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OBTAINING ORGANO-MINERAL FERTILIZER BY ABSORPTION OF CARBON DIOXIDE BY NATURAL HUMIC SUBSTANCES

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Abstract

Global warming caused by increased emissions of greenhouse gases such as carbon dioxide (CO_2), methane (CH4) 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.

The work describes research on the use of HAS (potassium and ammonium) for CO_2 capture. Laboratory tests have been carried out to evaluate the maximum absorption capacity and CO_2 absorption rate of aqueous solutions of HAS. It has been shown that the absorption capacity is more than 10 times lower than that of a benchmark solution of 30% MEA. However, the CO_2 absorption rate of a 30% AH solution is close to that of 30% MEA. Nevertheless, contrary to amines, after the CO_2 absorption HAS solutions can be used as fertilizers. This provides both CO_2 capture and utilization.

The resulting solutions were tested for microgreens, the biomass of microgreens and the length of sprouts of microgreens of the experimental and control groups were studied.

Key words: fertilizer; absorption; potassium humate; ammonium humate; CO_2 utilization.

Introduction

Kazakhstan holds about 28 000 million tons of coal reserves ranking 10th in the world. Coal is used to power most of the country's electricity generation (about 69%) and is also used for heating most of homes and greenhouses. This leads to significant greenhouse gas (GHG) emissions, placing Kazakhstan among 15 largest GHG emitters per capita. To address these issues, the government has made ambitious commitments to increase the role of renewable energy sources by up to 50% by 2050, as well as to reduce GHG emissions. However, strong dependence on large reserves of inexpensive coal, relatively low domestic energy prices and a lack of flexible energy generation capacity make this transition challenging.

The prerequisite for the development of this work in Kazakhstan was the implementation by the President of the country Tokayev K.K. "Doctrines of carbon neutrality until 2060" and Kazakhstan's energy transition to low-carbon fuel calculation technologies, thereby reducing greenhouse gas emissions, increasing the efficiency of services and goods on the world market. The President of the Republic of Kazakhstan dated February 2, 2023 No. 121, approved a decree on a strategy for achieving carbon neutrality of the Republic of Kazakhstan until 2060.

Today's development and advancement of CO_2 absorption methods shows that capture itself is not technologically problematic. Using amine scrubbing, we get almost pure CO_2 from the stripper. Nevertheless, in order to reduce CO_2 emissions into the atmosphere, its further use or storage is necessary. Humic acid salts may become a promising alternative. Humic acid is a complex mixture of many different acids containing carboxyl and phenolate gropus.

The structure is thereby complex and varies in a certain range, according to the origin, but the average properties of extracted humic substances are remarkably similar and resistant to further biodegradation. HAs are random polycondensates with polyelectrolyte/polyampholite behavior with a polyphenol or quinone-based aromatic core, in which functional side structures contain carboxylic, phenolic, and carbonyl groups, as well as sugar, peptide fragments. The subentities are connected by various connectors, such as –O–, –CH_2–, =CH–, –NH–, –S–S–, and similar groups. The contained chemical functionality determines its properties in ion exchange, water absorption, its dispersion and cohesion energy, as well as interactions and complexation. A scheme of the general structure is illustrated in Scheme 1. [1]

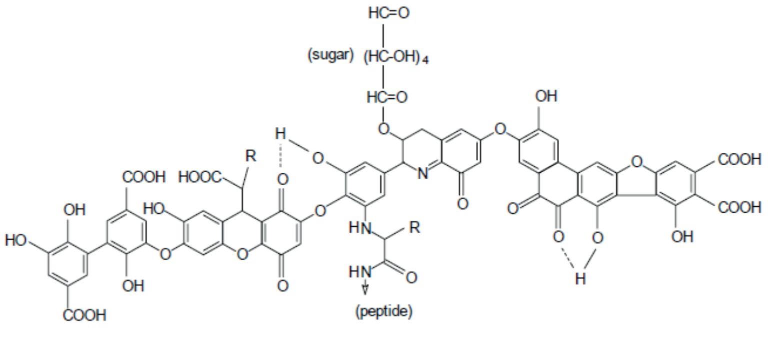

Figure 1 – Model structure of humic acid according to Stevenson (1982);
R can be alkyl, aryl or aralkyl

