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Controlled release fertilizers

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The efficiency of nitrogen assimilation by plants is rather low and this is a serious problem in view of environmental protection. Improvement of nitrogen absorption can be carried out through the developing, producing and applying the controlled release fertilizers. Biodegradable chitosan has been proposed as an alternative material in the production of controlled release fertilizers.

Keywords: controlled release fertilizers, chitosan.

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INTRODUCTION

Mineral fertilizers are some of the most important products of agricultural industry. While providing nutrients to crops, they increase their growth and at the same time play an important role in regulating both the pH and the fertility of the soil. Production of mineral fertilizers has risen along with the increase of human population and the need for increased food production[1]. However, an increased production of fertilizers and soil fertilization contrast with a relatively low nutrient assimilation by crops; it is estimated that for nitrogen the assimilation reaches 30 – 50%[2, 3]. The efficiency of nitrogen assimilation depends on complex interactions in crops' root systems, soil microorganisms, chemical reactions taking place in the soil and the processes leading to adverse elimination of nitrogen from the soil. Most fertilizers are easily soluble in water, thus during their application in water a soil solution with a given mineral compounds concentration is created. Nitrogen is absorbed from the soil by crops' root systems as NH_4^+ and NO_3^- mainly through mass transfer. In order to make nitrogen assimilation more effective, the fertilizer should be delivered no farther than 3 – 4 cm from the root system of a plant. If the amount of the delivered nitrogen exceeds the plant's intake capability, the processes leading to a decrease of its concentration are activated. These processes include both the physical processes (rinsing out, vaporization) and microbiological conversions (replacement, precipitation, hydrolysis). It is worth noting that an excessive concentration of mineral constituents and too high osmotic pressure of soil solution lead to a decrease of water content, withering and an abnormal crop growth.

Low effectiveness of nitrogen assimilation causes serious problems in view of environmental protection. Because of soil microorganisms mineral nitrogen undergoes transformation to nitrates easily soluble in the soil, which are later leached from the soil to ground and surface waters. An increased concentration of nitrates in waters can be connected with the methemoglobina related diseases found in children and in ruminant animals[3] as well as with other diseases (goitre, birth defects, heart diseases)[1]. The concentration of nitrides and nitrosamines, i.e. the derivatives of nitrides present in water, was also associated with the digestive system diseases[4]. Nitrides also lead to an increased eutrophication of surface waters[5]. An increased level of nitrates and nitrites in crops, which are the staple food for people and animals, can negatively affect their health[1]. It was pointed out that excessive amounts of fertilizers change the degree of salinity and pH of the soil, leading to its gradual degradation[5]. Urea and ammonium salt, used as mineral fertilizers, are potential sources of ammonia, which while migrating into adjacent ecosystems disturbs or destroys the vegetation of other plants[3]. A part of ammonia, after conversion into nitric acid, combines with sulphuric acid and in the form of acid rains badly affects vegetation and leads to erosion and soil depletion. As a result of the denitrification process taking place in the soil, both nitrous oxide and nitric oxide are created. They are responsible for the depletion of the ozone layer, subjecting people to the exposure of ultraviolet radiation. The production of mineral fertilizers is in itself a risky factor, during which hazardous substances are released into the environment. These substances include sulfur oxides, nitric oxides, fluorine compounds and dust.

Little assimilability of mineral components also has unfavorable effects in the economic aspect of the issue; nitrogen losses, spent energy and human work effort negatively affect the total economic balance of the whole agrochemical production process. At the same time, a consumption of non-renewable sources of energy (such as natural gas) used for the production of mineral fertilizers, should also be pointed out.

All the above mentioned factors seem to violate the basic rule of natural environment protection, which aims at reaching a sustainable development ensuring fulfilling the needs of present and future generations.

In the light of the above presented facts, it seems that the task of paramount importance is to increase the effectiveness of plants' nitrogen absorption and to decrease nitrogen losses, while at the same time to limit the amount of fertilizers' waste material produced by the industry. This can be carried out through:

– developing new technologies and methods of producing fertilizers (with a limited gas, dust and other waste material emissions)

– producing fluid – suspension fertilizers as well as those applied on plants' leaves (which eliminates the stages of drying and granulation)

– developing, producing and applying fertilizers with a delayed and controlled release of mineral nutrients (mainly nitrogen), i.e. the so-called *controlled release fertilizers (CRFs).*

NUTRIENT CONTROL RELEASE FERTILIZERS

According to specialists in fertilizers industry[6], fertilizers market in the world (including even the stable European market) is going to undergo significant changes in order to reduce costs and maximize profits. The development and application of the CRFs is going to be a basis of these processes.

