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The Influence of Algae as a Bioactive Additive on the Properties of Suspension Fertilizers

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Algae contain essential plant nutrients, various microelements and bioactive substances promoting full supply of nutritious substances to plants during their entire vegetation period. They are attractive because their cultivation does not require plots of agricultural land, and they use carbon dioxide as well as nitrogen and phosphorus compounds to accumulate biomass. Besides, they are environment-friendly and their use makes it possible to create a closed cycle. Chemical composition of algae shows that they are suitable for use as a fertilizer component, because they have no aluminium or silicon, and heavy metal concentration does not exceed permitted limits. The particles 106 – 212 μm in size contain mostly (65.4 %) algae, and are irregular in shape. By using algae, fine sediment remains in suspension 4 times longer and settles slowly to the bottom (with 4 % clay additive, the solid phase settles in 40 min, and with 4 % algae – in 130 min). Stable NPK 12-4-18 suspension fertilizers suitable for use during a warm period were obtained with 3.5 % algae additive. The main properties of such suspensions are: pH 6.3; crystallization temperature + 8.21 °C; density – 1226 kg/m^3, viscosity – 7.32 mm^2/s.

Keywords: suspension fertilizers, algae, clay, fine particle, stability.

1. INTRODUCTION

Nowadays all around the world a lot of attention is paid to the environmentally friendly and green biotechnological materials. Also, there is a continuous search for the most renewable energy sources whose proceedings will not harm the environment. One such idea is to use algae. Therefore commercial application of algae is very wide: as food and drink ingredient (jam, cheese, wine, tea, soup, noodles, pasta, beverages, powders, tablets, capsules, additives, antioxidants, colouring agent, hydrocolloids, fruit preserves, clarifying brewing agent), in aviation gas, biodiesel, bioethanol, biogas, bio-hydrogen, bio-methane. As bio-sorbents algae are used in ion exchange materials that bind strongly ions of heavy metals. In catalysis algae are important for their catalytic properties due to alkali and alkaline earth species. They are used in extraction processes in paper, textile printing, cosmetic and fertilizer industries, medicine (beta-carotene–supplement for vitamin C and precursor for vitamin A), and for other pharmaceutical and biological/microbiological leadings [1 – 3]. As it can be seen there are many ways in which algae can be used today, but the most relevant and widely explored are bioenergy and biofuels, biomedical, cosmetic products, fertilizers and pigments.

For biomass production, microalgae are cultivated in open ponds, closed photo-bioreactors or hybrid systems. After cultivation, microalgae biomass needs to be separated from the effluent of the bioreactor. The basic harvesting methods are sedimentation, centrifugation or manual removal. After harvesting there microalgae biomass is the subject to treatment which consists of mechanical, thermal hydrolysis, biological and chemical process. After all these steps microalgae biomass is suitable for general use or for biofuel production [4].

In biomedical use, macro algae produce a variety of natural bioactive compounds and metabolites, such as polysaccharides, polyunsaturated fatty acids, and phlorotannins. Polysaccharides play a role of structural support and perform a storage function in algae. Algae lipids consist of glycolipids, phospholipids and non-polar glycerolipids. Sterols, important structural components of cell membranes, can regulate membrane permeability and fluidity. As photosynthetic organisms, algae can synthesize three kinds of pigments: chlorophylls, carotenoids and phycobiliproteins. These bioactive compounds isolated from marine algae have been reported to have antibacterial, anti-inflammatory, antioxidant, anti-tumor properties, and thus have great prospects in the food, pharmaceutical, cosmeceutical, and nutraceutical industries [5].

Some types of brown and red macro algae are used in cosmetics due to the presence of vitamins, minerals, amino acids, sugars, lipids, and other biologically active compounds. Extracts of Monodus sp., Thalassiosira sp., Chaeloceros sp., and Chlorococcum sp. can be used in anti-aging products to intensify collagen stimulus. Chlorella vulgaris extracts stimulate collagen synthesis in skin, promoting tissue regeneration and wrinkle reduction [6].