Humic acids (HA) are a mixture of natural amorphous colloids formed as a result of various biological and abiotic decomposition processes of animal and plant residues, which are characterized by a complex molecular structure, chemical composition, chemical activity, and resistance to decomposition [2, 3]. HA are widely distributed in soil, coal, and natural reservoirs, and their composition, structure, and application have been widely studied in agriculture [4]. The percentage of HA present in various sources is the following: black peat: 10-40%, sapropel peat: 10-20%, brown coal: 10-30%, compost materials: 2-5%, and soil sludge: 1-5%. The extracted amount of HA depends on the type of organic material, the extractant, as well as the temperature and particle size of the substrate. In addition, the origin and source of HA are the main parameters for obtaining high-purity HA. As a rule, low-grade coals seem to be the main source of HA [5].

Humus is a complex polydisperse polymer mixture with diverse structures and aggregation states, which is widely distributed in natural soils, water, and minerals. It is mainly composed of C, O, H, and N, in which the proportion of organic carbon is generally between 40 and 60% [6,7]. According to its source, humus can be divided into soil humus, aquatic humus, and mineral humus. According to its composition and structure, humus can be divided into fulvic acid (FA), humic acid (HA), and humin. Among these three components of humus, FA is the alkali- and acid-soluble component, HA is the alkali-soluble and acid-insoluble component, and humin is the insoluble residue [8,9].

Humic substances (HS, fulvic and humic acids) are widely used as fertilizers or plant growth stimulants [10]. HA can increase soil organic matter, and fertilizer efficiency and improve the availability of nutrients in the soil, such as phosphates, potassium, nitrogen, etc. [11]. HA mainly contain hydroxyl, carboxyl, and quinone, which demonstrate excellent physiological activity, adsorption, exchange, and other properties [12]. However, considering the heterogeneity and complexity of the structure and composition, HA from different sources demonstrate different structures and properties. In addition, the characteristics of HA varied depending on the processing of raw materials and extraction technologies [13].

Humates have a complex effect on the soil, improving its physical, chemical and biological properties. Along with this, humates perform a protective function, binding heavy metals, radionuclides and organic toxicants, thereby preventing them from entering plants. Thus, by acting on the soil, humates indirectly affect plants, contributing to their more active growth and development.

As natural polyelectrolytes, the presence of HS is crucial to preserve the production and quality of soil, remove inorganic pollutants, improve industrial agents, and treat some diseases. Therefore, HS act as a important role in the fields of agriculture, environment, industry, human health, and medicine [14].

Biological sciences, including biotechnology and environmental microbiology, have thoroughly focused on the development of new technologies to tackle environmental priority issues related to the removal of several pollutants from wastewater and soils by using HS. Most of these developments rely on one of the most exploitable and versatile properties of HS, their redox activity [15]. Standard redox potential (E0') values for HS have been considered to range from−200 to +300 mV [16]; likewise, additional studies have determined values of E0' ranging from −300 to +150 mV [17]. This wide spectrum of redox potential is originated fromone of the primordial characteristics of this kind of compounds: their richness in chemical groups placed at the periphery of their aromatic structural core. Depending on the source and type of humic materials, these moieties can differ in number, chemistry, availability, and redox properties, thus resulting in variable reactivity and electron exchange capacity (EEC). The EEC is considered as the sum of the electron accepting (EAC) and donating capacities (EDC) [18]. The main functionalmoiety, which confers redox capacity to HS, has been proven to be the quinone chemical group. Depending upon the redox conditions of the environment in which HS prevail, their quinines may be on a fully reduced (hydroquinone; QH2), fully oxidized (quinone; Q), or in an intermediate oxidation state [18].

The main objective of the study [19] is to develop an environmentally friendly technology and organize the production of biological products, as well as to conduct laboratory and field tests to determine the effectiveness of the effect of chelate complex biological products based on potassium humate, enriched with NPK and Mo. The article presents the results of field trials on the effect of growth-stimulating organic fertilizer on hedge seedlings (elm and spirea) on the territory of the Astana Botanical Garden (Astana).As a result of vegetation experiments, an effective effect of modified organic biopreparations (MOB with NPK, MOB with Mo) was established, in which a stimulating effect on the growth of new shoots and a significant increase in the biomass of elm seedlings was observed. Biological preparations also had a beneficial effect on spirea hedge bushes, which manifested itself in a significant increase in plant height.

