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STUDY OF CO_2 ABSORPTION BY AN AQUEOUS SOLUTION OF POTASSIUM HUMATE WITH MICROSILICA

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The paper investigates the sorption of carbon dioxide by an aqueous solution of potassium humate with the addition of microsilica. Experimental studies of the kinetics of CO_2 sorption were conducted with different masses of microsilica (1, 5, 10, and 20 g) in the presence of 50 ml of potassium humate solution. The effect of contact time and the amount of sorbent on the efficiency of carbon dioxide sorption was determined. It was shown that an increase in the duration of the process leads to an increase in the amount of sorbed CO_2, with maximum efficiency achieved using 5 g of microsilica, for which the mass of sorbed carbon dioxide was 2.72 g. By the 160th minute of the experiment, the degree of CO_2 sorption reached approximately 15% based on the difference in gas concentrations at the inlet and outlet of the system. An analysis of the dynamics of changes in the CO_2 concentration was performed, and the integral values of the volume and mass of sorbed carbon dioxide were calculated. Based on experimental data, regression models were constructed and a generalized equation for predicting the sorption process was proposed. The results confirm the potential of the potassium humate-microsilica system for carbon dioxide capture and can be used in the development of technologies for reducing greenhouse gas emissions.

Keywords: carbon dioxide, CO_2, potassium humate, microsilica, sorption, carbon capture, gas purification, greenhouse gases.

КАЛИЙ ГУМАТЫНЫҢ МИКРОКРЕМНИЙМЕН СУЛЫ ЕРІТІНДІСІМЕН CO_2 СІҢІРУІН ЗЕРТТЕУ

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Мақалада микрокремний қосылған калий гуматының сулы ерітіндісімен көмірқышқыл газының сіңуі зерттеледі. CO_2 сорбциясының кинетикасын эксперименттік зерттеу 50 мл калий гуматы ерітіндісінің қатысуымен әртүрлі микрокремний массаларымен (1, 5, 10 және 20 г) жүргізілді. Байланыс уақыты мен сорбент мөлшерінің көмірқышқыл газын сіңіру тиімділігіне әсері анықталды. Процестің ұзақтығының артуы сіңірілген CO_2 мөлшерінің артуына әкелетіні, ең жоғары тиімділікке 5 г микрокремнийді қолданғанда қол жеткізілетіні көрсетілді, ол үшін сіңірілген көмірқышқыл газының массасы 2,72 г болды. Тәжірибенің 160-шы минутында CO_2 сіңу дәрежесі жүйенің кіріс және шығысындағы газ концентрацияларының айырмашылығына негізделген шамамен 15%-ға жетті. CO_2 концентрациясының өзгеру динамикасын талдау

жүргізілді және сіңірілген көмірқышқыл газының көлемі мен массасының интегралдық мәндері есептелді. Тәжірибелік деректер негізінде регрессиялық модельдер құрылды және сорбция процесін болжауға арналған жалпыланған теңдеу ұсынылды. Нәтижелер калий гуматы-микрокремний жүйесінің көмірқышқыл газын ұстап қалу әлеуетін растайды және парниктік газдар шығарындыларын азайту технологияларын әзірлеуде қолданылуы мүмкін.

Түйін сөздер: көмірқышқыл газы, CO_2, калий гуматы, микрокремний диоксиді, сорбция, көміртекті ұстау, газды тазарту, парниктік газдар.

ИССЛЕДОВАНИЕ ПОГЛОЩЕНИЯ CO_2 ВОДНЫМ РАСТВОРОМ ГУМАТА КАЛИЯ С МИКРОКРЕМНЕЗЕМОМ

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В работе исследован процесс поглощения углекислого газа водным раствором гумата калия с добавлением микрокремнезёма. Проведены экспериментальные исследования кинетики сорбции CO_2 при различных массах микрокремнезёма (1, 5, 10 и 20 г) в присутствии 50 мл раствора гумата калия. Установлено влияние времени контакта и количества сорбента на эффективность поглощения углекислого газа. Показано, что увеличение продолжительности процесса приводит к росту количества поглощённого CO_2, при этом максимальная эффективность достигается при использовании 5 г микрокремнезёма, для которого масса поглощённого углекислого газа составила 2,72 г. К 160-й минуте эксперимента степень поглощения CO_2 достигала около 15 % по разности концентраций газа на входе и выходе системы. Выполнен анализ динамики изменения концентрации CO_2, рассчитаны интегральные значения объёма и массы поглощённого углекислого газа. На основе экспериментальных данных построены регрессионные модели и предложено обобщённое уравнение для прогнозирования процесса сорбции. Полученные результаты подтверждают перспективность применения системы «гумат калия – микрокремнезём» для улавливания углекислого газа и могут быть использованы при разработке технологий снижения выбросов парниковых газов.

Ключевые слова: углекислый газ, CO_2, гумат калия, микрокремнезём, сорбция, улавливание углерода, газоочистка, парниковые газы.

Introduction. In recent decades, increasing atmospheric carbon dioxide (CO_2) concentrations have become one of the most serious environmental problems globally. The main causes of this process are the intensive combustion of fossil fuels, industrial development, and land-use change. According to the Intergovernmental Panel on Climate Change (IPCC), atmospheric CO_2 concentrations have increased from approximately 280 ppm in the pre-industrial period to more than 415 ppm in recent years, an unprecedented level in hundreds of thousands of years [1].

