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Gyrolite Adsorption of Zn^{2+} Ions in Acidic and Alkaline Solutions

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The influence of solution pH on gyrolite adsorption capacity of Zn^{2+} ions has been examined. Adsorption experiments were carried out in the thermostatic adsorber by stirring 1 g of gyrolite in 100 ml of $Zn(NO_3)_2$ solution containing 0.3 g/dm^3 of Zn^{2+} 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 Zn^{2+} ions (28.50 mg Zn^{2+}/g) intercalated in to gyrolite structure, whereas in acidic medium – 68 % of Zn^{2+} ions (20.43 mg Zn^{2+}/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 folowed by a pseudo-second order model and suggest that it is a process of chemosorption. 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 (Ca^{2+}or Si^{4+}) 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/SiO_2 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 $NaCa_{16}Si_{24}O_{60}(OH)_8{\cdot}14H_2O$. 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 Cu^{2+} 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. Kasperaviciute et al. [24] showed that in acidic medium gyrolite acts as chemosorbent which can adsorb only 41.48 % of Cu^{2+} ions. It should be noted that cation exchange capacity of gyrolite substituted with Na^+ ions increases to 92.30 mg Cu^{2+}/g and it is greater than tobermorite substituted with (Al^{3+}+Na^+) ions (53.22 mg Cu^{2+}/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

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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 $SiO_2 \cdot nH_2O$ ("Reaktiv", Russia, ignition losses 21.28 %, specific surface area $S_a = 1307$ m²/kg) and calcium oxide (CaO was burned at 950 °C for 0.5 h; $S_a = 1171$ m^2/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 $SiO_2 \cdot nH_2O$ 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 $Zn(NO_3)_2$ aqueous solution (pH ~ 5.6) containing 0.3 g/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 $Zn(OH)_2$ 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 °C ±5 °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 Largergren model [32, 33], assumes a first order adsorption kinetics and can be represented by the equation:

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

where q_e and q_t are adsorption capacity at equilibrium and at time t, respectively (mg·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:

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

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

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

where k_2 is the rate constant of the pseudo second order adsorption (g·mg^{-1}·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):

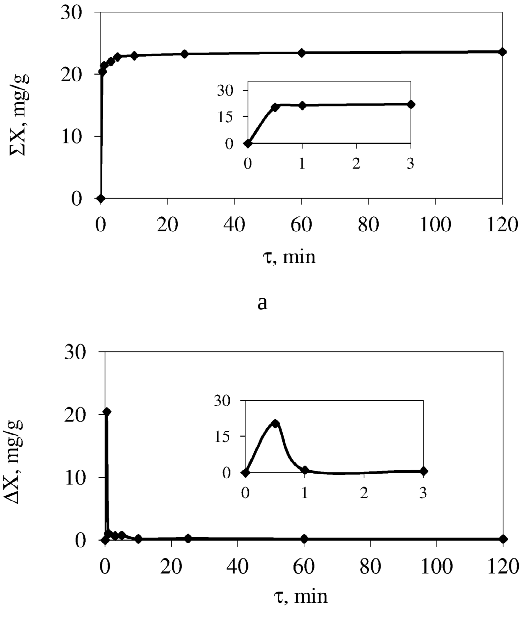
$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t. \tag{4}$$

The X-ray powder diffraction (XRD) data were collected with a DRON-6 X-ray diffractometer with Bragg-Brentano geometry using CuK_α 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°–60° (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 °C/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 $Zn(NO_3)_2$ solution which has pH ~ 5.6 and the initial concentration of Zn^{2+} ions equal to 0.3 g/dm^3, after 30 s more than 68 % Zn^{2+} ions (20.43 mg Zn^{2+}/g) intercalate into gyrolite crystal lattice (Fig. 1).



a

b

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 Zn^{2+}/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 Ca^{2+} ions are released in the first minutes because after 5 minutes them concentration (ΣX_{Ca2+}) is equal to 17.95 mg Ca^{2+}/g and after 2 h ΣX_{Ca2+} only increased till 18.79 mg Ca^{2+}/g (Fig. 2).

