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Modelling of kinetics of lithium sorption onto Mn-based adsorbents obtained via solid state reaction

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Abstract

Lithium recovery from brines (oilfield brines, geothermal waters, mine tailings) is reported as a sustainable method of lithium production. Mn-based adsorbents offer a high sorption capacity hence are often applied for lithium harvesting. In this study two Mn-based adsorbents were prepared via solid state reactions. The morphology of materials were evaluated with a scanning electron microscopy (SEM) confirming the high surface area. After activation the sorbents were contacted with a model brine to test sorption kinetics. Three different kinetic models including the pseudo-first order rate equation, the pseudo-second order rate equation and logistic model were fitted to the experimental data. The results indicate that experiments are well described by the pseudo-second order rate equation. Conditions for sorption to occur are favorable: sorbents reach a high sorption capacity of about 10-12 mg/g in a short time (less than 2 hour). Further research should focus on optimization of sorption conditions (pH, temperature, sorbent regeneration).

Keywords: oilfield brine; lithium recovery; sorption; kinetics; modelling

1. Introduction

The role of lithium is crucial to the development of electromobility, for one Tesla S model with a 70kWh battery about 63 kg of lithium carbonate is needed (**Goonan, 2012**). According to Bloomberg NEF, in 2030 global demand for lithium could reach 2 million tons of Li_2CO_3, or five times its sales in 2021 (**"BloombergNEF Ups Battery Demand Forecast", 2021**). Poland and the European Union are importers of lithium, there are no large and easily accessible deposits of lithium-bearing raw materials in Europe hence lithium was included in the list of critical elements (**Blengini et al., 2020**). Moreover, in Poland there is a significantly demand for lithium is growing due to the development of lithium-ion battery factories. In Lower Silesia two large lithium-ion battery factories are being built: the Korean LG Energy Solution in Kobierzyce and China's GTHR in Prusice. Similar factories are being built in neighboring countries. In view of the above, it is reasonable to start production of lithium from domestic resources. In Poland there are no recognized deposits of lithium-bearing minerals hence it can only be extracted from geothermal waters and formation brines (**Fijałkowska et al. 2008**). Thus, there is a need to develop a technology to recover lithium from brines. This issue strictly relates to another problem occurring in the mining industry - the increasing amount of waste water accompanying mineral extraction. In the final phase of exploitation of the hydrocarbons reservoir, mainly waste brine is extracted (as much as 15 m^3 of water per 1 m^3 of oil) (**Clark and Veil, 2009**). Similarly, in coal mining, about 3 m^3 of brine is extracted per 1 ton of coal mined (**Tsalidis et al., 2022**) and even after the mine is closed, dewatering of the pits is still required. In view of this, the method of brine treatment and management often determines the profitability of the entire project. Study of Miranda et al. (**2022)** estimates profits from recovering valuable resources from produced water in the Permian Basin, USA. Taking into account the composition and volume of produced water the metal revenue per single well could reach up to 16 000 USD in the case of lithium recovery. Trends in consumption and nominal price of lithium encourages to start new exploitation activities (**Shojaeddini et al. 2024**).

Different approaches were tested for direct lithium recovery from brines including advanced lithium ion-sieves (**Chen et al., 2024**; **Zhang et al., 2024**; **Yu et al., 2022**), membranes **(Guo et al., 2024; Zavahir et al., 2024)**, extractants (**Li et al. 2024**). Among these techniques adsorption is considered as a cost-efficient and easy-to-operate method. Mn-based materials are one of the most tested groups of sorbents for lithium recovery. The selectivity of these sorbents relies on the small ionic radius of lithium ions comparing to other alkali and earth alkali metal cations. The first proposed mechanism of lithium sorption was ion exchange reaction between Li^+ and H^+ according to the reaction **(Shen and Clearfield, 1986)**:

$HMn_2O_4 + Li^+ \rightarrow LiMn_2O_4 + H^+$

Further research of Feng et al. **(1992)** postuled that lithium incorporation into the λ-MnO_2 structure is related to the reduction of Mn(IV) to Mn(III) and release of oxygen. For many Mn-based sorbents the sorption mechanism is mixed especially that during the sorbent synthesis some undesirable impurities such as $LiMn_2O_4$ or Li_2MnO_3 may be produced and complicate sorption course. Mn-based sorbent can be synthesized by a simple solid state reaction (mixing between lithium and manganese salts followed by calcination) and this approach was used in this study as more roboust and less expensive. The alternative way to produce Mn-based materials is a hydrothermal reaction between γ -MnOOH and Li salts. The sorption capacities towards lithium for so obtained materials are high, up to 73 mg/g, but the wet chemistry route requires more advanced equipment and is time-consuming **(Safari et al., 2020)**. The activation and regeneration of all adsorbents requires an acid treatment (H^+ ions replace Li^+ in the crystal structure of sorbent). Li desorption from sorbents is accompanied by Mn loss which reduces the lifetime of the sorbent and poses a challenge in its commercialization **(Gao et al., 2019)**. Our previous study shows that Mn-based sorbents exhibit high sorption capacity and selectivity even in brines of very complex composition **(Knapik et al. 2023).** All large-scale recovery processes are carried out continuously so the kinetics of the sorption plays an important role. The aim of this paper was to study kinetics of lithium sorption from a model brine using previously synthesized sorbents to extend our findings. A novel modified logistic equation was proposed to better describe the experimental data.

2. Method section

2.1. Materials

Manganese(II) acetate tetrahydrate, hydrochloric acid and lithium carbonate were purchased from Vitaya, Poland. NaCl, KCl, $CaCl_2*2H_2O$ and $MgCl_2*2H_2O$ were analytical-grade and delivered by Pol Aura (Morąg, Poland). Standard solutions for AAS were produced by PerkinElmer (Waltham, MA, USA). The tests were performed using an artificial (model) brine containing 220 mg/kg of Li^+, 7.21 wt% of Na^+, 3.0 wt% of Ca^{2+} and 1000 mg/kg of Mg^{2+}.

2.2. Sorbents synthesis via solid state reaction

180 g of $Mn(CH_3COO)_2*4H_2O$ was mixed with 20 g of Li_2CO_3. The resulting mixture was crushed in a mortar and divided into two parts. The first batch of sorbent was calcinated at 400 ^oC for 4 hours (material denoted as MnT1) and the second at 600 ^oC (denoted as MnT2), both of which were then cooled freely (to ambient temperature). Calcination was carried out in a muffle furnace in air in an alumina crucible. The obtained materials were activated which means that Li ions were washed out from the structure using 0.1 M HCl. Delithation procedure was as follows: 5 g of sorbent

was mixed with 500 mL of distilled water and 8 g of 38% HCl. The sorbent dispersion was shaken for 1 h and left to settled down for 24 hours. After this time the solution was decanted and new portion of water and HCl was added. Washing with HCl was repeated 3 times, then the sorbent was washed similarly using 1 L of water. The concentration of Li and Mn was determined in solutions after each washing step to obtain lithium removal ratio and manganese losses. The obtained materials were dried in oven at temperature of 40 °C for 8 hours and used in kinetic study.

2.3. Analytical methods

The concentration of Li and Mn in water solutions was determined by flow injection atomic absorption spectrometry (FI-AAS) using the AAnalyst 100 Atomic Absorption Spectrometer by PerkinElmer. The surface morphology of obtained sorbents was analyzed with a scanning electron microscope (SEM, FEI Quanta FEG 250).

2.4. Kinetics of adsorption

0.5 g of sorbent was contacted with 75 g of modeled brine (alkalized with NaOH to pH=8) in 100 ml plastic container at a given contact time (from 1 minute to 24 hours). The pH was continuously monitored throughout the process. Samples of the sorbent suspension in brine with a volume of about 0.5 ml were centrifuged for 30 s at 2500 rpm and diluted to determine lithium content. Sorption capacity towards lithium at time *t* was calculated according to Eq. (1):

$$\mathrm{q_t} = V_s \frac{\mathrm{C_i - C_t}}{\mathrm{m_s}} \tag{1}$$

where C_i is the initial lithium concentration in brine (mg/L), C_t is the concentration of lithium in brine at given time *t* (mg/L), V_s is the volume of brine used in the experiment (L) and $\mathrm{m_s}$ is the mass of sorbent (g), respectively.

