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Adsorption Kinetic Parameters of Fe^{3+} and Ni^{2+} Ions by Gyrolite

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In this work the adsorption kinetic parameters for Fe^{3+} and Ni^{2+} ions by gyrolite are presented. Additionally, the adsorption mechanism was described by using pseudo first order and pseudo second order equations. It was determined that the adsorption capacity of gyrolite and intrusion of heavy metals ions in its structure depends on reaction time and the pH value of adsorptive. It was observed that the incorporation of Fe^{3+} ions occurs more intensive than Ni^{2+} ions. It was found that in the acidic solution the intrusion of Fe^{3+} ions into gyrolite structure proceeds by two types of chemical reaction mechanisms: substitution and addition. Meanwhile, nickel ions were participated only in substitution reaction: gyrolite-Ca^0 + Me^{x+} ↔ gyrolite-Me^0 + Ca^{2+}. It was observed that the pseudo second order model fit well for iron and nickel ions adsorption mechanism. It was estimated that the adsorption reactions are not reversible process and the crystal structure of gyrolite is stable. Moreover, synthetic adsorbent and the products of sorption were characterized by XRD, STA and FT-IR methods.

Keywords: gyrolite, inorganic adsorbents, heavy metal ions adsorption, kinetics parameters.

1. INTRODUCTION

Heavy metal ions are necessary for plants and animals if their concentration is low, however over and above this concentration becomes toxic [1]. The ions have been excessively released into the environment due to industrial activities (pigment manufacture, tanneries, metal plating, petroleum refining, battery manufacture, paint manufacture, pesticides, pigment manufacture and etc.) and have created a major concern [2 – 6]. Heavy metals are non-biodegradable waste often detected in industrial wastewaters therefore they must be removed before discharge [4, 7]. Nickel and iron are most of the dangerous toxic heavy metals for the environment and human health. The main sources of nickel element are electroplating, iron, steel industries, electrical, radio engineering and electronics manufacturing, chemical industry, plastics production, municipal sewage, coal burning [8]. It belongs to the second class of toxicity, characterizes low mutagenic and carcinogenic properties [8]. The iron is essential as a trace element. The main sources of this element are metallurgy, chemical, paint industry, textile dyeing and printing [8].

A large group of inorganic materials: zirconium phosphates, aluminosilicates, clay minerals, hydroxyapatite, and others are used as adsorbents for heavy metals or radioactive contaminated water [9 – 13]. Before four decades S. Komarneni et al. [12 – 16] announced that it has been found new adsorbent – 1.13 nm tobermorite. During that timed it has been explored in detail the calcium silicate hydrates adsorption properties of synthesized compounds embedded in the crystal lattice extraneous atoms, which significantly increased their ability to adsorb heavy metal ions from aqueous solutions [16 – 19]. Gyrolite is a mineral with most likely chemical formula $NaCa_{16}Si_{24}O_{60}(OH)_8 \cdot 14H_2O$, it can be synthesized by hydrothermal treatment in CaO and SiO_2 mixture [20]. The gyrolite was first synthesized by E. P. Flint et al. It should be underlined, that this synthesis route is a very complex and time consuming process [22 – 24].

The adsorption recognized as one of the most effective methods for the removal of heavy metals from the wastewaters [25]. Generally, the adsorption mechanism is determined by the pseudo first-order and pseudo-second order equations [26 – 30]. Mostly, kinetics have been described by the first-order equation was developed by S. Lagergren [30]. In this equation one can calculate the reaction rate constant and the equilibrium adsorption capacity. However, Y. S. Ho et al. [31 – 33] described sorption, which included chemisorption and provided a different idea to the second-order equation called a pseudo-second-order rate expression. The equation has the following advantages: the sorption capacity, the rate constant of pseudo-second-order, and the initial sorption rate can all be determined from the pseudo-second-order equation without knowing any parameter beforehand. In previous studies [34 – 36], it was declared that gyrolite shows a very good cation exchange properties, i. e. the removal efficiency of Cu^{2+} ions was equal to 99.5 % and of Zn^{2+} and Cd^{2+} ions – 98 % – 99 % in alkaline medium. V. Kasperaviciute et al. [36] showed that in acidic medium gyrolite acts as chemosorbent,which can adsorb only 41.48 % of Cu^{2+} ions.