Mineral constituent uptake (N, P, K) by plants in their vegetation cycle has a sigmoidal character[1]. An application of the CRFs which release their nutrients in a way better fitting plants' requirements ensures an improved effectiveness of fertilizing through minimizing the losses between application and absorption. At the same time using the CRFs allows to reduce the negative influence fertilizers have on the environment, largely due to high solubility of nitrogen compounds, which are left unused. In conventional fertilizing (e.g. with urea) nutrients release lasts 30 – 60 days, which given a 100 – 120 day long crops growth cycle means that a fertilizers must be applied 2 or 3 times. The CRFs release their nutrients slowly and gradually during the whole vegetation season and consequently need to be applied once only, which greatly reduces both time and energy consumption. A better and more efficient use of nutrients can lead both to a reduction of waste material produced by the fertilizers industry and to a reduction in natural gas consumption. It is also pointed out that using the CRFs increases the crops' yield[1, 7].

The CRFs are the fertilizers which gradually release their mineral nutrients, while at the same time providing proper nutrition to plants. They were first used in 1965[8]. Currently, the CRFs are produced mainly in the USA, Western Europe, Japan, South Korea, Israel and China.

Most studies quoted in the literature on the subject mention a system in which a granule of fertilizer is encapsulated, i.e. it is coated with an inert layer. After a fertilizer's application, water penetrates through a hydrophobic membrane into the inside of a granule. Then, nutrients are dissolved and the arising osmotic pressure leads to either a partial tearing off of the membrane or to its expansion, which allows ion transport through the coating into the soil[9] (Figure 1). The rate of nutrients' release is controlled by a coating diffusion coefficient.

SCU – sulfur-coated urea is an example of this kind of a fertilizer[10, 11]. Other examples include polysulfone-coated urea[12], polyethylene-coated urea[13], and polymer-coated superphosphate[14]. Other kinds of materials have also been used for the coating of fertilizers and these include[15]: natural gum, rosin, waxes, paraffins, various kinds of ester copolymers, urethane composites, epoxy and alkide resins, polyolefines, polyacrylic acid, polyvinyl alcohol, epoxidized soybean oil with a polyester as a curing agent or butadiene-methylstyrene block copolymers.

The second kind of fertilizers is a system where the active component is dispergated in a polymer matrix. Two processes affect the rate of nutrients' release: diffusion in pores and canals of a matrix and physical and biochemical degradation of a matrix. The system's great advantage is its simple construction. The first study into a matrix system was published in 1987[16], but up till now the system has not been thoroughly studied[17], nor has it been used in industrial applications.

A distinct category of the CRFs are systems in which there is no physical barrier in the form of a polymer material, and in which the release rate decisive factor is either solubility or degradability of a given fertilizer. Such fertilizers include[1]:
– inorganic materials of low solubility (e.g. ammonium and metallic phosphates)
– chemically or biologically degradable materials of low solubility (e.g. urea – formaldehyde condensates, oxamides, diurea.

The basis of selecting an appropriate fertilizer both the mechanism and the rate of nutrients' release are assessed. From the technological point of view the CRFs can be divided into these in which the release is controlled by coating diffusion, coating erosion, chemical reaction, osmosis or swelling[1]. The kinetics of nutrients' release is a process, which so far has not been entirely understood. Although the literature on the subject presents several kinetic equations describing the release rate, these equations mainly refer to the coating diffusion cases[18].

However, none of the earlier presented modern technologies assures a proper and full balance between a plant's changing biological needs for nitrogen and its release. Fer-