The increase in greenhouse gas levels leads to an increase in the greenhouse effect and causes significant changes in the Earth's climate system. According to the IPCC Sixth Assessment Report, the average global surface temperature for the period 2011–2020 was 1.09 °C above the 1850–1900 level, which is accompanied by an increase in extreme weather events, rising sea levels, and the degradation of natural ecosystems. Carbon capture and storage (CCS) is considered one of the important approaches for reducing CO_2 emissions from large stationary sources. Current CO_2 capture technologies include chemical and physical absorption, adsorption using solid sorbents, membrane separation, cryogenic separation, and related hybrid processes. Recent reviews emphasize that the development of new capture materials is focused on improving CO_2 capacity and selectivity while reducing energy consumption, regeneration requirements, and material costs [2-4].

Among alternative sorbents, humic substances and their salts have attracted increasing attention because of their availability, low cost, and abundance of oxygen-containing functional groups. Recent experimental studies have demonstrated the ability of humic acid salts to absorb CO_2. Spietz et al. [5] investigated potassium and ammonium humates prepared from oxidized lignite and experimentally determined their CO_2 absorption capacity and absorption rate. The reported absorption capacity of the humic acid salts reached up to 10.9 g CO_2/kg, confirming the potential of humate-based

materials for CO_2 capture. In addition, a recent study of humic substances obtained from brown coal in Kazakhstan reported the potential of potassium humate for CO_2 absorption, supporting the relevance of coal-derived humic substances as low-cost CO_2 sorbents [6].

Silica-based materials represent another important class of CO_2 sorbents. Their application is associated with high surface area, developed pore structure, thermal stability, and the possibility of surface functionalization. Amaraweera et al. [7] reviewed porous silica materials for CO_2 capture and highlighted the role of pore structure, surface area, and surface functional groups in determining CO_2 adsorption performance. More recent studies have demonstrated that modification of mesoporous silica can further enhance its interaction with CO_2. In particular, amine-functionalized mesoporous silica has been investigated as a promising class of regenerable solid sorbents, while hierarchical silica-containing composites have also been developed to improve surface accessibility and CO_2 capture performance [8].

The combination of organic and inorganic components provides an additional approach for controlling the surface properties and mass-transfer characteristics of CO_2 sorbents. In such systems, the organic component can provide chemically active functional groups, whereas the inorganic phase can contribute surface area, pore structure, dispersion, and mechanical stability. However, the effect of increasing the inorganic fraction is not necessarily proportional to the increase in CO_2 uptake because excessive mineral loading may alter the ratio of active organic groups to the mineral phase and affect the accessibility of the active sites [9].

These findings provide a basis for investigating potassium humate-microsilica systems as combined organic–inorganic CO_2 capture materials. At the same time, because potassium humate is prepared using KOH, the possible contribution of residual alkalinity to CO_2 uptake should be considered separately. Therefore, distinguishing the contributions of humate functional groups, residual alkaline species, and microsilica requires additional measurements of pH and residual alkalinity as well as characterization of the sorbent before and after CO_2 exposure.

An additional increase in sorption capacity can be achieved by introducing highly dispersed mineral components into the system. Of particular interest is microsilica (silica fume), an ultrafine amorphous silicon dioxide with a large specific surface area and high reactivity. Due to the presence of a large number of surface silanol groups, microsilica can increase the number of interaction sites with carbon dioxide and alter the structure of the liquid phase, facilitating the intensification of mass transfer processes [10-11].

In light of the above, studying the absorption of CO_2 by aqueous solutions of potassium humate modified with microsilica is relevant. Studying the influence of component concentration, contact time, and absorption conditions will allow us to evaluate the potential of this system for the development of environmentally friendly and cost-effective carbon dioxide capture technologies.

Scientific novelty. The scientific novelty of this study lies in the experimental determination of the effect of microsilica mass (1, 5, 10, and 20 g) on the kinetics and cumulative CO_2 uptake by an aqueous potassium humate solution under a constant solution volume of 50 mL and controlled experimental conditions. A non-monotonic dependence of CO_2 uptake on the microsilica loading was observed. The highest absolute CO_2 uptake within the investigated range was obtained with 5 g of microsilica and amounted to 2.72 g CO_2 after 160 min. The experimental data were further used to develop regression relationships describing the kinetics of the CO_2 sorption process.

Materials and methods. To evaluate the effectiveness of an aqueous solution of potassium humate modified with microsilica for CO_2 sorption, a laboratory experimental study was conducted. The primary objective was to determine the effect of microsilica content on the system's sorption properties and identify optimal sorption conditions.

The experiments were conducted in the laboratory of the Institute of Coal Chemistry and Technology (Astana, Kazakhstan) under controlled conditions. Oxidized brown coal from the Maikube deposit (Shoptykol site), containing humic substances and mineral impurities, including SiO_2, was used as the feedstock. The feedstock was crushed to a fraction of <0.5 mm and analyzed using standard methods (ISO, ASTM), including thermogravimetric analysis and determination of humic acids by acid-base extraction.

Oxidized brown coal from the Maikube deposit (Shoptykol site) was used as raw material for the study. This coal contains humic substances with a low sulfur content and medium ash content (25-28%). It also contains significant amounts of aluminum oxide (up to 30%) and phosphorus.

The calorific value of the combustible fraction of coal ranges from 29.3 to 31.4 kJ/kg. Total recoverable coal

reserves are estimated at 5.3 billion tonnes, of which 1.8 billion tonnes are suitable for open-pit mining with a low overburden ratio. For each experiment, 50 mL of potassium humate extract obtained from the same batch was used. The extract was prepared under identical extraction conditions, and no additional dilution or concentration step was applied before the CO_2 sorption experiments. Therefore, all experiments were performed using the same potassium humate solution to ensure identical initial conditions.

The feedstock was crushed to particles smaller than 0.5 mm and analyzed for the following parameters: A_d - 66.09%; W_r - 5.73%; V_d - 17.78%; S_{td} - 0.71%; C_{td} - 21.01%; H_{td} - 1.68%; N_{td} - 2.09%.

