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EXPLORING THE POTENTIAL OF HUMIC SUBSTANCES AS EFFECTIVE SORBENTS FOR REDUCING GREENHOUSE GAS EMISSIONS

This article explores the potential of humic substances, which are naturally occurring organic compounds found in soil, water, and coal, as a solution for reducing greenhouse gas emissions. The study specifically examines the humic substances extracted from the Maikube brown coal basin. The properties and mechanisms of humic substances that make them effective in mitigating greenhouse gas emissions are discussed, with early research results on the absorption processes of potassium humate provided. The article also reviews current research on the use of humic substances for carbon capture and storage and highlights the potential for scaling up this technology as a low-cost and efficient approach to reducing greenhouse gas emissions. The concentration of CO₂ was measured at the inlet and outlet of the gas in a gas chromatograph. Within 4 days, the absorption capacity of potassium humate (50%) was 4.99 g CO₂/kg. The IR spectrum of potassium humate is presented as well. The article concludes that while humic substances have the potential to be a promising solution for reducing greenhouse gas emissions, further research and development are required to determine their full potential.

Key words: greenhouse gases, humic substances, absorption, CO₂ capture, potassium humate.

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Парниктік газдар шығарындыларын азайту үшін тиімді сорбенттер ретінде гуминді заттардың әлеуетін зерттеу

Бұл мақалада парниктік газдар шығарындыларын азайту шешімі ретінде топырақта, суда және көмірде кездесетін табиғи органикалық қосылыстар болып табылатын гуминді заттардың әлеуеті қарастырылады. Зерттеу Майкубен қоңыр көмір бассейнінен алынған гуминдік заттарды арнайы қарастырады. Парниктік газдар шығарындыларын азайтуда тиімді ететін гуминді заттардың қасиеттері мен әсер ету механизмдері талқыланады, сонымен қатар калий гуматының сіңіру процестерін зерттеудің алғашқы нәтижелері келтірілген. Мақалада сонымен қатар көміртекті ұстау және сақтау үшін гуминді заттарды қолдану бойынша ағымдағы зерттеулер қарастырылады және парниктік газдар шығарындыларын азайтудың арзан және тиімді тәсілі ретінде осы технологияны кеңейту әлеуетіне баса назар аударылады. CO₂ концентрациясы газ хроматографындағы газдың кірісі мен шығысында өлшенді. 4 күн ішінде калий гуматының сіңіру қабілеті (50 %) 4,99 г CO₂ / кг құрады. Мақалада гуминдік заттар парниктік газдар шығарындыларын азайту үшін перспективалы шешім бола алатынымен, олардың толық әлеуетін анықтау үшін қосымша зерттеулер мен әзірлемелер қажет деген қорытындыға келеді.

Түйін сөздер: парниктік газдар, гуминді заттар, CO₂ сіңіру, калий гуматы.

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Изучение потенциала гуминовых веществ как эффективных сорбентов для снижения выбросов парниковых газов

В этой статье исследуется потенциал гуминовых веществ, которые являются естественными органическими соединениями, содержащимися в почве, воде и угле, в качестве решения для сокращения выбросов парниковых газов. В исследовании специально рассматриваются гуминовые вещества, извлеченные из бурогоугольного бассейна Майкубе. Обсуждаются свойства и механизмы действия гуминовых веществ, которые делают их эффективными в снижении выбросов парниковых газов, а также приводятся ранние результаты исследований процессов абсорбции гумата калия. В статье также рассматриваются текущие исследования по использованию гуминовых веществ для улавливания и хранения углерода и подчеркивается потенциал для расширения масштабов этой технологии как недорогого и эффективного подхода к сокращению выбросов парниковых газов. Концентрацию CO_2 измеряли на входе и выходе газа в газовом хроматографе. В течение 4 сут поглощающая способность гумата калия (50 %) составила 4,99 г CO_2 /кг. Также представлен ИК-спектр гумата калия. В статье делается вывод о том, что, хотя гуминовые вещества могут стать многообещающим решением для сокращения выбросов парниковых газов, для определения их полного потенциала необходимы дальнейшие исследования и разработки.

Ключевые слова: парниковые газы, гуминовые вещества, абсорбция, улавливание CO_2 , гумат калия.