2.5. Modeling approach

To describe sorption kinetics three different models were used including the pseudo-first-order equation, logistic equation and the pseudo-second-order equation. The pseudo-first order (PFO) model can be described as follows (**Płaziński and Rudziński 2011**):

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{2}$$

where q_t and q_e are the amount of lithium adsorbed by the sorbent at time *t* and at equilibrium, respectively (mg/g) and K_1 is the rate constant (1/min). The linearized form of Eq. 2 is expressed as:

$$\ln{(q_e - q_t)} = \ln{q_e} - K_1 t \tag{3}.$$

The PSO model well predicts the initial stage of the sorption before reaching the equilibrium stage (Tan and Hameed 2017).

The pseudo-second-order (PSO) kinetic model can be described as (**Płaziński and Rudziński 2011**):

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{4}$$

where K_2 refers to the adsorption rate constant of PSO kinetic model. This equation can be integrated for initial condition $\mathrm{q_t} = 0$ at $\mathrm{t} = 0$ and described according to Eq. (5):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{5}.$$

The applicability of PSO and PFO do not explain the mechanism of sorption process and other more realistic models are needed. In our previous study (**Knapik and Stopa 2021**) we developed an new modified logistic equation that provides more information about interactions in studied systems in the form:

$$\frac{1}{q_t}\frac{dq_t}{dt} = F(t)(q_e - q_t) \tag{6}$$

where *F(t)* is a function of time and can be expressed as:

$$F(t) = \frac{k_{lg}}{t^{\alpha}} \tag{7}$$

where k_{lg} is an adsorption rate constant (-) and α is a constant describing sorbent-sorbate interactions. After the integration with the initial condition $q_{t\to\infty} = q_e$ we obtain:

$$q_t = \frac{q_e}{1+C\cdot exp\left(\frac{-q_e\cdot k_{lg}}{1-\alpha}\cdot t^{1-\alpha}\right)} \tag{8}$$

where *C* is the model constant.

All three models were fitted to experimental data using nonlinear regression (the least squares method in the Mathcad software). To assess the goodness of fit the RMSE (root mean square error) and chi^2 statistical criteria were applied. These parameters were calculated according to formulas:

$$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(q_{e,exp} - q_{e,calc}\right)^2} \qquad (9),$$

$$chi^2 = \sum_{i=1}^{N}\frac{\left(q_{e,exp}-q_{e,calc}\right)^2}{q_{e,calc}} \tag{10}$$

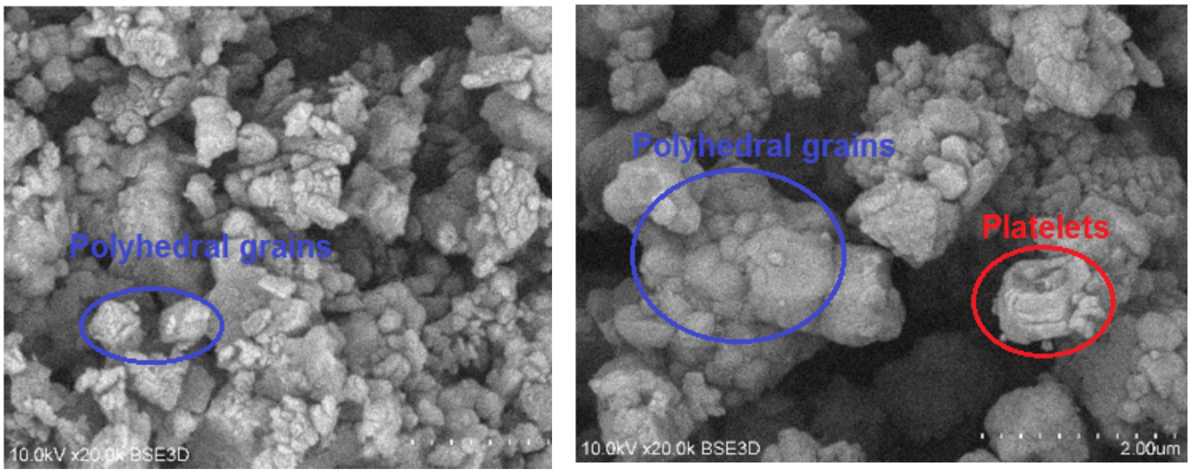
where *n* is the data numbers, $q_{e,exp}$ and $q_{e,calc}$ are the empirical and calculated values, respectively.

