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Mineral ammonium ion absorber as a fertilizer

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Abstract: The purpose of this paper was to study the usability of new ammonium absorber material as fertilizer. The vermiculite-material which effectively binds ammonium nitrogen to its structure has been developed to remove ammonium ions from waste waters. The material is further developed for fertilizer use. At first step the absorption material was processed with the reject water of biogas plant. Then it was utilized as the nutrient source of garden plants. Chinese cabbages were used as test plants in the work. Significant increase of the growth of the Chinese cabbage was observed when comparing to those cultivations where plants have got normal nitrogen fertilization.

Keywords: *ammonium, nutrient, vermiculite*

Introduction

Proper nutrient management of growing media is extremely important for production of food. Increased environmental awareness has increased the demand of sustainable production of plants, and reducing the use of artificial fertilizers. In this study growth experiments were performed. Nitrogen source of our experiments was a new sustainable fertilizer product.

Limited fossil energy resources and increasing growth in global energy consumption together with increasing amount of organic waste material have increased biogas production all over the world (Martinez et al. 2009, Perera et al. 2009). Within the last decade, biogas plants have consolidated their position in the recycling of organic wastes to energy. Biogas production has also become an important branch of agriculture, mainly due to continuously growing usage of agricultural raw materials for anaerobic digestion (Martinez et al. 2009). Besides biogas, process produces digestate, which consists of a mixture of liquid and solid fractions. This biogas plant digested slurry is a good source of plant nutrients (Möller and Stinner 2009). Manuring the farmland with the digested residue from biogas plant increases the yields of agricultural products. On the other hand, negative impacts such as eutrophication and acidification of soil can be even higher than with mineral fertilizers (Martinez et al. 2009; Möller and Stinner 2009). The usability of digestate is also adhering to hygiene requirements. Organic waste can contain infectious matters, which can result in new spreading of pathogens and transmission of disease between animals, humans, and environment (Pastor et al. 2008; Yan et al. 2008). An anaerobic digestion reduces the risk from pathogens, but contaminants in the digestion liquid and their affect to plants, soil and water are not well studied. For example heavy metals are not altered in the anaerobic digestate process (Schattauer, A. 2011) and the fate of organic pollutants and pesticides is unknown (Yan et al. 2008). Also PCB and PAH are reported not to be affected by anaerobic digestion (Yan et al. 2008).

We present now our latest growth experiments about feasibility of the plant availability of nitrogen recovered from biogas plant reject water. The nitrogen rich reject water of VamBio biogas plant was used as a nutrient source for loading filtering sand, GeoTrap (GT), with nitrogen and organic material. The absorption material that has been processed with the reject water of biogas plant (material that has been loaded with nitrogen is called NGT later in this article) was utilized as the nutrient source of garden plants. We also tested how well the plants are able to utilize nitrogen of the absorption material and if the amount of soluble nitrogen or of other nutrients will become harmfully high for the plants. Nitrogen fertilization is crucial for achieving high yields in field vegetables (Wu et al. 2011). Chinese cabbages were used as test plants in the work. Cabbage was selected for this work because of its short growth period and high N requirement. The objective was to evaluate the impact of rates of NGT or GT applied at planting on plant N fixation, heavy metal fixation and growth. We also wanted to test the possibility to reduce nitrogen loss from leaching by using this new material.

Methods

Substrate fertilizer material

In this study we have tested new ammonium absorber material. Vermiculite clay mineral, $(Mg,Ca)_{0.6\text{-}0.9}(Mg, Fe, Al)_6[(Al, Si)_8O_{20}](OH)_4{\cdot}nH_2O$, was pretreated with heat according to a reported patent (Eklund et al. 2005). So formed product is called GeoTrap (GT). It can be used to remove ammonium ions from waste waters. This mineral is widely available, easily handled and low-costly. It is a sheet aluminosilicate of the hydromica group and it has a sandwich-like structure. Its capability to intake ammonium ions has been improved with a special modification of the natural form (Eklund et al. 2005). During last years our research group has developed and tested this modification method, and we have made a product that works especially well for ammonium ions of waste-waters.