The aim of this work was determine adsorption kinetic parameters for Fe^{3+} and Ni^{2+} ions by gyrolite. Additionally, the adsorption mechanism was described by pseudo first-order equation and pseudo-second order equation.

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2. EXPERIMENTAL

Fine-grained $SiO_2 \cdot nH_2O$ ("Stanchem", ignition losses, 7.84 %; specific surface area $S_a = 1804\ m^2/kg$ by Blaine) and CaO (calcium hydroxide was burned 950 °C for 0.5 hours; $S_a = 1234\ m^2/kg$; purity 98.83 % was used as starting materials. Hydrothermal synthesis of gyrolite has been carried out in autoclave under the saturated steam pressure at 200 °C; the duration of isothermal curing was 48 hours, the molar ratio of primary mixture was $CaO/SiO_2 = 0.66$. These synthesis conditions were chosen according to previously published data [22]. The products of the synthesis have been filtered, rinsed with ethyl alcohol to prevent carbonization of materials, dried at the temperature of 50 ºC ±5 ºC and sieved through a sieve with a mesh width of 50 μm

Adsorption experiments were carried out at 25 °C temperature in the thermostatic absorber Grant SUB14 by stirring 1 g of gyrolite in 100 ml of $Ni(NO_3)_2 \cdot yH_2O$ and $Fe(NO_3)_3 \cdot yH_2O$ solutions containing $0.25\ g\ Me/dm^3$ (where Me^{x+} is Ni^{2+}, Fe^{3+} ions respectively) for 60 min. The concentrations of heavy metal ions were determined using a Perkin-Elmer Analyst 4000 spectrometer. The value of pH was taken by Hanna instrument (Hi 9321, microprocessor pH meter).

In order to determine kinetic parameters of adsorption reactions, a kinetic models have been developed and fitted for the adsorption process of the Ni^{2+} and Fe^{3+} ions into gyrolite. The S. Largergren model [30], 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 capacities at equilibrium and at time t_e, respectively ($mg \cdot g^{-1}$), 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 [31 – 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 ($g \cdot mg^{-1} \cdot min^{-1}$). 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):

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

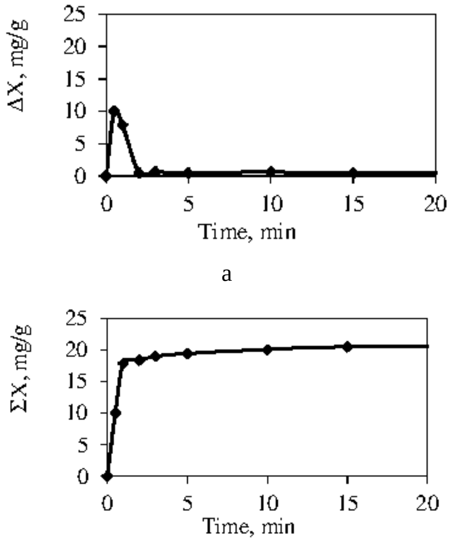
The X-ray powder diffraction (XRD) data were collected with a DRON-6 X-ray diffractometer with Bragg–Brentano geometry using Cu K_α radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range 2°– 60° (2θ) in steps of 2θ = 0.02°.

Simultaneous thermal analysis (STA: differential scanning calorimetry – DSC and thermogravimetry – TG) was also employed for measuring the thermal stability and phase transformation of samples at a heating rate of 15 °C/min, the temperature ranged from 30 °C up to 1000 °C under air atmosphere. The test was carried out on a Netzsch instrument STA 409 PC Luxx. The ceramic sample handlers and crucibles of Pt-Rh were used.