Introduction

Global warming caused by increased emissions of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4) and others has been recognized as a serious environmental problem for humanity. Today there is a massive production and consumption of fossil hydrocarbons, which leads to huge emissions of carbon dioxide into the atmosphere. Its concentration, which is a measure of human consumption of energy from fossil fuels, is growing rapidly. The natural utilization of CO_2 by plants and water bodies can no longer cope with such volumes. At present, the annual increase in CO_2 is 3200–3600 million tons. According to the calculations of the Intergovernmental Panel on Climate Change (IPCC), if CO_2 emissions continue to grow at such rates, the average annual temperature on Earth will increase by 1.5–4.5 °C by the end of the 21st century. This means an increase in temperature of 0.3°C per decade, which is three times the level of adaptability of natural ecosystems. Therefore, the effective utilization of carbon dioxide is an urgent scientific and environmental task of the world scientific community. This article considered the methods by which humic substances absorb greenhouse gas (GHG) pollutants from flue gases.

Humic acids are complex organic polymers of uncertain structure, containing acidic carboxylic and phenolic groups, which may be extracted from

coal, peat, and soil [1]. Humic substances, including humate and humic acid are types of amorphous organic molecular compounds, most of these extensively exist in nature. Due to its “sponge-like” structure, humic substances produce a large surface area (330–340 m^2/g) and surface energy and have a strong adsorption capacity. The adsorption capacity of humic acid is not only related to its surface area and surface energy, but also the swelling property of humic acid to water [2].

Humic substances also are known to have a high capacity for absorbing and binding a wide range of organic and inorganic compounds. This is due to their complex molecular structure, which includes a variety of functional groups such as carboxylic, phenolic, and hydroxyl groups. The adsorption mechanism involves both physical and chemical processes, including adsorption, complexation, and chelation. The adsorption process involves the binding of molecules to the surface of the humic substance, while complexation and chelation involve the formation of stable complexes with metal ions and other organic compounds. Additionally, humic substances have been found to have a high cation exchange capacity, which allows them to exchange cations with pollutants, further enhancing their adsorption capacity [3]. Functional groups, such as carboxylic and phenolic groups, present in humic substances form strong complexes with metal ions, and the adsorption of metal ions is influenced by the pH of the solution [4].

Humic substances have been found to play a significant role in various biological and chemical processes, including the suppression of GHG emissions and the absorption of metal ions and other contaminants from water and soil. In terms of GHG emission suppression, humic substances have been shown to act as electron acceptors in the decomposition process in wetlands, affecting the activity of methanogenic cultures and promoting direct interspecies electron transfer with activated carbon. Humic substances have also been found to interact with microorganisms and affect the biological transformation of organic pollutants in water and soil, shifting anaerobic microbial transformation towards CO₂ production instead of CH₄ generation. The redox properties of humic substances have been studied using electrochemical analysis, revealing their ability to transfer protons and electrons [5]. In terms of metal ion and contaminant absorption, the mechanism of absorption by humic substances is complex and involves several factors, including the chemical properties of the humic substances, the properties of the metal ions or contaminants being adsorbed, and the properties of the soil or water matrix.

Humic substances have also been found to adsorb other contaminants, such as arsenic and herbicides, with the absorption influenced by the chemical properties of the humic substances and the soil or water matrix. Further research is needed to fully understand the multifaceted mechanism of absorption by humic substances [4].

Humic substances are a complex organic compound with high molecular weight ranging from 700 to 20,000 amu, obtained from brown coal in Kazakhstan. These substances contain various functional groups, including positively charged groups such as peptide (-CO -NH-), azo groups (-N=N-), amines (-NH₂, -NH -, >N-), amides (-CO-NH₂), imines (>C=NH), and negatively charged groups such as alcohol, phenolic and hydroxyquinone hydroxyls (-OH), aldehyde, ketone and quinone carbonyls (>C=O), carboxyls (-COOH), methoxyls (-O-CH₃), and others. Therefore, humic substances are polyfunctional polyelectrolytes, specifically polyampholytes, allowing them to participate in various reactions such as carboxylation, polycondensation, copolymerization, nitration, amination, sulfonation, and complex formation. The interaction between humic acids and carbon dioxide, as well as hydrogen sulfide, follows several pathways due to the presence of potassium humate, amine, carboxyl, and hydroxyl groups.

Materials and Methods

The study was conducted at the Institute of Coal Chemistry and Technology LLP, Astana, Kazakhstan.

