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The Kinetics of Manganese Sorption on Ukrainian Tuff and Basalt—Order and Diffusion Models Analysis

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Abstract: The study aimed to determine the nature of the kinetics of the manganese sorption process on Ukrainian tuff and basalt at different temperatures characteristic of the natural water environment. The scope of the research included manganese sorption kinetic test on natural mineral sorbents at temperatures of 10, 17.5 and 25 °C in slightly acidic conditions. Sorption (pseudo-first order, pseudo-second order and Elovich models) and diffusion kinetic models (liquid film diffusion and intraparticle diffusion) were used in the analysis of test results. The manganese sorption process on both tuff and basalt proceeded quickly. The dynamic equilibrium state of manganese sorption settled after 35 and 45 min on tuff and basalt respectively. Although the process took place in a slightly acidic environment and below pH_{pZC} of the sorbents, possible electrostatic repulsion did not inhibit the removal of Mn. The Mn sorption on both materials followed the PSO kinetics model. Based on the diffusion kinetic models, it was determined that Mn sorption process on both materials was influenced by diffusion through the boundary layer and intraparticle diffusion. The differences in removal efficiency and rate of Mn sorption in the temperature range of 10–25 °C were not found.

Keywords: manganese removal; saponite; hematite; andesine; pseudo-first order; pseudo-second order; Elovich model; liquid film diffusion model; intraparticle diffusion kinetic model

1. Introduction

Natural mineral materials are widely applied in environmental engineering especially for soil remediation [1,2]. They are also used for water and wastewater treatment fundamentally as filtering beds [3–5]. Natural mineral materials are often used as adsorbents and ion exchangers [6–11], but also as coagulant aids [12,13] or deacidifying media [14]. Along with technical development the variety of mined minerals increases, while research methods for characterizing their properties are being developed. This results in diversity and precision of technological applications of minerals with specific properties.

Groundwater treatment technology is based on using mineral materials. The main metals and compounds removed from groundwater are iron, manganese, ammonium ion and hydrogen sulphide. Applying the various types of materials consisting of and coated with MnO_x is recognized in various technical solutions including mechanical, chemical and biological processes of contaminations removal [15]. These technologies are related to the granular filter media and the redox processes. An alternative approach, especially for manganese removal, may be adsorption-based fluidized bed

technology. Here it is also possible to use rock material, such as powdered clay minerals, zeolites or others. Clay minerals and zeolites are known for their high adsorption ability to remove heavy metals or ammonium ions [16–21]. Additionally, metal oxides, frequent components of soils and rocks, are also good adsorbents for heavy and transition metals removal [22,23]. The modification of clay minerals like smectites by iron or aluminum oxides leads to obtaining pillared materials with increased adsorption capacity [24].

However, in nature, it is also possible for such minerals to co-exist. The Ukrainian volcanic tuff from Ivanodolinsky quarry consists mainly of saponite and hematite [25], which provides the basis for research work to assess its adsorption properties for possible environmental applications. Natural materials may show mineral diversity within the deposit, therefore the production of synthetic minerals with repeatable and simultaneously modified properties is also a popular trend [21]. In the Ivanodolinsky quarry, tuffs occur together with basalt rock [25] and study of the properties of this rock is equally needed. Due to the lower price, unmodified natural materials are often tested for their ability to remove pollutants, especially as they are available locally [1,9,11,19,26].

Saponites are rated as a good low-cost sorbents for water purification from heavy metals [27]. As they are characterized by the ability of cation exchange, including ammonium ion, they are considered as the materials with potential use in water treatment [21,28]. Additionally the saponite's active centers can be heterogeneous as a result of coexisting other minerals, e.g., hematite [28]. These are the essential features of the material in terms of its practical application. The more that, the saponite can be effectively separated from water by the electrochemical method [29–31], which confirms the possibility of its use in fluidized bed reactors. However, when analysing the review [6,21] and research works [24,27,28,31–33] on the sorption of inorganic pollutants on smectites, it can be noticed that the researchers focus on removing the following ingredients: Cd, Cr, Cu, Hg, Li, Na, Ni, Pb, Zn, as well as the ammonium ion or radionuclides. Work on the removal of Mn on a saponite is definitely less common, although this removal is of course possible [33]. Due to the common Mn occurrence in groundwater and considering the use of saponite rock in groundwater treatment, the studies on Mn sorption seems to be necessary.