In work [20] studied the simultaneous removal of NO and SO_2 using a new process of oxidation-absorption of micro-nanobubbles based on HA-Na. HA-Na in the liquid phase is ionized to produce acidic groups, mainly including carboxyl (COO−) and hydroxyl (OH−), and can react rapidly with H+, then HA-Na is transferred to humic acid (HA) sediment.

In this paper reviews [14] the recent development of waste gas treatment by HA with special reference to HA for removal of SO_2, NOx, CO_2, H_2S, and heavy metals. Sun et al. [21] put forward a method to absorb CO_2 by humates and ammonia. This method involves CO_2 absorption by a mixture of humates and ammonia−water. The humates and ammonia−water are stirred to obtain a mixed aqueous solution into an absorbing tower, where insetting gas contains CO2 to generate a solution of ammonium hydrogen carbonate (NH_4HCO3) and HA−NH_4. The obtained solution is poured into a mechanical dewatering device. The obtained mixture of (NH_4HCO_3) and HA−NH_4 is a kind of compound fertilizer. This method provides a new route to reduce emissions of CO_2 from power plants, which contains a separation improvement in ammonia scrubbing by adding HA−Na. Therefore, it seems that employing HA as an additive to enhance on CCS of other absorbents is a good choice, before CO_2 sequestration mechanism by only HA is not reported [14].

The removal of waste gas from combustion flue gas by HA has been spotlighted in recent years as a potential way to reduce gas pollutants. The special physical and chemical characteristics of HA is a basis for waste gases treatment employing HA. Because of the great adsorption and weak alkalinity of HA−Na, it is used to remove the acidic waste gas SO_2, NOx, H_2S, and CO_2.

HS and their structural analogous possess the inherent potential to play key roles on preventing the release of GHG from natural environments [22].

As shown in the literatures, a study on the absorption of gases by humic substances used sodium humate, but there are no data on the use of potassium and ammonium humate as an absorbent, therefore, these studies are novel.

This paper presents the results of laboratory studies on CO_2 absorption in humic acid salts. Ammonium (AH) and potassium humate (KH) in various concentrations have been tested. The absorption potential of these solutions in removing CO_2 from synthetic flue gases (i.e., containing about 12% CO_2 and) was determined.

Work presented in this paper has been carried out as a part of collaboration between LLP Institute of Coal Chemistry and Technology and Institute of Energy and fuel processing technology (ITPE). The research has been carried out in the Institute of Energy and Fuel Processing Technology, in Zabrze, Poland.

Methods and Materials

LLP "Institute of Coal Chemistry and Technology" together with LLP "Research and Production Association "KazTechCoal" developed and introduced into production an innovative technology for the production of organomineral fertilizer "Kazuglegumus" from domestic oxidized brown coal (highly concentrated liquid solution). In the process of preparing humic preparations, a rotary-pulsation apparatus is used, then an ultrasonic reactor is used to bring the size of coal particles (19.2 nm - 3.57 μm) to a nano- and micro-size state. In both cases, air is supplied to oxidize the coal and increase the content of humic substances. In the process of dispersion and ultrasonic exposure, the temperature of the mixture reached no more than 50-55°C, which is acceptable for the oxidation of coal with atmospheric oxygen and the extraction of the formed salts of humic and fulvic acids, as well as amino acids. In the process of oxidation with air, a micellar dispersed system is formed - a solution of humic substances with a particle size of less than a micrometer.

As a feedstock for the production of humate, oxidized brown coal from the Sarykol deposit was used, which was previously crushed to a particle size of less than 0.5 mm and had the following characteristics (wt.%): A^d 66.09; W^r 5.73; V^d 17.78; S_t^d 0.71; C_t^d 21,01; H_t^d 1,68; N_t^d 2.09; Na

0.61; Al 0.89; K 0.58; Ca 0.31; Ti 0.22; Fe 1.11; Zr 0.08. The particle size of the coal was: 2.95 microns - 10%, 63.8 microns - 50%, 452 microns - 90%. X-ray phase composition of the sample contains: halloysite ($Al_2Si_2O_5(OH)_4$), silicon oxide (SiO_2), albite Na ($AlSi_3O_8$). The output of humic substances from brown coal was 56%. Next, the physicochemical properties of the resulting fraction were studied [22].

