorption decrease with further temperature rising. Although the enhanced sorption of sample RBRM600 was apparent in the entire investigated pH range, the major difference compared to other sorbents was observed at initial pH 2.

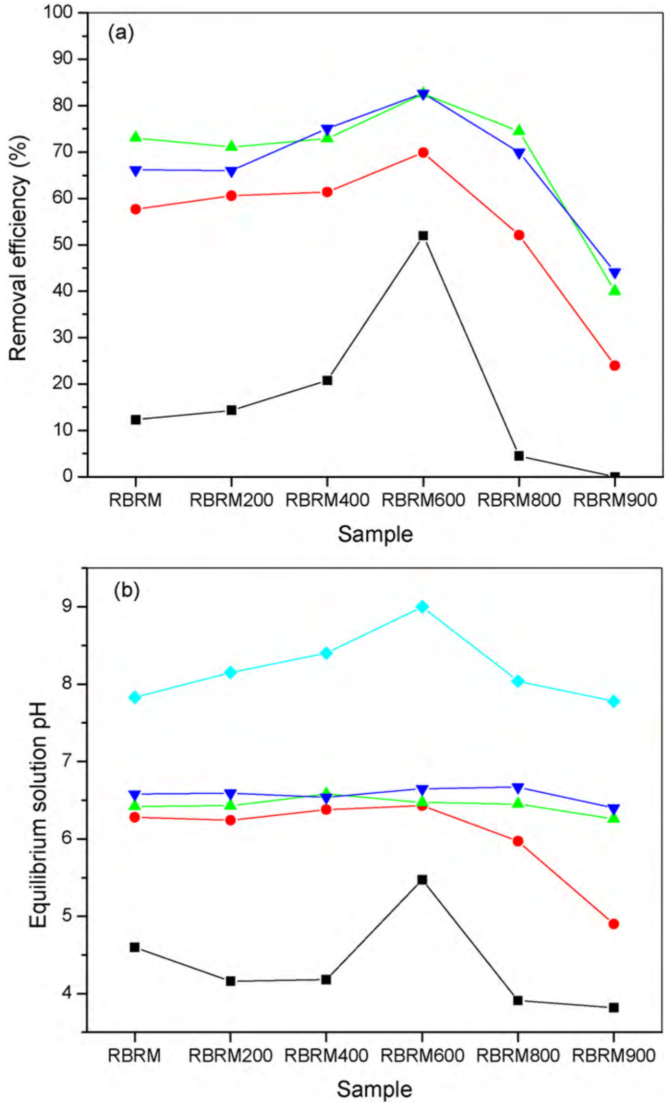

Fig. 9. The relationships between temperature treatments of RBRM, and: (a) Ni^{2+} removal efficiency from the solution of different initial pH (■ – pH 2, ● – pH 3, ▲ – pH 4, and ▼ – pH 5); (b) pH after interaction of RBRM samples and Ni-solution of different initial pH, or distilled water (♦).

Ni^{2+} uptake was greatly influenced by the structural state (amorphous or crystalline) and specific surface area of other sorbent materials [40]. In the case of red mud, heating have brought about both physical (change of grain size, change of pore shape and size), and chemical changes (decomposition, new phase formation, phase transformation, etc.) that resulted in alteration of its sorption properties. Enhanced sorption on powder calcinated at 600 °C, can be associated with water exclusion from gibbsite and bayerite phases, leading to improved porosity and surface area of such sorbent. In the same time, due to phase transition and increased solubility, the pH values after Ni^{2+} sorption (Fig. 9b), were highest for RBRM600, also influencing the improved metal removal. Quite the opposite, the progressive formation of crystalline mineral phases at $T > 600$ °C and sintering of calcinated red mud particles have contributed to lower Ni^{2+} sorption, by lowering the overall specific surface area and pH value.

Our results can be connected with the results of Altundogan and Tümen [41], who found that heating of bauxite at 600 °C, represents the optimum treatment for phosphate sorption improvement, due to an eight-fold increase in surface area via dehydration of boehmite and diaspore. In the work of Gupta and Sharma [42]

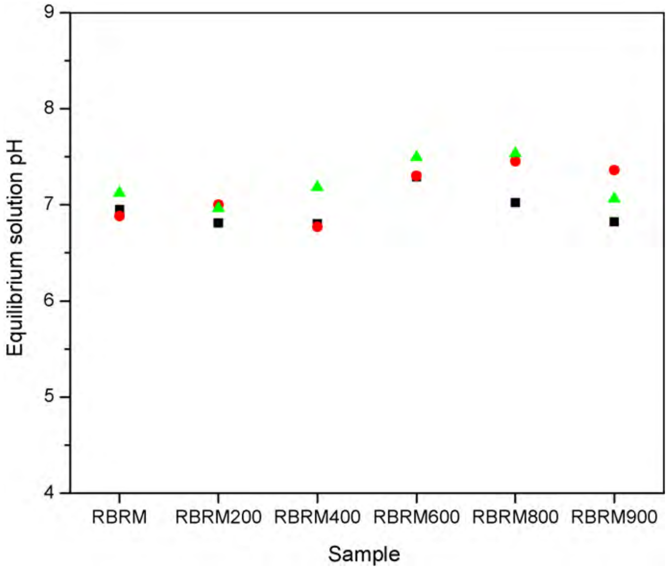

Fig. 10. Equilibrium pH values after desorption in distilled water (Ni^{2+} sorption experiments performed at initial pH 2 – ■, pH 3 – ● and pH 4 – ▲).

hydrogen-peroxide pretreated red mud sample from India, heated at 500 °C was used for Cd^{2+} and Zn^{2+} sorption experiments, as its best sorption capacity and optimum surface area were declared. Heating red mud from China at 700 °C produced the optimal sample for phosphate immobilization [16], while 400 °C was reported to be the optimal in the case of arsenate removal by red mud from Turkey [18].

