

Gyrolite Adsorption of Zn²⁺ Ions in Acidic and Alkaline Solutions

Aliona ILJINA *, Kęstutis BALTAKYŠ, Anatolijus EISINAS

Department of Silicate Technology, Kaunas University of Technology, Radvilenu 19, LT-50254 Kaunas, Lithuania

crossref <http://dx.doi.org/10.5755/j01.ms.21.1.5703>

Received 12 November 2013; accepted 16 June 2014

The influence of solution pH on gyrolite adsorption capacity of Zn²⁺ ions has been examined. Adsorption experiments were carried out in the thermostatic adsorber by stirring 1 g of gyrolite in 100 ml of Zn(NO₃)₂ solution containing 0.3 g/dm³ of Zn²⁺ ions. Duration of adsorption at 25 °C temperature was 0.5, 1, 3, 5, 10, 25, 60, 120 min. It was found that adsorption process in alkaline solution proceed faster and more efficiently as in acidic because after 30 s 95 % of Zn²⁺ ions (28.50 mg Zn²⁺/g) intercalated in to gyrolite structure, whereas in acidic medium – 68 % of Zn²⁺ ions (20.43 mg Zn²⁺/g). Substitution reaction was found typical for gyrolite in the alkaline solution because 82 % zinc ions participated in ion exchange reaction and other part of these ions were present in gyrolite according to an addition interaction. Cation exchange mechanism proceeded differ in acidic solution because all zinc ions participated only in ion exchange reaction. The adsorption process in alkaline solution followed by a pseudo-second order model and suggest that it is a process of chemisorption. Gyrolite recrystallized in to gyrolite gel and C-S-H(I) when reaction medium is acidic meanwhile in alkaline medium intercalated zinc ions do not affect the structural properties of gyrolite.

Keywords: gyrolite, calcium silicate hydrate, adsorption, kinetics, XRD.

1. INTRODUCTION

Zinc is one of the most dangerous toxic heavy metals for human health. The main sources of this element are abandoned disposal sites, galvanizing, iron, steel industries [1]. It belongs to the second class of toxicity, characterizes low mutagenic and carcinogenic properties [2].

Many methods have been proposed for removal of toxic heavy metals from wastewaters. Chemical precipitation, filtration, complexing, solvent extraction, electrochemical technique, ion exchange and adsorption are some of the commonly used processes [3–5]. However, many of these procedures vary in effectiveness and cost. Among various methods, adsorption a now recognized as one of the most effective methods for the removal of heavy metals from the environments [6, 7].

There are many types of inorganic (activated alumina, zeolites, some clays et al.), organic (activated carbon, polymers, peat, et al.) and synthetic (calcium silicate hydrates, silicas, zeolites et al.) adsorbents [8–11]. The most important attributes of an adsorbent for any application are: capacity, selectivity, regenerability, kinetics, compatibility and costs [12]. It should be underlined that natural organic and inorganic adsorbents have a lower adsorption capacity, adsorption process continues longer, or it is hard to regenerate adsorbents and repeatedly to use them. Many authors [13–16] have reported that calcium silicate hydrates (C-S-H) prepared under hydrothermal treatment act as cation exchangers with some metal cations (Ca²⁺ or Si⁴⁺) in their lattice structure. These compounds created a new family of inorganic cation exchangers. Use of synthetic adsorbents has more advantages: by changing synthesis conditions (CaO/SiO₂ and water/solid ratios, isothermal curing temperature and duration, stirring intensity, cooling rate),

synthesis products crystallite size, crystallinity, crystal shape, composition can be controlled and organic/inorganic anions/cations, which have low affinity for these compounds group can be intercalated [17].

Mineral gyrolite is one of this C-S-H with most likely chemical formula NaCa₁₆Si₂₄O₆₀(OH)₈·14H₂O. It is a good adsorbent for wastewater purification from hazardous heavy metals and as a new generation chemically modified filler for polymeric nanocomposites [18–21]. Gyrolite can adsorb more chemical elements than other C-S-H because the interlayer sheets, with a thickness of about 2.2 nm (one of the largest in all the C-S-H group) are available for the intercalation of a new guest by controlling the charge of the host [22].

In previous works [23, 24] it was determined that gyrolite shows a very good cation exchange properties because almost of all Cu²⁺ ions (99.5 % removal efficiency) were intercalated into structure of this compound depending on the initial concentration of copper ions in alkaline medium [23]. However, the experimental data obtained of V. Kasperavičiute et al. [24] showed that in acidic medium gyrolite acts as chemisorbent which can adsorb only 41.48 % of Cu²⁺ ions. It should be noted that cation exchange capacity of gyrolite substituted with Na⁺ ions increases to 92.30 mg Cu²⁺/g and it is greater than tobermorite substituted with (Al³⁺+Na⁺) ions (53.22 mg Cu²⁺/g) [25].

