1

Sepiolite functionalized with N-[3-(trimethoxysilyl)propyl]ethylenediamine triacetic acid trisodium salt. Part II: Sorption of Ni^{2+} ions from water

SLAVICA S. LAZAREVIĆ[*], IVONA M. JANKOVIĆ-ČASTVAN, BOJAN M. JOKIĆ, DJORDJE T. JANAĆKOVIĆ and RADA D. PETROVIĆ

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia

Abstract: The sorption of Ni^{2+} on the sepiolite functionalized by covalent grafting of *N*-[3-(trimethoxysilyl)propyl]ethylenediamine triacetic acid trisodium salt, MSEAS, was studied in batch experiments as a function of the initial metal concentration, the equilibration time, pH value, and temperature. The modification of sepiolite resulted in an enhanced Ni^{2+} retention with a capacity of 0.261 mmol/g at 298 K. The retention of Ni^{2+} ions occurred dominantly by specific sorption and exchange of Mg^{2+} ions from the sepiolite structure. The sorption process followed pseudo-second-order kinetics. The sorption equilibrium results were best described by the non-linear form of the Langmuir Sorption Equation. The values of the thermodynamic parameters (enthalpy, free energy and entropy) were calculated from temperature dependent sorption isotherms and these values showed that the sorption of Ni^{2+} onto modified sepiolite was endothermic.

Keywords: functionalized sepiolite, sorption, Ni^{2+} ions, kinetics, thermodynamics

RUNNING TITLE: Sorption of Ni^{2+} ions from water on functionalized sepiolite

30   INTRODUCTION

32   Water pollution by heavy metals is a serious environmental problem with harmful

33 impacts on the ecological balance and living organisms, including humans. The major

34 contributors to the high concentrations of Ni^{2+} ions in aqueous media are the industries related

35 to stainless steel, electroplating, jewelry, coinage, catalysts, batteries, and accumulators. Even

36 at low concentrations, nickel has a damaging effect on human health because it accumulates

37 in the lungs, kidneys, liver, intestines and heart. Higher concentrations of nickel cause various

38 diseases and disorders, including cancer of the lungs, nose and bone, chronic headaches,

39 sleeplessness and diarrhea.[1] Therefore, the removal of Ni^{2+} ions from water and wastewaters,

40 in order to reduce its concentration below the acceptable range, is highly warranted. The

41 remediation of heavy metals using a sorption technique is now progressing through numerous

42 researches aimed at the development of highly efficient, cost effective, and environmentally

43 friendly materials as sorbents.

44   In order to improve the sorption performance of sepiolite for the sorption heavy metal

45 ions, sepiolite was previously functionalized using different silane coupling agents.

46 Modification of sepiolite was performed using triethoxy-3-(2-imidazolin-1-yl)propylsilane in

47 toluene solution and the capacity of the material for Co^{2+}, Cu^{2+}, Cd^{2+}, Mn^{2+}, Fe^{3+} and Zn^{2+}

48 sorption was investigated.[2] Liang showed that the sorption capacities of

49 mercaptopropyltrimethoxysilane functionalized sepiolite for Pb^{2+} and Cd^{2+} were higher than

50 those of natural sepiolite.[3] The surface modification of sepiolite with [3-(2-

51 aminoethylamino)propyl]trimethoxy-silane and ability to sorb captions was investigated.[4] The

52 sorption capacity of the modified sepiolite was higher for zinc, copper and cobalt than those

53 for the other ions as a result of the specific interaction between metal ions and the amine

54 groups.

55   The removal of Cr(VI) from aqueous solution using adsorbents obtained by covalent

56 grafting of (3-mercaptopropyl) trimethoxy-silane and [3-(2-

57 aminoethylamino)propyl]trimethoxy-silane onto natural, acid activated and thermo-acid

58 activated sepiolites, was studied.[5-7] Adsorption capacities of amine-functionalized sepiolites

59 for chromium(VI) sorption were much higher than those of mercapto-silane functionalized

60 sepiolites under the same conditions.

61   In first part of this paper the modification of sepiolite with *N*-[3-
62 (trimethoxysilyl)propyl]ethylenediamine triacetic acid trisodium salt in order to obtain the
63 efficient sorbent for water treatment and characterization of prepared sorbent were reported.
64 In this second part of this paper, the adsorption properties of the functionalized sepiolite
65 sample, the sorption of Ni^{2+} on the MSEAS will be discussed. The batch sorption technique
66 was used to obtain sorption isotherms and to explore the effects of temperature, the initial pH
67 value and equilibrium time on the sorption capacity. The capabilities of the Langmuir,
68 Freundlich and Redlich−Peterson Isotherm Models to fit the equilibrium sorption data were
69 investigated, while the pseudo-first, pseudo-second order and intraparticle diffusion model
70 were used to fit the kinetic sorption data.