The sorption process is characterized in equilibrium and by the description of its kinetics. Kinetics and sorption equilibrium studies have been gaining popularity in recent decades and are the subject of many publications [6,14,26,34,35]. In literature, there are huge numbers of models enabling description of sorption kinetics. They may be divided into two basic groups: models based on chemical reaction order and models based on molecules diffusion. The most often found kinetic models based on reaction order are pseudo-first order (PFO), proposed by Lagergren [36] and pseudo-second kinetic model (PSO), also called Ho model [37]. The Elovich Equation neglects desorption and is known to describe chemisorption well [38,39]. The less common are models based on molecules diffusion: liquid film diffusion (IFM) [40] and intraparticle diffusion model (IPD) [41] broadening the scope of the sorption mechanism assessment. The temperature of the system in equilibrium studies is differentiated because of the evaluation of thermodynamic parameters. One of the research factors often applied in kinetics sorption studies is concentration of the contamination in the solution and dosage of adsorbent, but the influence of temperature on the kinetics is rarely analyzed. It is often tested at one temperature, often at room temperature (22–25 °C) [34,35,42–45], but also 30 °C and even 50 °C [6]. However, the temperature influences the adsorption rate of metal cations on inorganic sorbents and is important in the course of kinetic process [6]. As experimentally demonstrated, at low temperature (3–10 °C) the sorption efficiency on some mineral materials (halloysite, limestone sand, zeolite, diatomite) may decrease, especially in the case of the removal of the heavy metals [46]. The study of the temperature factor seems to be particularly important for the environmental applications of sorption materials, especially for groundwater treatment, which is the naturally cold water.

The study aimed to determine the nature of the kinetics of the manganese sorption process on Ukrainian tuff and basalt at different temperatures characteristic of the natural water environment. The scope of the research included manganese sorption kinetic test on natural mineral sorbents at

temperatures of 10, 17.5 and 25 °C in slightly acidic conditions. Sorption and diffusion kinetic models were used in the analysis of test results.

2. Materials and Methods

2.1. Preparation of Minerals

The volcanic tuff and basalt from the Ivanodolinsky quarry (Rivne region, Ukraine) were investigated. Both materials were used in the raw form and the physically bound water wasn't removed since the experiment covered the conditions for the practical use of minerals without thermal treatment. The materials were used in the form of powder. At the beginning they were grounded, then sieved to obtain a particle size lower than 0.1 mm.

2.2. Determination the Point of Zero Charge

The point of zero charge pH (pH_{PZC}) of materials tested was determined by the batch equilibration [34,47]. Accordingly, the samples of air-dried materials (0.2 g) were shaken in PVC vials for 24 h with 40 mL of 0.01 and 0.1 mol/L KNO_3 , at different pH values in the range 2.0–11.0. Initial pH values were obtained by adding an amount of KOH or HNO_3 solution (0.1 mol/L). Determination of the point of zero charge was performed in duplicate, and the mean values were presented. Hach HQ40D-Multimeter with gel electrode (Hach Company, Loveland, CO, USA) was used to mark pH of the sample.

2.3. Adsorption Kinetics Experiment

The kinetic experiment was carried out by a batch method at temperatures of 10, 17.5 and 25 ± 0.1 °C. Two liters of a $MnCl_2$ solution in double-distilled water with Mn concentration of 10 mg/L and a pH 6.0 were prepared. Then 2.0 g of the air-dried mineral material was added to the solution and it was kept mixed. At set time intervals, samples of 10 mL were taken to analyze the Mn concentration. The mineral powder was separated from the solution by two-minute centrifugation (10,000 rpm). The samples of the tested sorbents were collected after the time ranging from 5 to 100 min. Atomic absorption spectrophotometer AA990 (PG Instruments Ltd., Wibtoft, Leicestershire, UK) was used to determine the Mn concentration in solution. HQ40D-Multimeter with gel electrode was used to mark pH of the sample. Kinetics experiments were realized in duplicate series.