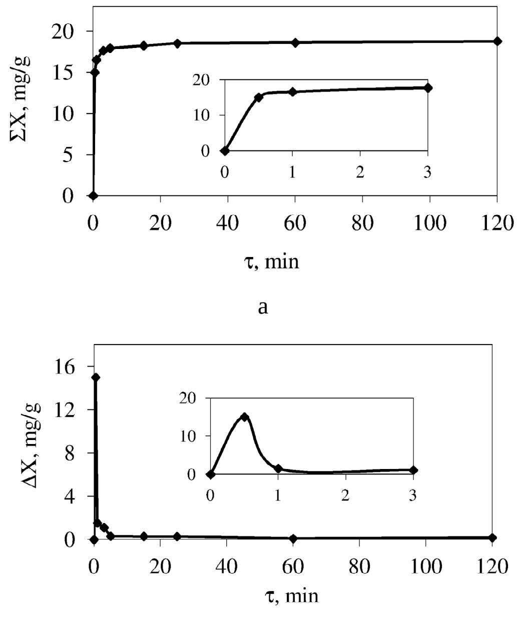


Fig. 2. Integral (a) and differential (b) kinetic curves of Ca^{2+} ions concentration variation in acidic solution

It was estimated that almost all zinc ions intercalated into gyrolite structure only by substitution reaction: gyrolite-Ca^0 + Zn^{2+} ↔ gyrolite-Zn^0 + Ca^{2+}. 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 Ca^{2+} ions quantity in solution.

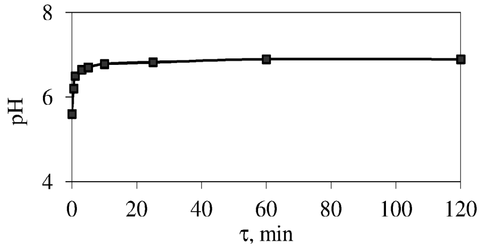


Fig. 3. Variation of acidic solution pH value

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. Kasperaviciute et al. [24] showed that in acidic medium gyrolite acts as chemosorbent which can adsorb only 41.48 % of Cu^{2+} 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).

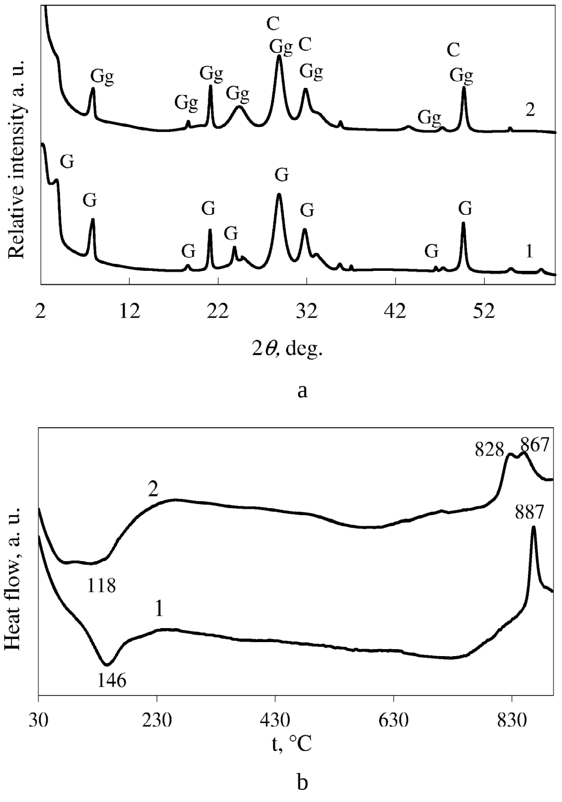


Fig. 4. X-ray diffraction patterns (a) and DSC curves (b) of gyrolite: 1 – before adsorption, 2 – after adsorption. Indexes: G – gyrolite; Gg – gyrolite gel; C – C-S-H(I)

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, wich are typical to gyrolite gel and CSH(I) respectively (Fig. 4, b, curve 2). It should be noted that these compounds recrystalizes 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).

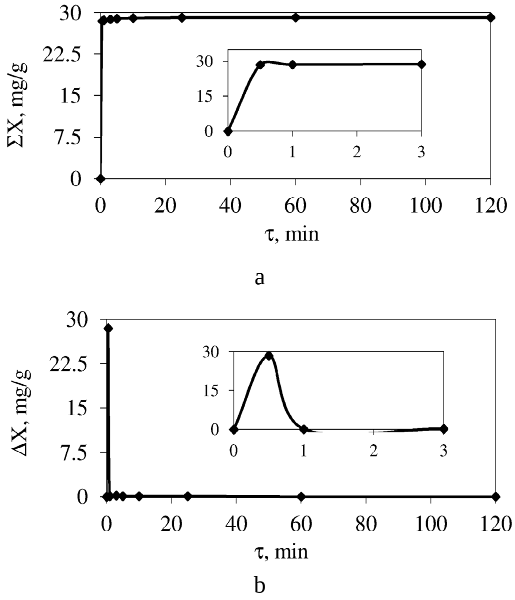


Fig. 5. Integral (a) and differential (b) kinetic curves of Zn^{2+} ions adsorption in alkaline solution

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 (ΣX_{Ca2+}) is equal to 13.92 mg Ca^{2+}/g and after 2 h ΣX_{Ca2+} 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·g^{-1}	$\Sigma X(Ca^{2+})$, mg·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+} ↔ 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).