Inorganic components included: Na (0.61%), Al (0.89%), K (0.58%), Ca (0.31%), Ti (0.22%), Fe (1.11%), and Zr (0.08%). Particle size distribution ranged from 2.95 μm (D_{10}) to 452 μm (D_{90}), with a median size of 63.8 μm. X-ray diffraction analysis revealed the presence of halloysite, SiO_2, and albite.

Potassium humate was obtained by alkaline extraction using a 3% KOH solution at a coal:solution ratio of 1:7. The residual alkalinity of the potassium humate extract was not separately adjusted before the sorption experiments; therefore, its contribution to CO_2 uptake was considered in the control experiments. The process was carried out at 50–55°C with mechanical and ultrasonic treatment, which ensured the transition of humic substances into a colloidal solution.

Modified samples were prepared by adding microsilica at concentrations of 1g, 5g, 10g and 20g to 50 ml of potassium humate solution, followed by stirring until homogeneous. The experimental design included four microsilica loadings (1, 5, 10, and 20 g) with a constant volume of potassium humate solution (50 mL). The contact time was varied from 10 to 160 min at 10-min intervals. The primary response parameter used for comparison was the cumulative mass of absorbed CO_2 at the end of the experiment. Because the potassium humate was prepared using KOH, determination of the pH and residual alkalinity of the resulting potassium humate solution would provide important information for evaluating the contribution of free alkaline species to CO_2 uptake. These parameters were not determined in the present experimental series and therefore represent an important limitation of the current interpretation. Further experiments should include pH measurements and, preferably, quantitative determination of residual alkalinity before and after CO_2 exposure. Microsilica was considered an active additive, increasing the contact area and intensifying CO_2 mass transfer. Microsilica is a highly dispersed amorphous silica with a predominant silicon dioxide content. The material is characterized by high chemical purity, a significant specific surface area, and the presence of trace amounts of alkali and alkaline earth metal oxides, as well as impurity elements. Due to this composition, it exhibits high reactivity and is widely used in composite and sorption systems (Table 1).

Table 1 - Chemical composition of microsilica

Chemical Component	Mass fraction, %
SiO_2	95–99.21
Al_2O_3	0.01–0.21
Fe_2O_3	0.05–0.10
CaO	0.53–0.68
MgO	0.20–0.30
Na_2O	0.05–0.10
K_2O	0.95–1.18
P_2O_5	0.05–0.07
TiO_2	0.02–0.04
C	0.5–1.10
LOI (Loss on Ignition)	1.30
Moisture	< 0.5
pH	8.0
Density	445–580

CO_2 sorption was carried out in a vertical glass column at 23°C. A gas mixture containing 30% CO_2 and 70% N_2 was continuously passed through the sorption solution. The inlet and outlet gas flow rates were monitored during the experiments and used in the calculation of CO_2 sorption. The inlet and outlet CO_2 concentrations were determined using a CrystalLux 4000-M gas chromatograph (Figure 1).

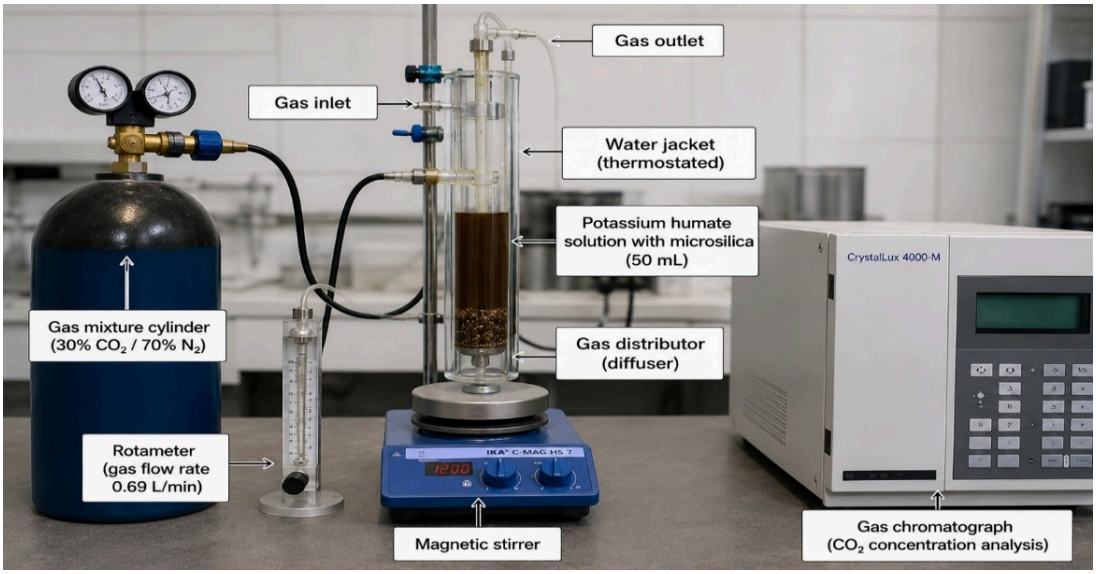

Fig. 1 - Schematic diagram of a laboratory setup for the sorption of carbon dioxide by potassium humate

The sorption capacity ($A_{(CO_2)}$) was calculated using the ideal gas equation, taking into account the volume of absorbed CO_2, pressure, and temperature. The process kinetics were described by a quadratic regression model as a function of time and microsilica concentration. The volume of absorbed CO_2 was expressed in m^3 in the calculation, while pressure was expressed in P_a and the gas constant in J/(mol·K), ensuring dimensional consistency of the equation.