71

72   EXPERIMENTAL

73

74   *Materials*

75

76   The functionalization of sepiolite was performed from aqueous solution using of *N*-[3-
77 (trimethoxysilyl)propyl]ethylenediamine   triacetic   acid   trisodium   salt
78 $((CH_3O)_3Si(CH_2)_3N(CH_2COONa)N(CH_2)_2N(CH_2COONa)_2)$,   MSEA,   Gelest).[8]
79 The morphological characteristics, X-ray diffraction, FTIR and DTA analyses, specific
80 surface areas and pore size distribution using B.E.T. method and point of zero charge (pH_{pzc})
81 were reported previously.[8]

82

83 *Determination of the point of zero charge of the MSEAS in solutions of Ni^{2+} ions*

84

85   The shift in the point of zero charge was investigated by the batch equilibration
86 method, using 0.01 and 0.001 mol dm^{-3} solutions of $Ni(NO_3)_2$ at different initial pH values,
87 ranging from approx. 3.5 to approx. 8. using the batch equilibration method described
88 previously.[9] Equilibration was attained by shaking for 24 h in a water bath thermostated at
89 298 K. The concentrations of Ni^{2+} and Mg^{2+} ions in the solutions after equilibration with
90 0.001 mol dm^{-3} solutions of $Ni(NO_3)_2$ were measured. The quantity of sorbed Ni^{2+} ions was
91 calculated in order to determine the effect of initial pH value on the sorption process.

92

93   *Sorption procedure*

94

95   All sorption experiments were conducted using the batch equilibration technique in

96   Ni^{2+} solutions prepared in demineralized water. A series of 25 cm^3 of each solution containing

97   0.05 g of sorbent in poly(vinyl chloride) (PVC) vessels were shaked in a water bath

98   thermostated at the desired temperature. The dispersions were filtered and the initial Ni^{2+}

99   concentration and metal ion remaining unadsorbed in the supernatant, as well as the

100   concentration of Mg^{2+} ions were determined using AAS. All the sorption studies were

101   repeated twice; the reported value is the average of two measurements.

102   The following conditions were maintained for different sets of experiments:

103   Effects of pH: Initial concentration of Ni^{2+} 0.01 and 0.001 mol dm^{-3}, pH values from

104   approx. 3.5 to approx. 8, equilibrium period of 24 h and temperature of 298 K.

105   Isotherms: Initial concentration of Ni^{2+} between 25 and 200 mg dm^{-3}, pH values of the

106   solutions 5.6 ± 0.1, equilibrium period of 24 h and temperature of 298 K.

107   Kinetics: Initial ion concentration of 100 mg dm^{-3}, pH value of 5.6 ± 0.1, temperature

108   of 298 K, contact times ranging from 1 h to 24 h. The final concentrations of Ni^{2+} and Mg^{2+}

109   ions were measured in the supernatant as dependent variables of time.

110   Thermodynamics: Initial concentration of Ni^{2+} between 25 and 200 mg dm^{-3}, pH

111   values of the solutions 5.6 ± 0.1, equilibrium period of 24 h, temperatures of 318, 328, and

112   338 K.

113

114

115

116   RESULTS AND DISCUSSION

117

118   *Determination of the point of zero charge of the MSEAS in solutions of Ni^{2+} ions*

119

120   As a result of specific sorption on the sorbent surface which lowers the number of

121   sites available for the sorption of H^+ ions, the pH_{pzc} in Ni^{2+} solutions were shifted to lower

122   values compared with those obtained in KNO_3 solutions.[10] From the dependences pH_f *vs*. pH_i,

123   (Fig. 1b) it can be seen that the pH_{pzc} of the modified sepiolite were 5.6 ± 0.1 for 0.01 mol dm^-

124   ^{3} and 5.8 ± 0.1 for 0.001 mol dm^{-3} $Ni(NO_3)_2$. The pH_{pzc} was also lower compared with values

125   obtained for natural sepiolite in Ni^{2+} solutions (6.5± 0.1 for 0.01 mol dm^{-3} and 6.8 ± 0.1 for