The concentrations of Mn retained in sorbent phase in time were calculated from the following expression (Equation (1)):

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad (1)$$

The removal efficiency of Mn was calculated from the following expression (Equation (2)):

$$R.E. = \frac{C_0 - C_e}{C_0} \cdot 100\% \quad (2)$$

2.4. Kinetics Models

The kinetic equations (Equations (3)–(10)) used in the work are presented in the Table 1. The PFO and PSO models have been applied in general form (nonlinear model). As shown in many works [37,39,48] regression analyses using linearized function of originally nonlinear PFO and PSO models often lead to incorrect results and false conclusions.

Table 1. Equations of the applied kinetic models.

Model	Equation	References
Models based on chemical reaction order		
PFO	(3) $q_t = q_e(1 - e^{-k_1 t})$	[36]
PSO	(4) $q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$	[37]
	(5) $R_w = \frac{1}{1 + k_2 q_e t_{ref}}$	[49]
Elovich	(6) $q_t = \frac{1}{b} \ln(1 + ab \cdot t)$	[38,39]
	(7) $R_E = \frac{1}{q_{ref} b}$	[50]
Models based on molecules diffusion		
LFM	(8) $\ln(1 - F) = -k_f d \cdot t$	[40]
	(9) $F = q_t / q_e$	
IPD	(10) $q_t = k_i t^{0.5} + c_i$	[41]

Usually one of mentioned models describes experimental points in a better way which authors mostly confirm by higher coefficient R^2 . Their validities can be determined by the calculation of the standard deviation. The best-fit model is the one with the lowest value of SD (Equation (11)), and the one in which the value of R^2 is closer to unity. The calculations were made in an Excel spreadsheet using Solver.

$$SD = \sqrt{\frac{\sum [(q_{exp} - q_{cal}) / q_e]^2}{N - 1}} \cdot 100 \quad (11)$$

For kinetic models based on the chemical reaction order (PFO, PSO and Elovich models) the error functions were also calculated as follows: the sum of the squares of the errors ERRSQ (Equation (12)), average relative error ARE (Equation (13)), Fisher's test TF (Equation (14)) and chi-square test χ^2 (Equation (15)) [51]:

$$ERRSQ = \sum_1^N (q_{exp} - q_{cal})^2 \quad (12)$$

$$ARE = \frac{100}{N} \sum_1^N \left| \frac{q_{exp} - q_{cal}}{q_{exp}} \right| \quad (13)$$

$$TF = \frac{(N - p) \sum_1^N (q_{exp} - \frac{1}{N} \sum_1^N q_{exp})^2}{(N - 1) \sum_1^N (q_{exp} - q_{cal})^2} \quad (14)$$

$$\chi^2 = \sum_1^N \left(\frac{(q_{exp} - q_{cal})^2}{q_{cal}} \right) \quad (15)$$

3. Results and Discussion

3.1. Characteristics of Minerals

The minerals have been described as sorbents in our previous studies [25]. Table 2 presents results of the nitrogen adsorption/desorption analysis. Comparing to other natural mineral materials, tuff and basalt are characterized by medium-sized specific surface area, yet the porous structure of tuff is more developed. The XRD analysis showed that volcanic tuff consists of saponite (58% *w/w*), quartz (22%), hematite (17%) and a small amount of analcime (3%), whereas in basaltic rock consists mainly of

andesine (93%), with an admixture of saponite (7%) [25]. The XRD diagrams of tuff and basalt are shown in Figure 1.

Table 2. Structure parameters of volcanic tuff and basalt from Ivanodolinsky quarry [25].

Material	SSA _{BET} (m ² /g)	Total Pore Volume (cm ³ /g)	Average Pore Radius (nm)
Volcanic tuff	79.3	0.113	2.76
Basaltic rock	28.6	0.048	2.37

Figure 1. X-ray diffraction patterns of (a) tuff and (b) basalt. Reprinted with permission from Reference [25].