The most important parameters for algae cultivation are light, nutrients, aeration, temperature and pH, which determine efficiency of biomass utilization. To cultivate microalgae two methods are used: photoautotrophic cultivation and heterotrophic cultivation. Using heterotrophic cultivation, the following pigments are obtained: lutein, astaxanthin, phycocyanin. Lutein is a

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primary xanthophyll pigment present in plants and green algae, involved in light harvesting during photosynthesis and protection of the photosystems from photo oxidative damage. Astaxanthin is the second xanthophyll and are the oxygenated derivatives of carotenoids. It is primarily produced by marine algae and bacteria. Phycocyanin is the blue colored phycobiliprotein found exclusively in cyanobacteria, cryptophytes and red algae [7, 8].

Biochar (carbon-rich charcoal of any kind of biomass) production from algal feedstock has a lower carbon content surface area and cation exchange capacity compared to lignocellulose biochar. It has higher pH, which can balance acidified soils and tends to have a higher content of nutrients including minerals such as nitrogen, ash and inorganic elements. Nitrogen-rich biochar produced from microalgae residue is useful in agriculture as a nitrogen-releasing fertilizer to the soil. Microalgae biomass also produced biochar with higher nitrogen content and other mineral elements such as sodium, magnesium, potassium, calcium and iron compared with biochar produced from lignocellulosic biomass [7].

Many scientific publications include studies on the conditions for algae cultivation, using algae for fertilization and their positive impact on agronomic effect. Because algae are used as a source of nitrogen, their influence on crop yields is appreciated [9 – 11]. However, what has not yet been analyzed is algae as bioactive substance, and its acting on the physico-chemical properties of a multi-component fertilizer system. Therefore, the aim of this work is to investigate the properties of traditionally used suspension fertilizers with clay and an algae additive.

2. MATERIALS AND METHODS

The basic solution of suspension fertilizers is its liquid phase after separation of $KH_2PO_{4(s)}$ crystals formed during interaction between potassium chloride and ammonium dihydrogen phosphate. Chemical composition of the solution includes: 1.6 % N, 3.75 % P_2O_5 ir 17.5 % K_2O. Its properties are as follows: crystallisation temperature +19 °C, pH 3.25; density – 1182 kg/m^3; viscosity – 1.322 mm^2/s [12, 13]; fractional composition was analized by sieve shakers „L3P Sonic Sifter“ for sieving analyse.

Clay whose fraction is 0.08 – 0.2 mm comes from the Neveroniai quarry. Its physical properties include: clay particle content not less than 25 %; plasticity number not less than 7; clay is free from tree roots, metal or other impurities. Clay’s chemical composition % is as follows: 46.25 – 69.82 of SiO_2; 7.05 – 17.47 Al_2O_3; 2.46 – 8.38 Fe_2O_3; 5.02 – 10.78 CaO; 2.27 – 4.32 MgO; radioactivity estimated below the regulatory recommended standard of (370 Bq/kg, 1 and 1) according to OECD 1979 and ICRP 2000 [14, 15].

Algae – Chlorella (protothecoides) was grown in the Laboratory of Chemical and Biochemical Research of the ASU Institute of Environment and Ecology (Lithuania). Algae was filtered, dried at 60 °C, and crushed using a vibratory mill. Before drying, algae contained 88.64 % moisture; after drying it was reduced to 8.108 %.

Chemical composition of algae was analysed by employing methods of chemical analysis: nitrogen concentration was measured by Kjeldahl method (Vapodest 45 s); phosphorus concentration was determined by photocolorimetrical method (T70/T80 UV–VIS); potassium concentration was calculated by marginal solutions method (flame photometer PFP–7). Concentration of micronutrients (MN) was established by atomic absorption spectroscopy (AAS) using Perkin Elmer Analyst instrument, gas mixture of acetylene (7.5 L/min) and air (10 L/min) was used for atomization. Also MN were investigated by X-ray fluorescence analysis (XRFA) using the Bruker X-ray S8 Tiger WD, with Rh tube, anode voltage up to 60 kV, with current strength up to 130 mA. The specimens were measured in an atmosphere of helium. Measurements were performed using the SPECTRA Plus QUANT EXPRESS method [16 – 20].

Fourier-transform infrared spectroscopy (FTIR) analysis was performed with spectrometer “Perkin Elmer FT – IR System”. A tablet pressed in a tablet press was used for the analysis (1 mg of substance mixed with 200 mg KBr). The analysis was implemented in the main range of the IR spectrum from 400 to 4000 cm^{-1} with Scanning was carried out at an interval of 2 %, recording interval of 1 cm^{-1}, 10 scans were performed [21].