The specific CO_2 absorption capacity of the potassium humate–microsilica system, $A(CO_2)$, expressed as g CO_2/kg of substance, was calculated using the ideal gas equation (Equation 1), taking into account the measured gas-phase parameters:

$$A_{CO_2} = \frac{PV}{RT} \cdot \frac{44.01}{m_s} \quad (1)$$

where:

- $A(CO_2)$ is the specific amount of absorbed CO_2 (g/kg);
- P is the absolute pressure (P_a);
- V is the volume of absorbed CO_2 (m^3);
- R is the universal gas constant (8.314 J/(mol K));
- T is the absolute temperature (K);
- 44.01 is the molar mass of CO_2 (g/mol);
- m_s is the mass of microsilica used in the experiment, kg (0.001, 0.005, 0.010, and 0.020 kg for the respective experimental samples).

The equation used allows us to quantify the sorption capacity of the potassium humate-microsilica system and compare the efficiency of various modified samples under identical experimental conditions. The calculation assumes ideal gas behaviour and uses the measured inlet and outlet gas flow parameters at each sampling interval. The inlet CO_2 flow rate was 0.69 L/min, corresponding to 0.00069 m^3/min. All gas volumes used in the calculation were converted to m^3 to maintain consistency with the SI units of pressure and the gas constant.

Results and discussion. The results of the CO_2 sorption experiments for potassium humate–microsilica systems are presented in Tables 2–6. The experiments were conducted using 50 mL of potassium humate solution with different amounts of microsilica (1, 5, 10 and 20 g). The CO_2 sorption was monitored at 10-minute intervals for a total duration of 160 min.

At the end of the experiment, the highest absolute amount of absorbed CO_2 was obtained for the system containing 5 g of microsilica and amounted to 2.72 g CO_2. For 1 g of microsilica, the absorbed amount reached 2.53 g CO_2, whereas increasing the microsilica loading to 10 and 20 g resulted in lower values of 1.76 and 1.06 g CO_2, respectively.

Therefore, under the investigated experimental conditions, increasing the microsilica loading did not result in a proportional increase in CO_2 uptake. The

maximum amount of absorbed CO_2 was observed at a microsilica loading of 5 g, reaching 2.72 g CO_2 after 160 min. Further increasing the microsilica loading to 10 and 20 g resulted in lower final CO_2 uptake values of 1.76 and 1.06 g CO_2, respectively. Thus, within the studied range, the dependence of CO_2 uptake on microsilica loading was non-monotonic, indicating that increasing the microsilica amount alone did not enhance the overall CO_2 capture capacity of the system (Figure 2).

Table 2 - CO_2 capture using microsilica sorbents in a 50 ml volume of potassium humate solution

Duration, min.	Mass of microsilica, g			
	1	5	10	20
10	0.22	0.23	0.21	0.17
20	0.43	0.46	0.42	0.35
30	0.62	0.67	0.65	0.54
40	0.79	0.88	0.88	0.74
50	0.96	1.09	1.10	0.91
60	1.12	1.28	1.33	1.06
70	1.28	1.47	1.54	1.06
80	1.44	1.66	1.76	1.06
90	1.59	1.82	1.76	1.06
100	1.74	1.97	1.76	1.06
110	1.90	2.12	1.76	1.06
120	2.07	2.27	1.76	1.06
130	2.22	2.42	1.76	1.06
140	2.38	2.57	1.76	1.06
150	2.53	2.72	1.76	1.06
160	2.53	2.72	1.76	1.06

Table 3 - Carbon dioxide sorption of 1 g of microsilica with 50 ml of potassium humate

Δt, min	Time of test (min)	V out gaz dm_3/ min	CO_2 % vol. outlet	CO_2 in - CO_2 out, % vol	Amount of absorbed CO_2, dm_3	Integral, calculation (total CO_2), dm_3	Absorbed g CO_2	g CO_2/ kg of the solution
10.000	10	0.05	5.25	24.75	0.013	0.122	0.22	0.010
10.000	20	0.05	7.18	22.82	0.012	0.241	0.43	0.019
10.000	30	0.05	7.52	22.48	0.012	0.351	0.62	0.028
10.000	40	0.05	11.12	18.88	0.010	0.450	0.79	0.035
10.000	50	0.06	12.78	17.22	0.010	0.543	0.96	0.043
10.000	60	0.06	13.71	16.29	0.009	0.635	1.12	0.050
10.000	70	0.06	13.32	16.68	0.009	0.726	1.28	0.057
10.000	80	0.06	14.13	15.87	0.009	0.813	1.44	0.064
10.000	90	0.06	14.91	15.09	0.009	0.899	1.59	0.071
10.000	100	0.06	15.07	14.93	0.008	0.985	1.74	0.077
10.000	110	0.06	14.55	15.45	0.009	1.075	1.90	0.084
10.000	120	0.06	13.24	16.76	0.009	1.169	2.07	0.092

10.000	130	0.06	13.18	16.82	0.009	1.259	2.22	0.099
10.000	140	0.06	14.74	15.26	0.009	1.344	2.38	0.106
10.000	150	0.06	15.16	14.84	0.008	1.429	2.53	0.112
10.000	160	0.06	15.08	14.92	0.008	1.429	2.53	0.112

