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#### Review

## Unique effects of alginite as a bituminous rock on soil, water, plants and animal organisms

Ján Brindza<sup>1</sup>, Ľuboš Vozár<sup>2</sup>, Marián Miko<sup>3</sup>, Ján Gažo<sup>3</sup>, Peter Kovár<sup>2</sup>, Vladimíra Horčinová Sedláčková<sup>1</sup>, Olga Grygorieva<sup>4</sup>

<sup>1</sup>Slovak University of Agriculture in Nitra, Institute of Biodiversity Conservation and Biosafety,

Faculty of Agrobiology and Food Resources, Slovakia

<sup>2</sup>Slovak University of Agriculture in Nitra, Faculty of Agrobiology and Food Resources,

Department of Crop Production and Grassland Ecosystems, Slovakia

<sup>3</sup>Slovak University of Agriculture in Nitra, Faculty of Agrobiology and Food Resources,

Department of Genetics and Plant Breeding, Slovakia

<sup>4</sup>M.M. Gryshko National Botanical Garden, National Academy of Sciences of Ukraine, Kyiv, Ukraine

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The publication aims to present some knowledge about the less-known but at the same time very scarce bituminous rock alginite with comprehensive practical use in the form of a brief overview. Alginite is an organic-bituminous rock that was formed about six million years ago from dead fossil algae *Botryococcus braunii* Kütz and diatoms in the area of today's Pannonian Basin. In Europe, alginite deposits have been discovered in Hungary, Austria and Slovakia in Pinciná village. Alginite mining is mostly used in Hungary in the Gerce area. Alginite is grey to dark grey, in the wet state dark laminated, clayey with the form of disintegrating clay. Alginite has very valuable physical, mechanical and chemical properties. It is a natural bituminous rock with a favourable content of basic nutrients (P, K, Ca, Mg and S) for plants except for nitrogen content. Alginite contains a large number of microelements, which increase the agrochemical possibilities of its use. It can be applied in its natural form without chemical treatment. It is an ecological raw material that improves the soil and does not negatively affec the environment. Alginite has become the subject of research in many workplaces. The overview presents the basic physical, mechanical and chemical properties of alginite and selected knowledge and research results that have enabled the practical use of alginite in natural or technologically modified form in agriculture in the formation of growth, development and crop formation and quality of seeds and fruits of cultivated crops, forestry, remediation and improvement of soil and water properties, decomposition of herbicides, stabilization of beneficial microorganisms in animal organisms and other areas.

**Keywords:** alginite, bituminous rock, organic matter, properties, knowledge, use, agriculture, forestry, remediation waters, decomposition of herbicides

#### Introduction

The basic purpose of modern agriculture to provide nutritious and safe raw materials for food by economic processes and sustainable and environmentally responsible production thereof. The duality of the agricultural production namely the connection between the saving of environment and the profitability is the most important question recently which can be solved only by the maintaining of the fertility of the soil. The fertility of soil can be adjusted by added minerals and nutrients. In the soil, which is an independent living media the nutrients are exposed most diverse of chemical and biological transformations before they are utilized by plants. The cultivation and fertilizing should keep the intensive soil life because intensive soil fertility without intensive soil life is not possible. As

\*Corresponding Author: Vladimíra Horčinová Sedláčková, Slovak University of Agriculture in Nitra, Faculty of Agrobiology and Food Resources, Institute of Biodiversity Conservation and Biosafety, Nitra, Slovakia Vladimira.sedlackova@uniag.sk a result of the agricultural practices of the last decades, the fertility of the soils is decreased considerably because the amount the organic materials which provide intensive soil life is reduced considerably. Our soils suffer from carbon-starvation which is enhanced by the fact that the produced primary and secondary organic products are transported from the production area for industrial use. Besides the lack of organic matters the microelement content of our soils also reduces.

For providing the proper agricultural functionality the organic content of the soil has to be at least 2 %. With this, the soil provides the life conditions of microorganisms that mineralize the organic materials and which activities determine basically the fertilizer capability of the soil. Soils having less organic content are unable to maintain the nutrients evolved from the mineralized organic compounds, thus these are washed out from the soil caused severe environmental problems e.g. the lack of microelements in food plants which cause severe health problems for humans at the end of the food chain. The forms of the disadvantageous changes of soils are the compactness of the soil, bad air and water management, the starting of the salinization on the watered areas, the erosion and deflation. The basic cause of these changes is the degradation of the organic-mineral colloids of soil which results that there are no reactants enough in suitable amount or composition for the chemical and biological reaction in the soil. In the soil, the mineral elements for the life of the microorganisms are provided by a so-called organicmineral, in other words, organomineral complex. The restoration of the structure and the function of these organomineral complexes are the primary purpose of soil improvement and soil conditioning.

### Bituminous rock alginite – a scarce natural raw material

Research institutes in many countries around the world are also looking for and testing several natural rocks. One of these mineral rocks is alginite.

Alginite as a bituminous rock is a scarce natural raw material. Hitherto, alginite has been discovered in Australia (Ozimic, 1982), Hungary (Solti, 1987), Austria (Solti et al., 1987), Slovakia (Vass et al., 1995, 1997a,b,c, 1998), USA (Stankiewicz et al., 1996) and China (Jia et al., 2013).

The first research and its practical use with bituminous rock in the Gerce region is in Hungary. Alginite from Hungary became the subject of follow-up research (Ravasz et al., 1994; Németh et al., 2008; Kádár et al., 2015; Vígh et al., 2016; Soós et al., 2018) and the search for practical possibilities of its use in Austria (Solti et al., 1987), the Czech Republic (Tužinský et al., 2015; Holzer et al., 2018), Spain (Mastalerz et al., 2013), Slovenia (Komac, 2016), Romania (Kentelki, 2010), Germany (Hippmann et al., 2016, 2018) and Russia (Motyleva et al., 2014).