We utilized various wet laboratory research methods in our investigation. The first method is thermogravimetric analysis, which allows us to determine the technical characteristics of coals such as moisture content, volatile substances, and ash, as per the ISO techniques ISO 589-81, ISO 562:1998, ISO 5071-1:1997, and ISO 1171:1997 [6-9]. This analysis was performed using an Eltra Thermostep thermogravimetric analyzer, as outlined in ASTM D7582-12. Another method we used is for determining humic acids, following the ISO 5073 [10] technique. We used a method for determining both the total yield of humic acids and free humic acids, involving processing an analytical fuel sample with an alkaline solution of sodium pyrophosphate, extraction with a solution of sodium hydroxide, and precipitation of humic acids with an excess of mineral acid. We will then determine the mass of the precipitate obtained.

We also employed methods for the determination of fulvic acids, involving determining the amount of carbon of fulvic acids by calculating the difference between the total carbon content in the extract and its content in humic acids. We will express this as a percentage of the mass of the soil and as a percentage of the total carbon content in the original soil.

In addition, we used gravimetric and titrimetric analysis methods for precipitation, isolation, stripping, and determining the mass of dried humic acids, mass of ash residue of humic acids, ash content in solution and ash content in dry humic preparation brought to air dry state (%), and alkali concentration in liquid humic acids (g/dm³).

IR analysis of potassium humate (HA-K) was performed at "Nazarbayev University Core Facilities" laboratories using Nicolet iS10 FT-IR spectrometer.

Coal samples were taken from the Maikube brown coal basin, the Shoptykol deposit. The Maikube section has a design capacity of 20 million tons/year [11]. The coals of the basin are humus, brown, with a high degree of carbonification (B3), and medium ash (25-28%). Refractory ash with a high content of Al₂O₃ (up to 30%), low-sulfur coals (0.5-1.0%) and multiphosphorous coals (0.1%). The heat of combustion per combustible mass is 29.3-31.4 kJ/kg. The total coal reserves of the basin are estimated at 5.3 billion tons, including 1.8 billion

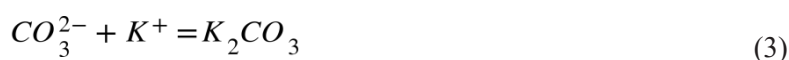
tons suitable for open-pit mining at stripping up to 10 m³/t [12].

Oxidized brown coal of the Maikube deposit, pre-crushed to a size of less than 0.5 mm and having the following characteristics (wt.%) was used as a feedstock for humate production: Ad 66.09; W r 5.73; V d 17.78; Std 0.71; Ctd 21.01; Htd 1.68; Ntd 2.09; Na 0.61; Al 0.89; K 0.58; Ca 0.31; Ti 0.22; Fe 1.11; Zr 0.08.

The size of coal particles was: 2.95 microns (10%), 63.8 microns (50%), and 452 microns (90%). The X-ray phase composition of the sample contains halloysite (Al₂Si₂O₅(OH)₄), silicon oxide (SiO₂), and albite Na (AlSi₃O₈). The yield of HS from brown coal was 56%. Further, the

physicochemical properties of the obtained fraction were studied.

The dissolution of CO₂ in the HA-K⁺ solution is as follows: first, CO₂ diffuses from the gas phase at the gas-liquid interface, where solubility equilibrium is established. CO₂ hydrate forms H⁺, HCO₃⁻ and CO₃²⁻ by ionization that diffuses into the liquid phase. HA-K⁺ in the liquid phase mainly ionizes carboxylic (COO⁻) acid groups and is transferred to the gas-liquid interface. H⁺ diffused into the liquid phase interacts with COO⁻. As a result, HA-K⁺ is converted to humic acid precipitation. In addition, K⁺ and CO₃²⁻ react to form potassium carbonate (K₂CO₃). Corresponding reactions are given in equations 1, 2, 3 [13].



HA-K⁺ solution is a pH buffer because it is a salt of a strong base and a weak acid. Therefore, it is necessary to consider the ionization equilibrium and the hydrolytic equilibrium in the solution. With the increase in the number of cycles, the concentration of K⁺ ions increases. An increase in the concentration of K⁺ ions can interfere with the ionization of K⁺ and reduce the amount of HA-K⁺, which reduces the hydrolysis of K⁺. Therefore, the concentration of H⁺ ions increases and the initial pH decreases [14].

The plant for saturating liquids with carbon dioxide consists of several sections. Carbon dioxide was released from a special cylinder, and the gas flow was monitored using a rotameter. The amount of primary gas was constant 15 %. An aqueous solution of potassium salt of humic acids was poured into the absorption column. Then the solution was saturated with CO₂ gas.