Scanning electron microscopy (SEM) method was employed to determine particle form and chemical composition of algae and clay. For SEM PhenomWorld ProX (G5) with integrated energy-dispersive X-ray spectroscopy (EDS) for elemental analysis of samples was used. Magnification ranged from 20 to 150,000, acceleration voltages adjustable range was from 4.8 kV to 15 kV.

Physical properties of solution were determined by using right and, if necessary, modified methods for solutions analysis. Glass capillary viscometer (capillary diameter 3 mm) was used to determine viscosity and aerometer (GOST 18481-81) was used to determine density. pH value was measured with HANNA instrument pH 211 microprocessor pH-meter using glass membrane electrode. KERN MLS_N electronic humidity analyser (precision of 0.001 g or 0.01 %) was used to determine humidity. Temperature of crystallisation (precision of ±0.05 °C) was determined by polythermic method using salt-ice cooling mixture. Temperature average (at least 5 measurements) between the first crystalline coming and the last crystalline disappearing is the crystallization temperature of the solution of particular composition.

3. EXPERIMENTAL RESULTS

The results of our previous studies [12] suggest that liquid phase (1.6 % N, 3.75 % P_2O_5 and 17.5 % K_2O), which remained after KCl and $NH_4H_2PO_4$ conversion, can be used as basic for manufacturing liquid fertilizers. NPK suspension fertilizers can be produced from base solution by adding $CO(NH_2)_2$ and NH_4NO_3 salts. In this work, nitrogen concentration was maximized and suspensions of 12-4-18 branded fertilizers were developed. The suspension fertilizer was obtained by adding 16 % urea and 8 % ammonium nitrate. The solid particles in these fertilizers are stable and do not dissolve, but phase stratification is observed over time. This process is typical of all suspension fertilizers, but is intended to be as slow as possible. To this end, a variety of suspension stabilizing additives are used in the fertilizer industry.

Two different additives have been selected to stabilize the 12-4-18 suspension fertilizer created in this work: clay (conventional additive) and algae (alternative bioactive additive). Chemical composition of these additives was initially analysed using different methods of chemical and instrumental analysis (AAS, XRFA, FTIR). The data obtained are presented in Table 1. Analysis these data shows that chemical composition of algae and clay is not very specific. Different methods produce different basic elements (N, P converted to P_2O_5, K converted to K_2O), secondary elements (Ca, Mg, S, Na), trace elements (Fe, Zn, Mn, Co, Cu, Cr), heavy metals (Pb, Cd) and other impurities (Al, Si, Br, Sr, Ti). These discrepancies can be explained by different sample preparation: chemical analysis and AAS – aqueous solution analysis; XRFA and FTIR – solid material with different accuracy and sensitivity of these methods.

However, it can be said that phosphorus (chemical analysis), calcium (XRFA, EDS), silicon (XRFA) are the main components of algae. They also contain elements needed for plants such as manganese, sodium, magnesium, zinc, iron, copper and very few heavy metals harmful to plants (lead, cadmium, titanium, strontium, and aluminium).

The biggest part of clay is silicon, which is not needed for plants, but is not harmful. There is also a lot of calcium, aluminium, iron, magnesium, which (excreted in aluminium) plants need as trace elements, i. e. in low doses.