An economically important deposit of alginite was also located in Slovakia in Maar near Pinciná village north-east of the town of Lučenec (Vass et al., 1997a). The exploitation of alginite from the deposit is only in the beginning stage. Nevertheless, alginite has become an important research object even in the conditions of Slovakia at the Geocomplex research workplace (Kovár et al., 2021), University of Veterinary Medicine and Pharmaceuticals in Košice (Nemcová et al., 2012–2015; Styková et al., 2016; Strompfová et al., 2018), Technical University of Zvolen (Bublinec and Gregor, 1997; Beláček, 1998, 2003, 2006; Beláček et al., 2002; Sarvašová, 2009), Slovak University of Agriculture (Kulich et al., 2001, 2002; Kovár et al., 2021), National Agriculture and Food Centre - Soil Science and Conservation Research Institute (Barančíková et al., 2003; Litavec and Barančíková, 2013; Barančíková and Litavec, 2016), State Geological Institute of Dionýz Štúr (Baláž et al., 2010), many research institutes (Elečko et al., 1998) and other universities (Bednárová, 2019).

Since 2016, significant research activities have been provided by several research teams at the Slovak University of Agriculture in Nitra. Research activities at the level of basic and applied research are focused on the development and application of various preparations developed from natural alginite on various plant species to recognize the effects of alginite on germination, plant growth and development, biomass formation, seed and fruit yields, tolerance of biotic and abiotic factor of the growing environment and the quality of plant parts.

Alginite, as an organic-bituminous rock, originates mainly from the bodies of dead algae (from the Latin algae). It formed as a rock during various geological periods, especially those that gave algae optimal conditions for growth and reproduction. Post-volcanic crater lakes or swamps were sites where alginite arising (Vass et al., 1995, 1997a,b,c, 1998).

The complex characterization of the alginite deposit in Pinciná in Slovakia was processed by Vass et al. (1995, 1997a,b,c) and other research teams (Kulich et al., 2001, 2002; Litavec and Barančíková, 2013).

#### **Basic characteristics of alginite**

Alginite, which fills a former inland sea at Pinciná, is a grey to dark grey laminated, clayey rock rich in organic substances, weakly strengthened organogenic sedimentary rock with a form of disintegrating clay (Vass, 2005). It was formed from algae in the aquatic environment. In the rock, the dark and light laminae of 0.5 to 2.0 mm in thickness are alternating (Figures 1 and 2). Dark laminae are rich in *Botryococcus* remains whose funnel cell covers consist of organic material similar to sporopoleminium (Vass, 1998). The light lamina is formed from clay material and contains repositories of diatoms formed by opal (Vass, 2005).

In the wet state, there is a dark-coloured unconsolidated clayey rock. This is confirmed by the results from various boreholes in the alginite deposit in Pinciná, which drilled in 2020 by Geocomplex (Figure 3).

Alginite has the characteristic of organic soil. Organic substances significantly increase humidity and plasticity. The humidity determined by drying at



Figure 1 Plates of natural alginite (Photo: J. Vrábel, 2020)

22–30 °C was in the range of 57.75–78.63 %. Samples from the top layer of the alginite showed 15 % higher humidity when dried at 60 °C than when open-air drying. When dried at 105 °C temperature, the humidity was



Figure 2 Natural alginite in the Pinciná deposit, Slovakia (Photo: Š. Hajdu, 2017)



Figure 3 Colour of wet alginite samples obtained from different depths at the Pinciná deposit (Photo: A. Oravec, 2020)

higher than 100 %. These data correspond well with the water absorption capacity (Vass et al., 1997a,b,c).

The specific weight of alginite was determined by Vass et al. (1997a,b,c) in the range of 2.06 to 2.35 g.cm<sup>-3</sup> and Kulich et al. (2002) 2.568 g.cm<sup>-3</sup>. The specific weight of alginite compared to standard soil (2.65–2.75 g.cm<sup>-3</sup>) is relatively low. The presence of organic matter affected the bulk density and specific weight of the dry rock.

Vass et al. (1997a,b,c) determined a porosity for alginite in the range of 62.44 to 68.45 % and Kulich et al. (2002) only 40.8 % and high absorbency of 82.0 % indicate a high sorption capacity, which originates in a polymineral composition of alginite containing clay minerals and organic matter.

The water absorption capacity of alginite (Aranyi coefficient) in alginite Pinciná was determined by Vass et al. (1997a,b,c) in the range of 80-108. This is more than the value of the water absorption capacity of alginite in natural soils. Heavy soil has the largest water absorption capacity, 61–80 (Vass et al., 1997a,b,c). The water balance of the soil depends on the content of the clay component in the soil and on its mineralogical composition. In the case of alginite, the absorption capacity also depends on the organic matter content.

Alginite from Pinciná is an important natural raw material for improving the absorption properties of the soil, as well as for increasing the water holding capacity. One kilogram of alginite from Pinciná can absorb and retain about 1 litre of water for a long time without expanding its volume. It also retains decay, similar to the unsaturated state. Therefore, alginite makes it possible to accelerate and improve the transport of water into plants according to the needs of individual plant species (Vass et al., 1997a,b,c).

Vass et al. (1995, 1997a,b,c) determined in alginite from Slovakia the pH values in the range 5.87-7.10, Litavec and Barančíková (2013) in the range of 5.50-7.20, which indicates a weakly acid to the neutral reaction of alginite. Only in the case of sampling point 11 at a depth of 8 m did they detect a weakly basic reaction of alginite (pH = 8.13), with a considerably high concentration of inorganic carbon of 4.6 %. Vass et al. (1997a,b,c) determined an average pH of 6.28in alginite. The results of the authors agree with the results of analyzes in the Algalit laboratory (Hungary), according to which the pH in alginite from Hungary was determined in the range of 4.79-6.94 (Ravasz et al., 1994). The basic pH values of alginite allow the classification of alginite among neutral natural raw materials with a higher humus content in the range of 6.53–33.10 % (Kulich et al., 2002).