3. Results and discussion

MnT1 and MnT2 materials differ in the calcination temperature during their synthesis which influences their structural properties. **Table 1** summarizes the process of sorbent synthesis and **Figure 1** shows the surface morphology of both materials.

Table 1: Differences during synthesis and activation of MnT1 and MnT2 sorbents

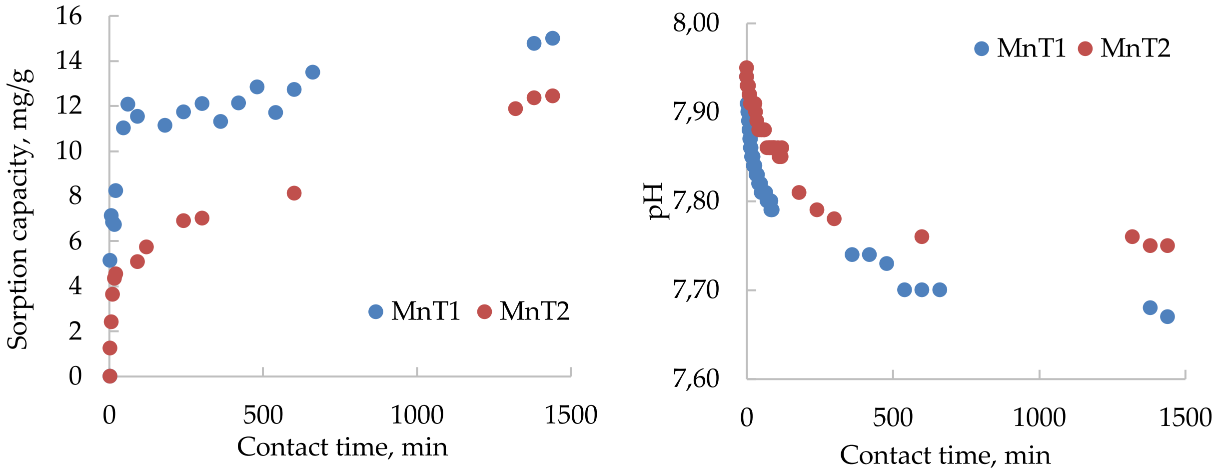
Material	MnT1	MnT2
Mass after calcination (as wt % of initial mass)	0.40	0.40
Bulk density, g/mL	0.77	0.86
Lithium removal during activation, %	96	91
Manganese losses, wt%	20	17



(a) **(b)**

Figure 1: SEM images of a) MnT1 and b) MnT2 materials

For both obtained materials the grain size is no larger than 5 µm, with most of the grains composed of smaller structures. There are both small grains in the form of platelets, strongly anisotropic as well as polyhedral grains typical for sintering process. Larger grains are covered by smaller ones. The surface area for MnT1 is larger than for MnT2, the surface of MnT2 is rougher (more fine grains). The morphology of the materials indicates that they are heterogeneous and may consist of several different crystalline structures. A higher surface area offers more active sites for sorption hence the MnT1 material has better sorption properties than the MnT2 (**Figure 2**).