Table 4 - Carbon dioxide sorption of 5 g microsilica with 50 ml potassium humate

Δt, min	Time of test (min)	V out gaz dm_3/ min	CO_2 % vol. outlet	CO_2 in - CO_2 out, % vol	Amount of absorbed CO_2, dm_3	Integral, calculation (total CO_2), dm_3	Absorbed g CO_2	g CO_2/ kg of the solution
10.000	10	0.05	3.14	26.86	0.013	0.132	0.23	0.010
10.000	20	0.05	4.06	25.94	0.013	0.259	0.46	0.020
10.000	30	0.05	6.19	23.81	0.012	0.381	0.67	0.030
10.000	40	0.05	6.57	23.43	0.012	0.499	0.88	0.039
10.000	50	0.05	7.94	22.06	0.012	0.614	1.09	0.048
10.000	60	0.05	8.45	21.55	0.011	0.725	1.28	0.057
10.000	70	0.05	10.75	20.25	0.011	0.831	1.47	0.065
10.000	80	0.05	10.69	19.31	0.010	0.937	1.66	0.074
10.000	90	0.05	10.29	19.71	0.011	1.032	1.82	0.081
10.000	100	0.06	15.14	14.86	0.008	1.117	1.97	0.088
10.000	110	0.06	14.89	15.11	0.009	1.200	2.12	0.094
10.000	120	0.06	15.1	14.1	0.008	1.283	2.27	0.101
10.000	130	0.06	15.23	14.77	0.008	1.368	2.42	0.108
10.000	140	0.06	14.69	15.31	0.008	1.454	2.57	0.114
10.000	150	0.06	15.17	14.83	0.009	1.539	2.72	0.121
10.000	160	0.06	15.04	14.96	0.009	1.539	2.72	0.121

Table 5 - Carbon dioxide sorption of 10 g microsilica with 50 ml potassium humate

Δt, min	Time of test (min)	V out gaz dm_3/ min	CO_2 % vol. outlet	CO_2 in - CO_2 out, % vol	Amount of absorbed CO_2, dm_3	Integral, calculation (total CO_2), dm_3	Absorbed g CO_2	g CO_2/ kg of the solution
10.000	10	0.05	8.89	21.11	0.011	0.116	0.21	0.009
10.000	20	0.05	6.78	23.22	0.012	0.240	0.42	0.019
10.000	30	0.05	4.94	25.06	0.013	0.368	0.65	0.029
10.000	40	0.05	4.54	25.46	0.013	0.497	0.88	0.039
10.000	50	0.05	4.61	25.39	0.013	0.625	1.10	0.049
10.000	60	0.05	4.96	25.04	0.013	0.750	1.33	0.059
10.000	70	0.05	5.78	24.22	0.012	0.874	1.54	0.069
10.000	80	0.05	6	24	0.012	0.998	1.76	0.078
10.000	90	0.05	6	24	0.012	0.998	1.76	0.078
10.000	100	0.05	6	24	0.012	0.998	1.76	0.078
10.000	110	0.05	6	24	0.012	0.998	1.76	0.078

10.000	120	0.05	6	24	0.012	0.998	1.76	0.078
10.000	130	0.05	6	24	0.012	0.998	1.76	0.078
10.000	140	0.05	6	24	0.012	0.998	1.76	0.078
10.000	150	0.05	6	24	0.012	0.998	1.76	0.078
10.000	160	0.05	6	24	0.012	0.998	1.76	0.078

Table 6 - Carbon dioxide sorption of 20 g microsilica with 50 ml potassium humate

Δt, min	Time of test (min)	V out gaz dm_3/ min	CO_2 % vol. outlet	CO_2 in - CO_2 out, % vol	Amount of absorbed CO_2, dm_3	Integral, calculation (total CO_2), dm_3	Absorbed g CO_2	g CO_2/ kg of the solution
10.000	10	0.06	12.41	17.59	0.010	0.097	0.17	0.008
10.000	20	0.06	12.43	17.57	0.010	0.200	0.35	0.016
10.000	30	0.05	I.66	20.34	0.011	0.307	0.54	0.024
10.000	40	0.05	10.41	19.59	0.011	0.417	0.74	0.033
10.000	50	0.05	8.19	21.81	0.011	0.518	0.91	0.041
10.000	60	0.06	14.81	15.19	0.009	0.601	1.06	0.047
10.000	70	0.06	15.78	14.22	0.008	0.601	1.06	0.047
10.000	80	0.06	15.78	14.22	0.008	0.601	1.06	0.047
10.000	90	0.06	15.78	14.22	0.008	0.601	1.06	0.047
10.000	100	0.06	15.78	14.22	0.008	0.601	1.06	0.047
10.000	110	0.06	15.78	14.22	0.008	0.601	1.06	0.047
10.000	120	0.06	15.78	14.22	0.008	0.601	1.06	0.047
10.000	130	0.06	15.78	14.22	0.008	0.601	1.06	0.047
10.000	140	0.06	15.78	14.22	0.008	0.601	1.06	0.047
10.000	150	0.06	15.78	14.22	0.008	0.601	1.06	0.047
10.000	160	0.06	15.78	17.59	0.008	0.601	1.06	0.008

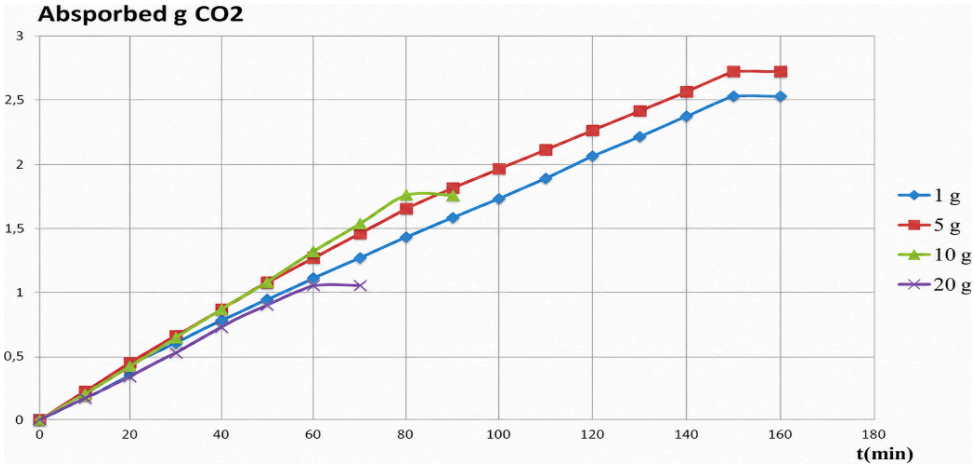

Fig. 2 - Dependence of CO_2 sorption on time during the interaction of potassium humate with microsilica (1 g, 5 g, 10 g, 20 g)

The difference between the inlet and outlet CO_2 concentrations varied during the experiment. This parameter represents the difference in gas-phase CO_2 concentration between the inlet and outlet streams and was used to estimate the amount of CO_2 removed from the gas stream over each sampling interval. It should not

be interpreted directly as the total CO_2 sorption capacity, which was calculated from the integral volume and corresponding mass of absorbed CO_2.