The relatively low content of  $CaCO_3$  in alginite from Pinciná was caused by geological conditions. There are no carbonate rocks around the deposit. The authors (Vass et al., 1997a,b,c) determined the content of  $CaCO_3$ in alginite in the range of 1.16-3.72 % (mean 2.17 %) by atomic absorption spectrometry. In the alginite from the borehole VPA-7, it determined the  $CaCO_3$  content from 1.06 to 14.74 % (mean 2.61 ±3.03 %). Ravasz et al. (1994) determined a  $CaCO_3$  content ranging from 0.0 to 14.0 % (mean 0.7 ±2.16 %).

Salt content is an important indicator in the evaluation of fertilizers and soil activators. Soils should contain as few salts as possible to avoid the salinity of the soil. According to the total salt content, the following are distinguished: soils with a trace salt content (<0.05 %), slightly saline soils (0.05–0.15 %), saline soils (0.15–0.40 %) and highly saline soils (>0.40 %). Plants sensitive to soil quality do not grow on weakly saline soil, on saline soil only the most resistant plants and on strongly saline soil no plants grow (Ravasz et al., 1994). The salt concentration was determined by the laboratory Algalit (borehole VPA-1 and 3) and GS SR (borehole VPA-7). The average salt content was determined to be 0.1, respectively 0.041 %. Kulich et al. (2001) determined the salt content in alginite samples in the range of 0.04–0.05 %. According to Vass et al. (1997a,b,c) alginite from the Pinciná deposit with salt content corresponds to weakly saline soil, respectively soil with a trace salt content.

Vass (1998) determined an average  $C_{org}$  content of about 9 % from analyzes of organic matter of alginite. The distribution of organic carbon is unequal. From the contents of  $C_{org}$  by multiplying a Welt coefficient of 1.72 (Valla et al., 1980), the humus content was calculated to be about 15 % (Vass et al., 1998).

Although alginite from the Pinciná deposit contains a higher content of organic carbon in the alginite, the content of humified organic matter is low. Type II kerogen predominates in organic matter of algal origin (Vass, 1998). The fractional composition of the humified organic matter has a higher content of fulvic acids than humic acids. This is evidenced by the low value of the carbon ratio of humic acids to fulvic acids (Litavec and Barančíková, 2013).

The proportion of the clay fraction in the alginite from the Pinciná deposit was determined to be in the range of 11–79 %. Of the clay minerals, illite and kaolinite predominate, the most represented mineral is

Minerals	Diffraction max. values	Minerals	Diffraction max. values
Smectite	14–15 Ä	Kaolin	7.0–3.6 Ä
Quartz	4.2–3.3 Ä	Dolomite	2.8 Ä
Illit-mica	10.0-5.0-3.3 Ä	Chlorite	7.0-4.7-3.6 Ä
Calcite	3.8–3.0 Ä	Feldspars	3.7–3.2 Ä

Table 1	Mineralogical composition of alginite according to the values of diffraction maximum values (Kulich et al., 2001)
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smectite. The specific surface area of alginite confirms its high sorption capacity with a specified range of 313–654 m<sup>2</sup>.g<sup>-1</sup> (Vass et al., 1997b). There is a direct linear relationship between the specific surface area and the smectite content as well as the organic matter content. Sorption tests confirmed the ability of alginite to bind lead from polluted waters, cadmium sorption is less efficient (Vass et al., 1997a).

Clay minerals (smectite, illite), carbonates (calcite, dolomite) and amorphous quartz and silica are the dominant mineral components of alginite, while gypsum, plagioclase, K-feldspar, siderite, goethite, pyrite and magnesite can also be found in smaller amounts. In 1974, within the framework of the mapping research programme of the Geological Institute of Hungary (MÁFI), Solti (1999) explored one-time volcanic craters buried in alginit and basalt bentonite. The mineralogical composition of alginite is also reported by the team of Kulich et al. (2001), which documents the data in Table 1.

### Chemical composition of alginite

Concerning biogenic elements, in addition to the nitrogen content, the presence of P, K, Ca, Mg and S can be positively assessed for alginite (Table 2). A comparison of the content of macroelements shows significant variability between alginite samples. This is because alginite as a sedimentary rock is not homogeneous (Russell, 1990; Vass et al., 1997a,b,c; Kulich et al., 2001).

Alginite contains a large number of microelements that increase the agrochemical value of alginite (Table 3). Regarding the risk elements (As, Cd, Pb, Ag, Cr, Se) in no case were the values of the limit contents according to the standard valid in the territory of the Slovak Republic exceeded (Kulich et al., 2001). The comparison of the content of microelements shows significant variability between alginite samples.

Regarding the nutrients available to plants from natural alginite, the contents of phosphorus, potassium, calcium and magnesium are higher than the optimal contents of these elements in agricultural

Table 2Basic chemical composition of samples of powdered alginite (% of dry matter) from the Pinciná deposit according<br/>to the results of the accredited laboratory Reg. No. 038 / S-025