It should be noted that adsorption kinetics was not fitted for gyrolite adsorption process yet [18, 23, 24]. However, it is important to ascertain the influence of kinetic parameters (k and q_e , where k – is the rate constant of adsorption, q_e – adsorption capacity at equilibrium) on adsorption reactions because kinetics gives ideal about the mechanism of adsorption [26]. Adsorption kinetics are mostly described by the pseudo first and pseudo second order empirical kinetic equations [27, 28]. One more important problem concerned with adsorption is the

* Corresponding author. Tel.: +370-37-300161; fax.: +370-37-300152.
E-mail address: aliona.iljina@ktu.lt (A. Iljina)

utilization of contaminated adsorbents. Ordinary Portland cement (OPC) is the most adaptable binder currently available for the immobilisation of heavy metals. In previous works A. Eisinas et al. [29, 30] examined that gyrolite substituted with Cd^{2+} ions can be immobilise in OPC. It was determined that the additive of gyrolite increases both the heat evolution rate and the amount of heat hydration of OPC samples. After 28 h of hardening, the mineral compositions of samples of pure OPC and OPC with additive of gyrolite are similar.

The aim of this work was to evaluate the influence of adsorptive pH value on gyrolite adsorption capacity of Zn^{2+} ions. The kinetic parameters (k , q_e) of adsorptions reaction are represented.

2. EXPERIMENTAL

In this study the following reagents for gyrolite synthesis were used as starting materials: fine-grained $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ("Reaktiv", Russia, ignition losses 21.28 %, specific surface area $S_a = 1307 \text{ m}^2/\text{kg}$) and calcium oxide (CaO was burned at 950°C for 0.5 h; $S_a = 1171 \text{ m}^2/\text{kg}$; purity 97.68 %).

The synthesis of gyrolite has been carried out in unstirred suspensions in the vessels of stainless steel within 48 hours at 200°C temperature from a stoichiometric composition (the molar ratio of CaO/SiO_2 was equal to 0.66 where water/solid ratio of the suspension was equal to 10.0) of the initial CaO and $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ mixture. These synthesis conditions were chosen according to previously published data [31].

Adsorption experiments were carried out at 25°C temperature in the thermostatic adsorber Grant SUB14 by stirring 1 g of gyrolite in 100 ml of $\text{Zn}(\text{NO}_3)_2$ aqueous solution (pH ~ 5.6) containing $0.3 \text{ g}/\text{dm}^3$ of Zn^{2+} ions for 0.5, 1, 3, 5, 10, 25, 60, 120 min. In order to maintain the alkaline of solution (pH ~ 9.0) and to prevent $\text{Zn}(\text{OH})_2$ precipitation, the aqueous solution ($c = 10\%$) of NH_4OH was used. The percentage of exchange was determined on the basis of the variations in the concentration of the cations in the solution and in gyrolite. The saturated adsorbent was rinsed with distilled water, dried at $50^\circ\text{C} \pm 5^\circ\text{C}$, and dissolved in HCl (1:1). The concentration of Ca^{2+} and Zn^{2+} ions was determined using an atomic absorption spectrometer – Perkin-Elmer Analyst 4000 with parameters: wavelength of Zn^{2+} is 213.86 nm; wavelength of Ca^{2+} is 422.67; the hollow cathode lamp current (I) is 30 mA; type of flame is C_2H_2 -air; oxidant air 10 l/min; acetylene 2.5 l/min. The value of pH was taken by Hanna instrument (Hi 9321, microprocessor pH meter).

In order to determined kinetic parameters of adsorption reactions, a kinetic models have been developed and fitted for the adsorption process of the Zn^{2+} ions into gyrolite. The Lagergren model [32, 33], assumes a first order adsorption kinetics and can be represented by the equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \quad (1)$$

where q_e and q_t are adsorption capacity at equilibrium and at time t , respectively ($\text{mg} \cdot \text{g}^{-1}$), k_1 is the rate constant of pseudo first order adsorption (min^{-1}). After integration and

applying boundary conditions $t = 0$ to $t = t_e$ and $q_t = 0$ to $q_t = q_e$, the integrated form becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t. \quad (2)$$

The pseudo second order adsorption kinetic rate equation [32, 33] is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \quad (3)$$

where k_2 is the rate constant of the pseudo second order adsorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$). For the boundary conditions $t = 0$ to $t = t_e$ and $q_t = 0$ to $q_t = q_e$, the integrated form of the equation becomes (the integrated rate law for the pseudo second-order reaction):

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t. \quad (4)$$

The X-ray powder diffraction (XRD) data were collected with a DRON-6 X-ray diffractometer with Bragg-Brentano geometry using $\text{CuK}\alpha$ radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range $2^\circ - 60^\circ$ (2θ) in steps of $2\theta = 0.02^\circ$.

Simultaneous thermal analysis (STA) was carried out on a Netzsch STA 409 PC Luxx instrument. DSC parameters: heating rate was $15^\circ\text{C}/\text{min}$; the temperature ranged from 30°C up to 1000°C , under air atmosphere.