3.2. Point of Zero Change

Experimental results of the pH_{PZC} determination are illustrated in Figure 2. The pH_{PZC} of tuff is at pH 8.9. This is consistent with the identified pH_{PZC} values of the minerals that form it: 8.2 of smectite [52], 6.0 of smectite-rich clay soil [53], 6.5–8.5 of hematite [54] and <5 of quartz [54]. The pH_{PZC} of Ukrainian basalt rock consists mainly of plagioclase (andesine) equals 8.5. Similar result (pH_{PZC} 7.6) was obtained in the case of volcanic basalt rock from Ethiopia, also rich in plagioclases [34]. By analyzing the research system, the pH of solution (6.0) was lower than pH_{PZC} of used sorbents. In this case, the surfaces of aluminosilicate minerals receive a slightly positive charge, because the protonation of silanol groups occurs at very low pH and only aluminol groups are easy protonated [55]. However, the pH-dependent charge is lesser for smectite and makes up 5–10% of the surface. Studies on the removal of Cd, Pb and Cu on Turkish smectite have shown that the sorption process is inhibited only in an acidic environment at pH < 4 [56]. Only hematite's adsorption properties significantly depends of the pH of the solution [55]. Therefore, the slightly acidic pH of the solution, typical for

groundwater, can a bit adversely affect the adsorption by an electrostatic repulsion, but does not exclude it.

Figure 2. Determination of pH_{PZC} of tuff and basalt in KNO_3 solutions.

3.3. Effect of Contact Time

Figure 3 shows the impact of contact time on Mn ion sorption on tested materials at temperatures of 10, 17.5 and 25 °C. The equilibrium state of Mn sorption on tuff settled in a relatively short time after about 35 min at all tested temperatures. In the case of basalt, the dynamic equilibrium of Mn sorption was established after 45 min. During the first 15 min, the Mn sorption process on both tuff and basalt proceeded quickly due to the high availability of active sites on the surface of each of the sorbents tested. They are the favorable results comparing with other minerals characterized by equilibrium adsorption time 30–180 min [6]. Adsorption of Mn on another rock material Turkish kaolinite, required even up to 120 min to reach equilibrium [57].

Figure 3. The equilibrium state of Mn sorption on tuff (T) and basalt (B) at temperature 10, 17.5 and 25 °C.

The degree of Mn ion removal efficiency during sorption on tuff and basalt at the temperatures tested is summarized in Table 3. The lowering of Mn concentration at all temperatures tested was higher on tuff, about 50%. In the case of basalt, it was 21.5%. No influence of temperature (in the tested range) on the effectiveness of Mn removal was found. This is beneficial while using these materials for treatment of low temperature water. pH has been changing during manganese sorption in the Mn–tuff and Mn–basalt systems (Figure 4). Simultaneously with the removal of

Mn cations from the solution, its pH was increasing. In both analyzed systems the pH was rising from 6.0 to 6.5. As stated above, tuff contains a significant amount of saponite, and basalt consists mainly of andesine. Saponite is the phyllosilicate of the smectite group with the chemical formula $(\text{Ca}_{0.5},\text{Na})_{0.3}(\text{Mg},\text{Fe}^{2+})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and andesine belonging to plagioclases is expressed as $\text{Na}_{0.7-0.5}\text{Ca}_{0.3-0.5}\text{Al}_{1.3-1.5}\text{Si}_{2.7-2.5}\text{O}_8$ [58]. Changes in pH may indicate that the alkali and alkaline earth metals present in the minerals are exchanged with the Mn present in the solution. The MnCl_2 , salt of weak base and strong acid, dissociates in water and causes $\text{pH} < 7$ (6.0). When Mn is exchanged for Ca and Na, salts of strong bases and strong acids begin to dominate in the solution, and the pH tends to 7. The increase in pH may also be partly due to the dissolution of the alkaline components of the rock, not associated with Mn removal. This applies to basalt, the series of which is ascending and not flattened like a kinetic curve. From a technological point of view, a slight increase in water pH is acceptable.

Table 3. R.E. of Mn sorption on tuff and basalt at 10, 17.5 and 25 °C in a state of equilibrium (tuff–35 min, basalt–45 min).