(a) **(b)**

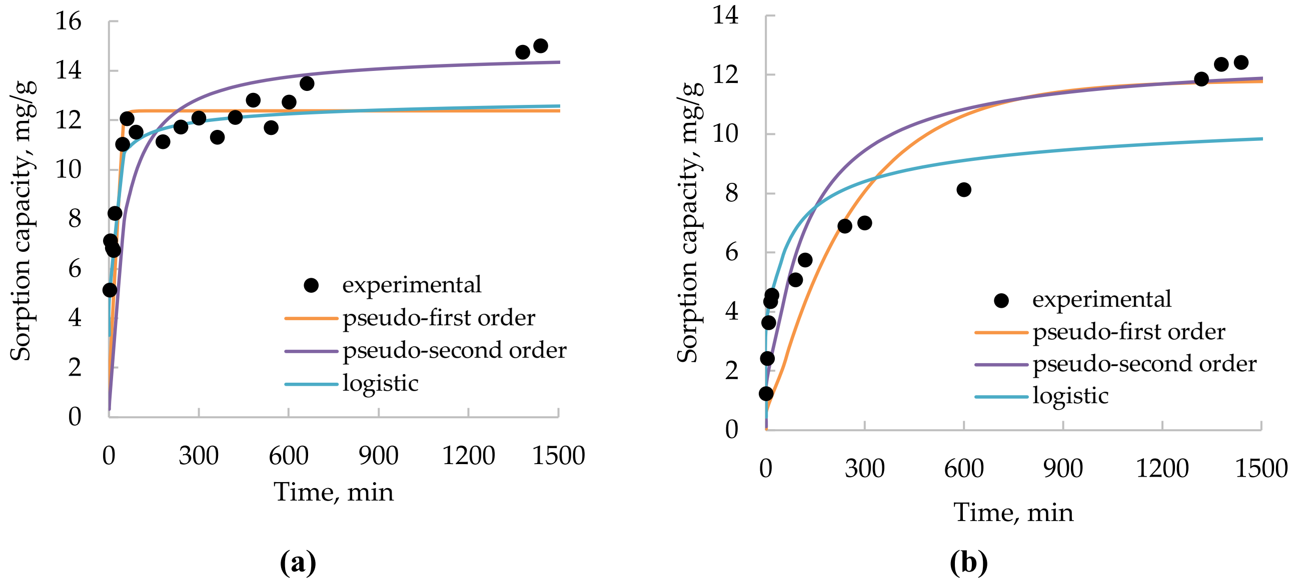
Figure 2: Changes in a) sorption capacity towards lithium and b) pH during lithium recovery from a model brine

The contact time significantly affects the sorption of lithium as shown in **Figure 2**. The MnT1 material is almost twice as effective as material MnT2 (at least during the initial sorption period). Changes in sorption capacity are strictly correlated with changes in pH value which is related to the mechanism of the process itself. Obtained results confirm that adsorbents work on the principle of ion exchange. Lithium, which incorporates into the structure of the sorbent, displaces H^+ ions from it, which causes a decrease in pH. It is an equilibrium exchange, 1 mole of Li^+ ions displaces 1 mole of H^+. The sorption occurs relatively fast, after 2 hours of contact both materials reach about 80% of available capacity. The sorption equilibrium is established after 24 hours of contacting. The maximum sorption loading for lithium is 15.004 and 12.435 mg/g for MnT1 and MnT2 materials, respectively. The obtained materials have better (or at least similar) sorption capacities to other Mn-based materials reported in the literature as shown in **Table 2**. The initial composition of brine and synthesis path of sorbent strongly influence sorption capacity. The direct comparison is difficult because test conditions differ greatly and for each raw material (seawater or brine) sorption needs to be tested individually.

Table 2: Comparison of sorption capacities of selected Mn-based sorbents

Sorbent (name or structure)	Synthesis	Brine	Sorption capacity, mg/g	Reference
MnT1	Solid-state reaction	Artificial brine (Li^+: 220 mg/L)	15.004	this study
MnT2	Solid-state reaction	Artificial brine (Li^+: 220 mg/L)	12.435	this study
λ-MnO_2	Hydrothermal synthesis	Salt lake at pH 8 (Li^+: 20 mg/L)	1	Marthi and Smith, 2019
λ-MnO_2	Solid-state reaction	Spiked seawater (Li^+: 3.5 mg/L)	1.7	Chitrakar et al., 1990
$H_{1.6}Mn_{1.6}O_4$	Hydrothermal synthesis/calcination	LiCl solution (Li^+: 150 mg/L)	6.22	Herrmann et al., 2022
$Li_{1.6}Mn_{1.6}O_4$	Sol–gel, hydrothermal and heat treatment	Seawater (Li^+: 6.08 mg/L)	10.05	Liu et al., 2015
$Li_{1.5}Mn_2O_4$	Hydrothermal reaction	Artificial seawater (Li^+: 10 mg/L)	15.3	Kitajou et al., 2003
$Li_{1.33}Fe_xMn_{1.67-x}O_4$	Solid-state reaction	Salt lake brine from the Salar de Uyuni, Bolivia (Li^+: 1630 mg/L) at pH 7.2	28	Chitrakar et al., 2014

Figure 3 and **Table 3** summarize the fitting of kinetic models to experimental data.