126   0.01 mol dm^{-3} $Ni(NO_3)_2$)[11]   due to the presence of additional groups originating from

modifier, located on the external sites of the sepiolite, which interact with the Ni^{2+} ions by forming stable surface complexes. In this way, the quantity of specifically sorbed Ni^{2+} ions was increased.
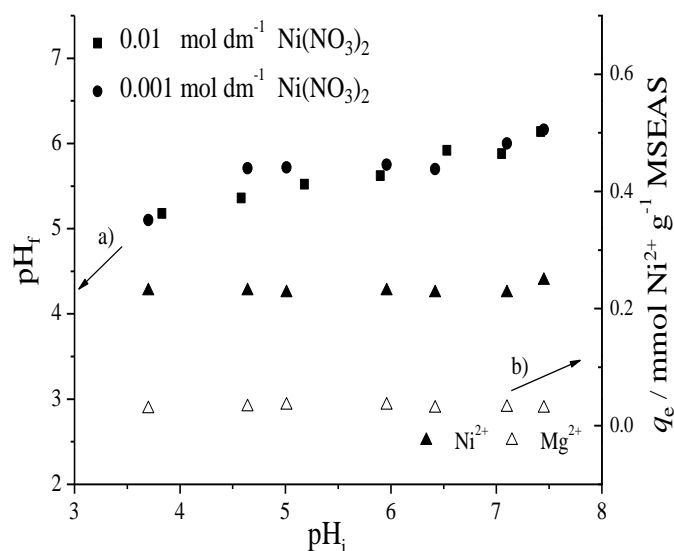
Fig. 1. a) Dependences of pH_f on pH_i during the equilibration of MSEAS in 0.01 mol dm^{-3} and 0.001 mol dm^{-3} Ni(NO$_3$)$_2$ solutions; b) effect of initial pH on the amount of Ni^{2+} sorbed on MSEAS and quantity of ion exchanged Mg^{2+} ions

The quantities of sorbed Ni^{2+} ions from 0.001 mol dm^{-3} Ni(NO$_3$)$_2$ solution at different pH values and the amounts of Mg^{2+} ions present in the solutions as result of ion exchange are also shown in Fig. 1. The sorption of Ni^{2+} ions was examined in the pH range from approx. 3.5 to approx. 8, in order to avoid ion hydrolysis at higher pH values and the dissolution of sepiolite at lower pH values.

Effect of initial pH value

The solution pH can have a significant effect on the uptake of metal, since it determines the surface charge of the adsorbent and the degree of ionization and speciation of the sorbate. The effect of initial pH on the adsorption of Ni^{2+} by modified sepiolite adsorbent was observed at different pH (3.5–8) simultaneously with determination of point of zero

5

150   charge of the MSEAS in solutions of Ni^{2+} ions. To prevent the precipitation of Ni^{2+} from

151   solution at high pH values, the solution pH was maintained at pH less than the pH of

152   precipitation formation.

153   The quantity of exchangeable Mg^{2+} ions was determined as the difference between the

154   total amount and the amount of Mg^{2+} ions released into the solution by the dissolution (0.05

155   mmol g^{-1} MSEAS). The amount of nickel ion sorbed per unit mass of MSEAS was almost

156   constant, amounting to $\approx$ 0.032 mmol $Ni^{2+}g^{-1}$ MSEAS. It is obvious that the change in the

157   initial pH value of the metal ion solutions in investigated range did not affect a change in the

158   sorption capacity.

159   The quantity of Mg^{2+} ions released into the solution during the ion exchange process

160   with Ni^{2+} ions was also almost constant at different pH values, meaning that the process of ion

161   exchange was of the same intensity. During the ion exchange process, Mg^{2+} ions are displaced

162   from the MSEAS lattice and released into solution. This process does not influence a change

163   in the pH_{pzc} because H^{+} ions are not involved in the ion exchange process.

164   The final pH values determined during the pH_{pzc} determination was similar for all the

165   investigated initial pH values, *i.e.*, the process of the specific sorption of Ni^{2+} onto MSEAS in

166   this pH range was not significantly affected by the pH value. As a result of the simultaneously

167   occurring specific sorption and ion exchange, as the main mechanisms of sorption, the total

168   amount of metal ion sorbed per unit mass of MSEAS remained almost constant in the

169   investigated pH range.