Material	R.E., %		
	10 °C	17.5 °C	25 °C
Tuff	50.4	48.6	49.7
Basalt	21.4	21.5	21.5

Figure 4. Changes of pH in the solution during Mn sorption on the tested materials.

3.4. Models Based on Chemical Reaction Order

Figure 5 shows the experimental data of the sorption of Mn on tuff and basalt at the tested temperatures together with the curves calculated from the three kinetic models based on reaction order (pseudo-first order, pseudo-second order and Elovich models). Points from the equilibrium area were excluded when experimental results were fitted by models [39,59]. It was found that PSO equation is superior to other two ones for the description of kinetic data. The fitness is justified based on the fact that R^2 are within 0.8528–0.9918 and 0.8375–0.9354, respectively (Table 4). At the same time, analyzing the SD standard values for Mn sorption kinetics models on the tested tuff and basalt materials, the low SD values obtained for the PSO and Elovich models indicate a better fit of the experimental data with the pseudo-second order kinetics model. This [60] could suggested chemical nature of the sorption of Mn on tuff and basalt. Similar phenomena has been observed for various mineral materials [6,16,34,61].

Figure 5. Regression analysis of the sorption on Mn on tuff and basalt by PFO (dashed line), PSO (solid line) and Elovich (dotted line) models.

The error functions used for the reaction-order models (Equations (12)–(15)) confirm that the PSO model best approximates the experimental data. However, the coefficient of determination R^2 does not always give an unequivocal result; sometimes between individual model the insignificant differences make it difficult to unambiguously analyze and indicate a specific model. As shown by Chutkowski et al. [51], relying on one selected optimization criterion may result in the risk of incorrect indication of the optimal sorption kinetics model. The parallel occurrence of several other errors can eliminate the risk of making mistakes. The results of applied error functions (ERRSQ, ARE, TF and χ^2) presented in Table 4 made it possible to confirm the course of sorption in accordance with the PSO model.

Table 4. Parameters of sorption kinetics models based on reaction order, characterized by coefficient of determination, standard deviation and the error functions.

Tuff									
PFO Model	q_e mg/g	k_1 1/min	R^2	SD		ERRSQ	ARE	TF	χ^2
10 °C	5.2	0.23	0.9362	0.036		0.1418	2.5373	12.0966	0.0288
17.5 °C	5.1	0.21	0.9404	0.021		0.0529	1.3014	36.9299	0.0105
25 °C	5.0	0.27	0.8177	0.046		0.2478	3.7851	4.8286	0.0498
PSO Model	q_e mg/g	k_2 g/(mg·min)	R^2	SD	R_W	ERRSQ	ARE	TF	χ^2
10 °C	5.6	0.065	0.9918	0.012	0.01	0.0177	0.9335	97.1013	0.0035
17.5 °C	5.5	0.062	0.9791	0.037	0.02	0.1469	2.6028	13.3081	0.0326
25 °C	5.3	0.095	0.8528	0.043	0.01	0.2203	3.1705	5.4315	0.0433
Elovich Model	a mg/g·min	b g/mg	R^2	SD	R_E	ERRSQ	ARE	TF	χ^2
10 °C	55.0	1.57	0.7667	0.048	0.13	0.1800	3.2419	9.5294	0.0394
17.5 °C	101.5	1.80	0.7881	0.087	0.11	0.5762	6.1464	3.3932	0.1370
25 °C	196.0	1.89	0.7337	0.066	0.11	0.3984	4.5675	3.0036	0.0797
Basalt									
PFO Model	q_e mg/g	k_1 1/min	R^2	SD		ERRSQ	ARE	TF	χ^2
10 °C	2.4	0.13	0.8537	0.094		0.1811	8.1872	4.9676	0.0893
17.5 °C	2.2	0.35	0.8501	0.029		0.0203	2.1287	5.3365	0.0094
25 °C	1.8	0.22	0.6209	0.102		0.1369	7.3550	2.0458	0.0792
PSO Model	q_e mg/g	k_2 g/(mg·min)	R^2	SD	R_W	ERRSQ	ARE	TF	χ^2
10 °C	2.8	0.059	0.9354	0.056	0.04	0.0738	4.5153	12.1924	0.0326
17.5 °C	2.3	0.352	0.8733	0.027	0.01	0.0172	2.0998	6.3122	0.0079
25 °C	2.0	0.131	0.8375	0.068	0.02	0.0577	4.9277	4.8569	0.0355
Elovich Model	a mg/g·min	b g/mg	R^2	SD	R_E	ERRSQ	ARE	TF	χ^2
10 °C	1.9	2.14	0.9728	0.054	0.19	0.0626	4.3843	14.3639	0.0279
17.5 °C	5.1	2.60	0.8382	0.120	0.18	0.2780	9.4243	0.3897	0.1203
25 °C	8.1	4.19	0.9503	0.239	0.21	0.1072	6.5275	2.6125	0.0634