The CO₂ absorption process was carried out at constant temperature (23°C). The concentration of CO₂ was measured at the inlet and outlet of the gas in a gas chromatograph "CrystalLux". The experiment was carried out until the concentration of carbon dioxide reached the initial concentration and became saturated.

Results and Discussion

The IR spectrum of potassium humate (HA-K) in nujol is depicted in Fig. 1. The adsorption bands of HA-K were observed at the wave numbers of 3500-3000 cm⁻¹ (-OH stretching phenols, carboxylic acids and water, as well as -NH stretch of amines and carboxamides), 2919 cm⁻¹ (refers to the asymmetric and symmetrical features of the methylene (-CH₂-) group, which is typical for aliphatic and undeformed cyclic hydrocarbons, but is also masked and may be the corresponding N-H/O-H signal), 2880 cm⁻¹ and 2823 cm⁻¹ (both correspond to aliphatic C-H stretching), 1560 cm⁻¹ (could be referred to asymmetrical vibration of carboxylate -COO⁻ ion; a shoulder of this band towards higher wavenumbers could be related to double bond stretching, e.g. -C=C-, and -C=N-), 1425 cm⁻¹ and 1370 cm⁻¹ (correspond to a combination of O-H bending, CH₂ and CH₃ deformation, alkene C-H bending, carboxamide C-N stretching and symmetric -CO₂- stretching vibrations of carboxylate ion), 1200 cm⁻¹ (C-O stretching), 1033 cm⁻¹, 1007 cm⁻¹ (C-O stretching vibrations in polysaccharides or polysaccharide-like substances), 914 cm⁻¹ and 882 cm⁻¹ (C-N/C-C

stretching vibrations), 756 cm^{-1} (out-of-plane bending vibrations of aromatic C-H), 541 cm^{-1} , 468 cm^{-1} and 440 cm^{-1} (out-of-plane bending vibrations of aromatic $-(\text{CH}_2)_n-$ groups), which were ascribed to humate and humic species.

Other investigations have been conducted to explore the potential absorption capabilities of humic substances.

The mechanism of carbon dioxide absorption with potassium humate (HK) solution is as follows:

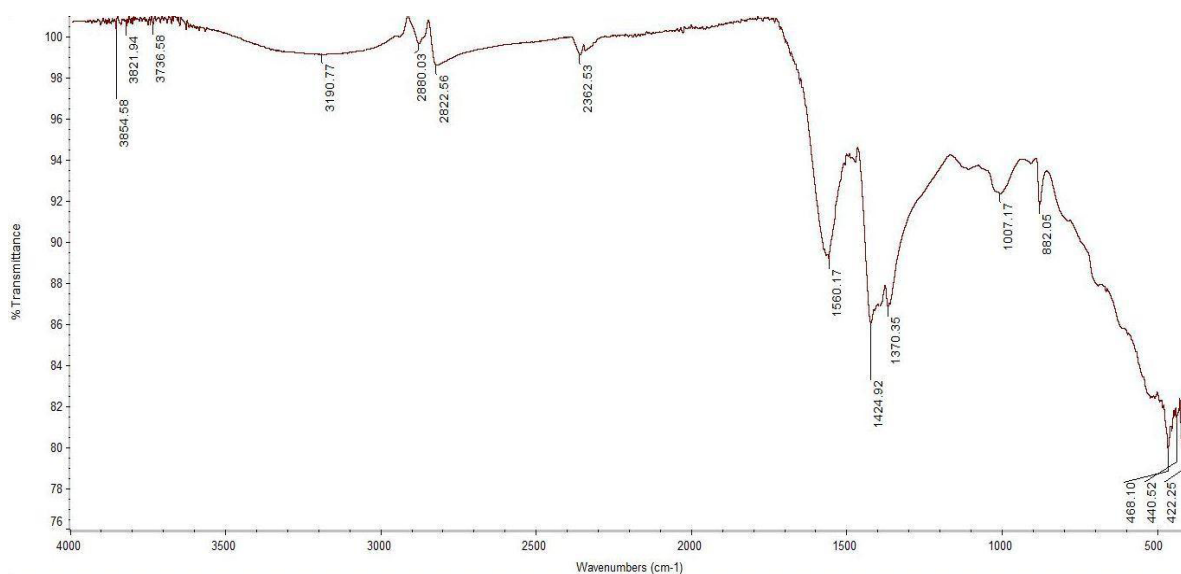
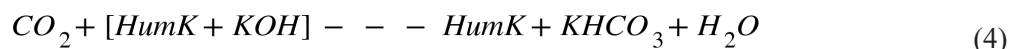


Figure 1 – IR spectrum of potassium humate (HA-K)

Carbon dioxide is converted into potassium bicarbonate or potassium carbonate.