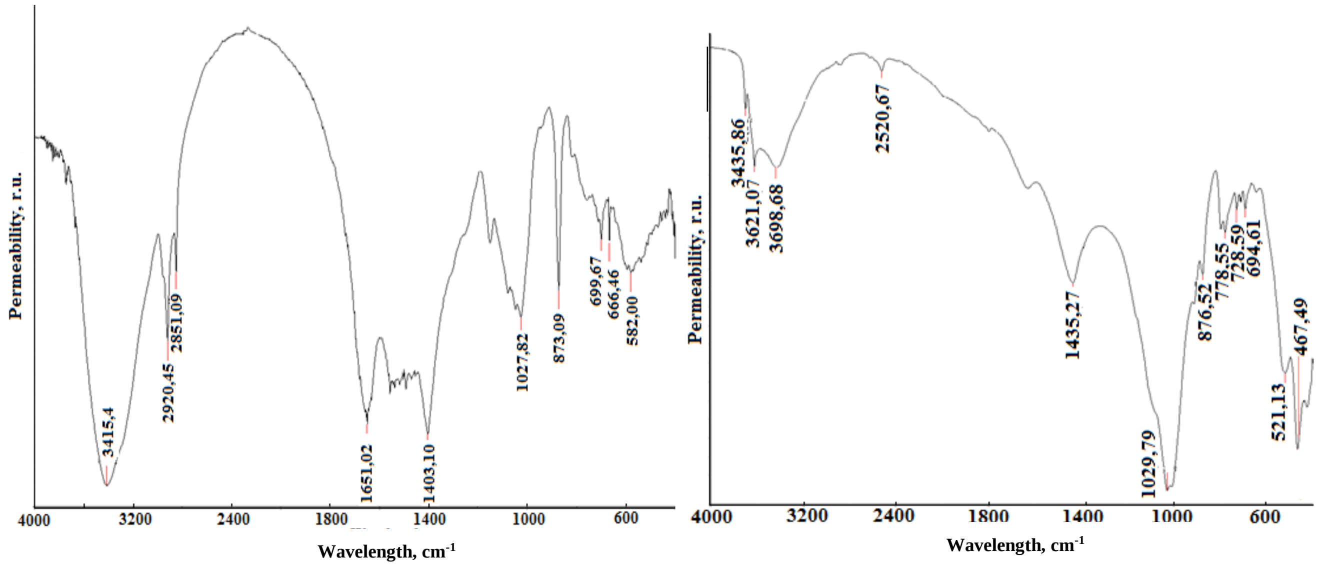
Comparing chemical composition of these two additives it is obvious that algae are more suitable for use as a component of solution than clay.

To obtain a more detailed analysis of the suspension stabilization additives, the IR spectra of these materials were recorded (Fig. 1). As can be seen from Fig. 1 a clay IR spectrum has a wide absorption band at 3415.40 cm^{-1} in the -OH functional group. Absorption Band peaks 2920.45 – 2851.09 cm^{-1} are characteristic of the -CH functional valence oscillations. These results of IR analysis are consistent with those of Y. Shi, J. Sheng, F. Yang, Q. Hu [22]. The absorption band peaks in the 1651.02 – 1403.10 cm^{-1} spectra can be classified as -CO and -NO plane vibrations, and the peaks in the spectra of 1027.82 – 873.09 cm^{-1} are O-C-O, Si-O, Cl-O plane vibrations. Absorption bands that are visible in the 699.67 – 582.00 cm^{-1} spectrum can also be assigned to O-Si-O, O-Cl-O functional groups and PO_4^{3-} functional groups with metal ions for plane vibrations. Identification of the above mentioned functional groups in the IR spectrum correlates with the chemical algal composition determined by chemical analysis methods.

According to data provided by B. Tyagi in a scientific publication [23], the curve of Fig. 1 b, in the 3698.68 – 3435.86 cm^{-1} frequency range the oscillations characteristic of the -OH group are visible. It can be stated that the peak of the absorption bands is 1029.79 cm^{-1} characteristic of the valence oscillations of the Si-O-Si group, and 876.52 cm^{-1} is characteristic of the Si-OH valence oscillations. The peak of the absorption bands is 778.55 – 694.61 cm^{-1} and the peak in the 521.13 – 467.49 cm^{-1} frequency in this case is attributable to the plane oscillations of the Si-O-Si functional group, because the PO_4^{3-} functional groups were not confirmed in clay nor by chemical or instrumental analysis methods.