The enhanced CO_2 uptake observed for the potassium humate–microsilica system at a microsilica loading of 5 g may indicate a possible beneficial interaction between the components. However, the present experimental design does not provide sufficient evidence to conclusively establish a synergistic effect, since separate control experiments with potassium humate and microsilica under identical conditions were not included. Therefore, the observed improvement is described here as an enhanced CO_2 uptake of the modified system rather than as a confirmed synergistic effect.

The table presents the results of a laboratory experiment studying the dynamics of CO_2 sorption by a composite system based on silica and potassium humate. Measurements were carried out for 160 minutes with a 10-minute increment. The following parameters were recorded for each time point: the volume of outgoing gas, the outlet CO_2 concentration, the difference between the inlet and outlet carbon dioxide concentrations, the amount of absorbed CO_2 in dm^3, the integral cumulative value of the volume of absorbed CO_2, the mass of sorbed gas in grams, and the mass of sorbed CO_2 recalculated per 1 kg of solution. At the initial stages (up to 30 min), an active increase in CO_2 sorption is observed. Then, the rate of sorption increase stabilizes, and in the range from 140 to 160 minutes, a plateau is reached with an absorbed mass of carbon dioxide of approximately 2.53 g, which corresponds to 0.112 g CO_2/kg of solution. The experimental profiles demonstrate that CO_2 uptake increases with contact time, particularly during the initial stage of the experiment. With increasing contact time, the rate of uptake decreases, and a plateau-like region is observed for the systems containing 10 and 20 g of microsilica. For the 10 g system, the cumulative uptake reached approximately 1.76 g by 80 min, while for the 20 g system approximately 1.06 g was reached by 60 min. These observations may indicate that the readily accessible reactive or sorption sites had been substantially occupied under the experimental conditions. However, the observed plateau should be considered an apparent or quasi-equilibrium state rather than definitive evidence of thermodynamic equilibrium (Figure 3).

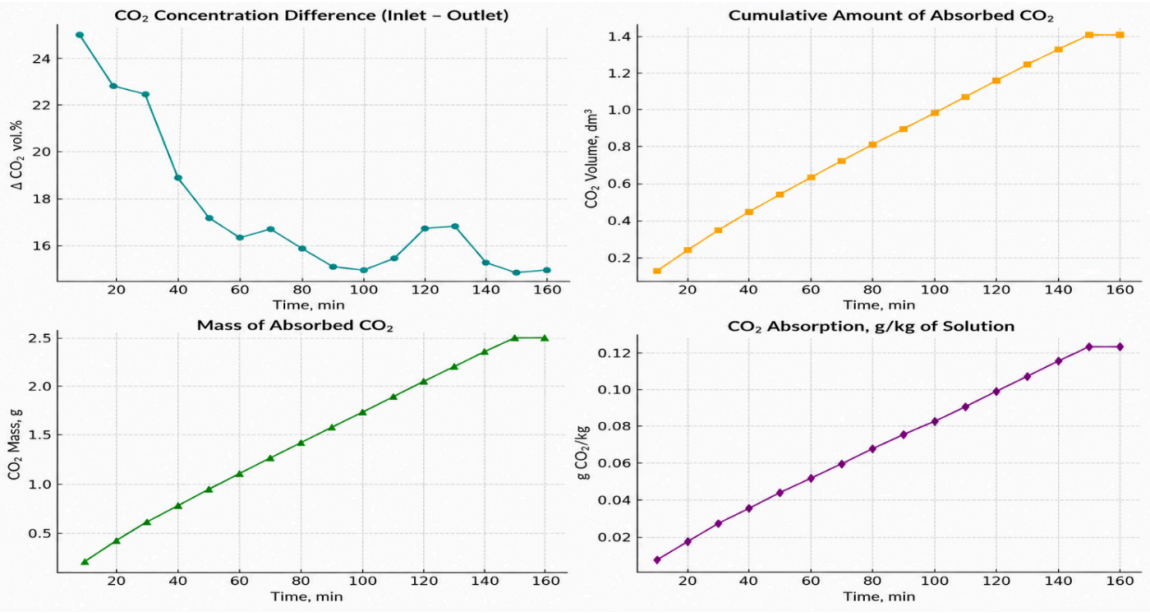

Fig. 3 - Dependence of CO_2 sorption rates on time for the "potassium humate – microsilica" system

CO_2 concentration difference (inlet - outlet) - shows how sorption efficiency changes over time.Integral amount of absorbed CO_2 (dm^3) - the cumulative value of the volume of gas absorbed. Mass of absorbed CO_2 (g) the increase in the mass of gas absorbed with increasing interaction time. CO_2 sorption per 1 kg of solution (g/kg) - the specific sorption capacity of the solution.

Below is a table 7 summarizing the regression equations for various parameters associated with the carbon dioxide (CO_2) sorption process by a silica-potassium humate composite. Each equation describes the dependence of the corresponding parameter on test time and can be used to analyze sorption kinetics.