3. RESULTS AND DISCUSSION

The results of adsorption showed that in $\text{Zn}(\text{NO}_3)_2$ solution which has pH ~ 5.6 and the initial concentration of Zn^{2+} ions equal to $0.3 \text{ g}/\text{dm}^3$, after 30 s more than 68 % Zn^{2+} ions ($20.43 \text{ mg Zn}^{2+}/\text{g}$) intercalate into gyrolite crystal lattice (Fig. 1).

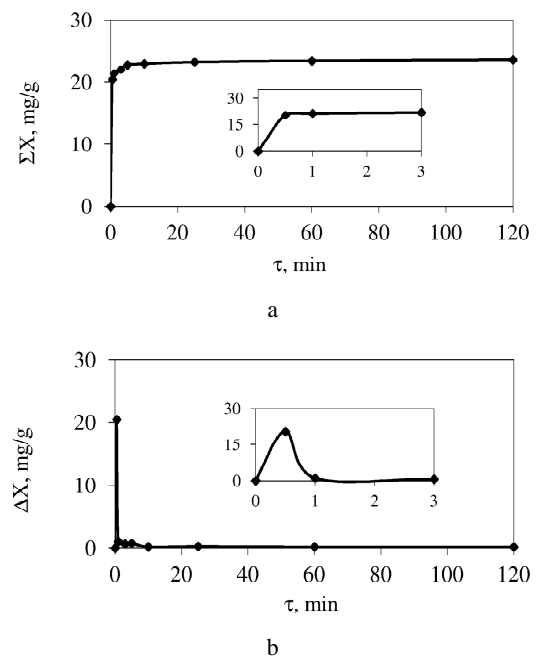


Fig. 1. Integral (a) and differential (b) kinetic curves of Zn^{2+} ions adsorption by gyrolite in acidic solution

After increase duration of the interaction, the zinc ions concentration in the solution decreases steadily. It should be noted that gyrolite adsorption occurs within 5 min, because amount of intercalated zinc ions into gyrolite structure increase only to 22.82 mg Zn²⁺/g and later does not vary (Fig. 1, a).

It should be noted that when zinc ions intercalate into gyrolite structure, calcium ions are released from the crystal lattice of adsorbent into the solution. Most of Ca²⁺ ions are released in the first minutes because after 5 minutes their concentration ($\Sigma X_{Ca^{2+}}$) is equal to 17.95 mg Ca²⁺/g and after 2 h $\Sigma X_{Ca^{2+}}$ only increased till 18.79 mg Ca²⁺/g (Fig. 2).

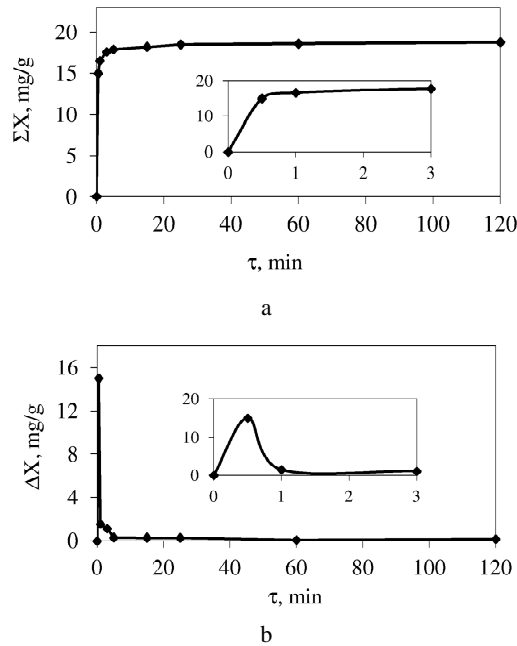


Fig. 2. Integral (a) and differential (b) kinetic curves of Ca²⁺ ions concentration variation in acidic solution

It was estimated that almost all zinc ions intercalated into gyrolite structure only by substitution reaction: gyrolite-Ca⁰ + Zn²⁺ ↔ gyrolite-Zn⁰ + Ca²⁺. The main reason could be pH of initial cation metal solutions.

It should be noted that the significant change of pH value in reaction medium was observed at the beginning of adsorption (3 min – 5 min) because the value of pH varied from 5.6 to 6.5 (Fig. 3). Presumable that mentioned variation of pH value depends on increment of Ca²⁺ ions quantity in solution.

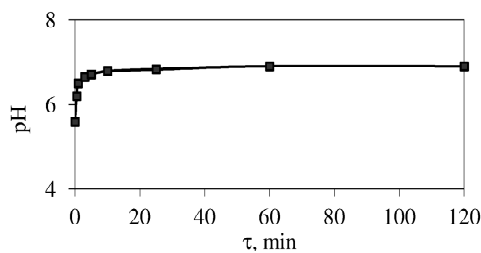


Fig. 3. Variation of acidic solution pH value

After adsorption experiment gyrolite powder was dried and poured into decarbonized water for the leaching test. It was determined that zinc ions concentration in

solution after 120 minutes at 25 °C did not exceed over ~0.008 %.