Table 1. Chemical composition of algae and clay determined by different methods

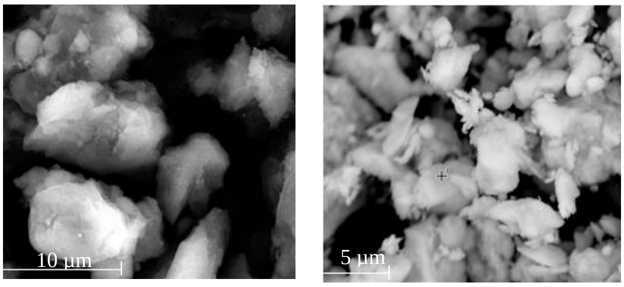
Macro nutrients concentration, %			Micro elements concentration by method					
N	$P_2O_{5(total)}$	K_2O	AAS, mg/g		XRFA, %		EDS, %	
Algae								
0.8*	10.5*	0.5*	Fe	2.813	Ca	22.00	Ca	9.17
–	2.5**	0.2**	Cu	2.643	Na	2.31	Si	7.39
5.2***	–	2.4***	Zn	2.295	Mg	0.323	Mg	1.50
			Mn	288.0	S	0.782	S	3.34
			Co	0.131	Cl	0.151	Br	2.04
			Pb	0.031	Sr	0.106		
			Cd	0.021	Si	0.0715		
					Ti	0.0249		
Clay								
–	1.2*	0.9*	Fe	1.119	Si	21.1	Si	16.49
–	0.7**	4.5**	Cu	–	Ca	9.37	Ca	8.32
2.3***	–	–	Zn	0.012	Al	5.59	Br	1.23
			Mn	0.002	Fe	5.27	Al	1.16
			Co	–	Mg	1.66	S	0.69
			Pb	0.028	Na	0.171	Mg	0.64
			Cd	0.012	S	0.132		
					Mn	0.0812		
					Zn	0.0127		
					Cr	0.0118		
Note: * – method of chemical analysis; ** – XRFA method; *** – EDS method.								



a b

Fig. 1. FTIR analysis spectrum: a – Chlorela Vulgaris algae; b – clay for Neveroniai career

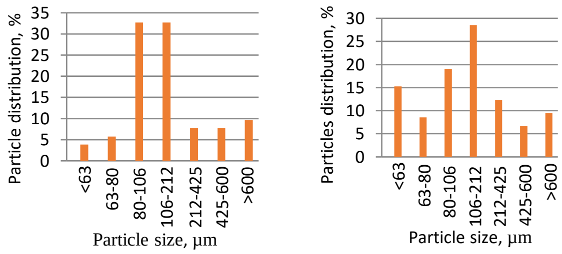
Since the suitability of materials used to stabilize suspensions is determined not only by their chemical properties but by their surface properties, analysis of the particle size distribution of the algae and clay particles was performed (Fig. 2, Fig. 3).



a b

Fig. 2. SEM analysis (acceleleration voltages adjustable range from 4.8 kV to 15 kV): a – Chlorela Vulgaris algae; b – clay for Neveroniai career

SEM photos show that algae and clay particles are irregular in shape, with many corners and irregularity. However, algae particles (Fig. 2 a) are more homogeneous in comparison to clay particles. Clay particles are very diverse, in some places adhering to agglomerates of particles of different shapes and sizes (Fig. 2 b).

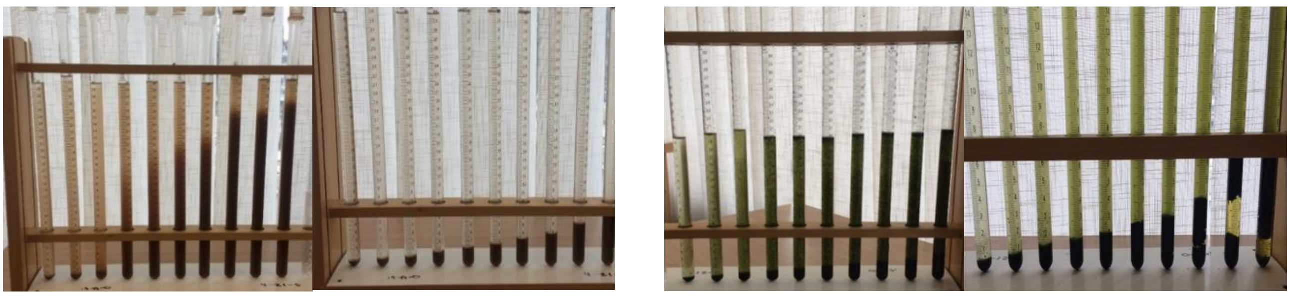


a b

Fig. 3. Particle size distribution: a – Chlorela Vulgaris algae; b – clay for Neveroniai career

SEM data is also confirmed by particle size distribution analysis (Fig. 3). Particles of 106 – 212 µm are predominant in algae (65.4 %). In clay, particles of different sizes are distributed evenly, and the largest part (~ 28.6 %) consists of 106 µm particles.