170

171   *Sorption isotherm studies and modeling*

172

173

174   The amount of nickel ions sorbed onto MSEAS at 25 °C at a pH_i of 5.6±0.1, and the

175   dependence of the quantity of Mg^{2+} ions ion exchanged as functions of the equilibrium
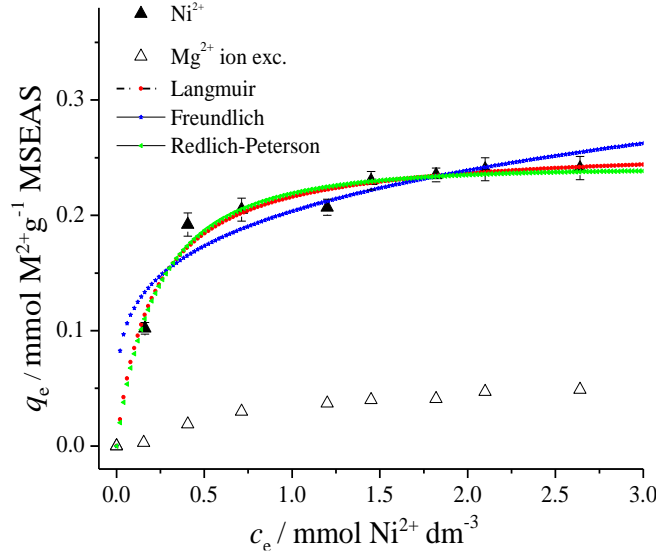
176   concentration are shown in Fig. 2.

177

178

Fig. 2. Sorption isotherm for Ni^{2+} ions onto MSEAS and the dependence of q_e (mmol Mg^{2+}g^{-1}) on c_e (mmol Ni^{2+} dm^{-3}) and the fitting of the experimental data to different isotherm models

According to Fig. 2, the modified sample had a higher sorption capacity (≈0.23 mmol g^{-1} MSEAS) than the natural sepiolite,[11] *i.e.*, an improvement of the sorption efficiency was accomplished by modification with *N*-[3-(trimethoxysilyl)propyl]ethylenediamine triacetic acid trisodium salt from an aqueous solution. Nickel sorption on the natural sepiolite sample was attributed to cation exchange and the formation of surface complexes through Si–OH groups. When a dispersion of natural sepiolite was treated with a silane solution, the reactive silanol groups exhibit a high affinity for –Si–OH groups on the sepiolite surface thereby forming –Si–O–Si–bonds and retaining three free –COO$^-$ groups. Vasiliev et al. investigated metal complexes based on grafted *N*-[3-(trimethoxysilyl)propyl]ethylenediamine triacetic acid onto silica by nuclear magnetic resonance (NMR) and electron spin resonance (ESR) and showed that metals form several complexes with carboxyl groups of the ligand.[12] These complexes have different structures with a different degree of substitution of the water molecules on the ligand in the plane of the coordination sphere.

The amount of Mg^{2+} ion exchanged (Fig. 2) increased with increasing amount of Ni^{2+} sorbed on the mineral, which corroborates ion exchange, *i.e.,* replacement of Mg^{2+} on the edges of the octahedral layer of sepiolite with Ni^{2+} ions, as one of the main mechanisms of sorption. It can be seen that the MSEAS had a slightly lower ion exchange capacity for Ni^{2+}

ions than the natural sepiolite sample.[11] Grafting of organosilanes on sepiolites is limited to the external surface of sepiolite.[13] The Mg–OH groups at the edges of the sepiolite channels responsible for ion exchange with metal cations from solution remain unaffected by process of silane functionalization. In this way, the ion exchange capacity remained and was similar to that of natural sepiolite. The increase in Ni^{2+} sorption on the functionalized sepiolite could be explained by an increase in specific sorption, *i.e.*, the interaction of both surface silanol groups and additional groups originating from modifier, that exhibit a high binding affinity toward Ni^{2+} ions.

The equilibrium sorption data were analyzed by three isotherm models: Langmuir, Freundlich and Redlich−Peterson using nonlinear fitting (presented in Fig.2). The Langmuir Model[14] assumes monolayer sorption at specific homogeneous sites, with no interactions between the sorbed species. The Freundlich Equation[15] describes sorption (possibly multilayer in nature) on a heterogeneous surface consisting of non-identical and energetically non-uniform sites. The Redlich−Peterson Model[16] is represented by a three-parameter, empirical equation featuring both Langmuir and Freundlich isotherms. This Model approaches the Freundlich Isotherm Model at high concentrations (when β is equal to 0) and predicts behaviors corresponding to the Langmuir form at the low concentration limits (when the β values are close to 1). The sorption isotherms constants for Ni^{2+} sorption onto MSEAS, determined by non-linear regression analysis using the Easy Plot, are summarized in Table I.