Thus, it was found that the adsorption of zinc ions by gyrolite is irreversible in acidic solution.

Obtained data showed that adsorptive nature has a determinant influence for gyrolite adsorption capacity because V. Kasperavičiute et al. [24] showed that in acidic medium gyrolite acts as chemisorbent which can adsorb only 41.48 % of Cu²⁺ ions.

In order to identify the stability of gyrolite after adsorption, it was characterized by XRD and STA methods.

XRD analysis showed that gyrolite in acidic solution is unstable because after 2 h of adsorption, the intensity of gyrolite main diffraction peak (*d*-spacing – 2.273 nm) decreases (Fig. 4, a, curve 2). It was determined that gyrolite recrystallized into gyrolite gel (*d*-spacing – 2.205, 1.106, 0.830, 0.304, 0.279, 0.183 nm) and variable (undefined) composition of the semi-crystalline compound – CSH(I) (*d*-spacing – 0.304, 0.279, 0.183 nm) (Fig. 4, a, curve 2).

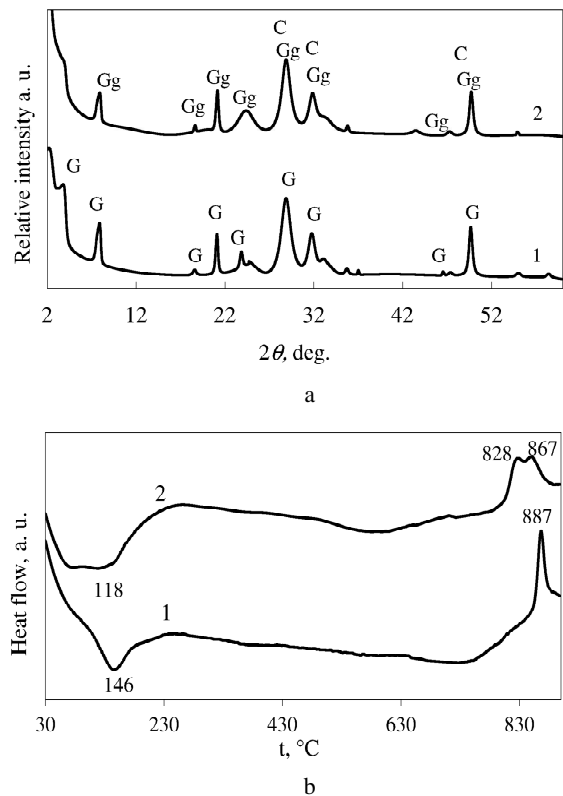


Fig. 4. X-ray diffraction patterns (a) and DSC curves (b) of gyrolite: 1 – before adsorption, 2 – after adsorption. Indexes: G – gyrolite; Gg – gyrolite gel; C – C-S-H(I)

These results were confirmed by DSC data: typical an endothermic effect at ~146 °C is of gyrolite (Fig. 4, b) moved to a lower temperature at ~118 °C after 2 h of adsorption (Fig. 4, b, curve 2). Also, it was identified two exothermic effects at 828 °C and 867 °C temperatures, which are typical to gyrolite gel and CSH(I) respectively (Fig. 4, b, curve 2). It should be noted that these compounds recrystallizes into the wollastonite at lower temperatures compared to the pure gyrolite sample (Fig. 4, b, curve 1).

These data agree with A. Stumm et al. [34] results, which have indicated that zinc incorporation into synthetic gyrolite is possible up to $Zn/(Zn+Ca) = 1/6$, corresponding to approximately 6 wt.%. Increasing zinc content led to a gradual diminishing of the basal reflection (001) of gyrolite, as for the nanocrystalline phases [34].

In order to increase stability of adsorbent, adsorption reactions of zinc ions were studied in alkaline medium.

It was determined that in alkaline solution (pH ~ 9.0) adsorption proceeded faster and more efficiently as in acidic. After 30 s more than 95 % of Zn^{2+} ions (28.50 mg Zn^{2+}/g) intercalated into gyrolite crystal lattice (Fig. 5, a). It should be noted that the ion exchange in gyrolite occurred within 1 min because almost all the Zn^{2+} ions (29.12 mg Zn^{2+}/g) intercalated in the structure of this compound (Fig. 5, b).