As a result of the experiment, the sorption capacity of the humic absorbent was calculated according to the following formula (6):

$$A_{\text{CO}_2} = \frac{\rho V}{RT} \cdot 44,01 \cdot \frac{1}{m_s} \quad (6)$$

Here, A_{CO_2} is the amount of absorbed CO_2 (gCO_2/kg), P -atmospheric pressure, Pa, V - volume of CO_2 released, dm^3 , R – gas constant, 8314 J/mol , T -temperature, K, 44.01 - CO_2 molar mass, g/mol ; m_s -sample mass, kg. The calculation results are given in Table 1.

Table 1 – Absorption capacities of humic absorbent

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
1 day								
10,000	10	0,41	1,51	28,49	0,117	1,166	2,06	0,092
10,000	20	0,41	1,93	28,07	0,116	2,323	4,11	0,182
10,000	30	0,41	2,16	27,84	0,115	3,479	6,15	0,273

Table continuation

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	40	0,41	1,97	28,03	0,116	4,646	8,21	0,365
10,000	50	0,41	1,43	28,57	0,117	5,820	10,29	0,457
10,000	60	0,41	1,5	28,5	0,117	6,993	12,36	0,549
10,000	70	0,41	1,47	28,53	0,117	8,166	14,43	0,642
10,000	80	0,41	1,49	28,51	0,117	9,310	16,46	0,731
10,000	90	0,42	3,46	26,54	0,111	9,310	16,46	0,731
2 day								
10,000	10	0,41	1,02	28,98	0,119	1,172	2,07	0,092
10,000	20	0,41	1,99	28,01	0,116	2,336	4,13	0,184
10,000	30	0,41	1,61	28,39	0,117	3,509	6,20	0,276
10,000	40	0,41	1,4	28,6	0,118	4,680	8,27	0,368
10,000	50	0,41	1,7	28,3	0,117	5,848	10,34	0,459
10,000	60	0,41	1,66	28,34	0,117	7,004	12,38	0,550
10,000	70	0,42	2,45	27,55	0,114	8,150	14,41	0,640
10,000	80	0,42	2,38	27,62	0,115	9,294	16,43	0,730
10,000	90	0,42	2,52	27,48	0,114	10,440	18,45	0,820
10,000	100	0,41	2,29	27,71	0,115	11,586	20,48	0,910
10,000	110	0,42	2,51	27,49	0,114	12,733	22,51	1,000
10,000	120	0,41	2,25	27,75	0,115	13,887	24,55	1,091
10,000	130	0,41	2,05	27,95	0,116	15,044	26,59	1,182
10,000	140	0,41	2	28	0,116	16,202	28,64	1,273
10,000	150	0,41	1,97	28,03	0,116	17,356	30,68	1,363
10,000	160	0,42	2,35	27,65	0,115	18,503	32,71	1,454
10,000	170	0,42	2,38	27,62	0,115	19,649	34,73	1,544
10,000	180	0,42	2,41	27,59	0,115	20,793	36,75	1,634
10,000	190	0,42	2,52	27,48	0,114	20,793	36,75	1,634
3 day								
10,000	10	0,41	1,18	28,82	0,118	1,176	2,08	0,092
10,000	20	0,41	1,61	28,39	0,117	2,336	4,13	0,184
10,000	30	0,41	2,22	27,78	0,115	3,482	6,16	0,274
10,000	40	0,42	2,58	27,42	0,114	4,618	8,16	0,363
10,000	50	0,42	2,92	27,08	0,113	5,751	10,16	0,452
10,000	60	0,42	2,79	27,21	0,113	6,887	12,17	0,541
10,000	70	0,42	2,65	27,35	0,114	7,956	14,06	0,625
10,000	80	0,44	7,08	22,92	0,100	8,933	15,79	0,702
10,000	90	0,44	8,48	21,52	0,095	9,910	17,52	0,779
10,000	100	0,44	7,04	22,96	0,100	10,900	19,27	0,856
10,000	110	0,44	7,68	22,32	0,098	11,891	21,02	0,934
10,000	120	0,44	7,04	22,96	0,100	12,838	22,69	1,009
10,000	130	0,45	10,2	19,8	0,089	13,718	24,25	1,078
10,000	140	0,46	10,96	19,04	0,087	14,612	25,83	1,148