FT-IR spectra have been recorded out with the Perkin Elmer FT-IR Spectrum X system apparatus. Specimen were prepared by mixing 1 mg of the sample with 200 mg of KBr. The spectral analysis was performed in the range of $4000\ cm^{-1} – 400\ cm^{-1}$ with spectral resolution of $1\ cm^{-1}$.

3. RESULTS AND DISCUSSION

It was found that the adsorption of nickel ions proceeds intensively at the beginning of the process because after 30 s the amount of adsorbed ions by gyrolite was equal to 10 mg Ni^{2+}/g when the initial concentration of Ni^{2+} ions was 0.25 g Ni^{2+}/dm^3 (Fig. 1, a). It was determined that the adsorption rate slightly increases by prolonging the experiment duration due to exchange in the quantity of incorporated Ni^{2+} ions. After 15 min, the equilibrium (20.84 mg Ni^{2+}/g) is attained and the removal of mentioned ions is complete (Fig. 1, b).

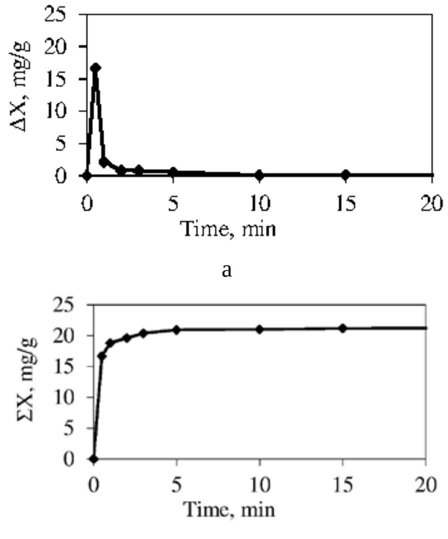


a

b

Fig. 1. Differential (a) and integral (b) kinetic curves of Ni^{2+} ions adsorption by gyrolite

In this case, calcium ions are released from the crystal lattice of gyrolite into the solution when the charge of the host is changed in order to maintain its neutrality. Most of Ca^{2+} ions (16.7 mg Ca^{2+}/g) are released in the first minutes of adsorption. Later on, the concentration of Ca^{2+} ions increases slightly with increase of adsorption duration. These results are in good agreement with the data of previuos work [11, 14, 34 – 36]. It was observed that the desorption process of calcium ions ended within 5 min (21.3 mg Ca^{2+}/g) (Fig. 2, b). It should be underlined that pH value of medium rapidly increases when adsorbent was mixed with solution (Fig. 3). This change is attributed to the degree of release of Ca^{2+} ions from the structure of the gyrolite solid in solution during the reaction. Therefore, it is no coincidence that the pH value of solution varied from 5.39 to 7.68 only at the beginning of reaction (Fig. 3). It was determined that the intrusion of metal ions into adsorbent structures depends also on the pH of solution due to the extremely high and selective uptake of Fe^{3+} ions (Table 1). It was determined that the elimination of mentioned ions is completed within 30 s because all iron ions (24.5 mg Fe^{3+}/g, i. e. 98 % – 99 %) are adsorbed. Also, the additional amount of Ca^{2+} ions (20.96 mg Ca^{2+}/g) were realised from undefined structure of gyrolite crystal lattice, i. e. interlayers, which contain Ca^{2+} ions and H_2O molecules (Table 1).



a

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

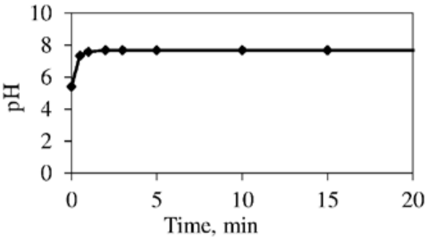


Fig. 3. Variation of acidic solution pH value

Table 1. Variation of adsorbed Fe^{3+} ions, desorbed Ca^{2+} ions and pH during adsorption