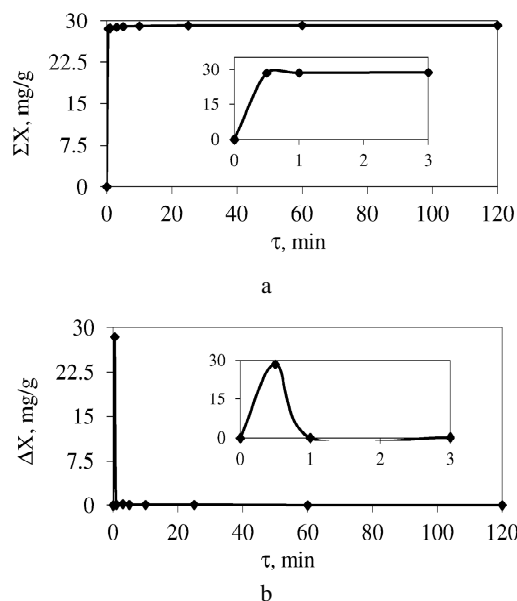


Fig. 5. Integral (a) and differential (b) kinetic curves of Zn^{2+} ions adsorption in alkaline solution

It should be noted that amount of calcium ions released from gyrolite crystal structure in alkaline solution is significantly lower than in acidic. Most of Ca^{2+} ions are released after 5 minutes because concentration of them ($\Sigma X_{Ca^{2+}}$) is equal to 13.92 mg Ca^{2+}/g and after 2 h $\Sigma X_{Ca^{2+}}$ only increased till 14.53 mg Ca^{2+}/g (Table 1).

Table 1. The amount of desorbed Ca^{2+} ions in alkaline solution

Time, min	$\Delta X(Ca^{2+}), mg \cdot g^{-1}$	$\Sigma X(Ca^{2+}), mg \cdot g^{-1}$
0	0	0
0.5	10.82	10.82
1	1.20	12.02
3	1.00	13.02
5	0.90	13.92
15	0.30	14.22
25	0.20	14.42
60	0.10	14.52
120	0.01	14.53

It was determined that substitution reaction was typical of gyrolite in the alkaline solution because 82 % of

Zn^{2+} ions participated in the substitution/chemical reaction ($gyrolite-Ca^0 + Zn^{2+} \leftrightarrow gyrolite-Zn^0 + Ca^{2+}$), whereas the rest of these ions were present in gyrolite according to an addition interaction.

It was found that pH value in alkaline solution during adsorption process does not vary: pH is equal to 9.0 ± 0.1 (Fig. 6).

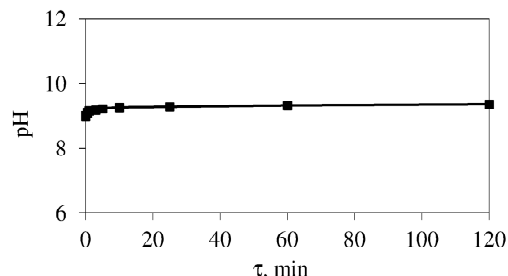


Fig. 6. Variation of alkaline solution pH value

In order to identify the stability of gyrolite, the products of sorption were characterized by XRD and DSC analysis (Fig. 7).

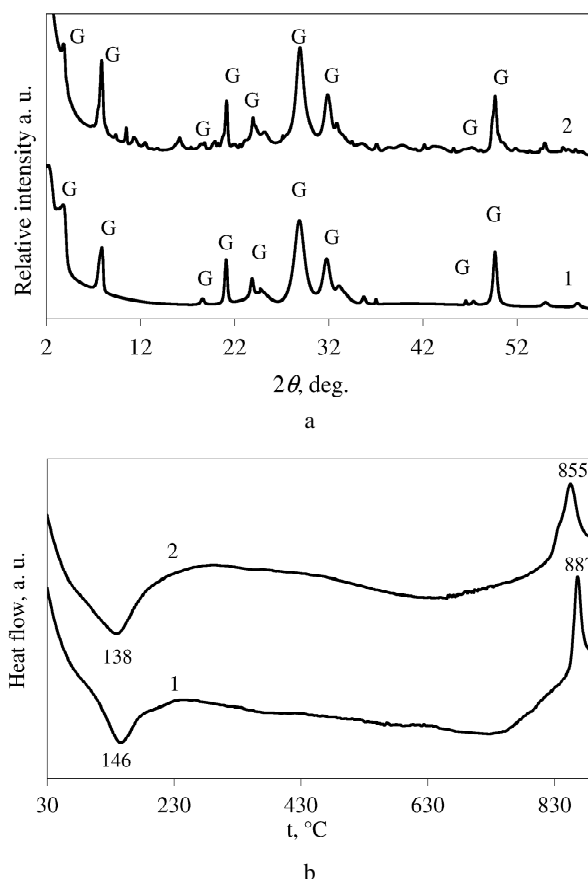


Fig. 7. X-ray diffraction patterns (a) and DSC curves (b) of gyrolite: 1 – before adsorption, 2 – after adsorption. Indexes: G – gyrolite

The X-ray powder diffraction analysis showed that the structure of gyrolite did not change during the adsorption process. In the X-ray diffraction pattern, the most characteristic peak (d -spacing – 2.273 nm) of gyrolite was identified. This principal reflection did not change over the duration of the adsorption reaction (Fig. 7, a, curve 2). In

DSC curve the same thermal effects (endothermic effect at 138 °C of water dehydration and exothermic effect at 855 °C of recrystallization to wollastonite) were identified (Fig. 7, b, curve 2) as in pure gyrolite (Fig. 7, b, curve 1). It should be noted that gyrolite substituted with Zn²⁺ ions recrystallizes into wollastonite at lower temperature (855 °C).