In this study we used reject water of VamBio biogas plant to load GeoTrap with nitrogen. The VamBio biogas plant is a relatively large biogas plant. The production is based mainly on animal manure from local farms, together with waste from food industry and municipal sewage sludge. The material is mixed into homogeneous slurry in a reception tank, after which it is pasteurized for 1 h at 70 °C by steam-heating, in order to kill bacteria. After cooling, the material is pumped into a digester to be broken down by different types of micro-organisms in an anaerobic environment at about 38 °C. The plant produces electricity (8 000 MWh/a), heat (9 000 MWh/a), biogas for industry and different types of digestates. Solid waste is rich in phosphorus and can be used as fertilizer. Reject water is rich in nitrogen, especially ammonium nitrogen, and organic matter. For this study 30 kg of GeoTrap was treated with a reject water of VamBio Biogas plant. About 70 l of water was used for every 10 kg of GeoTrap. GeoTrap and water were mixed for 2 hours. Material (NGT) was then dried at room temperature for about one week. NGT contains about 0,6-1,5 mass-% of nitrogen and half of it is in the form of ammonium nitrogen.

Plant Production

Four different substrate mixtures were used. A commercially available peat (Luonnonturve, Kekkilä, Finland) was mixed with clean GeoTrap (GeoSmart, St. Petersburg, Russia) or with GeoTrap that has been treated with reject water of biogas plant (NGT). Two rates of mixtures were done. Amount of GeoTrap (GT) or NGT in the mixture was 1/3 or 2/3 of total amount (1 l). 100 ml of garden lime was added for every 10 l of peat. Substrate pH was between 6.5 and 7.5. Chinese cabbages were sown in 1 litre pots 10 seeds to each pot at the end of March 2011. The plants were harvested in the beginning of May at first to five plants and then to three plants per pot. The experiment with Chinese cabbage was arranged with four different substrate materials, 2 different liquid fertilizer formulations, and 3×3 single-plant replications per treatment combination. Total amount of 72 plants were studied in this experiment.

Plants were irrigated every other day with tap water, depending on their requirements. Plants were separated into two groups in the greenhouse and one group was fertilized with full strength Hoagland's nutrient solution (+H) and one group of plants was fertilized with Hoagland's without nitrogen (-H). Fertilizer solution was given for the plants once per week. Nutrient concentrations of full strength Hoagland solution are follows: 2 M KNO_3, 2 M $Ca(NO_3)_2 \cdot 4H_2O$, 1 M FeEDTA, 2 M $MgSO_4 \cdot 7H_2O$, 1 M NH_4NO_3, 1 M KH_2PO_4 and minors H_3BO_3, $MnCl_2 \cdot 4H_2O$, $ZnSO_4 \cdot 7H_2O$, $CuSO_4$ and $H_3MoO_4 \cdot H_2O$. For Hoagland solution without nitrogen (-H) compounds KNO_3, $Ca(NO_3)_2$ and NH_4NO_3 were not added to the solution. Temperature of the greenhouse was about 25 °C and light period was 16 h light and 8 h dark.

Analysis

In order to evaluate fertilizing potential of the material clean GeoTrap and GeoTrap that has been treated with reject water from a biogas plant are analysed at Actlabs, Canada. Actlabs is a commercial laboratory that is accredited to both ISO 17025 with CAN-P-1579 and NELAP for specific registered tests. Analysis package 'WRA+trace 4Lithoresearch' was performed for all solid samples. The chemical composition of GeoTrap (GT) and loaded GeoTrap (NGT) are presented in Table 1.

Before and after the growth period chemical composition of all substrate materials were analysed at Actlabs, Canada. The growth of plants was monitored throughout the experiment. At the end of the experiment tissue was harvested for analysis. Fresh and dry weight of plants was analysed with an analytical balance. For the analysis of dry weight samples were dried in a forced-air oven at 60 °C until constant weight was obtained. Chemical analysis of the plants was performed at commercial laboratory Viljavuuspalvelu Oy, Finland. Analysis is accredited (ISO/IEC 17025).