Measured	Evaluation of an alginite sample by authors' results of this article		Results from literary data		
parameter	alginite sample 3533	alginite sample 3548	alginite sample 3536	Vass et al. (1997) borehole VPA1,3,4,5	Kulich et al. (2001)
SiO <sub>2</sub>	47.55	47.29	47.10	39.1-53.04	37.50-53.30
Al <sub>2</sub> O <sub>3</sub>	17.85	18.31	18.44	13.06-17.89	11.05-22.50
N	-	-	-	0.10-23.80	_
TiO <sub>2</sub>	1.11	1.11	1.11	0.90-1.30	1.10-1.34
Fe	6.86	7.08	7.03	0.97-5.75	5.85-8.00
Ca0	1.07	0.97	0.90	0.93-2.32	0.80-8.40
MgO	1.43	1.42	1.39	0.62-1.92	0.60-4.02
MnO	0.04	0.04	0.04	0.01-0.36	0.04-0.30
P <sub>2</sub> O <sub>5</sub>	0.12	0.13	0.13	0.42-0.92	0.15-1.64
Na <sub>2</sub> 0	0.30	0.45	0.43	0.33-0.81	0.33-0.74
K <sub>2</sub> 0	1.09	1.54	1.54	1.05-1.85	1.05-1.37
SO <sub>2</sub>	-	-	-	0.42-2.47	_
Humidity	8.65	1.71	1.58	_	_

Cr		Alginite sample 3548	Alginite sample 3536	Vass (1997a)
	138	183	145	18-68
Ag	<0.1	<0.1	<0.1	0.1-2.19
As	4.87	6.22	4.94	1.48-9.35
Ba	364.2	374.3	386.0	196-1109
Be	1.8	2.3	2.3	0.93-1.85
Bi	0.25	0.53	0.58	<10
Cd	<0.5	<0.5	<0.5	0.010-0.145
Со	25.8	34.4	32.6	4-29
Cs	<5	5.2	5.1	_
Cu	30.9	40.5	43.7	31-83
Ga	24	20	20	9–20
Ni	123	173	146	43-209
Pb	10.7	17.3	20.6	6-58
Sn	5	6	11	<3
Sr	59.8	58.9	59.4	51-123
V	121	124	121	30-75
Zn	85	109	119	76-120
Zr	137	130	132	135-321
Sb	0.92	0.51	3.56	0.04-7.80
Rb	27	88	86	45-98
Se	<0.1	<0.1	<0.1	0.01-0.05
Те	<0.5	<0.5	<0.5	-
La	34	34	35	-
Nb	23	26	26	_
Се	64	64	64	_
Y	21	22	22	_

Table 3Content of microelements in powder alginite (mg/kg of dry matter) from the Pinciná deposit according to the<br/>results of an accredited laboratory Reg. No 038/S-025

soils. Only the nitrogen content is insufficient (Kulich et al., 2001).

### Organic matter of alginite

Ognjanova-Rumenova and Vaas (1998) found that the dark layers of alginite are rich in residues of the algae *Botryococcus braunii* Kütz. The finer, lighter layers of alginite are rich in diatoms. In the published study a total of 181 taxa are observed in the present study. They refer to 35 genera, 128 species, 37 varieties and 6 forms, and belong to 13 families, 4 orders and classes Centrophyceaea and Pennatophyceaea. Diatoms were identified to species whenever possible; however ten entities could be assigned to the genus only. The diatom flora mostly consists of modern species – 92.4 %, but the group of extinct species (7.6 %) is abundant in

some levels (i.e. *Pliocaenicus omarensis* (Kütz.) Round & Hak., *Aulacoseira distans* var. *scala* (Ehr.) nov. comb, etc.). In general, pennate forms are the most varied (94.5 %). The species-rich genera *Navicula* Bory and *Cymbella* Ag. can be distinguished, they account for 26.5 % of the entire flora. These are followed by the genera *Pinnularia* Ehr. (8.8 %), *Fragilaria* Lyngb. (7.2 %), *Achnanthes* Bory (7.2 %) and *Gomphonema* Ehr. (6.1 %). The class Centrophyceae accounts for 5.5 % of the diatom flora. More of its representatives are widely spread, in some levels they are rock-forming and occur as dominants or subdominants.

The authors of the presented publication analyzed more than 200 samples of alginite from different parts of the Pinciná deposit and confirmed the results of the

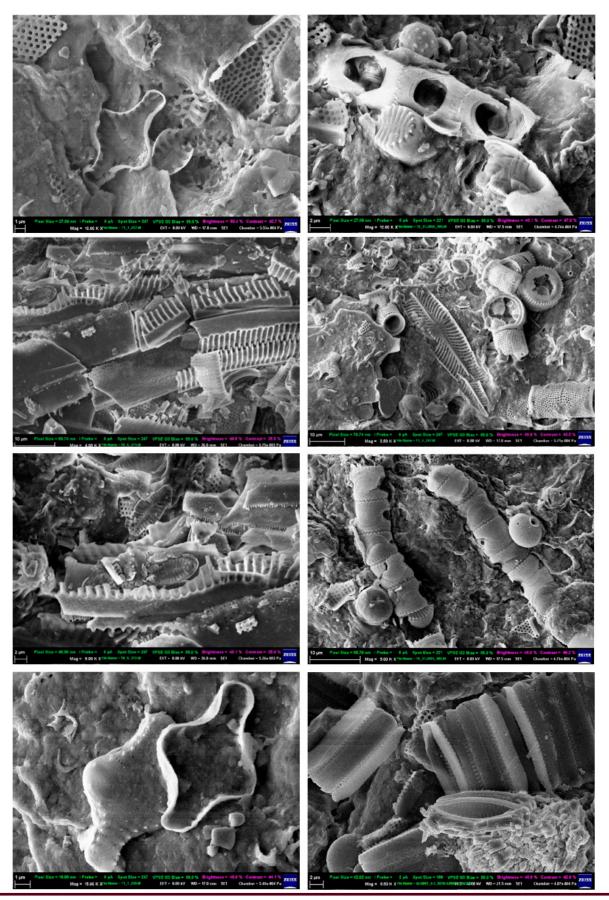


Figure 4Demonstration from some species of diatoms found in alginite samples from the Pinciná deposit (Photo:<br/>R. Ostrovský, 2017)

works of Ognjanova-Rumenova and Vaas (1998), which we also document in Figure 4.