TABLE I. Sorption parameters and coefficients of correlation according to the Langmuir, Freundlich and Redlich−Peterson Models for the sorption of Ni^{2+} ions onto MSEAS at 298 K

Langmuir			Freundlich			Redlich−Peterson			
$q_e = \dfrac{q_m K_L c_e}{1 + K_L c_e}$			$q_e = K_f \cdot c_e^{1/n}$			$q_e = \dfrac{K_R c_e}{1 + a_R \left(c_e\right)^{\beta}}$			
K_L / dm^3 mmol^{-1}	q_m / mmol g^{-1}	R^2	K_f / mmol$^{1-1/n}$·dm$^{3/n}$g^{-1}	n	R^2	K_R / dm^3 g^{-1}	a_R / (dm^3 mmol^{-1})$^{\beta}$	β	R^2
4.77	0.261	0.984	0.204	4.33	0.954	1.06	3.86	1.04	0.985

227   According to presented results, both the Langmuir and Redlich−Peterson isotherms
228   showed better correlation with the experimental data than the Freundlich isotherm, as
229   expressed by the higher correlations coefficients. Figure 2 shows that the Langmuir and the
230   Redlich−Peterson isotherms overlapped one another. The value of the Redlich−Peterson
231   parameter β was ≈ 1.0, indicating that the Redlich−Peterson isotherm adopts the Langmuir
232   isotherm, and that experimental data for sorption of Ni^{2+} ions onto the modified sepiolite
233   sample could be best described by the Langmuir sorption model. The results of the isotherm
234   modeling indicate monolayer coverage of the MSEAS by Ni^{2+} ions and a homogenous
235   distribution of the active sites on the MSEAS surface.

236

237   *Effect of contact time*

238

239   The kinetics of Ni sorption on the MSEAS at 100 mg dm^{-3} initial Ni^{2+} concentration at
240   a temperature of 298 K is illustrated in Fig. 3. The sorption of Ni^{2+} was initially fast with >80
241   % of Ni^{2+} sorbed in the first 60 min. This initial rapid sorption was followed by a much
242   slower period. After 1000 min, an apparent equilibrium was achieved. In addition to Ni^{2+}
243   sorption, the quantity of Mg^{2+} ions released into the solution as a result of the ion exchange
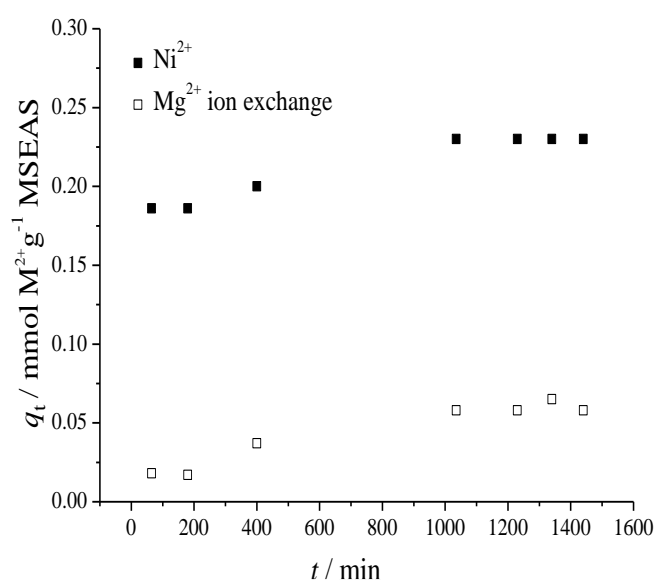244   process was also examined (Fig. 3) and a similar dependence was registered.

245
246

249   Fig. 3. Effect of contact time on the amounts of Ni^{2+} sorbed onto MSEAS and Mg^{2+} ion
250   exchanged ($c_i = 100$ mg dm^{-3}, at a temperature of 298 K and pH of 5.6 ± 0.1)

In addition to equilibrium isotherms, information on sorbate transport is essential for analyzing the dynamic behavior of sorption. Three stages are considered to be involved during the sorption of metal ions onto sorbents:

1. Transfer of the sorbate molecules from the bulk solution to the solid surface, i.e. film diffusion;
2. Intraparticle diffusion within the interior of the adsorbent;
3. Adsorption of the adsorbate on active sites (physisorption or chemisorption).

The third step is considered to be so rapid that never constitute the rate-limiting step. Steps (1) and (2) can be considered to be acting individually or in combination.[17] Rate of sorption processes depend on parameters like structural properties of the sorbent (e.g., porosity, specific area and particle size), the properties of the ions (e.g., ionic radius and number of coordination), the concentration of the metallic ions and the interactions between metallic ions and active sites of the sorbent.

Three kinetic models were employed to describe the mechanism of sorption on modified sepiolite: the pseudo-first-order equation proposed by Lagergren,[18] the pseudo-second-order kinetic model proposed by Ho and G. McKay,[19] and the intraparticle diffusion model proposed by Weber and Morris[20]. The rate constant k_1 / min^{-1} was calculated from the slope of the $\ln(q_e - q_t)$ $vs.$ t plot, the second-order rate constant k_2 / g mmol^{-1}·min^{-1} and the equilibrium sorption capacity q_e, from linear plot of t/q_t $vs.$ t, by considering the values of the slope and the intercept, respectively.