Table 1. Chemical composition of GeoTrap (GT), and GeoTrap after treatment with reject water of a biogas plant (NGT).

analyte	unit	GT	NGT
SiO2	%	36.50	35.60
Al2O3	%	12.25	12.63
Fe2O3	%	6.01	5.62
FeO	%	0.50	0.73
MnO	%	0.083	0.074
MgO	%	25.57	24.88
CaO	%	1.41	1.22
Na2O	%	0.08	0.05
K2O	%	0.09	0.19
TiO2	%	0.922	0.977
P2O5	%	0.04	0.03
C	%	0.32	0.35
S	%	<0.01	<0.01
F	%	<0.01	<0.01
Cl	%	<0.01	0.02
N	%	<0.01	0.64
B	ppm	<2	2
Sc	ppm	16	15
Be	ppm	<1	<1
V	ppm	26	24
Cr	ppm	920	940
Co	ppm	50	49
Ni	ppm	620	620
Cu	ppm	<10	<10
Zn	ppm	80	80
Ga	ppm	19	19
Ge	ppm	1.4	1.4
As	ppm	<5	<5
Rb	ppm	4	6
Sr	ppm	58	25
Y	ppm	<0.5	<0.5
Zr	ppm	51	38
Nb	ppm	39.5	38.0
Mo	ppm	<2	<2
Ag	ppm	<0.5	<0.5
In	ppm	<0.1	<0.1
Sn	ppm	1	1
Sb	ppm	<0.2	<0.2
Cs	ppm	1.0	0.9
Ba	ppm	237	164

Results and Discussion

Nutrient treatments significantly affected the growth of seedlings. Plants were grown for two months and after one month the positive effect of reject water loaded GeoTrap (NGT) on the growth was clearly visible (Figure 1). As it was expected, plants growing in the substrate with no nitrogen and getting no liquid fertilizer with nitrogen (GT-H) were very small. At this time of growth plants getting nitrogen from the substrate (NGT-H) or from liquid fertilizer (GT+H) were about similar size. The biggest plants were those growing in the nitrogen containing substrate and getting liquid fertilizer (NGT+H).

Figure 1. General view of seedlings after one month from sowing. Substrate depending size difference of plants is clearly visible. All of these substrates contain 2/3 of peat. In addition to peat substrates contain 1/3 of clean GeoTrap (GT) or 1/3 of GeoTrap after reject water treatment (NGT). Plants on the left have got Hoagland’s solution without nitrogen (-H) and plants on right have got normal Hoagland’s solution (+H).

After two months growth plants were harvested. Fresh and dry masses of total biomass after the growth period are presented in the Figure 2. Loading the GeoTrap with reject water seems to produce a good fertilizer. Shoot mass is highly dependent on the amount of N in the substrate. The greatest dry mass (36.3 ± 2.9 g) was observed for plants fertilized with nutrient solution without nitrogen and having 2/3 of NGT and 1/3 of peat in the substrate. Liquid N fertilizer (Hoagland solution, +H) increased the size of those plants, which didn’t get nitrogen in the substrate. Anyway, liquid N fertilizer decreased the size of those plants having N also in the substrate. The smallest dry mass was supposedly measured from plants irrigated with tap water and having no N fertilizing (1.6 ± 0.48). The growth of these plants ceased soon after the beginning of the trial, most probably because of nutrient deficiency.