In 74 samples of alginite, Vass (1998) determined a humus content in the range of 6.88–45.37 %. Kulich et al. (2001) determined the humus content in the range of 6.53–31.1 % and Pichler et al. (2001) document a humus content of 15.5 % in alginite.

In experiments, Litavec and Barančíková (2013) found that alginite, despite a sufficient content of organic carbon (OC = 5.5 %), contains relatively little humified organic matter. Its fractional composition has a higher content of fulvic acids than humic acids.

Vass (1998) determined an average  $C_{org}$  content of about 9 % from analyzes of organic matter of alginite. The distribution of organic carbon is unequal. From the contents of  $C_{org}$  by multiplying a Welt coefficient of 1.724 (Valla et al., 1980), the humus content was calculated to be about 15 %.

Organic matter in alginite is converted to kerogen. Kerogen (gr.) is a complex mixture of organic chemical compounds that make up the most abundant fraction of organic matter in sedimentary rocks. As kerogen is a mixture of organic materials, it is not defined by a single chemical formula. Its chemical composition varies substantially between and even within sedimentary formations. Kerogen is insoluble in normal organic solvents in part because of the high molecular weight of its component compounds. The soluble portion is known as bitumen. When heated to the right temperatures in the earth's crust, (oil window c. 50-150 °C, gas window c. 150-200 °C, both depending on how quickly the source rock is heated) some types of kerogen release crude oil or natural gas, collectively known as hydrocarbons (fossil fuels). When such kerogens are present in high concentration in rocks such as organic-rich mudrocks shale, they form possible source rocks. Shales that are rich in kerogen but have not been heated to the required temperature to generate hydrocarbons instead may form oil shale deposits (Vandenbroucke and Largeau, 2007).

### Practical use of alginite

Alginit as a natural material and its organicmineralogical composition to give a possibility to use in organic farming system management. As mineralrich in high organic matter content, biogenic and trace elements have excellent preconditions for use mainly in agriculture as a natural fertilizer increasing fertility. Alginit is also very interesting for the high content of humic substances, which are an important component of natural organic matter in soil and sediment. Humic substances heterogeneous organic compounds are environmentally important substances that can improve soil fertility. With its hydro-saving properties, it is one of the excellent water absorbent material with the potential to regulate the distribution of water toward the plant roots.

In more than 40 years since the discovery of alginite as a bituminous rock and knowledge of its properties, significant research has gained significant knowledge of its comprehensive use. The next part of the review presents some results and findings from various areas of research, which documents (...research, which documents...) that alginite is a unique, but still little known bituminous rock.

### Effects of alginite application on plant germination

The influence of alginite and extracts from it on germination of Kentucky bluegrass (Poa pratensis L.) researched Kovár et al. (2021). The effect of alginite (powder, crushed alginite) and extracts from it (ALGEX 2 – "sodium solution", ALGEX 4 – "potassium solution") was observed in a controlled condition of a climatic chamber (26 °C/15 °C; 12 h light/12 h dark; 70 % rh) in an experiment with *Poa pratensis* L. on parameters as germination dynamics, average germination, germination rate and mean germination time. There were 5 treatments in this experiment: V1 - control without alginite and extracts from it; V2 - alginite powder 10 % vol.; V3 - crushed alginite 10 % vol.; V4 - 1.5 % extract ALGEX 2 and V5 - 1.5 % extract ALGEX 4. A significant increase in the germination of *Poa pratensis* L. was recorded as early as the 7<sup>th</sup> day of the experiment, using the ALGEX 4 extract, where the germination reached 340.00 % compared to the control. From the overall point of view, the positive and at the same time significant (p = 0.0000) effect of alginite and its extracts were manifested. The application of the solid form of alginite increased the average germination by 51.70 % (powder) and 201.70 % (crushed alginite), while the use of alginite extracts increased by 33.33 % (ALGEX 2) and 334.20 % (ALGEX 4) compared to the control. Alginite and its products can also be positively evaluated in terms of their effect on the germination rate, which they increased by 0.04-1.52 seeds/day in *Poa pratensis* L. compared to the control. The most apparent acceleration of germination was achieved with the application of alginite in liquid form (ALGEX 4) – 1.57 seeds/day, respectively alginite in solid form (crushed alginite) - 0.75 seeds/day with significant (p=0.0052) differences between treatments. The values of the mean germination time showed a shortening

of the germination time in all treatments using alginite, namely by 2.82 days with powder application, by 3 days with crushed alginite, by 1.31 days with ALGEX 2 extract and by 4.95 days with extract ALGEX 4.

### Effects of alginite application on soil improvement and crop production

Vass et al. (2002) in a three-year experiment, the authors tested the effect of alginite from the Pinciná deposit on the chemical properties of soils in three sites - light soil, agglomerated brown soil, sandy-clay soil with a comparison of unfertilized parcels and other fertilization combinations. At the end of the experiment, the decrease in pH of alginite-fertilized soils was the lowest of all fertilization combinations. The content of plant-acceptable P and K in the soil decreased significantly, which means that alginite facilitates nutrient uptake by plants. The humus content also decreased but in the alginite-treated soil the least. The content of exchangeable bases was higher than in unfertilized soil. The sorption capacity level at one site reached the fully saturated degree, decreased at other sites, but relatively least in alginitetreated soils. The contents of heavy metals in the soils changed slightly, with exception of the site in Pitelová, where the contents before and after the end of the experiment exceeded the indicator value, which is probably a consequence of the floods of the river Hron. Relatively higher concentrations of heavy metals in alginite-treated soil indicate a higher sorption capacity of alginite, which protects plants from increased uptake of toxic metals.