Time, min	Adsorbed Fe^{3+}ions		Desorbed Ca^{2+} ions		pH
	ΔX, mg/g	∑X, mg/g	ΔX, mg/g	∑X, mg/g	
0.5	24.49	24.49	18.02	18.02	2.10
1	0.09	24.58	1.00	19.02	2.51
2	0.10	24.69	1.50	20.52	2.59
3	0.14	24.83	0.19	20.71	3.64
5	0.03	24.86	0.07	20.78	4.79
10	0.03	24.89	0.07	20.85	5.24
15	0.05	24.93	0.10	20.95	6.09
60	0.04	24.97	0.01	20.96	6.39

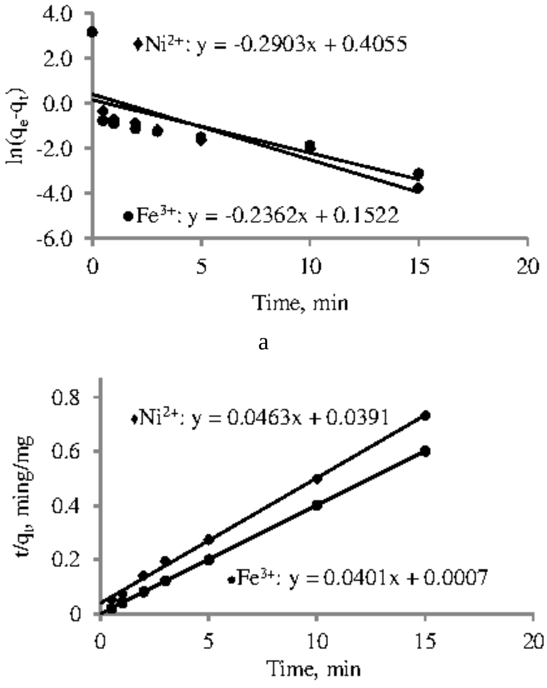
In this case, the significant change of pH value in reaction medium was observed at the beginning of adsorption (3 min – 10 min) because the value of pH varied from 2.10 to 6.39 (Table 1).

Thus, it is clearly seen that the adsorption of Ni^{2+} and Fe^{3+} ions from aqueous solutions by gyrolite is a quite complex process. Several authors [11, 13, 21] reported that the partial exchange $Ca^{2+} \leftrightarrow M^{x+}$ proceeds at the same time in both directions, i. e. the cation exchange reaction of these ions is reversible. Meanwhile, our results have shown that gyrolite acts as a chemisorbent but not like usual adsorbent. In order to confirm this fact, after adsorption process gyrolite substituted with Ni^{2+} or Fe^{3+} ions was dried up and immersed in distilled water. It was proved that Me^{x+} ions did not appear in the solution after 60 minutes at 25 °C. Thus, the latter process is irreversible.

It was found that in the acidic solution the intrusion of Fe^{3+} ions into gyrolite structure proceeds by two types of chemical reaction mechanisms: substitution and addition. It was estimated that the ion exchange occurs between divalent and trivalent ions because Ca^{2+} ions were replaced 77 % of Fe^{3+} ions as remaining part of these ions are combined by gyrolite according to addition reaction. Meanwhile, nickel ions were participated only in substitution reaction: gyrolite-Ca^0 + $Me^{x+} \leftrightarrow$ gyrolite-Me^0 + Ca^{2+}.

In order to determine adsorption kinetic parameters, the mentioned reactions were described by pseudo first-order equation and pseudo-second order equation.

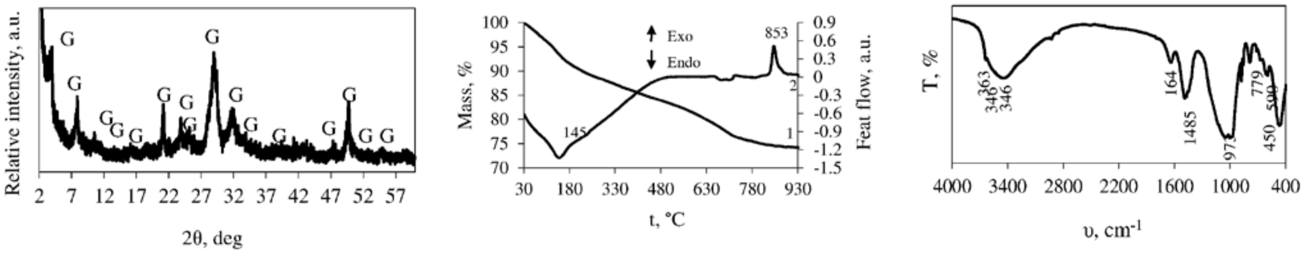
A Largergren equation (2) was used to calculate the rate constants (k_1) of reaction and the equilibrium concentrations (q_e) of heavy metals (Table 2). It was found that the calculated $q_{e(cal)}$ values disagreed with the experimental $q_{e(exp)}$ values as well as the values of correlation coefficients (R^2) are quite low: for Fe^{3+} ions – $R^2 = 0.48$ and for Ni^{2+} ions – $R^2 = 0.96$.



