Abstract

Nitrogen fertilization is a key factor influencing both the efficiency of agricultural production and the quality of the obtained crop. Mineral fertilizers are the main source of nitrogen, and their application to arable land contributes to enriching the soil with nutrients that are necessary for the proper growth of cultivated plants. Urea is a mineral fertilizer that contains nitrogen in the highest concentration - 46%. It is estimated that the share of urea fertilizers in the total global consumption of mineral fertilizers exceeds 50%. The use of urea fertilizers to fertilize agricultural fields is associated with the unfavorable phenomenon of ammonia emission from the fertilized soil, which results in ineffective use of the nitrogen dose supplied to the plants, and thus reduces the economic efficiency of the crops. Estimated data of ammonia emissions into the atmosphere indicate a 60% level of N losses, which depends on many soil and climate factors.

Directive (EU) 2016/2284 of the European Parliament and of the Council of 14 December 2016 on the reduction of national emissions of certain atmospheric pollutants, amending Directive 2003/35/EC of the European Parliament and of the Council of 26 May 2003 and repealing Directive 2001/81/EC of the European Parliament and of the Council of 23 October 2001, which led to restrictions on the use of both urea and fertilizers based on it in the European Union, due to the level of emissions associated with the use of the mentioned fertilizers.

Grupa Azoty Zakłady Azotowe "Puławy" S.A., as the main producer of urea, had to take action to reduce ammonia emissions to the level acceptable in the NEC Regulation. One way to implement the changes mentioned above is to use urease inhibitors, which, combined with fertilizer, would create a finished product that can be used in agriculture. Due to the fact that no potentially negative consequences resulting from long-term use of commercially available urease inhibitors have been identified so far, Grupa Azoty Zakłady Azotowe "Puławy" S.A. has started to work in order to find out for natural substances that are harmless to the environment, the application of which, together with fertilizer products manufactured by the Azoty Group, would enable the reduction of ammonia emissions.

The first stage of work carried out as part of this doctoral dissertation included the selection of plant raw materials that would contain substances that inhibit the activity of urease. Then, two stages of laboratory tests were carried out, i.e. incubation tests and pot tests. In both mentioned experiments, two types of soil with different properties were used - luvisols with a granulometric composition of sandy clay (pH 5.4) and podzolic soil with a granulometric

composition of clayey sand (pH 7.4). During both experiments, a constant substrate humidity was maintained, corresponding to the soil suction force (pF) value of 1.9.

In a 14-day incubation experiment, the influence of 6 plant extracts (obtained from the fruits of three plant species: blueberries, raspberries and black mulberries in two concentrations, i.e. 10% and 25%) on ammonia emission was verified. Ammonia emissions were measured using the GASMET DX 4040 analyzer based on the Fourier transform infrared absorption spectroscopy (FTIR) method. The dose of urea fertilizer (granulated urea) applied in the experiment together with the tested plant extracts was 240 kg N ha^{-1}. Almost all tested plant extracts resulted in a significant reduction in NH_3 emissions. Moreover, the incubation experiment provided information on the influence of the mentioned plant extracts on the activity of the urease enzyme and the content of various forms of nitrogen (total, nitrate and ammonium) in the soil. Urease activity depended on the type of soil used for the experiment, the type of extract applied, and the date of sampling. The influence of the tested extracts on the content of nitrate and ammonium nitrogen in the soil was also observed. Based on the results obtained, the most effective plant extracts were selected, i.e. 25% blueberry extract (reduction of cumulative NH_3 emissions in the range of 49-90% compared to the control, depending on the type of soil used in the research) and 10% black mulberry extract (78-87%), the effectiveness of which was then checked in pot tests.

A pot experiment using spring wheat of the Rusałka variety was conducted until the earing phase of wheat for a period of 67 days. The amount of nitrogen applied to the soil in the experiment was a total of 140 kg N ha^{-1} and, in accordance with the recommendations of the the code of good agricultural and forest practice developed by the Institute of Soil Science and Plant Cultivation – State Research Institute, it was divided into two doses (applied together with the tested plant extracts). The first dose of 90 kg N ha^{-1} was applied before sowing, while the second dose of 50 kg N ha^{-1} was applied during the shooting phase. In a pot experiment, a 13-day measurement of ammonia emissions from the soil was carried out. Moreover, the influence of the tested extracts on: urease activity and the content of various forms of nitrogen in soil samples, the content of macroelements and chlorophyll in the above-ground parts of the plant and the intensity of the photosynthesis process were determined. Additionally, next-generation sequencing was performed, which provided information on the impact of blueberry and mulberry extracts on soil microorganisms (bacteria and fungi). The influence of extracts on ammonia emission from soil in the pot experiment depended on the soil type. The results of the research presented in this study confirmed the effectiveness of the tested plant extracts in reducing NH_3 emissions into the environment (reducing the cumulative ammonia emission by

31% and 40% compared to the control when applying 25% blueberry extract and 10% black mulberry extract, respectively) in the case of podzolic soil. The influence of plant extracts on the content of ammonium nitrogen in the soil and macronutrients in plants was observed. The obtained results of next-generation sequencing indicate the possibility of modifying the structure and number of microorganisms in the soil using plant extracts used together with urea.

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