TABLE II. Kinetic parameters for Ni^{2+} sorption onto MSEAS

Pseudo-first-order			Pseudo-second-order				Intra-particle diffusion			
$\log (q_e - q_t) = \log q_e - \dfrac{k_1}{2.303} \cdot t$			$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} + \dfrac{1}{q_e} t$				$q_t = k_i \cdot t^{1/2} + C$			
k_1 / min^{-1}	q_e / mmol g^{-1}	R^2	k_2 / g mmol^{-1} min^{-1}	q_e / mmol g^{-1}	R^2	h / mmol g^{-1} min^{-1}	k_i / mmol g^{-1} min$^{-1/2}$	C mmol g^{-1}	R^2
0.0023	0.070	0.954	0.093	0.238	0.998	0.0053	0.174	0.0012	0.799

10

276   For pure intraparticle diffusion to take place, the plot of q_t *vs*. $t^{1/2}$ should be linear
277   passing through the origin with no intercept. But if the plot shows multilinearity, then the
278   sorption process may be controlled by the combination of film and intraparticle diffusion, *i.e.*
279   more than one step is involved in the sorption process.

280   The values of k_i (intra-particle diffusion rate constant, mmol/g·min) and a constant C
281   reported in Table 3 were calculated by the extrapolation of the second portion of the curve q_t
282   *vs*. $t^{1/2}$ back towards the *y*-axis. Intraparticle diffusion was not the only rate-limiting step
283   because the plot does not pass through the origin.

284   The results presented in Table II show that the pseudo-second-order model fitted the
285   sorption data much better then the pseudo-first-order and intraparticle diffusion models (Table
286   II). The pseudo-second-order rate law expression is based on the assumption that the rate
287   limiting step is chemical sorption, which is in agreement with finding that the main
288   mechanisms of sorption of Ni^{2+} ions onto MSEAS are chemical processes: specific sorption
289   and ion exchange of Mg^{2+} from the sepiolite structure with Ni^{2+} ions from the solutions.

290   Many investigations demonstrated that the kinetic behavior of heavy metal sorption
291   studies has been satisfactorily explained with the pseudo-second-order sorption equation.[21-23]
292   This trend suggests that the rate-limiting step in heavy metal sorption is chemisorption, which
293   involves valence forces through sharing or exchange of electrons between sorbent and
294   sorbate, complexation, coordination and/or chelation, rather than physisorption.

295

296   *Effect of temperature*

297

298   The effect of temperature on sorption of nickel ions onto modified sepiolite is shown
299   in Fig 4. In the experimental temperature range, the quantity of nickel ions sorbed by MSEAS
300   increased with increasing temperature, demonstrating that the process of nickel sorption was
301   endothermic. Non-linear fitting of experimental data for Ni^{2+} sorption onto MSEAS using the
302   Langmuir Isotherm at various temperatures are also presented in Fig. 4. The values of the
303   sorption parameters and coefficients of correlation (given in Table III) confirmed that the
304   Langmuir Isotherm Equation not only represents the sorption process at 298 K very well, but
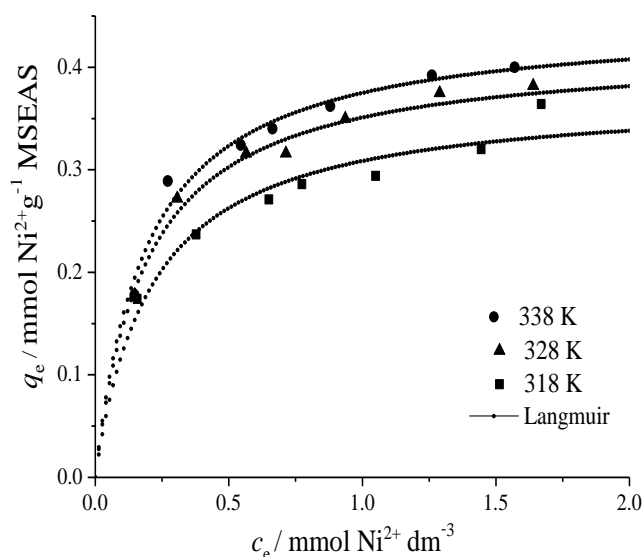305   also in the temperature range 318–338 K.