To present chemisorption the PSO and Elovich models, the approaching equilibrium factors R_W and R_E were calculated (Table 4). The values of the R_W in the Mn–tuff system are in the range 0.01–0.02, while in the Mn–basalt system 0.01–0.04 at applied temperatures. Therefore, in both cases of tuff and basalt are in the range of $0.1 > R_W > 0.01$, which allows classifying the considered sorptive–sorbent system into zone II. That means the equilibrium in both sorption systems is not complicated to achieve [49]. The values of the R_E factor are within 0.11–0.13 and 0.18–0.21 in the Mn–tuff and Mn–basalt sorption system respectively. They are consistent with the chemical nature of Mn sorption on the both materials. The R_E values are in the region of $0.3 > R_E > 0.1$ corresponding to zone II with the curve of sorption with “mildly rising”. In contrast to R_W the values of R_E for basalt are higher at each temperature than those obtained for tuff as sorbent, which confirms that Mn sorption on basalt occurs more slowly than on tuff [50]. Obtained values of reaction rate k_2 as well as R_W and R_E factors show no dependence of temperature that means the sorption occurs with the relatively same speed in the range of 10–25 °C.

3.5. Diffusion Kinetic Models

Liquid film diffusion model is applicable at slow processes of adsorbate flow through the liquid film surrounding the adsorbent particles, which determines kinetics of the process [40]. A linear plot of $\ln(1 - q_t/q_e)$ vs. t with zero intercepts suggests that adsorption kinetics is controlled by a diffusion

through liquid film surrounding the solid sorbents. The k_{fd} was calculated from the slope of the straight line plot and its values are presented in Figure 6, along with R^2 . The similarity to the unity value of R^2 (0.8154–0.9365) for tuff and (0.7921–0.9526) for basalt respectively indicated an adequate fitting of film diffusion model. However, the straight lines did not pass through the origin thereby suggesting that film diffusion might not be the sole rate-limiting step [62,63].

Figure 6. Liquid film diffusion kinetic plot for Mn sorption on: (a) tuff and (b) basalt.

The mass transfer into the interior of the particle, characterized by an intraparticle diffusion coefficient, can be the slowest step. The most commonly used is the intraparticle diffusion model (IPD) of Weber and Morris. The IDP model for Mn on tuff and basalt is shown in Figure 7. The slope of the plots gave the values of k_i presented in Table 5. The plots are not linear over the whole time range, indicating that more than one step is involved in the sorption of Mn on tuff and basalt. The intraparticle diffusion kinetic plots in fragmented form showed two types of linearity indicating two diffusion stages of Mn adsorption onto tuff and basalt. For Mn sorption on both tuff and basalt, at tested temperature range the first stage plot passed near the origin, whereas the second one did not. It was concluded that the second stage was controlled by both film and intraparticle diffusions. For Mn sorption on both mineral sorbents, at all temperatures tested, the $k_{i1} > k_{i2}$ was attributed to the faster rate of film diffusion than intraparticle diffusion. It was concluded that the sorption kinetics might be controlled by film diffusion and intraparticle diffusion simultaneously.

Figure 7. Intraparticle diffusion kinetic plot for Mn sorption on: (a) tuff (T) and (b) basalt (B) in fragmented form.