In order to assess the suitability of algae as a suspension fertilizer stabilizing additive, the effect of algae on the deposition rate of particles in the fertilizer suspension has been investigated over time. In parallel, the same studies were carried out with clay used in the production of suspension fertilizers (Fig. 4).



a b

Fig. 4. 2-4-18 suspension fertilizers with additive: a – clay for Neveroniai quarry after 10 min and after 100 min; b – Chlorela Vulgaris algae after 10 min and after 100 min

The tests were carried out using special tube sets. Each graduated single-tube tube was filled with 30 cm^3 of 12-4-18 suspension slurry and 0.5 % to 5 % of clay or algae added. The pictures in Fig. 4 show that suspended fertilizers using clay are unstable (100 % completely stratified after 100 min), and the algae additive has a positive effect on the stability of the suspension. Visual evaluation of these pictures shows that clay with solid fertilizer particles settles on the bottom while the resulting layer of fertilizer particles and algae is not continuous. Part of the solid particles have settled on the bottom, the other part remains suspended throughout the solution volume. Therefore, the leaching speed of suspension fertilizers was analyzed further using both accessories.

Fig. 5 shows volume dependence of the deposited suspension particles on clay content and retention time. It is evident from the nature of the curve that at very low clay content (up to 1 %), the maximum degree of particle deposition is reached after the first 10 minutes. When clay concentration is increased to 4.0 %, the slurry is slower and all the solids settle in 25 – 40 minutes. Increasing clay concentration (up to 9 %) further increases the formation of a stable sediment layer (90 – 100 min).

The nature of the curves in Fig. 6 is fundamentally different from the curves in Fig. 5. The suspension particle layer increases not only with increasing concentration but also with longer storage life.

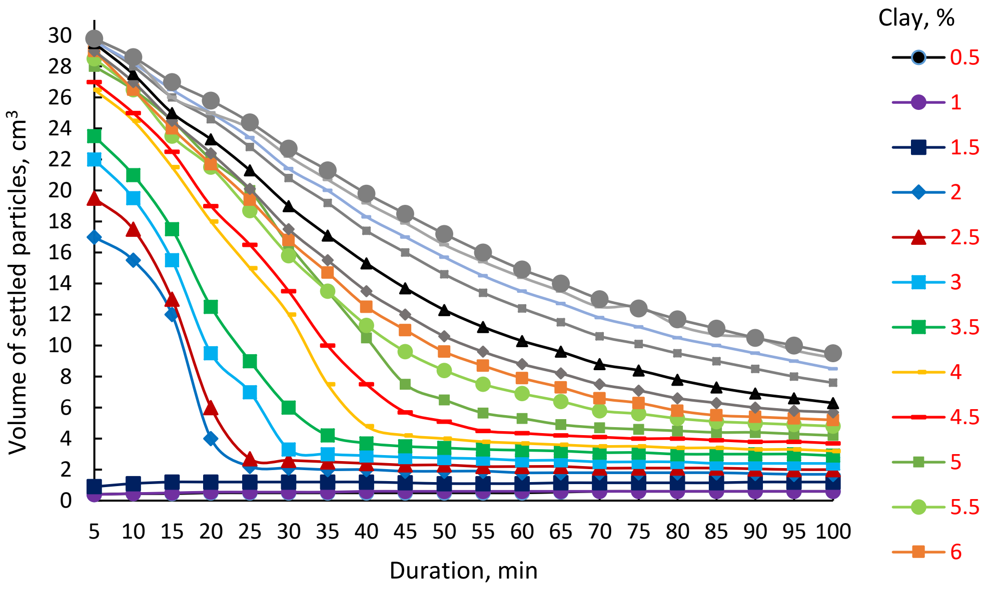


Fig. 5. Dependence of the volume of particles deposited in 12-4-18 suspension fertilizers on the duration of the experiment and the clay additive