These equations allow us to model and predict the behavior of a CO_2 sorption system over time, which is important for process optimization and sorbent efficiency assessment.

Table 7 – Regression equations for CO_2 sorption parameters

№	Parameter	Regression equation	Model Type	Symbols
1	CO_2 concentration difference (inlet-outlet), vol. %	$y = -0.067t + 25.35$	Linear	y – CO_2 concentration difference (% vol.), t – test time (min)
2	Integral amount of absorbed CO_2, dm³	$y = 0.0006t^2 + 0.010t + 0.01$	Polynomial	y – accumulated CO_2 (dm³), t – test time (min)
3	Mass of absorbed CO_2, g	$y = 0.011t + 0.01$	Linear	y – mass of sorbed CO_2 (g), t – test time (min)
4	CO_2 sorption per 1 kg of solution, g/kg	$y = 0.0007t + 0.0005y$	Linear	y – CO_2 sorption per 1 kg of solution (g/kg), t – test time (min)

Based on the regression equations presented for various parameters of the carbon dioxide (CO_2) sorption process by a silica-potassium humate composite, we can propose a generalized equation describing the kinetics of CO_2 sorption over time.

Since the integral amount of CO_2 absorbed (in dm³) reflects the cumulative nature of the process and takes into account changes in concentration, mass, and specific sorption, its equation can be considered generalized in formula 2:

$$V_{CO_2} = -1.159 \times 10^{-8}t^2 + 1.090 \times 10^{-5}t + 2.406 \times 10^{-5} \quad (2)$$

where:

1. $V_{CO2}(t)$ is the integral amount of absorbed CO_2 in dm³ at time t (min);
2. t is the test time in minutes.

This equation reflects the nonlinear nature of the accumulation of adsorbed CO_2 over time, consistent with experimental observations. The equation can be used for:

1. Predicting sorbent efficiency at various stages of the process;
2. Optimizing the contact time of the gas mixture with the sorbent to maximize CO_2 sorption;
3. Comparative analysis of various sorption systems and experimental conditions.

The equation serves as a useful tool for modeling and analyzing CO_2 sorption processes in laboratory and industrial settings.

Assuming a linear relationship between the sorbent mass and the volume of sorbed CO_2, the generalized equation for mass m (g) takes the formula 3:

$$\begin{aligned} V_{CO_2} = &-1.007 \times 10^{-4} + 1.358 \times 10^{-5}t - 2.070 \times 10^{-8}t^2 \\ &+3.015 \times 10^{-4}m - 1.362 \times 10^{-6}m^2 - 1.386 \times 10^{-8}mt - 2.093 \times 10^{-9}mt^2 \end{aligned} \quad (3)$$

where: m - mass of silica in grams.

Based on the data, the equations for different sorbent masses will be as follows:

For 1 g of sorbent (Formula 4):

$$V_{CO_2} = -1.159 \times 10^{-8}t^2 + 1.090 \times 10^{-5}t + 2.406 \times 10^{-5} \quad (4)$$

For 5 g of sorbent (Formula 5):

$$V_{CO_2} = -2.349 \times 10^{-8} t^2 + 1.361 \times 10^{-5} t - 5.179 \times 10^{-5} \quad (5)$$

For 10 g of sorbent (Formula 6):

$$V_{CO_2} = -7.445 \times 10^{-8} t^2 + 1.835 \times 10^{-5} t - 8.575 \times 10^{-5} \quad (6)$$

For 20 g of sorbent (Formula 7):

$$V_{CO_2} = -4.863 \times 10^{-8} t^2 + 1.095 \times 10^{-5} t + 3.333 \times 10^{-5} \quad (7)$$

An analysis of the results presented in Figures 4-5 shows that the carbon dioxide sorption process depends significantly on both the duration of contact between the gas and the sorbent and the mass of silica modified with potassium humate solution. As the experimental time increases, a steady increase in the amount of CO_2 absorbed is observed for all samples studied. However, the effect of sorbent mass is not proportional: under the investigated conditions, the maximum final CO_2 uptake was observed at a microsilica loading of 5 g, while further increases in microsilica loading to 10 and 20 g resulted in lower CO_2 uptake values.

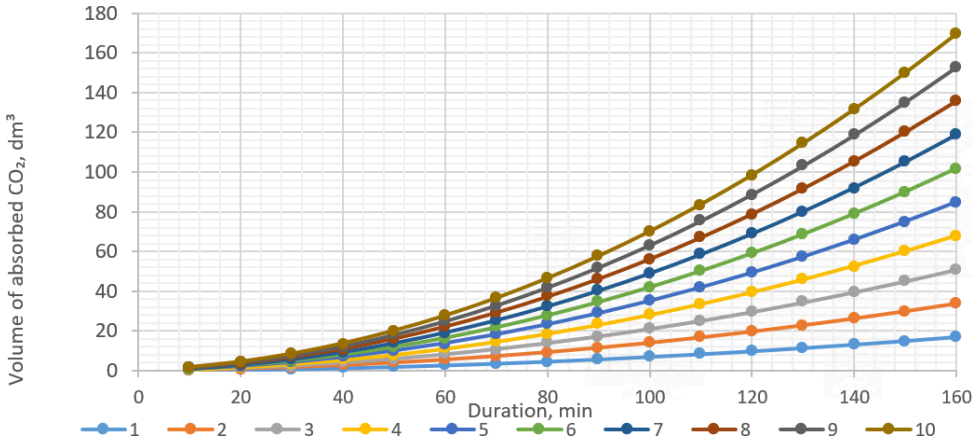

Fig. 4 - Dependence of the volume of absorbed CO_2 on time and the mass of the sorbent (silica) modified with a solution of potassium humate