Gömöryová et al. (2009) tested the effect of the amendment with alginite, an organic rock originating from the biomass of fossilized unicellular algae, on microbial activity of forest soils using a pot experiment. Five variants of soil-alginite mixtures were tested in three replicates with two forest soils: a loose sandy soil and a sandy loam. Gravimetric moisture closely correlated with the dose of alginite in both soils. Basal respiration and catalase activity increased with the dose of alginite in the sandy soil, but not in the sandy loam, where the highest response was observed at intermediate doses of alginite. The correlations of microbial activity parameters with moisture in the sandy soil were also much closer than in the sandy loam. The amendment with alginite was thus effective in improving some of the selected microbial activity indicators, but the optimum dose of alginite strongly depended on soil texture.

### Effects of alginite application on growth, development, crop formation and quality

Kádár et al. (2015) studied the effect of alginit on the soil and triticale over three years (2012-2014), in a long-term field experiment set up on acidic sandy soil in Nyirlugos. A 100 t.ha<sup>-1</sup> rate of alginit was applied in concentrations 0, 50, 100 and 150 kg.ha<sup>-1</sup>.year<sup>-1</sup> N. On alginit-treated plots, the pH (KCl) increased from 3.9 to 6.2 Every year the application of alginite increased the yield of straw and grain triticale. Alginit treatment generally doubled the yields, especially on plots treated with 150 kg.ha<sup>-1</sup>.year<sup>-1</sup> N, which became acidified and impoverished in Ca, Mg, K and P. Alginit treatment increased the Mg, Mo and Cd uptake and reduced that of Mn, Zn and Ba by triticale seeds. The Ca, Mg, S and Mo concentrations increased in the straw, while the incorporation of Mn, Zn, Ba, Cu, Ni and Co was inhibited by alginit. Alginit is a suitable mineral for the amelioration of similar acid sands, which may eliminate the acidity caused by excessive N supplies and improve the water holding capacity, colloidal and nutrient status and drought-tolerance, and thus their fertility.

Komac (2016) determined the application of alginite as an additive for improving water-retention properties of soil, and if its use improves the quality and increases crop yields. An experiment carried out with a Chinese cabbage (*Brassica rapa* subsp. *pekinensis* (Lour.) Hanelt) and a germination test with cress. Even the highest dose of alginit (A2 = 60 t.ha<sup>-1</sup>) did not alter the soil water capacity. Germinating cress test showed that alginit is not phytotoxic but encourages the emergence and growth of seedlings. Alginit increased the yield of the fresh mass of cabbage compared with unfertilized control of 22–30 % and had a similar effect as the bovine farmyard manure.

Vígh et al. (2016) studied "P37N01" hybrid maize (Zea mays L.) in a large-plot fertilization experiment on brown forest soil. Two various nitrogen fertilizers (Nitrosol - 30 % N and Pétisó - 27 % N) were applied. Five various treatments were conducted with 130 kg.ha<sup>-1</sup>, and one with 165 kg.ha<sup>-1</sup> specific amount of nitrogen active ingredient. At three treatments the "Nitro-sol 130 kg.ha-1" was applied altogether with additives: Alginit 10 l.ha<sup>-1</sup>, Dudarit 10 l.ha<sup>-1</sup> and Dudarit 10 l.ha<sup>-1</sup> + Alginit 10 l.ha<sup>-1</sup>. It was found that the nitrogen uptake in the leaves was highest at "Nitrosol 130" treatment; the phosphorus uptake was the highest at "Nitrosol + Alginit + Dudarit" treatment. The highest boron concentration in leaves was observed at "Nitrosol 165" treatment; the copper and manganese concentrations were the highest at "Nitrosol 130"

treatment; the molybdenum at "Nitrosol + Alginit + Dudarit" treatment, while zinc uptake was the highest at "Nitrosol + Alginit" culture. Dudarit and alginit mixed with Nitrosol facilitate primarily the incorporation of essential macro- and microelements in the seeds (not to leaves) of maize.

Oravcová et al. (2018) researched the content of mercury in soil and in plants grown in contaminated soil with the addition of Alginite. Samples of soil contaminated with mercury were taken from the locality of Malachov and then mixed with Alginite in a 1 : 3 and 1 : 1 ratio. These substrates were applied on *Brassica napus* L. var. napus. (rape). Plant and soil samples were analyzed on a dedicated spectrophotometer - AMA 254. In the samples of substrates used for growing rape, we found a mercury content from 0.0929 to 2.9085 mg/kg. The mercury content in the above - rape biomass from 0.0425 to 0.3302 mg/kg. The sorption properties of Alginite were most pronounced in the above-mentioned rape biomass when a drop-in mercury content of 0.2005 mg/kg was recorded. The resulting values were compared with the limit values that were exceeded in many cases. From the values, it has found, that Alginite has confirmed its sorption properties, which can be further used in the treatment of the physical-chemical properties of lighter soils, the decontamination of soils devastated by anthropogenic activity.

### Effects of alginite application on rooting and growth of forest plant species

Tužinský et al. (2015) evaluated the effect of alginite on the growth parameters of seedlings of Douglasfir, Scots pine and line mixture of pedunculate oak, red oak and Norway maple (broadleaves) on former agricultural land with an unfavourable hydrophysical regime. The following doses of alginite were tested in the experiment: control (variant A without alginite), 0.5 kg of alginite (B) and 1.5 kg of alginite (C) when planting both conifers and mixtures of broadleaves. The number of seedlings on the sub-plots was 400 individuals, only in the case of Douglas-fir, the number was 200 individuals. Therefore every combination of tree species and the amount of alginite had 4 replications. The parameters of growth and development of individual trees (height, increment and mortality) show that after 2 years, both doses of alginite had statistically positive effects on height increments.

Sarvašová (2009) tested the effects of the alginite on growth and development of 4-years-old European silver fir (*Abies alba* Mill.) and Norway spruce (*Picea abies* (L.) Karst.) plants. The best results as measured by the height of the aboveground part, length of the root system and root-collar diameter. The positive effect of alginite for silver fir was observed only at the height of the aboveground part and the length of the root system, for spruce as well as in thickness root neck. Alginite belongs to perspective natural soil conditioners.