Table continuation

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	150	0,45	9,44	20,56	0,092	15,492	27,38	1,217
10,000	160	0,46	11,69	18,31	0,084	16,337	28,88	1,283
10,000	170	0,46	11,41	18,59	0,085	17,140	30,30	1,347
10,000	180	0,47	13,95	16,05	0,076	17,158	30,33	1,348
10,000	190	0,46	12,38	17,62	0,082	17,177	30,36	1,349
10,000	200	0,46	11,29	18,71	0,085	17,196	30,40	1,351
10,000	210	0,46	12,49	17,51	0,081	17,215	30,43	1,352
10,000	220	0,46	12,62	17,38	0,081	17,234	30,46	1,354
10,000	230	0,47	13,91	16,09	0,076	17,234	30,46	1,354
4 day								
10,000	10	0,42	2,85	27,15	0,113	1,130	2,00	0,089
10,000	20	0,42	3,02	26,98	0,113	2,253	3,98	0,177
10,000	30	0,42	3,31	26,69	0,112	3,370	5,96	0,265
10,000	40	0,42	3,46	26,54	0,111	4,362	7,71	0,343
10,000	50	0,45	10,86	19,14	0,087	5,225	9,24	0,410
10,000	60	0,46	11,25	18,75	0,086	6,045	10,69	0,475
10,000	70	0,47	13,21	16,79	0,078	6,786	11,99	0,533
10,000	80	0,48	15,46	14,54	0,070	7,533	13,31	0,592
10,000	90	0,47	12,89	17,11	0,080	8,350	14,76	0,656
10,000	100	0,46	11,72	18,28	0,084	9,163	16,20	0,720
10,000	110	0,47	13,17	16,83	0,079	9,934	17,56	0,780
10,000	120	0,47	13,94	16,06	0,076	10,707	18,93	0,841
10,000	130	0,47	13,06	16,94	0,079	11,471	20,28	0,901
10,000	140	0,47	14,37	15,63	0,074	12,212	21,59	0,959
10,000	150	0,47	14,32	15,68	0,074	12,938	22,87	1,016
10,000	160	0,48	15,15	14,85	0,071	13,647	24,12	1,072
10,000	170	0,48	15,14	14,86	0,071	14,340	25,35	1,127
10,000	180	0,48	15,98	14,02	0,068	14,340	25,35	1,127

As can be seen from table 1, within 4 days, the absorption capacity of potassium humate (50%) was 4.99 g CO₂/kg.

Unfortunately, obtained absorption capacities are much lower than for benchmark 30% MEA. The MEA solution reached maximum saturation after 187 and 154 minutes at 25°C and 40°C respectively. Despite the significantly lower absorption capacity compared to MEA, the use of humic salts for CO₂ capture can be justified. Namely, the advantage is that the solution of humic salts after absorption can be used as a fertilizer.

In addition, it is harmless and non-toxic. Therefore, it can probably be considered a green solvent.

Further research is needed to determine the effect of temperature and to learn more about the chemistry between humic salts and CO₂.

After absorption of carbon dioxide with humate potassium salt, methods of back titration with acetate Ca are used for determination of carboxyl groups, and method of titration with Ba(OH)₂ for determination of total acidity. The result of the study is presented in Table 2.