After adsorption experiment gyrolite powder was dried and poured into decarbonized water for the leaching test. It was determined that zinc ions concentration in solution after 120 min at 25 °C did not exceed over 0.1 %. Thus, adsorption process in alkaline solution is irreversible.

Thus, our research allows to state that the cation exchange reactions are specific to chemisorption process. In order to determine kinetic parameters of adsorption reactions in alkaline solution, a kinetic models have been developed and fitted for the adsorption reaction of the Zn²⁺ ions by gyrolite.

By using pseudo first order kinetic rate equation in a linear form (2), the equilibrium adsorption capacity ($q_{e(\text{exp})}$) and the first order constant k_1 (min⁻¹) was determined experimentally from the slope and intercept plot of $\log(q_{e(\text{exp})} - q_t)$ versus t . It was observed that the pseudo first order model did not fit well because the calculated $q_{e(\text{cal})}$ value disagreed with the experimental $q_{e(\text{exp})}$ value and value of correlation coefficient (R^2) was very low – 0.557 (Table 2).

Table 2. The kinetic parameters of the pseudo first and pseudo second order kinetic models in alkaline solution

$q_{e(\text{exp})}$	Pseudo first order			Pseudo second order		
	k_1, min^{-1}	$q_{e(\text{cal})}, \text{mg}\cdot\text{g}^{-1}$	R^2	$k_2, \text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$	$q_{e(\text{cal})}, \text{mg}\cdot\text{g}^{-1}$	R^2
29.120	0.088	1.265	0.557	1.176	29.154	1.000

$q_{e(\text{exp})}$ – the equilibrium adsorption capacity, mg·g⁻¹, calculated from experimental data;

$q_{e(\text{cal})}$ – the equilibrium adsorption capacity, mg·g⁻¹, calculated by using equations (3) and (4) of kinetic models.

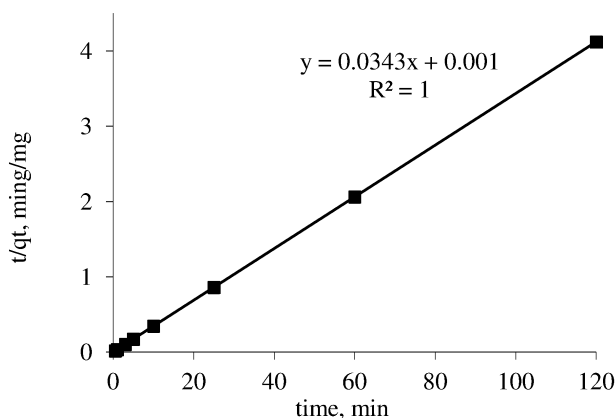


Fig. 8. Pseudo-second order kinetic plot in alkaline solution

By using the pseudo second order kinetics equation (4), the equilibrium adsorption capacity ($q_{e(\text{exp})}$) and the second-order constants k_2 (g·mg⁻¹·min⁻¹) was determined experimentally from the slope and intercept of plot t/q_t

versus t (Fig. 8). The values of the calculated $q_{e(\text{cal})}$ and experimental $q_{e(\text{exp})}$ are represented in Table 2.

An agreement between $q_{e(\text{exp})}$ experimental and $q_{e(\text{cal})}$ calculated values for the pseudo second order model was observed. Also, the correlation coefficient (R^2) for the second order increase to 1 and adsorption rate constant (k_2) is equal to 1.176.

Hence, the pseudo second order model followed by adsorption kinetics and suggest that the process of adsorption in alkaline solution is chemisorption.

CONCLUSIONS

It was found that the penetration of Zn²⁺ ions into structure of gyrolite depends on the pH value of the Zn(NO₃)₂ solution because after 30 s 95 % of Zn²⁺ ions (28.50 mg Zn²⁺/g) intercalated in to gyrolite structure in alkaline solution (pH ~ 9.0), whereas in acidic solution (pH ~ 5.6) only – 68 % (20.43 mg Zn²⁺/g).

It was determined that in alkaline solution 82 % of Zn²⁺ ions participated into gyrolite by the substitution reaction (gyrolite-Ca⁰ + Zn²⁺ ↔ gyrolite-Zn⁰ + Ca²⁺), whereas the rest of these ions were present in gyrolite according to an addition interaction. Meanwhile, in acidic solution adsorption reaction proceeded differ because almost all zinc ions participated only in substitution reaction.

It has been proven that independently of the solution pH value the adsorption reactions are irreversible. It was found that the adsorption processes in alkaline solution followed by a pseudo second order model and suggest that it is process of chemisorption.