Beláček et al. (2002) documented that alginite in forestry can be used not only as a fertilizer. Fundamental to the argument is the following observation that alginite improves; supports the entrance of water to plants that is very important mainly after forest planting. During the first years, the root system of plants is not able to gather water from deeper horizons of soil. Grounds for supposing that alginite can be used mainly for sandy types of soil (spread mostly in Záhorie and Cerová vrchovina highlands) are just because these types of soil are with underdeveloped structure. They are very light, permeable and without the ability of water retention for a longer time.

### Effects of alginite application on water remediation

One class of contaminants gathering increasing concern is endocrine-disrupting chemicals (EDCs). This pollution stems from one of three sources: agriculture (pesticides), industry (plasticizers, etc.), and pharmaceutical products. With the multitude of chemical additives, nature-based solutions are in particular demand. Alginite, mined in Hungary, has been studied regarding its potential for EDC remediation in polluted water. Alginite is immature oil shale, consisting of clay minerals, feldspars, quartz, accessories, and an organic component. This organic component, mainly derived from ancient algae and pollen, has been diagenetically modified and is now harmless, rendering Alginite a safe material for treating water. Although the material is already approved and in use for soil amelioration, technologies for water treatment are still missing. Guhl et al. (2018) found the extensive capability of Alginite to immobilise EDCs, such as 17b- estradiol, diclofenac, and others. Adsorption isotherms have been determined for a multitude of compounds; the general capability of Alginite to remedy endocrine-disrupting contamination has thus been shown. However, the actual mechanism of EDC removal by Alginite remains elusive. Acknowledging the heterogeneous nature of this material, a fractionation of the material into clay-rich and organic-rich parts aims at understanding the individual component's action towards pollutants. Interestingly, ethinylestradiol- and carbamazepine-polluted waters react differently to Alginite components. However, it has already been

published that organo-clay materials are suitable for treating diclofenac-polluted waters (diclofenac adsorbs poorly onto untreated clay).

The adsorptive removal of endocrine-disrupting chemicals (EDC) from municipal wastewater is a problem of wastewater treatment technology that has not yet been fully resolved (Kropp et al., 2021). Tröbs and Bertau (2017) examined alginite for its suitability as an adsorbent for water purification. Nevertheless, alginite (43 m<sup>2</sup>.g<sup>-1</sup>) compared to activated carbon (594 m<sup>2</sup>.g<sup>-1</sup>) has a lower specific surface area, the area-related loading capacity compared to activated carbon is high and is only below the values found for activated carbon in the case of EDC with a high degree of dissociation. This is the result of the interaction of kerogens as a nonpolar organic phase as well as basic seam-neutral crystal surfaces of the inorganic matrix. The adsorption of the EDC takes place primarily at the kerogen phase of the alginate. The differently realizable equilibrium loads can be explained well by the different lipophilia of the investigated EDC model substances. The adsorption behaviour on alginite is strongly influenced by the degree of dissociation dependent on the pH value. Considering the economic application of alginite in municipal wastewater treatment technology, the adsorbent must be assessed with regards to its arearelated, weight-related loading capacity. This shows that alginate and activated carbon can complement each other extremely effectively and develop an improved cleaning effect in combination. From an economic point of view, the significantly lower price of alginite (approx. 50–100 €.t<sup>-1</sup> vs. 1000–2000 €.t<sup>-1</sup>) has a positive effect. For these reasons, alginite seems highly interesting for wastewater treatment. Due to its high carbonate content, alginite also shows a buffering effect, so that the addition of chalk (lime) to the revitalization basin could be minimized.

Frišták et al. (2015) used Alginite, as a component of some types of kerogen alongside amorphous organic matter for adsorptive separation and removal of  $Cd^{2+}$ ions from aqueous solutions. Alginite material was characterized by X-ray diffraction, ATR-FTIR, cation exchange-capacity and specific surface area analyses. Evaluation of alginite sorption properties showed the effect of solution pH value in the range from 2 to 6 on the sorption capacity of alginite. At slightly acidic conditions (pH 6.0–6.5), the alginite samples exhibited a sufficient sorption capacity and stability. The pseudosecond-order kinetic model described the sorption data better than the pseudo-first-order kinetic model. The equilibrium of cadmium sorption by alginite was reached within 120 min. Maximal sorption capacity  $(Q_{\max})$  calculated from experimental equilibrium data (Langmuir adsorption isotherm) was 23.62 mg.g<sup>-1</sup>. Sorption energy of Cd<sup>2+</sup> ions calculated from the Dubinin–Kaganer–Radushkevich model confirmed the ion-exchange mechanism of cadmium removal for alginite sorbent. The alginite from central European geological maar (Pula, Hungary) can be utilized for the production of new non-conventional sorbents or mineral filters for the removal of toxic metals.

### Effects of alginite application on herbicide degradation

Rauch and Földényi (2012) studied the catalytic effect of an alginite was studied under laboratory conditions on the decomposition of herbicide propisochlor. The breakdown process was followed in four parallel experiments: buffered solution (pH = 7), in buffer solutions containing alginite or bentonite (a common rock), also in the solution obtained from the extraction of the alginite (alginate/buffer = 1/10). In the aqueous phase, the decomposition of the herbicide was followed by using HPLC-UV and the metabolites of degradation were identified by GC-MS techniques. For the phenomenological description of the experimental decay curves, two parallel reactions with first-order kinetics were taken into account. During the time of experiments, no significant decomposition was observed either in the pure buffer solution or in the presence of bentonite. When, however, alginite was added to the system the degradation of propisochlor was accelerated dramatically: after 5 days, its concentration dropped below 50 % of the initial value. The identified degradation products indicate both reductive as well as oxidative biological mechanisms operating under anoxic conditions. It was proved earlier that the sulfenic and sulfinic acid ester derivatives of the propisochlor appeared in the metabolic pathways of animals and plants, but they were not detected yet in the degradation process occurring in the soil environment. Among the degradation products, a dehydrochlorinated derivates is a new metabolite identified in experiments. Results corroborate the algae-related origin of the alginite and forecast its application as a soil ameliorating agent.