a

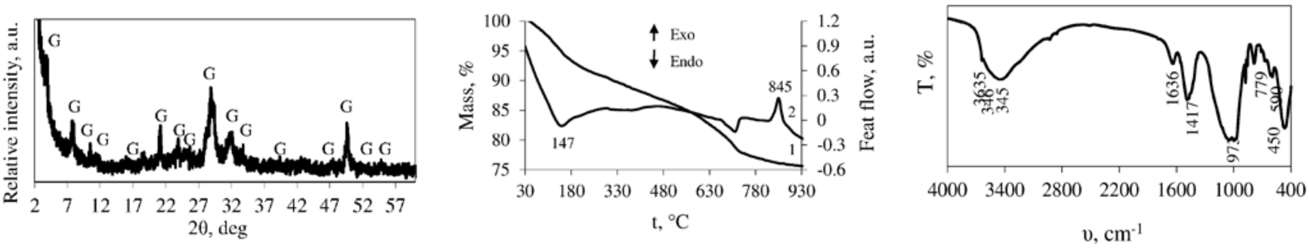
b

Fig. 4. Pseudo first-order (a) and pseudo-second order (b) kinetic plots in acidic solutions



a b c

Fig. 5. X-ray diffraction pattern (a), DSC – TG curves (b) and FT-IR spectrum (c) of gyrolite. Duration of hydrothermal synthesis at 200 °C is 48 h. Indexes: G – gyrolite



a b c

Fig. 6. X-ray diffraction pattern (a), DSC – TG curves (b) and FT-IR spectrum (c) of gyrolite substituted wit Fe^{3+} ions. Indexes: G – gyrolite

Thus, the obtained results suggest that the pseudo first order equation did not fit well for iron and nickel ions adsorption mechanism description (Fig. 5, a, Table 2).

By using the pseudo second order kinetics equation (4), the equilibrium adsorption capacity ($q_{e(exp)}$) and the second order constants k_2 ($g \cdot mg^{-1} \cdot min^{-1}$) was determined experimentally from the slope and intercept of plot t/q_t versus t (Fig. 4, b). 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. It was found that the Fe^{3+} ions adsorption rate ($k_2 = 2.30\ g \cdot mg^{-1} \cdot min^{-1}$) 46 times is higher than the nickel ion ($k_2 = 0.05\ g \cdot mg^{-1} \cdot min^{-1}$) (Table 2). These data agree with experimental results: Fe^{3+} ions adsorption reactions (Table 1) proceed more rapid than nickel ions (Fig. 1).

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

Me^{x+}	R^2	$q_{e(exp.)}$, $mg \cdot g^{-1}$	$q_{e(cal.)}$, $mg \cdot g^{-1}$	k, $g \cdot mg^{-1}\ min^{-1}$
Pseudo first-order kinetic models				
Ni^{2+}	0.96	20.84	11.99	–
Fe^{3+}	0.48	24.97	1.02	–
Pseudo second-order kinetic models				
Ni^{2+}	0.99	20.84	21.60	0.05
Fe^{3+}	1	24.97	24.94	2.30

R^2 – correlation coefficient; $q_{e(exp)}$ – the equilibrium adsorption capacity, $mg \cdot g^{-1}$, calculated from experimental data (Fig. 1, Table 1); $q_{e(cal)}$ – the equilibrium adsorption capacity, $mg \cdot g^{-1}$, calculated by using equations (3) and (4) of kinetic models.