Humidity, ash content and volatility of the samples were determined on a thermogravimetric analyzer *"TGA-701, Leco"*. Mass fraction of humic acids (in terms of dry matter) determined according to GOST 9517-94. The following instruments were used to determine the quality of raw materials and the content of humic substances: IR-Fourier spectrometer (*NicoletiS 10*), elemental analyzers *CHNS 628*, as well as *CS 632 CHNS/O* (*Perkin Elmer*), particle size analyzer (*Mastersizer 3000*), analyzer for determining total organic carbon (*VarioMAXcube TOC-automatic TOC analyzer*), ion chromatograph (*JONOWY ICS 5000 from DIONEX*), gas analyzer (*GA-40Tplus*), thermostat (*Thermo Scientific*), pH meter (*ProfiLine pH 3110 from WTW*).

The setup and procedure for conducting the experiment (CO_2 uptake) was as follows.

Installation for saturation of liquids with carbon dioxide consists of several sections. The gas preparation section consists of a carbon dioxide cylinder and an air compressor. Air and pure CO_2 are mixed in a gas mixer and the correct ratio is ensured by mass flow controllers. The total flow is checked with a rotameter.

The jacketed (i.e. double-walled) absorber is a column filled with 6 mm glass Raschig rings. The column has an overall height of approximately 1.2 m and a diameter of approximately 30 mm. The column is thermostated using a Thermo Scientific oven.

The CO_2 concentration was measured at the inlet and outlet of the gas. The first sampling point is located before the rotameter, and the second - after the impinger. The analyzer continuously measures the concentration of carbon dioxide at the outlet of the column. The inlet gas concentration is checked only before and after the test.

As a raw material for the experiment, carbon dioxide was taken in a cylinder with a CO_2 content of 13.6 % vol. Because, in the flue gases of CHP, the content of CO_2 reaches up to 13%.

An aqueous solution of a salt of humic acids (potassium or amine) was poured into an absorption column (a description of the installation is given in Fig. 1). Then the solution was saturated with a gaseous mixture of CO_2 and air. The content of carbon dioxide at the inlet to the gas was fixed and amounted to about 13.6% vol. Two solutions, namely potassium humate and ammonium humate, were tested independently of each other at different concentrations.

The CO_2 absorption process was carried out at constant temperatures (25°C and 40°C, 75°C respectively). The volume of the absorbing liquid was also known and used in the calculations. The concentration of CO_2 in the outgoing gas was measured continuously during the experiment (using an IR gas analyzer). The process was carried out until the outlet CO_2 concentration was close to the inlet concentration. The absorption capacity was calculated from the gas balance (it was based on the measured CO_2 content and known gas flow rates). In addition, the absorption capacity was checked using a Scheibler (it is based on volumetric analysis, it is a kind of gas burette). The pH of the solution was also checked before and after saturation with CO_2.

To determine the effect of the resulting aqueous solutions of HAS on plants, experiments were carried out on the microgreens "Cress-lettuce". 7 experimental and 1 control groups (water) were formed: potassium humate, ammonium humate, test 5 - 30% potassium humate (T=25 °C), test 6 - 30% ammonium humate (T=25 °C), test 7 – 50% potassium humate (T=25 °C), test 8– 50% ammonium humate (T=25 °C), test 11– 50% potassium humate (T=40 °C). Watering with 0.1% solutions was carried out every 7 days.

Results

Data on the elemental composition of humic substances isolated from the oxidized coal "Sarykol" from the Maikuben deposits are shown in Tables 1 and 2.

Table 1 – Average content of carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O)

Name	Technical specification, %				Content, %			
	Wrt	Ar	Vd	C	H	N	S	O
Potassium humate	44.80	11.64	42.69	34.31	1.66	0.80	0.43	19,03
Ammonium humate	56.46	31.76	14.90	53.21	2.70	13.89	0.48	12,70

Table 2 – Sample characteristics

Name	Chemical formula	O/C	H/C	P_2O_5, %	K_2O, %
Potassium humate	$C_{290}H_{160}O_{120}N_6S$	0.55	0,048	0.31	24.65
Ammonium humate	$C_{440}H_{270}O_{80}N_{10}S$	0.24	0,051	0.26	9.48

The potassium humate was not toxic or flammable and belonged to the 4th hazard class. The isolated fraction contained 34.31 % C and 19,03 % O, which characterizes it as saturated with these elements. The H and N content was at the level of 1.66 and 0.80 %, respectively. The S content was the lowest (0.43 %), which is typical for HS. The carbon content in ammonium humate is higher (53.21 %) compared to potassium humate. The nitrogen content is 13.89 %, which is 17 times higher than that of potassium humate, which will contribute to the absorption of CO_2.