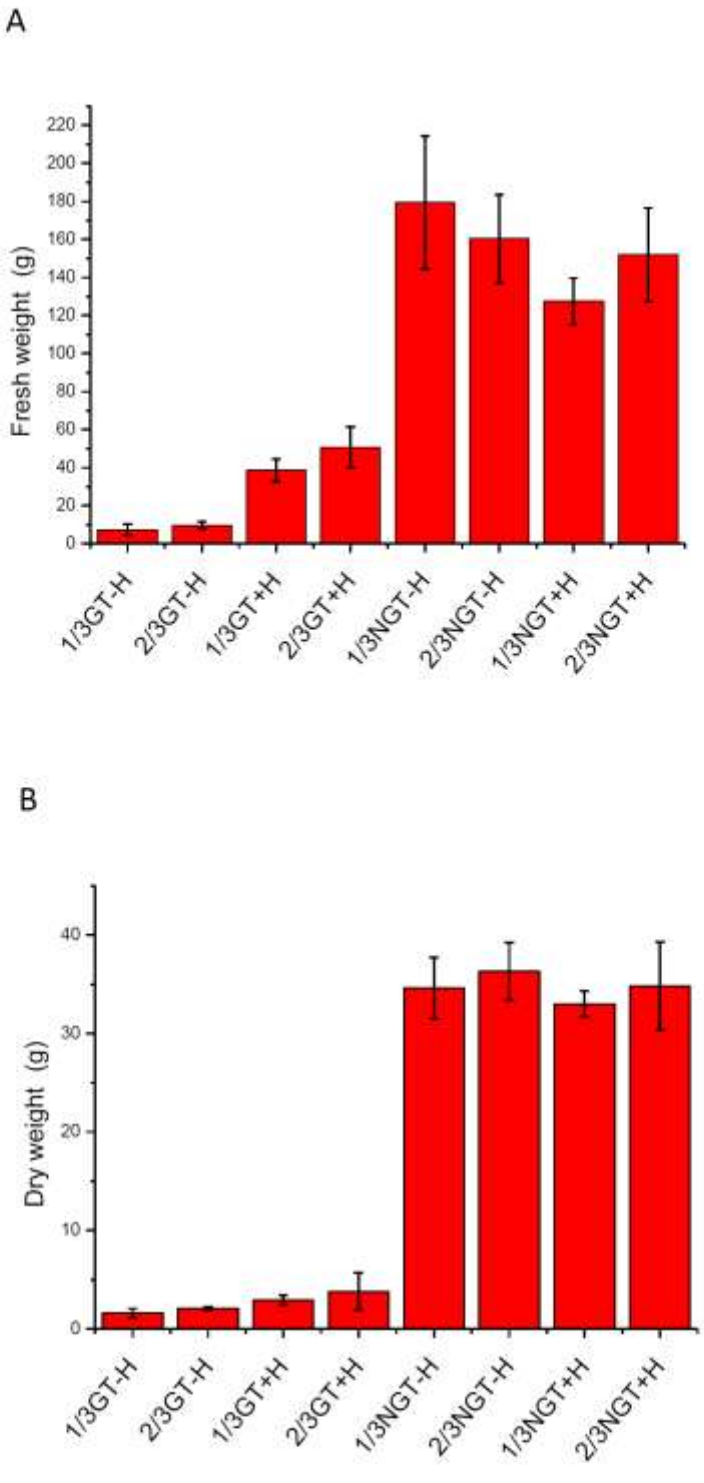

Figure 2. Shoot fresh (A) and dry (B) mass after the growth period. Substrates contain GeoTrap with no added nitrogen (1/3 GT and 2/3 GT) or GeoTrap loaded with nitrogen from the reject water of a biogas plant (1/3 NGT and 2/3 NGT). All plants have got Hoaglands solution for nutrition. Some plants got it without nitrogen (-H) and some with nitrogen (+H).

Chemical analysis of plants was performed in order to get information about the amount of nitrogen and other elements in plant. Chemical composition is presented in Table 2. For Chinese cabbage the recommended amount of nitrogen is 45-55 g/kg solid dry weight. Samples 1/3NGT and 1/3NGT have nitrogen concentration 59 and 57 g/kg, respectively. That is about the upper limit of recommended amount. These plants were the biggest ones. If the samples have nitrogen in the substrate and they have got even more nitrogen with fertilizing solution (1/3NGT+H and 2/3NGT+H), the nitrogen amount increases to 68 or 60 g/kg, respectively. In this latter case the level of available N has been too high for Chinese cabbage and has actually inhibited the growth (Staugaitis 2008). Chinese cabbage crop is particularly demanding for nitrogen fertilizers. Insufficient supply of nitrogen results in lower yields and smaller vegetable heads, while excess of nitrogen leads to a high concentration of nitrates in the heads, lower amount of total solids and consequently shorter shelf-life (Staugaitis 2008). Worst of all, the high nitrate accumulation in plants is not only inhibiting plant growth, but it is also harmful to human health (Chen 2004).

Table 2. Chemical composition of Chinese cabbages.

sample	elements										
	g/kg solid dry weight						mg/kg solid dry weight				
	N	P	K	Ca	Mg	S	Fe	B	Cu	Mn	Zn
1/3GT-H	18	1	22	16	3	5	57	8	<5	78	<20
2/3GT-H	7	4	33	9	3	-	240	12	<5	32	<20
1/3GT+H	7	5	27	10	3	-	120	14	6	42	28
2/3GT+H	18	1	26	17	5	5	60	7	<5	130	<20
1/3NGT-H	59	2	28	35	6	9	78	28	<5	100	47
2/3NGT-H	57	2	16	22	5	9	97	22	<5	76	48
1/3NGT+H	68	2	11	46	8	13	71	20	6	140	39
2/3NGT+H	60	2	27	25	6	8	130	18	6	100	45

Biogas reject water treatment of GeoTrap (samples NGT) has added nitrogen, calcium, magnesium, sulphur, boron, manganese and zinc concentration of plants. Amount of iron varies a lot, but variation can’t be connected to different substrate materials. Small amount of nitrogen in the plant samples 1/3GT+H and 2/3GT+H refers to the possibility that GeoTrap in the substrate might have captured nitrogen from liquid fertilizer. Residual nitrogen concentration of some of the used growth substrates were performed in order to check if the nitrogen concentration of these two substrates is increased during the growth period due to the nutrient absorption into GeoTrap during liquid fertilization (Table 3). Analysis results do not show gathering of nitrogen to the substrate.