306

307

Fig. 4. Sorption isotherms for the sorption of Ni^{2+} ions onto MSEAS at different temperatures

TABLE III. Sorption parameters and coefficients of correlation according to the Langmuir Model for the sorption of Ni^{2+} ions onto MSEAS at different temperatures

Sample	$T/$ K	Langmuir		
		R^2	$q_m/$ mmol g^{-1}	$K_L \cdot 10^{-3} /$ dm^3 mol^{-1}
	318	0.980	0.374	4.71
MSEAS	328	0.995	0.425	5.10
	338	0.970	0.460	5.24

In order to understand the sorption process from the aspect of energy change, the standard enthalpy change (ΔH^{Θ}, kJ mol^{-1}) and standard entropy change (ΔS^{Θ}, J mol^{-1} K^{-1}) were determined graphically from the slope and intercept, respectively, of the straight line obtained by plotting ln K_L $vs.$ $1/T$. The values of the obtained thermodynamic parameters ΔH^{Θ}, ΔS^{Θ} and Gibbs free energy change (ΔG^{Θ}, kJ mol^{-1}) are listed in Table IV.

The Gibbs free energy change (ΔG^{Θ}) indicates the degree of spontaneity of a sorption process and the higher the negative value is, the more energetically favorable is the sorption. For all the investigated temperatures, the ΔG^{Θ} values were negative. The value of ΔG^{Θ} became more negative with increasing temperature, indicating that the spontaneous nature of

12

326 the adsorption of Ni(II) was proportional to the temperature. Such a dependence of ΔG^Θ on

327 temperature and positive ΔH^Θ values confirmed the endothermic nature of sorption of Ni^{2+}

328 ions onto MSEAS. The ΔS^Θ was calculated to be 78.0 J mol^{-1} K^{-1}, which on the one hand

329 showed the affinity of the sorbent for Ni^{2+} ions, on the other hand, indicated the increase in

330 randomness at the solid/liquid interface after sorption.[24]

331   Positive ΔS value occurs as a result of redistribution of energy between the adsorbate

332 and the adsorbent. Before adsorption occurs, the heavy metal ions near the surface of the

333 adsorbent will be more ordered than in the adsorbed state and the ratio of free heavy metal

334 ions to ions interacting with the adsorbent will be higher than in the adsorbed state. As a

335 result, the distribution of rotational and translational energy among a small number of

336 molecules will increase with increasing adsorption by producing a positive value of ΔS.[21]

337

338 TABLE IV. Thermodynamic parameters for the sorption of nickel ions onto MSEAS

339

Sample	$\Delta H^\Theta/$ kJ mol^{-1}	$\Delta S^\Theta/$ J $mol^{-1}K^{-1}$	ΔG^Θ / kJ mol^{-1}			
			298 K	318 K	328 K	338 K
MSEAS	2.34	78.0	−20.92	−24.80	−25.60	−26.37

340
341
342
343 CONCLUSIONS
344

345   The sorption capacity shown by sepiolite functionalized with *N*-[3-

346 (trimethoxysilyl)propyl]ethylenediamine triacetic acid trisodium salt for Ni^{2+} from aqueous

347 solutions was higher than that of the natural sepiolite sample, suggesting that this

348 modification process is an effective method for obtaining sorbent for removal of Ni^{2+} ions

349 from highly polluted waters. The equilibrium sorption data were adequately described by the

350 Langmuir Isotherm Equation.

351   The retention of Ni^{2+} ions occurred dominantly by specific sorption and exchange of

352 Mg^{2+} ions from the sepiolite structure. The kinetic study of the sorption showed that the

353 pseudo-second-order model best described the experimental data, indicating that the sorption

354 may be controlled by chemical sorption and that chemisorption might be the rate-limiting step

355 that controls the sorption process.

The amount of Ni^{2+} sorbed onto the modified sepiolite increased with increasing temperature. The sorption thermodynamics indicates the endothermic and spontaneous nature of sorption process. On the contrary, the sorption capacity was not significantly changed on changing the initial pH value.

ИЗВОД

ФУНКЦИОНАЛИЗАЦИЈА СЕПИОЛИТА ПРИМЕНОМ СОЛИ НАТРИЈУМА N-[(3-ТРИМЕТОКСИ)ПРОПИЛ]ЕТИЛЕНДИАМИНТРИАЦЕТАТНЕ КИСЕЛИНЕ. ДРУГИ ДЕО: СОРПЦИЈА ЈОНА НИКЛА ИЗ ВОДЕНИХ РАСТВОРА

Славица С. Лазаревић, Ивона М. Јанковић-Частван, Бојан М. Јокић, Ђорђе Т. Јанаћковић и Рада Д. Петровић

Технолошко-металурши факултет Универзитета у Београду, Карнегијева 4, 11 000 Београд, Србија