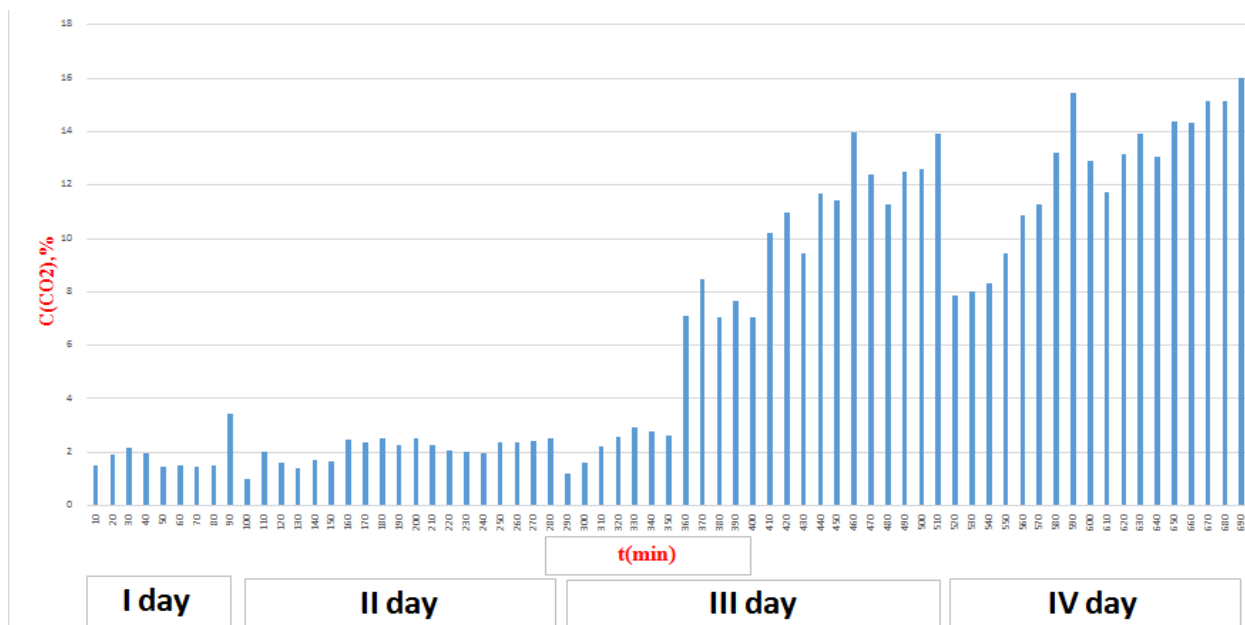


Figure 2 – Time dependence of non-absorbed carbon dioxide by humic absorbent

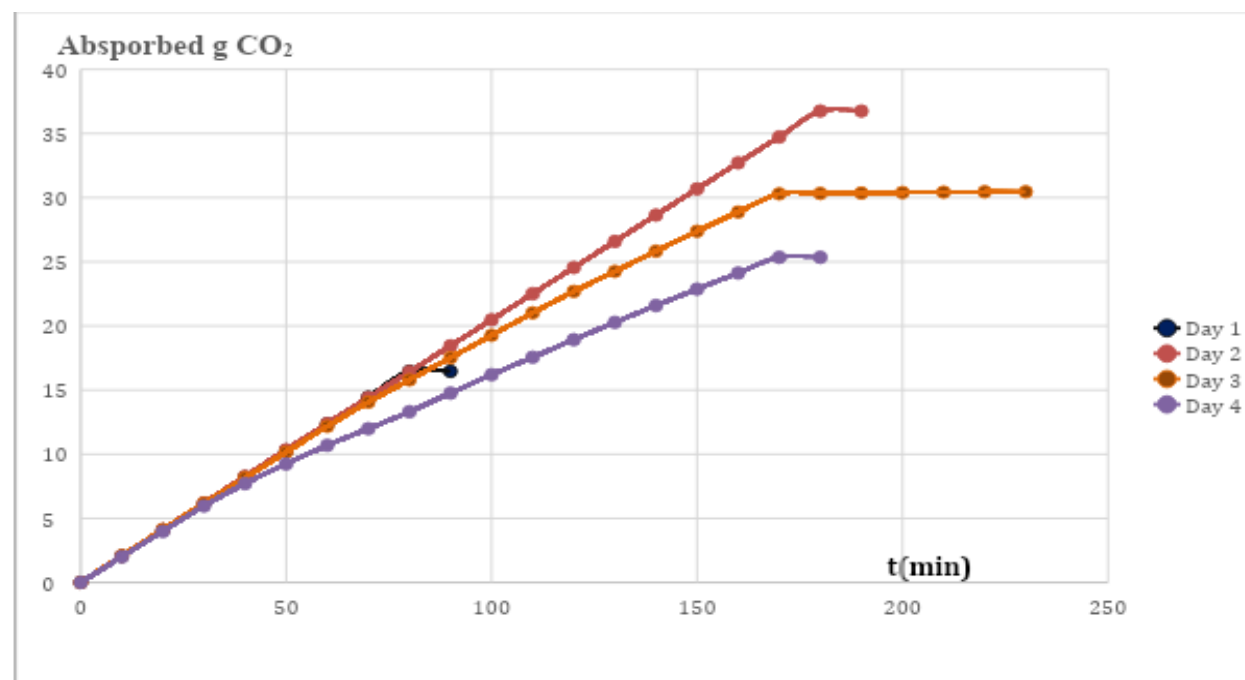


Figure 3 – Absorbed (g CO₂) CO₂ in potassium humate over time

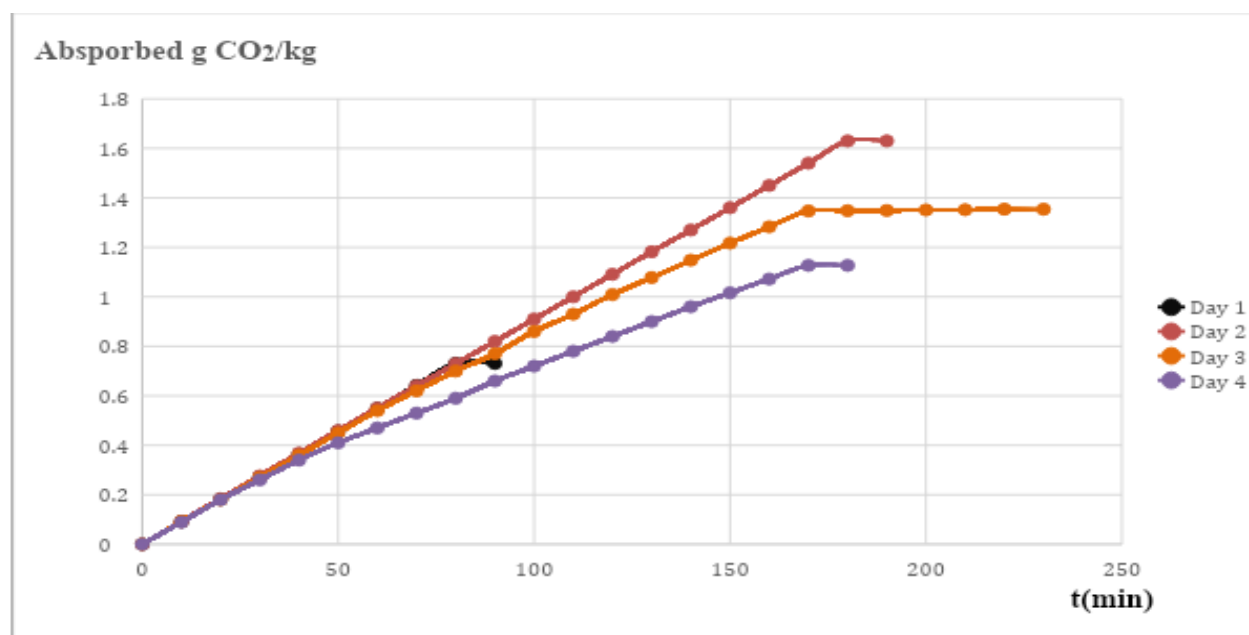


Figure 4 – Absorbed (g CO₂/kg) CO₂ in potassium humate over time

Table 2 – Results of functional groups research

Name	Total acidity, mmol/g	Phenol groups, mmol/g	Carboxyl groups, mmol/g
HA-K ⁺ before sorption	6,60	5,029	1,517
HA-K ⁺ after sorption	10,17	6,688	3,482
Sediment	12,85	8,654	4,196

Based on the results, it can be observed that the content of carboxyl groups increased by 2.3 times, phenolic groups by 1.3 times, and total acidity by 1.5 times, compared to the original solution.

Conclusion

In conclusion, the sorption capacity of CO₂ absorption with 50% potassium humate solution was equal to 4,99 g CO₂/kg at room temperature (230C). The considered method has the following advantages: it avoids the regeneration of the absorbent, reduces capital costs, the absorbent-organic substrate is saturated with carbon dioxide, when it is used, it accelerates the growth process of plants, the used absorbent is a polymeric substance capable of forming complex compounds with many metals, sulfur, and greenhouse gases, the obtained product is used as an organic

polymicrocomponent fertilizer saturated with CO₂. That is, the advantage of using humic salts is that the solution after absorption of CO₂ can be widely used in agriculture as an organo-mineral fertilizer saturated with K₂CO₃.

Overall, humic substances have unique physical and chemical characteristics that make them a promising candidate for developing effective CO₂ capture methods.

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