It is recommended to use gyrolite when pH of adsorptive is alkaline because in solution with lower pH value (~ 5.6), this compound recrystallized into gyrolite gel and variable (undefined) composition of the semi-crystalline compound CSH(I).

Acknowledgments

This work was partly supported by project "Promotion of Student Scientific Activities" (VP1-3.1-ŠMM-01-V-02-003) from the Research Council of Lithuania (A. Iljina). This project is funded by the Republic of Lithuania and also, the present work was funded by a grant (No. MIP-025/2014) from the Research Council of Lithuania.

REFERENCES

1. Agarwal, S. K. Heavy Metal Pollution. New Delhi, 2009: pp. 7 – 14.
2. Cesur, H., Balkaya, N. Zinc Removal from Aqueous Ssolution Using an Industrial By-product Phosphogypsum *Chemical Engineering Journal* 131 2007: pp. 203 – 208.
3. Montanher, S. F., Oliveira, E. A., Rollemberg, M. C. Removal of Metal Ions from Aqueous Solutions by Sorption onto Rice Bran *Journal of Hazardous Materials* B 117 2005: pp. 207 – 211.
4. Arambula-Villazana, V., Olguin, M. T. Sorption of Cadmium from Aqueous Solutions at Different Temperatures by Mexican HEU-type Zeolite Rich Tuff *Journal of Inclusion Phenomena and Macrocyclic Chemistry* 55 2006: pp. 237 – 245.
<http://dx.doi.org/10.1007/s10847-006-9048-7>