The oxygen to carbon ratio (O/C) indicated the typical polarity, i.e., abundance of polar oxygen functional groups on the surface. Results showed that O/C ratio of studied samples varied between 0.24 and 0.55. Potassium humate has a more polar surface than ammonium humate. As follows from the data on the elemental composition of humic substances, the H:C ratio for HA is slightly higher than for HK. This indicates the presence of fragments saturated with hydrogen in the molecular structure of HA.

Table 3 – Chemical composition of samples

Sample	The content of elements, wt. %											
	C	O	Na	Al	Mg	Si	K	Ti	Fe	S	F	Ca
Potassium humate	35.95	30.16	0.44	8.57	0.25	1.12	21.05	-	1.47	0.14	0.84	-
Ammonium humate	56,09	31,08	0,19	2,84	0,30	7,25	0.65	0,36	0,74	-	-	0,49
	Content of cations, mg/l						Anion content, mg/l					
	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}		Cl^-		$NO3^-$		SO_4^{2-}	
Potassium humate	442,247	34,715	14658,859	128,441	762,297		137,361		77,657		550,928	
Ammonium humate	375,111	7144,666	1722,679	134,351	674,456		135,948		28,447		227,898	

Table 4 – Sample characteristics

Name	HA^{daf}, %	TOC, %	pH	Elec. cond., мСм/см	SBET, m^2/g	The content of functional groups, mmol/g		Particle size, μm		
						carboxyl	phenolic	10 %	50 %	90 %
Potassium humate	81,48	2.82	12.33	20.44	0,55	0.241	0.549	0.02	0.36	3.57
Ammonium humate	80,70	17.36	10.94	12.18	3.96	0.304	0.126	0,69	7,21	296,00

One of the main indicators of the quality of HK is the particle size, which determines the availability of HS for plants, their solubility in soil, and the absence of large agglomerates.

After the rotary cavitation machine and the ultrasound machine, the particle size averaged from 19.2 nm to 3.57 microns (Tabl.4). According to the results, two fractions with a particle size from 0.01 to 0.1 microns were isolated, with a maximum content of more than 40% of the volume, as well as the second fraction containing particles from 0.15 to 1.0 microns in size.

According to the results of the study of the particle size of ammonium humate, one fraction was isolated with a particle size of 0.687 to 296 microns.

As can be seen from the results, the absorption capacities varied depending on concentration and used humate salt. It is clearly seen that ammonium humate (AH) featured better performance than

KH. This solution showed an increase in the ability to absorb CO2 with increasing concentration. There is a carbon dioxide absorption mechanism according to the following equation:

$$CO_2+[HumNH_4+NH_4OH] \text{ - - - } HumNH_4+NH_4HCO_3+H_2O$$
$$CO_2+[HumNH_4+NH_4OH] \text{ - - - } HumNH_4+(NH_4)_2CO_3+H_2O$$

Carbon dioxide is converted into ammonium bicarbonate or ammonium carbonate, which are valuable nitrogen fertilizers. The highest absorption capacity of 9.66 gCO_2/kg was obtained for 50% AH at 25°C. The highest absorption capacity for 50% KH was 3.86 g CO2/kg. As could be expected, the absorption capacity increased with increasing HAS concentration/ This effect was more prominent for AH. Unfortunately, obtained absorption capacities are much lower than for benchmark 30% MEA. Even the best result (obtained for 50% AH) has about 10 times less maximum absorption capacity than 30% MEA. The MEA solution reached maximum saturation after 187 and 154 minutes at 25°C and 40°C respectively.

There is a mechanism for the absorption of carbon dioxide by potassium humate according to the following equation:

$$CO_2+[HumK+KOH] \text{ - - - } HumK+KHCO_3+H_2O$$
$$CO_2+[HumK+KaOH] \text{ - - - } HumK+K_2CO_3+H_2O$$

Carbon dioxide is converted to potassium bicarbonate or potassium carbonate.

The tests were carried out in such a way that the salt concentration was first increased, and then the temperature was changed to achieve the best result. As with ammonium humate, the absorption capacity increases with the concentration of the solution. However, the HA solution showed 2-3 times lower capacity than HA.