In order to identify the stability of adsorbent, gyrolite was characterized by numerous methods of instrumental analysis.

X-ray diffraction analysis showed that after adsorption experiment the structure of gyrolite remains stable in the solution, although the intensity of typical diffraction peaks slightly decreases due to calcium ions desorption into the solution (Fig. 5, a; Fig. 6, a). It should be noted that no other compounds were observed after adsorption in XRD pattern.

The XRD results were confirmed by STA and FT-IR analysis. In DSC curve were identified the same thermal effects in both samples (before and after the adsorption process): endothermic effect at 145 °C typical to water dehydration and exothermic effect at 853 °C – characterizes the formation of wollastonite (Fig. 5, b; Fig. 6, b).

The FT-IR spectrum showed a sharp peak near $3639\ cm^{-1}$, which is visible only in the gyrolite spectrum and proves that clearly distinguished OH– [37] positions exist in the structure of this compound, which are connected only with Ca atoms and are not influenced by hydrogen bridge links. A wide absorption band near $3457\ cm^{-1}$ means the opposite that molecular water forms hydrogen bridge links in the interlayers. The bands in the range of $1636\ cm^{-1}$ frequency are assigned to $\delta(H_2O)$ vibrations and confirm this presumption. Also, it was determined a doublet near ~ 590 and ~ $612\ cm^{-1}$ due to Si-O-Si bending vibrations, the band at ~ $973\ cm^{-1}$ due to the Si-O stretching mode of nonbinding oxygens, and the band at ~ $645\ cm^{-1}$ due to the Si-O-Si bonds [37] (Fig. 5, c; Fig. 6, c).

CONCLUSIONS

The adsorption capacity of gyrolite and intrusion of heavy metals ions in its structure depends on reaction time and the pH value of adsorptive. It was determined that the incorporation of Fe^{3+} ions occurs more intensive than Ni^{2+}

ions because after 30 s only 40 % of them (10 mg Ni^{2+}/g) are intercalated into the structure of gyrolite, whereas Fe^{3+} ions – almost 98 % (24.49 mg Fe^{3+}/g).

It was found that in the acidic solution the intrusion of Fe^{3+} ions into gyrolite structure proceeds by two types of chemical reaction mechanisms: substitution and addition. Meanwhile, nickel ions were participated only in substitution reaction:

$$\text{gyrolite-Ca}^0 + \text{Me}^{x+} \leftrightarrow \text{gyrolite-Me}^0 + \text{Ca}^{2+}.$$

It was observed that the pseudo second order model fit well for iron and nickel ions adsorption mechanism description because the calculated $q_{e(\text{cal})}$ values agreed with the experimental $q_{e(\text{exp})}$ values. By the way, it was found that the Fe^{3+} ions adsorption rate ($k_2 = 2.30\ \text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) 46 times is higher than the nickel ion ($k_2 = 0.05\ \text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$). These data agree with experimental results.

It was estimated that the adsorption reactions are not reversible process, because almost all heavy metal ions are chemisorbed by gyrolite.

It was found that the crystal structure of gyrolite is stable in acidic solutions and its stability does not depend on examined adsorption conditions (60 min, 25 °C) and the concentration of heavy metals ions.