Taking into account the significant differences in the composition of starting red mud samples, as well as in investigated sorbates, the variation between optimum heating temperatures between studies are realistic.

By observing pH values after contact of red mud sorbents and aqueous solutions with and without Ni^{2+} ions (Fig. 9b), some conclusions about sorption mechanism can be derived. The pH values of distilled water followed the same temperature trend as discussed previously in the Section 3.1.3, with the maximum at 600 °C, but they were lower than ones obtained by EPA method, due to much lower solid/solution ratio and different contact times (solid/solution ratio 1:200 and equilibration time of 24 h). Although all final pH values increased in respect to initial ones, pH values measured in distilled water were higher in comparison with values obtained after Ni^{2+} sorption (pH drifted by 1–4 pH units, depending on initial pH). The results indicated that inner-sphere complexes formation between surface groups and Ni^{2+} ions, followed by H^+ release, contributed in the overall removal mechanism of all investigated sorbents.

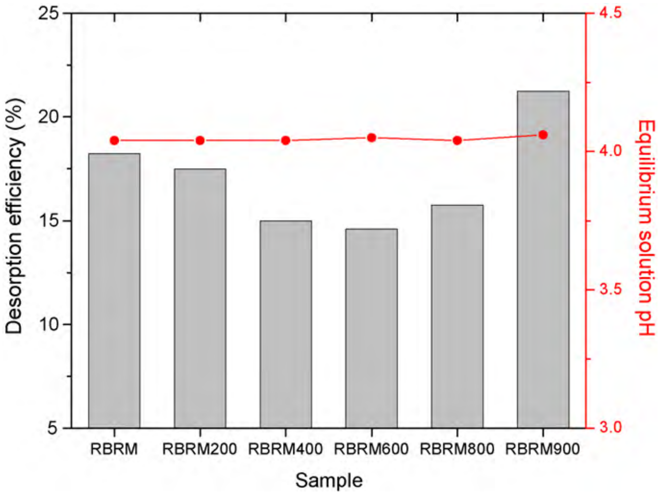

Fig. 11. Efficiency of Ni^{2+} desortpion from variously treated RBRM sorbents in TCLP2 solution, and equilibrium pH values.

In the work of Zouboulis and Kydros [19] nickel precipitation as insoluble hydroxide was found to be the main Ni^{2+} removal mechanism, because the addition of 5 g/L of rinsed Greek sample to a solution containing 50 mg/L of Ni^{2+} led to the shift of pH to >8. Considering that all final pH values obtained in this study were <7, using 5 g/L of rinsed as well as thermally treated samples, it can be concluded that precipitation of nickel-hydroxide was not a key mechanism of Ni^{2+} removal. The differences in Greek and Bosnian red mud alkalinity may be a consequence of their different compositions, as well as of rinsing procedures.

The stability of sorption products obtained at initial pH 2, 3 and 4, tested using distilled water as leaching media, was found to be extremely high. Concentrations of Ni^{2+} cations in distilled water, after 24 h of contact with loaded sorbents, were below detection limit, regardless the sorption pH and sorbent pretreatment. Such low leachability was most likely a consequence of rather high pH values measured after desorption experiments (Fig. 10).

In addition, stability of the products obtained at initial pH 5 was tested using acidic TCLP2 solution (Fig. 11). The released Ni^{2+} quantities varied in the range between 14.6 and 21.3%, while the final pH values were rather constant (∼4). However, it is important to notice that RBRM600 sample that exhibited highest sorption efficiency, showed highest stability, as well. Although the sorbed amounts of Ni^{2+} were comparable at pH 4 and 5, desorption efficiency of TCLP2 solution was much higher in respect to distilled water, signifying that Ni^{2+} leachabillity was controlled by leaching solution pH.

4. Conclusion

The Bosnian red mud was thoroughly rinsed in order to remove the Na_2O residues from technological process and evaluated as a potential removal agent for heavy metal cations. Hematite, bayerite, gibbsite and quartz were found to be major constituents of this composite sorbent. pH values of examined industrial waste increased significantly with solid/solution increase. The largest increase of Ni^{2+} sorbed amounts were produced by initial pH increase from 1 to 3. Sorption kinetics was significantly influenced by initial cation concentration, and equilibrium times varied from 5 min to 24 h with the initial concentration increase from 10^{-4} to 8×10^{-3} mol/L. The addition of 5 g/L of RBRM caused 100% removal of Ni^{2+} from the solutions of 10^{-4} to 5×10^{-4} mol/L, whereas with the further increase of Ni^{2+} concentration in the investigated range, the removal efficiency decreased to 26%. Using Langmuir theoretical model the maximum sorption capacity of RBRM sample was found to be 0.372 mmol/g. Desorbed amount of Ni^{2+} in acidic leaching media (TCLP2) increased with the increase of previously sorbed amounts, but overall desorption efficiency decreased from ∼33 to ∼10%.

The influence of annealing temperature on RBRM physico-chemical and sorption characteristics was studied in the range 200–900 °C. The amounts of cation sorbed, from the solution of different initial pH, increased with the temperature rise to 600 °C, whereas decreased with further temperature increase. The superior sorption properties of RBRM600 sample were associated with temperature induced physical and chemical changes of the sorbent. The stability of sorption products in distilled water was extremely high regardless the sorption pH and sorbent pretreatment, whereas the quantities of Ni^{2+} desorbed from variously treated sorbents, varied between 14.6 and 21.3% when acidic TCLP2 solution was applied.

The sample RBRM600, beside highest sorption efficiency, has also shown the highest stability.

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