Benei and Rauch (2016) performed adsorption experiments with alginite with acetochlor, propisochlor and 2,4-dichlorophenol. The alginite has a high content of organic matter, but its composition differs significantly from the humic substances in the soils. In alginite, humic substances make up only a quarter of all organic matter, 75 % of which is kerogen, which, according to the test results, plays a significant role in the binding of organic pollutants. This is supported by the adsorption experiments performed on humusdepleted alginite and, as the main mineral constituent, bentonite. Humic substances on the surface have been shown to inhibit access to kerogen, so the tested substances bound in the highest amount in all cases of demineralized alginite. Studies have also shown that due to the excellent buffering capacity of alginite, media with different pH do not cause a significant change in the amount of material bound.

### Humic acids of soils and alginite

Barančíková and Litavec (2016) examined the differences in chemical composition between humic acids (HA) from alginite and humic acids isolated from different soil types. The differences in elemental analysis and ash proportion in HA extracted by modified IHSS (International Humic Substances Society) method (C = 35.4, H = 43 atomic %, ash content = 0.08 %) and simplified extraction method (C = 31, H = 31 atomic %, ash content = 7.42 %) can be caused by different concentration of extraction solution, and also differences in the purification of HA. The differences in chemical structure between alginate HA and HA isolated from different soil types according to the data of elemental analysis (C content of alginite HA = 35.4 atomic %, C content in soils HA = 38.2-49.1 atomic %) and 13C nuclear magnetic resonance (NMR) spectra (degree of aromaticity of alginite HA = 24.4 % and soil HA= 35.9-53 %) were found. Results of 13C NMR show that the content of aromatic carbon was decreasing in the following order: Haplic Chernozem HA > Andic Cambisol HA > Haplic Cambisol HA > alginite HA. Based on the obtained results, it can be concluded that the differences in the chemical structure of alginite and soil HA can be explained by the difference in the origin of organic matter in alginite and soil samples. The source of organic matter in alginite is mainly type II kerogen from algae and that of soil is lignin and cellulose (type III kerogen) of higher plants.

# Effects of application of alginite on stabilization of beneficial microorganisms in animal organisms

Strompfová et al. (2018) investigated the effects of dietary supplementation with canine-derived probiotic strain *Lactobacillus fermentum* CCM 7421 in combination with alginite in dogs. Alginite is a loam-like material of volcanic origin composed of clay minerals and fossilised unicellular algae. The effects of these additives on faecal microbiota, faecal characteristics, short-chain fatty acid profile, haematology, serum biochemistry and cellular immunity parameters were monitored. The results of this straightforward experiment showed beneficial effects in the combined Alginite + *L. fermentum* group. In detail, a decrease in faecal coliforms and clostridia and an increase in lactic acid bacteria, haemoglobin and serum magnesium levels compared to baseline were observed in the A + LF group (p < 0.05). In contrast, sole application of alginite (A group) led to several unexpected effects such as an increase in clostridial population and serum alanine aminotransferase and a decrease in haemoglobin concentration (p <0.05). The addition of alginite prevented a decrease in faecal pH and serum mineral content observed in the LF group. This indicates the possibility of applying alginite in dogs' nutrition as a combinative additive with probiotic bacteria for restoring optimal acid-alkali balance without affecting positive probiotic effects.

Nemcová et al. (2012–2015) investigated the potential utilization of alginite and its humin extracts for stabilisation of beneficial microorganisms intended for the development of new application forms of these microorganisms. Procedures for preparation of laboratory extracts of alginite suitable for preparation of optimum alginite skeleton for solid substrate fermentation of beneficial bacteria and production of alginate containing cultivation media were developed and validated. A patent proposal was prepared to consist of the description of the way of stabilisation of beneficial micro-organisms by cultivation on alginite grains. Binding to an alginite carrier saturated with a suitable cultivation medium stabilizes probiotic micro-organisms during production and their application. The probiotic microorganisms capable of producing biofilm on alginite grains are in a dormant (quiescent) state with minimal metabolic processes, exhibit resistance to stress and multiply in the body after passaging in the body intestinal or skin microenvironment with a positive biological effect.

### Conclusions

The report presents only very brief information and knowledge about alginite. Alginite is a natural and non-toxic organic-bituminous rock, with a significant content of basic nutrients (P, K, Ca, Mg and S) for plants except for nitrogen and content of more than 60 microelements, which increase its agrochemical value. Alginite can be practically used in its natural and technologically modified form. The application of alginite does not damage the soil or the environment. The physical, mechanical, chemical, pedological, agrochemical and other properties of alginite confirm that alginite as a bituminous rock has unique possibilities for practical use in agriculture, forestry, remediation and soil and water improvement, pesticide decomposition and stabilization of microorganisms in animal organisms and various other fields. Alginite applied to the soil can retain water and nutrients dissolved in it, which it gradually releases to the roots of plants during periods of precipitation deficit. When applied correctly, it significantly affects the yield and quality of seeds and fruits of crops. It actively affects the biological, physiological and biochemical processes of plants. Despite many findings, alginite is still a lessknown bituminous rock. The least knowledge is about the chemical composition and thus about the effects of the organic part of alginite, which is referred to as type II kerogen.

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#### **Conflict of interest**

The authors declare no conflict of interest.

#### **Ethical statement**

This article does not contain any studies that would require an ethical statement.

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