У раду је испитана ефикасност уклањања јона никла из водених раствора на сепиолиту који је модификованом применом соли натријума N-[(3-триметокси)пропил]етилендиаминтриацетатне киселине (МСЕАС). Испитан је утицај почетне концентрације јона никла, времена уравнотежавања, pH вредности и температуре на процес сорпције применом методе уравнотежавања посебних проба. Поступак модификације природног сепиолита довео је до пораста капацитета сорпције јона никла. Сорпција је последица истовременог одигравања процеса специфичне сорпције и јонске измене са јонима магнезијума из структуре сепиолита. Поређењем експерименталних резултата са три модела сорпционих изотерми утврђено је да се процес сорпције јона никла на модификованом сепиолиту може описати моделом

14

389   Langmuir-ове сорпционе изотерме. Испитивање кинетике сорпције показало је да се
390   процес сорпције у складу са кинетичким моделом псеудо-другог реда. Вредности
391   термодинамичких параметара (промене енталпије, ентропије и слободне енергије
392   сорпције) одређене на основу зависности сорпције од температуре, указују на то да је
393   процес сорпције јона никла на узорку MCEAC ендотерман.
394
395

REFERENCES

1. R. P. Beliles, *The lesser metals. In: Toxicity of Heavy Metals in the Environment*, Marcel Dekker Inc, New York, 1979

2. Y. Turhan, P. Turan, M. Dogan, M. Alkan, H. Namli, O. Demirbas *Ind. Eng. Chem. Res.* **47** (2008) 1883

3. X. Liang, Y. Xu, G. Sun, L. Wang, Y. Sun, Y. Sun, X. Qin, *Chem. Eng. J.* **174** (2011) 436

4. M. Dogan, Y. Turhan, M. Alkan, H. Namli, P. Turan, O. Demirbas, *Desalination* **30** (2008) 248

5. V. Marjanović, S. Lazarević, I. Janković-Častvan, B. Jokić, A. Bjelajac, Dj. Janaćković, R. Petrović, *Hem. Ind.* **67** (2013) 715

6. V. Marjanović, S. Lazarević, I. Janković-Častvan, B. Jokić, Dj. Janaćković, R. Petrović, *Appl. Clay. Sci.* **80–81** (2013) 202

7. V. Marjanović, S. Lazarević, , B. Potkonjak, Dj. Janaćković, R. Petrović, *Chem. Eng. J.* **166** (2011) 198

8. S. Lazarević, I. Janković-Častvan, B. Jokić, Dj. Janaćković, R. Petrović, J. Serb. Chem. Soc. (2015) doi: 10.2298/JSC150219038L

9. S. Milonjic, A. Ruvarac, M. Susic, *Thermochim Acta* **11** (1975) 261

10. N. Kallay, V. Hlady, J. Jednačak-Bišćan, S. Milonjić, *Investigations of surfaces and interfaces – part A. In: Physical methods of chemistry series*, Wiley, New York, 1993, p73

11. S. Lazarević, I. Janković-Častvan, V. Djokić, Ž. Radovanović, Dj. Janacković, R. Petrović, *J. Chem. Eng. Data* **55** (2010) 5681

12. A.N. Vasiliev, L.V. Golovko, V.V. Trachevsky, G.S. Hall, J. Khinast, *Microporous Mesoporous Mater.* **118** (2009) 251

13. G. Tartaglione, D. Tabuani, G. Camino, Thermal and morphological characterisation of organically modified sepiolite. *Microporous Mesoporous Mater.* **107** (2008)161–168

14. I. Langmuir, *J. Am. Chem. Soc.* **40** (1918) 1361

15. H.M.F. Freundlich, *J. Phys. Chem.* **57** (1906) 385

16. O. Redlich, D.L. Peterson, *J. Phys. Chem.* **63** (1959)1024

17. G. McKay, V.J.P. Poots, *J. Chem. Technol. Biotechnol.* **30** (1980) 279

429   18. S. Lagergren, *K. Sven. Vetenskapsakad. Hand.* **24** (1898) 1

430   19. Y.S. Ho, G. McKay, *Process. Biochem.* **34** (1999) 451

431   20. Jr.W.J. Weber, J.C. Morris, *J. Sanit. Eng. Div. ASCE* **89** (1963) 31

432   21. A.R. Kul, H. Koyuncu, *J. Hazard. Mater.* **179** (2010) 332–339

433   22. A. Oliveira, L. Coelho, S. Gomes, I. Costa, M. Fonseca, K. de Sousa, J. Espinola, E.
434   da Silva Filho, *Water Air Soil Pollut.* 224 (2013) 1687

435   23. S. Wan, Z. Ma, Y. Xue, M. Ma, S. Xu, L. Qian, Q. Zhang, *Ind. Eng. Chem. Res.* **53**
436   (2014) 3629

437   24. H. Baker, *Desalination* **244** (2009) 48

438

439

440

441

442

443

444

445

446