Table 3. Residual nitrogen concentration of soil substrates after the growth experiment.

sample	N
	mass-%
2/3GT-H	0.04
2/3GT+H	<0.01
2/3NGT-H	0.45
2/3NGT+H	0.47

More research on this topic needs to be done in order to better understand processes at the GT and NGT substrates affecting the nitrogen usage of Chinese cabbage. This study gives information on the optimum dosage of NGT on the growth substrate, but the matter is complicated because Chinese cabbage crop is particularly demanding for nitrogen fertilizers. Selection of nitrogen fertilizer levels should take into account season, variety, its earliness and productivity, the amount of nitrogen in the soil and local climate conditions (Staugaitis 2008).

Conclusions

Fertilizer value of vermiculite based nutrient-rich bio-fertilizer GeoTrap was evaluated. Vermiculite material was loaded with nitrogen at the biogas plant to produce a fertilizer. So produced nitrogen fertilizer was mixed with peat and used as a growth substrate. Nutrient of the substrate significantly affected the growth of Chinese cabbage. Full strength Hoagland's solution favored growth, but much bigger growth was obtained with using new ammonium absorber material as fertilizer. At this time of growth (two months), threefold difference of growth of plants was observed for plants getting nitrogen as solution or getting nitrogen in the substrate.

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References

Chen, B.-M., Wang, Z.-H., Li, S.-X., Wang, G.-X., Song, H.-X., Wang, X.-N. (2004). Effects of nitrate supply on plant growth, nitrate accumulation, metabolic nitrate concentration and nitrate reductase activity in three leafy vegetables. Plant Science 167, 635–643.

Eklund, O., Shebanov, A., Toropainen, V., Åkerback, N., Engblom, S. (2005). Methods for improving vermiculite´s intake of ammonium ions, absorbation material, its uses and method of removing ammonium from environment. Patent US 7,927,038 and other members of the same patent family.

Martinez, J., Dabert, P., Barrington, S. and Burton, C. (2009). Livestock waste treatment systems for environmental quality, food safety, and sustainability. Bioresource Technology, 100, 5527-5536.

Möller, K. and Stinner, W. (2009). Effects of different manuring systems with and without biogas digestion on soil mineral nitrogen content and on gaseous nitrogen losses (ammonia, nitrous oxides). European Journal of Agronomy, 30, 1-16.

Pastor, L., Marti, N., Bouzas, A. and Seco, A. (2008). Sewage sludge management for phosphorus recovery as struvite in EBPR wastewater treatment plants. Bioresource Technology 99, 4817–4824.

Perera, P.W.A., Wu, W.-X., Chen, Y.-X. and Han, Z.-Y. (2009). Struvite recovery from swine waste biogas digester effluent through a stainless steel device under constant pH conditions. Biomedical and Environmental Sciences, 22, 201-209.

Schattauer, A., Abdoun, E., Weiland, P., Plöchl, M. and Heiermann, M. (2011). Abundance of trace elements in demonstration biogas plants. Biosystems engineering 108, 57-65.

Staugaitis, G., Viškelis, P. and Venskutonis, P.R. (2008). Optimization of application of nitrogen fertilizers to increase the yield and improve the quality of Chinese cabbage heads. Acta Agriculturae Scandinavica Section B – Soil and Plant Science, 58, 176-181.

Wu, X.-Y., Zhang, L.-P., Fu, X.-T., Wang, X.-Y. and Zhang, H.-S. (2011). Nitrogen loss in surface runoff from Chinese cabbage fields. Physics and Chemistry of the Earth 36, 401-406.

Yan, X., Jin, J., He, P. and Liang, M. (2008). Recent advances on the technologies to increase fertilizer use efficiency. Agricultural Sciences in China 7 (4), 469-479.