5. **Barakat, M. A.** New Trends in Removing Heavy Metals from Industrial Wastewater *Arabian Journal of Chemistry* 4 2010: pp. 361–377.
6. **Malakootian, M., Nouri, J., Hossaini, H.** Removal of Heavy Metals from Paint Industry's Wastewater Using Leca as an Available Adsorbent *International Journal of Environmental Science and Technology* 6 2009: pp. 183–190.
7. **Gupta, S. S., Bhattacharyya, K. G.** Immobilization of Pb(II) Cd(II) and Ni(II) Ions on Kaolinite and Montmorillonite Surfaces from Aqueous Medium *Journal of Environmental Management* 87 2008: pp. 46–58.
8. **Li, G., Zhaob, Z., Liua, J., Jianga, G.** Effective Heavy Metal Removal From Aqueous Systems by Thiol Functionalized Magnetic Mesoporous Silica *Journal of Hazardous Materials* 192 2011: pp. 277–283.
9. **Motsa, M. M., Thwala, J. M., Msagati, T. A. M., Mamba, B. B.** The Potential of Melt-mixed Polypropylene-zeolite Blends in the Removal of Heavy Metals from Aqueous Media *Physics and Chemistry of the Earth* 36 2011: pp. 1178–1188.
10. **Babel, S., Kurniawan, T. A.** Low-cost Adsorbents for Heavy Metals Uptake from Contaminated Water: a Review *Journal of Hazardous Materials* B 97 2003: pp. 219–243.
11. **Fenga, Y., Gongga, J. L., Zenga, G. M., Niua, Q. Y., Zhanga, H. Y., Niua, C. G., Denga, J. H., Yana, M.** Adsorption of Cd (II) and Zn (II) from Aqueous Solutions Using Magnetic Hydroxyapatite Nanoparticles as Adsorbents *Chemical Engineering Journal* 162 2010: pp. 487–494.
12. **Branvall, E., Mažeikienė, A., Valentukevičienė, M.** Experimental Research on Sorption of Petroleum Products from Water by Natural Clinoptilolite and Vermiculite *Geologija* 56 2006, pp. 5–12.
13. **Coleman, N. J., Trice, C. J., Nicholson, J. W.** 11 Å Tobermorite from Cement Bypass Dust and Waste Container Glass: A Feasibility Study *International Journal of Mineral Processing* 93 2009: pp. 73–78.
<http://dx.doi.org/10.1016/j.minpro.2009.06.002>
14. **El-Korashy, S. A.** Hydrothermal Synthesis and Transition Metal Cations Exchange Characterization of Titanium and [Titanium+Alkali Metals] Substituted-11Å Tobermorites *Journal of the Korean Chemical Society* 48 2004: pp. 129–36.
15. **El-Korashy, S. A.** Synthetic Crystalline Calcium Silicate Hydrate (I): Cation Exchange and Caesium Selectivity *Chemical Monthly* 133 2002: pp. 333–343.
<http://dx.doi.org/10.1007/s007060200012>
16. **Mostafa, N. Y., Kishar, E. A., Abo-El-Enein, S. A.** FTIR Study and Cation Exchange Capacity of Fe³⁺- and Mg²⁺-Substituted Calcium Silicate Hydrates *Journal of Alloys and Compounds* 473 2009: pp. 538–542.
<http://dx.doi.org/10.1016/j.jallcom.2008.06.029>
17. **Baltakys, K., Siauciunas, R.** Influence of Gypsum Additive on the Gyrolite Formation Process *Cement and Concrete Research* 40 (3) 2010: pp. 376–383.
18. **Winter, M. A., Richter, J. D., Sagar, S. L., Lee, A. L., Lander, R. J.** Plasmid DNA Purification by Selective Calcium Silicate Adsorption of Closely Related Impurities *Biotechnology Progress* 19 2003: pp. 440–447.
19. **Baltakys, K., Eisinas, A., Barauskas, I., Prichockienė, E., Zaleckas, E.** Removal of Zn(II), Cu(II) and Cd(II) from Aqueous Solution Using Gyrolite *Journal of Scientific and Industrial Research* 71 2012: pp. 566–572.
20. **Baltakys, K., Siauciunas, R.** The Influence of Gamma-Al₂O₃ and Na₂O on the Formation of Calcium Silicate Hydrates in the CaO-quartz-H₂O System *Materials Science-Poland* 25 (1) 2007: pp. 185–198.
21. **Baltušnikas, A., Lukošiušė, I. K.** XRD Characterization of Organically Modified Gyrolite *Materials Science (Medžiagotyra)* 15 (4) 2009: pp. 325–328.
22. **Shaw, S., Henderson, C. M. B., Clark, S. M.** In-situ Synchrotron Study of the Kinetics, Thermodynamics, and Reaction Mechanisms of the Hydrothermal Crystallization of Gyrolite Ca₁₆Si₂₄O₆₀(OH)₈·14H₂O *American Mineralogist* 87 2002: pp. 533–541.
23. **Bankauskaitė, A., Baltakys, K.** The Sorption of Copper Ions by Gyrolite in Alkaline Solution *Materials Science-Poland* 27 (3) 2009: pp. 899–908.
24. **Kasperaviciute, V., Baltakys, K., Siauciunas, R.** The Sorption Properties of Gyrolite for Copper Ions *Ceramics-Silikaty* 52 2008: pp. 95–101.
25. **Baltakys, K., Siauciunas, R.** Gyrolite Formation in CaO–SiO₂–nH₂O–γ-Al₂O₃–Na₂O–H₂O System under Hydrothermal Conditions *Polish Journal of Chemistry* 81 2007: pp. 103–114.
26. **Abechi, E. S., Gimba, C. E., Uzairu, A., Kagbu, J. A.** Kinetics of Adsorption of Methylene Blue Onto Activated Carbon Prepared from Palm Kernel Shell *Archives of Applied Science Research* 3 2011: pp. 154–164.
27. **Coleman, N. J., Trice, C. J., Nicholson, J. W.** 11 Å Tobermorite from Cement Bypass Dust and Waste Container Glass: A Feasibility Study *International Journal of Mineral Processing* 93 2009: pp. 73–78.
<http://dx.doi.org/10.1016/j.minpro.2009.06.002>
28. **Malamis, S., Katsou, E.** A Review on Zinc and Nickel Adsorption on Natural and Modified Zeolite, Bentonite and Vermiculite: Examination of Process Parameters, Kinetics and Isotherms *Journal of Hazardous Materials* 252–253 2013: pp. 428–461.
29. **Eisinas, A., Baltakys, K., Siauciunas, S.** The Effect of Gyrolite Additive on the Hydration Properties of Portland Cement *Cement and Concrete Research* 42 2012: pp. 27–38.
<http://dx.doi.org/10.1016/j.cemconres.2011.07.003>
30. **Eisinas, A., Baltakys, K., Siauciunas, S.** Utilization of Gyrolite with Impure Cd²⁺ Ions in Cement Stone *Advances in Cement Research* 25 2013: pp. 69–79.
31. **Šiaučiušas, R., Baltakys, K.** Formation of Gyrolite During Hydrothermal Synthesis in the Mixtures of CaO and Amorphous SiO₂ or Quartz *Cement and Concrete Research* 34 2004: pp. 2029–2036.
32. **Hameed, B. H., Mahmoud, D. K., Ahmad, A. L.** Equilibrium Modeling and Kinetic Studies on the Adsorption of Basic dye by a Low-cost Adsorbent: Coconut (*Cocos nucifera*) Bunch Waste *Journal of Hazardous Materials* 158 2008: pp. 65–72.
<http://dx.doi.org/10.1016/j.jhazmat.2008.01.034>
33. **Qiu, H., Lv, L., Pan, B., Zhang, Q., Zhang, W., Zhang, Q.** Critical Review in Adsorption Kinetic Models *Journal of Zhejiang University Science A* 10 2009: pp. 716–724.
<http://dx.doi.org/10.1631/jzus.A0820524>
34. **Stumm, A., Garbev, K., Beuchle, G., Black, L., Stemmermann, P., Nuesch, R.** Incorporation of Zinc into Calcium Silicate Hydrates, Part I: Formation of C-S-H(I) with C/S=2/3 and Its Isochemical Counterpart Gyrolite *Journal of Cement and Concrete Research* 35 2005: pp. 1665–1675.