(a) **(b)**

Figure 3: Fitting of kinetic models to experimental data for a) MnT1 and b) MnT2 materials

Table 3: Kinetic parameters for the recovery of Li from model brine

Model	Parameters	MnT1	MnT2
Pseudo-first order	K_1, 1/min	0.076	0.0038
	q_e, mg/g	12.38	11.811
	chi^2	24.381	114.636
	RSME	1.665	2.087
Pseudo-second order	K_2, g/(mg*min)	0.0015	0.0008
	q_e, mg/g	14.763	12.697
	chi^2	108.409	31.492
	RSME	2.669	1.848
Modified logistic	q_e, mg/g	18.607	13.392
	k_{lg}	0.023	0.086
	C	0.04	0.1
	α	1.098	1.203
	chi^2	1.628	4.866
	RSME	0.911	1.506
Maximum sorption capacity determined experimentally, q_{exp}, mg/g		15.004	12.435

Lower values of the RSME and chi^2 for the PSO model than for the PFO model confirm that the PSO model is more effective when describing the sorption of lithium on the tested sorbents. The maximum sorption capacities predicted by PSO model are consistent with experimental values. Despite the used model the constant rate for MnT1 material are higher than for MnT2 which suggest that sorption is more intense/privileged for the MnT1. The proposed logistic equation offers the best match to experiments based on the lowest chi^2 and RSME values but overestimates maximum sorption capacities. Kinetics favours lithium sorption and high lithium uptake may be achieved under relatively short time of contact which suggest that obtained materials could be applied in real-field lithium production facilities.

4. Conclusions

The mechanism of lithium incorporation into Mn-based sorbents is well-known and current research activities focus on cost-effective and reliable synthesis of these materials. The proposed solid state reaction was successful in obtaining cheap and effective sorbents. Synthesis conditions like calcination temperature influence the sorption properties - the MnT1 material obtained at 400 ^{o}C was more effective than the MnT2 calcinated at 600 ^{o}C. The adsorption process complies well with the pseudo-second-order model. The logistic model gives a better fit to the experimental results but it requires fitting of 4 parameters while PSO only 2 and for this reason the PSO model is more useful. Different parameters (like pH, sorption, mixing method) may influence sorption effectiveness and further research should focus on process optimization.

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SAŽETAK

Modeliranje kinetike sorpcije litija na temelju manganskih adsorbenata postignutom rekacijom čvrstog stanja

Pridobivanje litija iz otopine (slojne vode, geotermalne vode, rudničke jalovine) smatra se održivom metodom za pridobivanje litija. Adsorbenti temeljeni na manganu imaju visok kapacitet sorpcije te su stoga često primijenjeni kod proizvodnje litija. Ovdje su prikazana dva adsorbenta na temelju mangana dobivena reakcijama čvrstoga stanja. Ocijenjena je morfologija materijala uporabom skenirajućeg elektronskog mikroskopa (SEM-a) na velikoj površini. Sorbenti su nakon aktivacije reagirali s testnom otopinom, a kako bi se testirala kinetika sorpcije. Uporabljena su tri različita kinetička modela: (1) jednadžbe pseudo-prvoga reda, (2) one pseudo-drugoga reda i (3) logistički model. Svi su podešeni prema eksperimentalnim podatcima. Rezultati su ukazali na najveću podudarnost kod uporabe jednadžbi pseudo-drugoga reda. Ocrtani su povoljni uvjeti za sorpciju, tj. sorbenti su u manje od dva sata dosegli visok kapacitet sorpcije od oko 10-12 mg/g. Daljna istraživanja bit će usmjerena na optimizaciju uvjeta sorpcije (pH, temperatura, regeneracija sorbenata).

Ključne riječi: slojna voda; pridobivanje litija; sorpcija; kinetika; modeliranje

Author's contributions

Ewa Knapik (Assistant Professor, PhD) - conceptualization, methodology, software, validation, investigation, resources, data curation, writing - original draft preparation, visualization, supervision, project administration, funding acquisition. **Grzegorz Rotko** (Assistant Professor, PhD) - conceptualization, investigation, writing - original draft preparation, visualization. **Marek Leszek Solecki** (Assistant, MSc.) - validation, writing - original draft preparation, writing - review and editing. **Katarzyna Chruszcz-Lipska** (Assistant Professor, PhD) - investigation, writing - original draft preparation.

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