The concentration of 0.1% HA had a capacity similar to water and was 1,04 g/kg. The highest absorption capacity for CO2 was obtained for 50% KH and was 2.7 times lower than for the KA solvent under the same conditions.

KH 50% was tested at three temperatures (25, 40, 75°C). There is an increase in capacitance with increasing temperature. An increase in temperature from 25ºC to 75ºC caused an increase in absorption capacity by about 36 %. As with the HA solvent, foaming increases with temperature. However, this effect was greater than in the case of the ammonium humate solvent. At 75°C, the solution loss (due to foaming) was more than 40%. For optimal solutions, the following characteristics were studied:

Table 5 – Characteristics of samples before and after absorption of CO_2

№	Name	Content, %				TOC, %	The content of functional groups, mmol/g	
		C	H	N	S		carboxyl	phenolic
1	Potassium humate (100%)	34,310	1,660	0,771	0,432	2,820	0,241	0,549
2	30% Potassium humate (after CO_2 sorption), T=25ºC	40,793	1,136	0,947	-	3,258	0,145	0,585
3	50% Potassium humate (after CO_2 sorption) T=25ºC	39,423	1,158	0,919	-	2,990	0,107	0,773
4	50% Potassium humate (after CO_2 sorption) T=40ºC	40,724	1,149	0,966	-	3,099	0,107	0,683
5	Ammonium humate (100%)	53,210	2,700	13,890	0,475	17,360	0,304	0,126

Continuation of Table 5

6	30% Ammonium humate (after CO_2 sorption)	59,809	2,264	14,791	-	19,493	0,152	0,638
7	50% Ammonium humate (after CO_2 sorption)	61,324	2,231	15,194	-	22,564	0,268	0,662

The content of functional groups for the initial 30% potassium humate solution was, mmol/g: carboxyl - 0.063; phenolic-0.737; for the initial 50% potassium humate solution was mmol/g: carboxyl - 0.045; phenolic-0.795. The content of functional groups for the initial 30% ammonium humate solution was, mmol/g: carboxyl - 0.089; phenolic-0.661; for the initial 50% ammonium humate solution was mmol/g: carboxyl - 0.071; phenolic-0.819.

Compared to the initial solution of 100% potassium and ammonium humate, after the absorption of CO_2, an increase in C, N and organic emissions, the emission content is observed. However, it should be taken into account that not a 100% solution of humic substances was used for absorption, but 30, 50% dilute solutions, in this case an increase in hydrogen after sorption is also observed. When comparing functional groups, a decrease in carboxyl groups and a corresponding increase in hydroxyl groups were revealed, which may be due to the fact that phenolic and alcohol groups dissociate under alkaline conditions, therefore, the active potassium ions associated with hydroxyl substances interact with HCO_3^- and CO_3^{2-} forming a soluble salt of $KHCO_3$ and K_2CO_3 or NH_4HCO_3 and $(NH_4)_2CO_3$. pH value of the absorbing solution drops rapidly from 9-11 to 6-8 due to faster consumption of OH– in the absorption solution.

The results of the experiment on the study of the influence of aqueous solutions of HAS are shown in Figures 2 and 3.

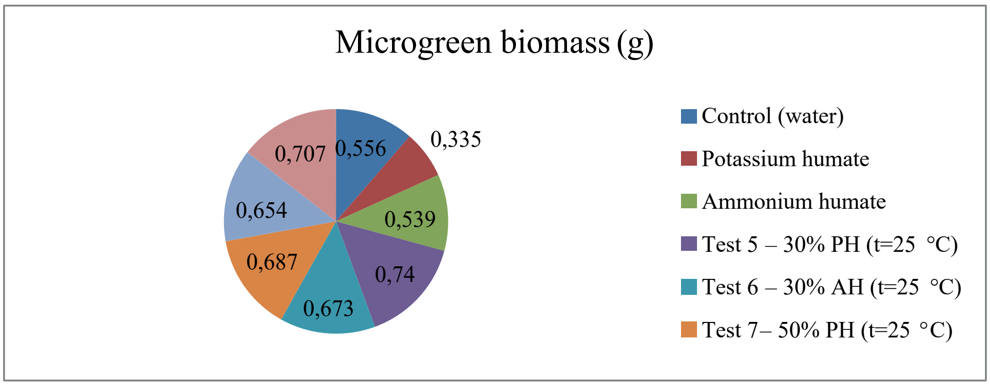

Figure 2 – Comparative diagram of microgreen biomass results of experimental and control groups