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REFERENCES

1. **Siegel, F. R.** Environmental Geochemistry of Potentially Toxic Heavy Metals. Springer-Verlag, Berlin Heidelberg, 2002: 223 p. http://dx.doi.org/10.1007/978-3-662-04739-2
2. **Parmar, M., Thakur, L. S.** Heavy Metal Cu, Ni and Zn: Toxicity, Health, Health Hazards and Their Removal Techniques by Low Cost Adsorbents: a Short Overview *International Journal of Plant, Animal and Environmental Sciences* 3 2013: pp. 143 – 157.
3. **Renge, V. C., Khedkar, S. V., Pandey Shraddha, V.** Removal of Heavy Metals from Wastewater Using Low Cost Adsorbents: a Review *Siences Review Chemical Communications* 2 (4) 2012: pp. 580 – 584.
4. **Wan Ngah, W. S., Hanafiah, M. A. K. M.** Removal of Heavy Metal Ions from Wastewater by Chemically Modified Plant Wastes as Adsorbents: A Review *Bioresource Technology* 99 2008: pp. 3935 – 3948. http://dx.doi.org/10.1016/j.biortech.2007.06.011
5. **Kadirvelu, K., Thamaraiselvi, K., Namasivayam, C.** Removal of Heavy Metal from Industrial Wastewaters by Adsorption onto Activated Carbon Prepared from an Agricultural Solid Waste *Bioresource Technology* 76 2001: pp. 63 – 65.
6. **Williams, C. J., Aderhold, D., Edyvean, G. J.** Comparison Between Biosorbents for The Removal of Metal Ions from Aqueous Solutions *Water Research* 32 (1) 1998: pp. 216 – 224.
7. **Barakat, M. A.** New Trends in Removing Heavy Metals from Industrial Wastewater *Arabian Journal of Chemistry* 4 (4) 2011: pp. 361 – 377.
8. **Agarwal, S. K.** Heavy Metal Pollution *New Delhi* 2009: pp. 7 – 14.
9. **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.
10. **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.
11. **Labhasetwar, N., Shrivastava, O. P.** $Ca^{2+}\leftrightarrow Pb^{2+}$ Exchange Reaction of Calcium Silicate Hydrate: $Ca_5Si_6O_{18}H_2\cdot 4H_2O$ *Journal of Materials Science* 24 1989: pp. 4359 – 4362. http://dx.doi.org/10.1007/BF00544512
12. **Komarneni, S., Roy, D. M., Roy, R.** Al-substituted Tobermorite: Shows Cation Exchange *Cement and Concrete Research* 12 (6) 1982: pp. 773 – 780. http://dx.doi.org/10.1016/0008-8846(82)90041-2
13. **Komarneni, S., Roy, D. M.** Tobermorites: a New Family of Cation Exchangers *Nature* 221 1983: pp. 647 – 648.
14. **Komarneni, S., Roy, R., Roy, D. M.** Pseudomorphism in Xonotlite and Tobermorite With Co^{2+} and Ni^{2+} Exchange for Ca^{2+} at 25 °C *Cement and Concrete Research* 16 (1) 1986: pp. 47 – 58. http://dx.doi.org/10.1016/0008-8846(86)90067-0
15. **Komarneni, S., Tsuji, M.** Selective Cation Exchange in Substituted Tobermorites *American Ceramic Society* 72 (9) 1989: pp. 1668 – 1674.
16. **Komarneni, S., Roy, D. M., Fyfe, C. A., Kennedy, G. J., Bothner-By, A. A., Dadok, J., Chesnick, A. S.** 27Al and 29Si Magic Angle Spining Nuclear Magnetic Resonance Spectroscopy of Al-substituted Tobermorites *Materials Science* 20 1985: pp. 4209 – 4214.
17. **Lopes, C. B., Coimbra, J., Otero, M., Pereira, E., Duarte, A. C., Lin, Z., Rocha, J.** Uptake of Hg^{2+} from Aqueous Solutions by Microporous Titano- and Zircono-silicates *Quimica Nova* 31 (2) 2008: pp 321 – 325.
18. **El-Korashy, S. A.** Studies on Divalent Ions Uptake of Transition Metal Cations by Calcite through Crystallization and Cation Exchange Process *Journal of Materials Science* 38 (8) 2003: pp. 1709 – 1719.
19. **Lujaniene, G., Meleshevych, S., Kanibolotskyy, V., Mazeika, K., Strelko, V., Remeikis, V., Kalenchuk, V., Sapolaite, J.** Synthesis and Characterization of Inorganic Sorbents and Their Application to Sorption of Radionuclides *Lithuanian Journal of Physic* 48 2008: pp. 107 – 114.
20. **Baltušinkas, A., Lukošiūtė, I., Levinskas, R., Gybėnas, A., Baltakys, K., Eisinas, A.** Analysis of Rietveld Method Application for Gyrolite Crystal Structure Refinement *Materials Science* (*Medžiagotyra*) 18 (4) 2012: pp. 379 – 384.
21. **Šiaučiunas, R., Janickis, V., Palubinskaite, D., Ivanauskas, R.** The Sorption Properties of Tobermorite Modified with Na^{2+} and Al^{3+} Ions *Ceramics Silikaty* 48 (2) 2004: pp. 76 – 82.
22. **Merlino, S.** Gyrolite: Its Crystal Structure and Crystal Chemistry *Mineralogical Magazine* 52 1988: pp. 377 – 387.
23. **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, $Ca_{16}Si_{24}O_{60}(OH)_8·14H_2O$ *American Mineralogist* 87 2002: pp. 533 – 541.