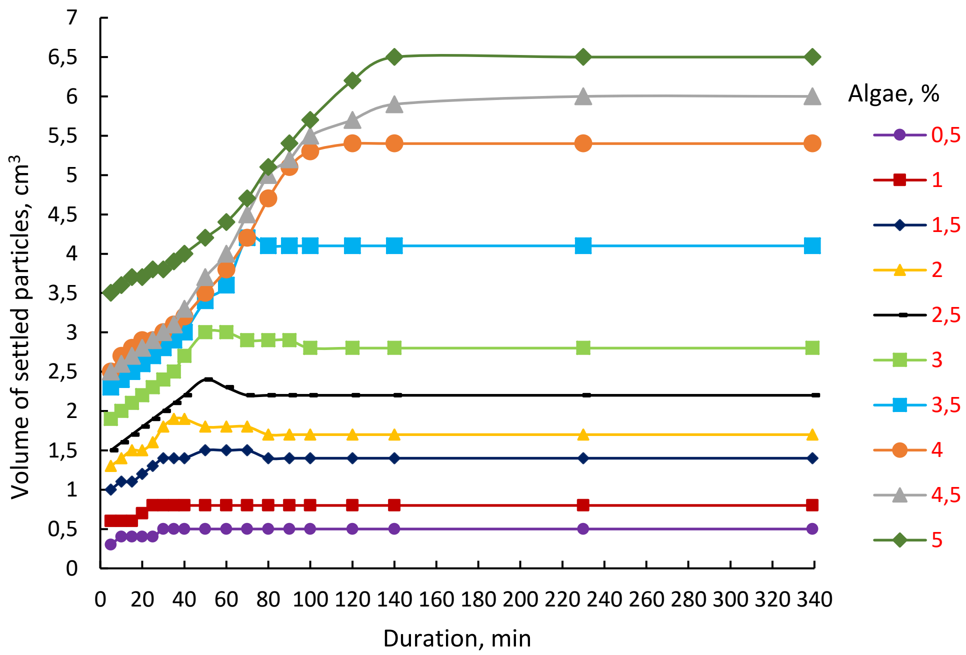


Fig. 6. Dependence of the volume of particles deposited in 12-4-18 suspension fertilizers on the duration of the experiment and the algae additive

When algae concentration is up to 1 %, the volume of precipitate formed does not change for 20 minutes. At a concentration of 1.0 – 3.0 %, the solids settle down more slowly. The maximum volume of precipitated particles at a concentration of more than 3 % is formed within 75 – 140 min.

According to the obtained results of suspension stratification, clay in the 12-4-18 fertilizer suspension, retains much shorter particles than algae. Using more than 3 % algae, a relatively stable suspension is formed, and the particles remain longer in suspension throughout the volume of the solution. It has also been observed that after a long period of time (1 – 3 days), the layer of solid fertilizer particles and algae remains non-continuous and continuous layer movement and mixing takes place. By using algae in this way, a relatively stable (non-stratified) fertilizer suspension is obtained.

The most important properties of the 12-4-18 suspension fertilizer with 3.5 % algae additives were determined: pH of 6.3 and crystallization temperature of 8.21 °C. The determined pH value corresponds to the requirements for liquid fertilizers, and the temperature above 0 °C limits the production and use of such fertilizers during the cold season. Physical properties of suspension fertilizers such as density and viscosity (density 1226 kg/m^3, viscosity – 7.32 mm^2/s), which meet the requirements for liquid fertilizers and are important for the design of pumps, pipelines, mixing, were also identified, when producing, transporting and spraying fertilizers in the fields. This quite concentrated suspension fertilizers, designed to meet plant nutrient demand, supplement soil nutrient and bioactive components supply and respectively new fertilizer strategies.

4. CONCLUSIONS

1. Results of chemical analysis show that algae are suitable for use as a fertilizer component, because they have neither aluminium nor silicon, and heavy metal concentration does not exceed permitted limits.
2. The particles of 106 – 212 µm in size contain most (65.4 %) algae, are irregular in shape but not agglomerated like clay.
3. Using algae, fine sediment remains in suspension much (4 times) longer and settles slowly to the bottom (with 4 % clay additives, the solid phase settles in 40 min, and with 4 % algae – in 130 min).
4. Stable 12-4-18 suspension fertilizers suitable for a warm period were obtained with 3.5 % algae additive. The main properties of such suspensions are: pH 6.3; crystallization temperature 8.21 °C; density – 1226 kg/m^3, viscosity – 7.32 mm^2/s.

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