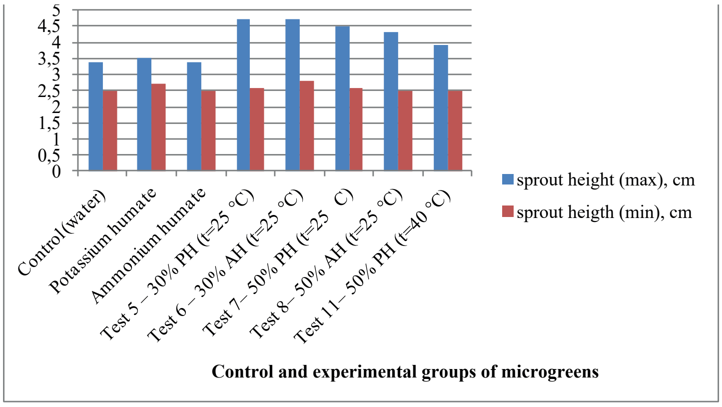

Figure 3 – Comparative diagram of the length of microgreen sprouts of the experimental and control groups

According to the results of the experiment, it can be seen that of the studied samples, the best indicators were observed in groups Test 5,6,7 and 11. The best biomass indicators were noted in Test 5 - 30% potassium humate (T = 25 ° C) and Test 11 - 50% potassium humate (T=40 °C), which is higher than the control group by 0.184 grams and 0.151 grams, respectively. Also, in the group where watering was carried out with Test 11–50% potassium humate solution (T=40 °C), the largest number of adult shoots was observed. The maximum length of sprouts was obtained in the experimental groups Test 5 - 30% potassium humate (T=25 °C) and Test 6 - 30% ammonium humate (T=25 °C), which amounted to 4.7 cm.

Discussion

Compared to the initial solution of 100% potassium and ammonium humate, after the absorption of CO_2, an increase in C, N and organic emissions, the emission content is observed. However, it should be taken into account that not a 100% solution of humic substances was used for absorption, but 30, 50% dilute solutions, in this case an increase in hydrogen after sorption is also observed. When comparing functional groups, a decrease in carboxyl groups and a corresponding increase in hydroxyl groups were revealed, which may be due to the fact that phenolic and alcohol groups dissociate under alkaline conditions, therefore, the active potassium ions associated with hydroxyl substances interact with HCO_{3-} and CO_3^{2-} forming a soluble salt of $KHCO_3$ and K_2CO_3 or NH_4HCO_3 and $(NH_4)_2CO_3$. pH value of the absorbing solution drops rapidly from 9-11 to 6-8 due to faster consumption of OH^- in the absorption solution. On the titration curves of humic substances, three clear inflections are usually observed in the range of pH 10÷11 (phenolic hydroxyls), pH 6.5÷9.5 (carboxyl groups at the aromatic ring), pH 2.5÷6.5 (carboxyl groups at hydrocarbon chains).

The dissolution of CO_2 in the HA-K+ solution is as follows: first, CO_2 diffuses from the gas phase at the gas-liquid interface, where solubility equilibrium is established. CO_2 hydrate forms H^+, HCO_3^- and CO_3^{2-} by ionization that diffuses into the liquid phase. $HA\text{-}K^+$ 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, $HA\text{-}K^+$ is converted to humic acid precipitation. In addition, K^+ and CO_3^2- react to form potassium carbonate (K_2CO_3).

Conclusion

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 CO_2. That is, the advantage of using humic salts is that the solution after absorption of CO_2 can be widely used in agriculture as an organo-mineral fertilizer saturated with K_2CO_3 or $(NH_4)_2CO_3$. Overall, humic substances have unique physical and chemical characteristics that make them a promising candidate for developing effective CO_2 capture methods.