Table 5. Parameters of intraparticle diffusion model, characterized by coefficient of determination and standard deviation.

Temperature	k_{i1} mg/g·min ^{0.5}	c_{i1} mg/g	R^2	SD	k_{i2} mg/g·min ^{0.5}	c_{i2} mg/g	R^2	SD
Tuff								
17.5 °C	0.56	2.45	0.9852	0.002	0.06	4.91	0.7885	0.006
	0.58	2.18	0.8179	0.094	0.09	4.47	0.4602	0.020
25 °C	0.58	2.34	0.8179	0.081	0.09	4.63	0.4600	0.019
Basalt								
10 °C	0.33	0.62	0.9847	0.028	0.04	2.00	0.7198	0.012
17.5 °C	0.23	1.10	0.8515	0.005	0.01	2.14	0.2515	0.005
25 °C	0.22	0.81	0.9999	0.001	0.12	1.12	0.0849	0.075

4. Conclusions

The Mn sorption process on both tuff and basalt proceeded quickly and the dynamic equilibrium state was achieved after 35 and 45 min respectively. Although the process took place in a slightly acidic environment and below pH_{PZC} of the sorbents, possible electrostatic repulsion did not inhibit the removal of Mn. During the kinetic studies the systems reached the equilibrium and in this state the sorption capacity of the tuff was twice as high as on the basalt (5.5 mg/g and 2.4 mg/g respectively). The better sorption properties of the tuff was due of high content of saponite (58% *w/w*), the layered mineral from the smectite group characterized by ion-exchange properties, as well as hematite (17%) the well-known metals sorbent.

The Mn sorption on both materials follows the PSO kinetics model. Based on R_W factor values in both sorption systems the achievement of equilibrium is not complicated. The reaction rate k_2 and R_E factor confirm that Mn sorption on basalt occurs more slowly than on tuff. Research has shown that in the temperature range of 10–25 °C there are no differences in removal efficiency and rate of Mn sorption. This is beneficial while using these materials for treatment of low temperature water. Based on the diffusion kinetic models, it was determined that Mn sorption process on both materials is influenced by diffusion through the boundary layer and intraparticle diffusion.

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Nomenclature

a	initial sorption rate, mg/g·min
ARE	average relative error
b	desorption constant related to the extent of surface coverage and activation energy for chemisorption, g/mg
B	basalt
c_i	intercept of IPD model, mg/g
C_0	initial concentration of Mn, mg/L
C_e	equilibrium concentration of Mn, mg/L
C_t	concentration of Mn at defined time, mg/L
ERRSQ	the sum of the squares of the errors

F	fractional attainment of equilibrium, equals q_t/q_e
IPD	intraparticle diffusion model
k_{fd}	film diffusion rate constant, min^{-1}
k_i	intraparticle diffusion rate constant, $\text{mg/g}\cdot\text{min}^{0.5}$
k_1	pseudo-first constant, min^{-1}
k_2	pseudo-second constant, $\text{g}/(\text{mg}\cdot\text{min})$
LFM	liquid film diffusion model
m	mass of sorbent, g
N	number of data points
PFO	pseudo-first order model
PSO	pseudo-first order model
p	number of model parameters
pH_{PZC}	point of zero change, -
pH_i	initial value of pH, -
pH_f	final value of pH, -
q_t	sorption capacity in time, mg/g
q_{cal}	calculated sorption capacities, mg/g
q_e	amount of sorption at equilibrium, mg/g
q_{exp}	experimental sorption capacities, mg/g
q_{ref}	amount of sorption at time $t = t_{\text{ref}}$, mg/g
$R.E.$	removal efficiency, %
R^2	coefficient of determination, -
R_E	approaching equilibrium factor based on Elovich equation, -
R_W	approaching equilibrium factor in the PSO model, -
SD	standard deviation, %
SSA_{BET}	specific surface area by Brunauer-Emmett-Teller (BET) method, m^2/g
T	tuff
TF	Fisher's test
t	time, min
t_{ref}	longest time of sorption process, min
V	volume of sample, L
χ^2	chi-square test

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