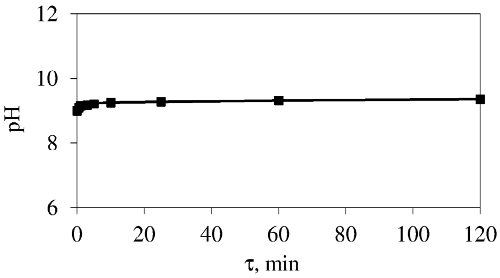


Fig. 6. Variation of alkaline solution pH value

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

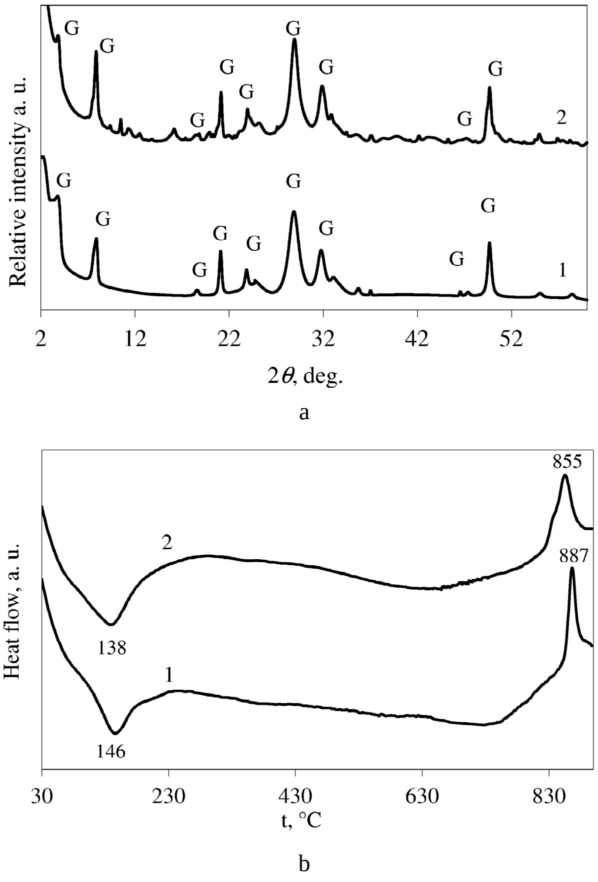


Fig. 7. X-ray diffraction patterns (a) and DSC curves (b) of gyrolite: 1 – before adsorption, 2 – after adsorption. Indexes: G – gyrolite

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 dehydratation 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 Zn^{2+} 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 Zn^{2+} ions by gyrolite.

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

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

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

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

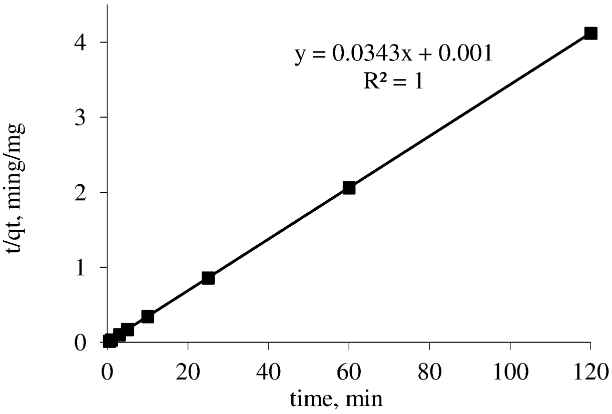


Fig. 8. Pseudo-second order kinetic plot in alkaline solution

By using the pseudo second order kinetics equation (4), the equilibrium adsorption capacity ($q_{e(exp)}$) 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 $q_{e(cal)}$ and experimental $q_{e(exp)}$ are represented in Table 2.

An agreement between $q_{e(exp)}$ experimental and $q_{e(cal)}$ 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 chemosorption.

CONCLUSIONS

It was found that the penetration of Zn^{2+} ions into structure of gyrolite depends on the pH value of the $Zn(NO_3)_2$ solution because after 30 s 95 % of Zn^{2+} ions (28.50 mg Zn^{2+}/g) intercalated in to gyrolite structure in alkaline solution (pH ~ 9.0), whereas in acidic solution (pH ~ 5.6) only – 68 % (20.43 mg Zn^{2+}/g).

It was determined that in alkaline solution 82 % of Zn^{2+} ions participated into gyrolite by the substitution reaction (gyrolite-Ca^0 + Zn^{2+} ↔ gyrolite-Zn^0 + Ca^{2+}), 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 chemosorption.

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

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