24. **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.
25. **Cheung, C. W., Porter, J. F., McKay, G.** Sorption Kinetic Analysis for The Removal of Cadmium Ions from Effluents Using Bone Char *Water Research* 35 (3) 2001: pp. 605 – 612.
26. **Ho, Y. S.** Selection of Optimum Sorption Isotherm *Carbon* 42 (10) 2004: pp. 2115 – 2116.
27. **Ho, Y. S., McKay, G.** The Kinetics of Sorption of Divalent Metal Ions onto Sphagnum Moss Peat *Water Research* 34 (3) 2000: pp. 735 – 742. http://dx.doi.org/10.1016/S0043-1354(99)00232-8
28. **Ho, Y. S., McKay, G.** Sorption of Dyes and Copper Ions Onto Biosorbents *Process Biochemistry* 38 (7) 2003: pp. 1047 – 1061.
29. **Ho, Y. S., Wang, C. C.** Pseudo-isotherms for the Sorption of Cadmium Ion onto Tree Fern *Process Biochemistry* 39 (6) 2004: pp. 759 – 763. http://dx.doi.org/10.1016/S0032-9592(03)00184-5
30. **Lagergren, S.** About the Theory of So-called Adsorption of Soluble Substances *Kungliga Svenska Vetenskapsakademiens Handlingar* 24 (4) 1898: pp. 1 – 39.
31. **Ho, Y. S. Wase, D. A. J., Forster, C. F.** The Adsorption of Divalent Copper Ions from Aqueous Solution by Sphagnum Moss Peat *Trans IChemE Part B* 17 1994: pp. 94 – 185.
32. **Ho, Y. S., Wase, D. A. J., Forster, C. F.** Batch Nickel Removal from Aqueous Solution by Sphagnum Moss Peat *Water Research* 29 (5) 1995: pp. 1327 – 1332.
33. **Ho, Y. S., Wase, D. A. J., Forster, C. F.** Kinetic Studies of Competitive Heavy Metal Adsorption by Sphagnum Moss Peat *Environmental Technology* 17 (1) 1996: pp. 71 – 77.
34. **Bankauskaitė, A., Baltakys, K.** The Sorption of Copper Ions by Gyrolite in Alkaline Solution *Materials Science-Poland* 27 (3) 2009: pp. 899 – 908.
35. **Kasperaviciute, V., Baltakys, K., Siauciunas, R.** The Sorption Properties of Gyrolite for Copper Ions *Ceramics-Silikaty* 52 (2) 2008: pp. 95 – 101.
36. **Baltakys, K., Eisinas, A., Barauskas, I., Prichockiene, E., Zaleckas, E.** Removal of Zn(II), Cu(II) and Cd(II) from Aqueous Solution Using Gyrolite *Journal of Scientific and Industrial Research* 71 (8) 2012: pp. 566 – 572.
37. **Garbev, K.** Structur, Eigeschaften und Quantitative Rietveldanalyse von Hydrothermal Cristallisierten Calciumsilikthydraten (C-S-H-Phasen) *Dissertation*. Forschungszentrum Karlsruhe GmbH, 2004: 241 p.