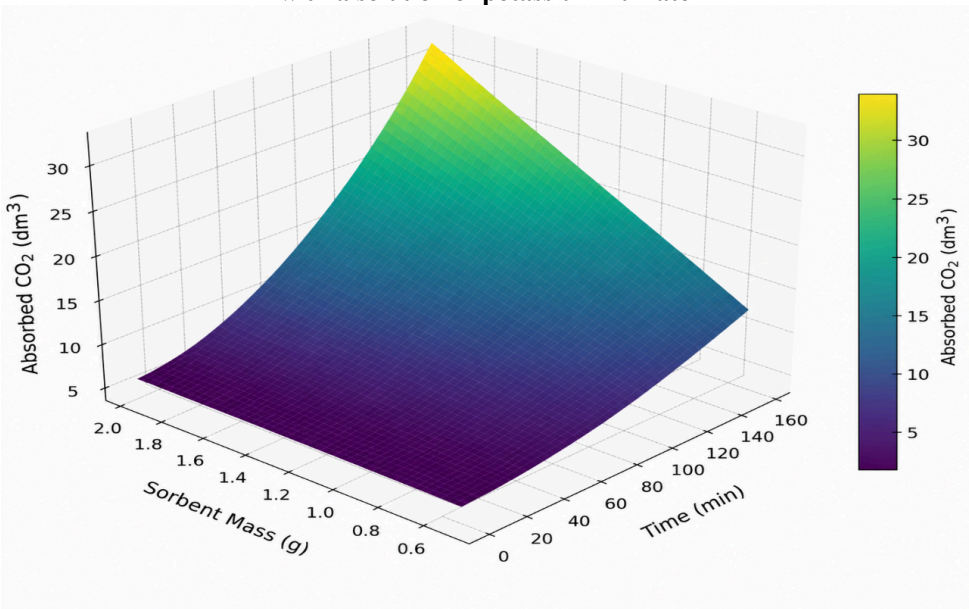

Fig. 5 - Graph of the dependence of the volume of absorbed CO_2 on time (X-axis) and the mass of the sorbent (silica) (Y-axis) modified with a potassium humate solution

Figures 4 and 5 illustrate the dependence of CO_2 uptake on contact time and microsilica loading. The graphical results confirm that contact time has a positive effect on cumulative CO_2 uptake during the initial stage of the experiment. However, the effect of microsilica loading is non-monotonic. The highest final CO_2 uptake was obtained at 5 g of microsilica, whereas increasing the loading to 10 and 20 g resulted in lower final uptake values.

Therefore, the graphical analysis does not support the assumption that increasing the microsilica mass continuously increases CO_2 capture. Instead, the results indicate the presence of an optimum microsilica loading under the selected experimental conditions. This optimum may reflect the balance between the amount of microsilica, the potassium humate concentration, the accessibility of active sites, and mass-transfer limitations within the system.

Overall, the obtained results demonstrate that the potassium humate–microsilica system is capable of capturing CO_2 under the investigated experimental conditions, with the highest measured uptake of 2.72 g CO_2 obtained at a microsilica loading of 5 g per 50 mL of potassium humate solution. Increasing the microsilica loading to 10 and 20 g decreased the measured CO_2 uptake to 1.76 and 1.06 g, respectively.

The results indicate that CO_2 uptake is controlled by the combined properties of the potassium humate and microsilica phases and does not depend solely on the amount of microsilica. Because KOH was used during humate preparation, the possible contribution of residual alkalinity cannot be excluded. Therefore, the present results should be interpreted as the overall CO_2 capture performance of the potassium humate–microsilica system. Determination of pH and residual alkalinity, together with characterization of the material before and after CO_2 exposure, is required to establish the relative contribution of alkaline species, humate functional groups, and microsilica to CO_2 capture.

Conclusion. The study examined the carbon dioxide sorption efficiency of an aqueous potassium humate solution supplemented with varying amounts of microsilica. The results showed that CO_2 sorption significantly depends on both the duration of contact between the gas mixture and the sorbent and the microsilica content in the system. All samples studied showed an increase in the amount of carbon dioxide absorbed over time, demonstrating the high sorption activity of the developed composite material.

Among the investigated microsilica loadings, the highest absolute CO_2 uptake was obtained at 5 g, reaching 2.72 g CO_2 after 160 min. This result identifies 5 g as the most effective loading within the tested range; further studies including control experiments and replicate measurements are required to establish statistical significance and determine the optimal composition of the system. For samples with microsilica masses of 1, 10, and 20 g, the amount of carbon dioxide adsorbed was 2.53, 1.76, and 1.06 g, respectively. However, for samples with 10 and 20 g of microsilica, earlier stabilization of the process was observed, indicating that sorption saturation had been reached.

Based on the experimental data, graphical dependences were constructed and regression equations were derived describing the kinetics of CO_2 sorption. It was shown that the accumulation of adsorbed carbon dioxide is nonlinear and can be described by a polynomial relationship, enabling prediction of process efficiency under various operating conditions.

Modeling for the silica-potassium humate system showed that the effect of sorbent mass on CO_2 uptake was non-monotonic under the investigated conditions. According to the calculations, increasing the silica content to 10 g resulted in a calculated CO_2 uptake value of 169.7 conventional units by the 160th minute. These results indicate that increasing the sorbent quantity alone does not necessarily lead to a proportional increase in the CO_2 sorption capacity of the material.

Based on the obtained data, the study confirms the potential of using a composite sorbent based on microsilica and potassium humate for carbon dioxide capture. Maximum CO_2 sorption efficiency was achieved with a microsilica content of 5 g, ensuring the extraction of up to 15% of CO_2 from the gas stream by the end of the experiment. These results can be used in the development of technologies for reducing greenhouse gas emissions and the creation of effective sorption materials for environmentally friendly applications.

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