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ТАБИҒИ ГУМИНДИК ЗАТТАРМЕН КӨМІРҚЫШҚЫЛ ГАЗЫН СІҢІРУ АРҚЫЛЫ ОРГАНОМИНЕРАЛДЫ ТЫҢАЙТҚЫШТАРДЫ АЛУ

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Түйін

Көмірқышқыл газы (CO_2), метан (CH_4) және т.б. парниктік газдар шығарындыларының артуына байланысты жаһандық жылыну адамзат үшін күрделі экологиялық проблема ретінде танылды. Бүгінгі таңда көмірсутектерді жаппай өндіру және тұтыну атмосфераға көмірқышқыл газының үлкен шығарындыларына әкеледі. Адамның қазба отындарынан алынатын энергияны тұтыну көрсеткіші болып табылатын оның концентрациясы қарқынды өсуде. Өсімдіктер мен су объектілерінің CO_2-н табиғи пайдалануы бұдан былай мұндай көлемдерді көтере алмайды. Қазіргі уақытта CO_2 жыл сайынғы өсімі 3200-3600 млн тоннаны құрайды. Климаттың өзгеруі жөніндегі үкіметаралық топтың (IPCC) есептеулеріне сәйкес, егер CO2 шығарындылары осы қарқынмен өсе берсе, онда 21 ғасырдың аяғында Жердегі орташа жылдық температура 1,5–4,5 °С артады. Бұл онжылдықта температураның 0,3°С жоғарылауын білдіреді, бұл табиғи экожүйелердің бейімделу деңгейінен үш есе жоғары. Сондықтан көмірқышқыл газын тиімді пайдалану әлемдік ғылыми қауымдастықтың өзекті ғылыми және экологиялық міндеті болып табылады.

Бұл мақалада CO_2-ны ұстау үшін гуминді заттарды (калий және аммоний) пайдалану бойынша зерттеулер сипатталған. ГЗ ерітінділерінің CO_2 сіңіру жылдамдығы мен максималды сіңіру қабілетін бағалау үшін зертханалық сынақтар жүргізілді. Сіңіру қабілеті 30% МЭА эталондық ерітіндісінен 10 есе төмен екендігі көрсетілген. Дегенмен, 30% АГ ерітіндісінің CO_2 жұту жылдамдығы 30% МЭА-ға жақын. Дегенмен, аминдерден айырмашылығы, ГЗ ерітінділерін CO_2 сіңіргеннен кейін тыңайтқыш ретінде пайдалануға болады. Бұл CO_2-ны ұстауды және пайдалануды қамтамасыз етеді.

Кілт сөздер: тыңайтқыш; сіңіру; калий гуматы; аммоний гуматы; CO_2 пайдалану.

ПОЛУЧЕНИЕ ОРГАНОМИНЕРАЛЬНЫХ УДОБРЕНИЙ ПУТЕМ ПОГЛОЩЕНИЯ УГЛЕКИСЛОГО ГАЗА ПРИРОДНЫМИ ГУМИНОВЫМИ ВЕЩЕСТВАМИ

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Аннотация

Глобальное потепление, вызванное увеличением выбросов парниковых газов, таких как двуокись углерода (CO_2), метан (CH_4) и других было признано серьезной экологической проблемой для человечества. Сегодня происходит массовое производство и потребление ископаемых углеводородов, что приводит к огромным выбросам углекислого газа в атмосферу. Его концентрация, которая является мерой потребления человеком энергии из ископаемого топлива, быстро растет. Естественная утилизация CO_2 растениями и водоемами уже не справляется с такими объемами. В настоящее время годовой прирост CO_2 составляет 3200–3600 млн тонн. По расчетам Межправительственной группы экспертов по изменению климата (МГЭИК), если выбросы CO_2 будут продолжать расти такими темпами, то к концу XXI века среднегодовая температура на Земле повысится на 1,5–4,5 °С. Это означает повышение температуры на 0,3°С за десятилетие, что в три раза превышает уровень приспособляемости природных экосистем. Поэтому эффективная утилизация углекислого газа является актуальной научной и экологической задачей мирового научного сообщества.

В работе описаны исследования по использованию гуминовых веществ (калий и аммоний) для улавливания CO_2. Были проведены лабораторные испытания для оценки максимальной абсорбционной способности и скорости абсорбции CO_2 водных растворов ГВ. Показано, что поглощающая способность более чем в 10 раз ниже, чем у эталонного раствора 30% МЭА. Однако скорость поглощения CO_2 30% раствором АГ близка к скорости 30% МЭА. Тем не менее, в отличие от аминов, растворы ГВ после поглощения CO_2 можно использовать в качестве удобрений. Это обеспечивает как улавливание, так и утилизацию CO_2.

Ключевые слова: удобрение; абсорбция; гумат калия; гумат аммония; утилизация CO_2.