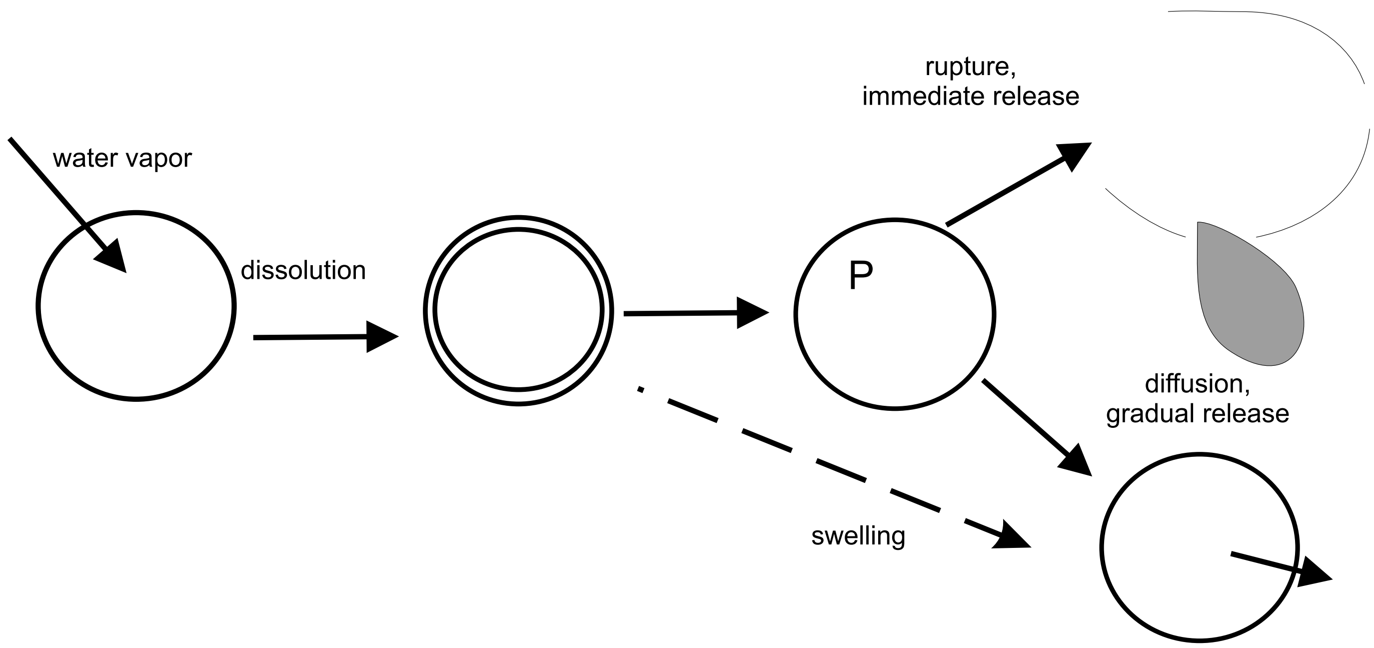

Figure 1. Stages of the release from a polymer-coated granule

tilizers coated with sulfur have a high initial release rate (as a result of badly damaged coating), whereas for the polymer coated fertilizers nitrogen release rate is at first low and it gradually increases along with the increase of water penetrating the inside of a granule. As for formaldehyde - urea resins coatings, they release nitrogen at a slow and constant rate. To sum up, it would seem reasonable to look for complementary materials that would combine a high rate and the stability of nutrients' release, while at the same time fulfilling crops' nutritious needs.

Despite the CRFs's many advantages and the fact that they have been constantly developed, their use is still very limited. It is estimated that the CRFs constitute a mere 1 per cent of the total amount of used fertilizers. This is due to the CRFs's high prices; they are from 2 to 8 times more expensive than the commonly used fertilizers[1].

Making good use of the enormous potential connected with the CRFs's market, which in fact means developing, producing and applying the CRFs requires solving how to:

– produce fertilizers at a cost lower than the presently manufactured CRFs

– control the features of the currently developed fertilizers

– understand the mechanism of the controlled release better

– develop the kinetic models of the controlled release for new systems

– develop new research methods of the controlled release

– carry out the initial assessment of a selected CRF group on the environment

THE POSSIBILITY OF USING CHITOSAN IN CRFs

One of the CRFs' drawbacks, and particularly the polymer-coated CRFs, is that after nutrients' consumption there is still a considerable amount of useless polymer left in the soil. A good and possible solution, although not as yet used on a technological scale, is to produce the CRFs using biodegradable materials[17], manufactured from raw materials renewable in the process of biosynthesis. Chitosan is one of such materials. It is a natural polysaccharide produced commercially by deacetylation of chitin, which is the structural element in see crustaceans. Chitosan easily undergoes biodegradation in natural environment and it is highly biocompatible. Additionally, it has unique polycationic properties. Owing to its features it is being intensively investigated in the pharmaceutical field, as it might be used in the systems of controlled drugs release[19 – 21]. For several years now, researchers have been investigating the possibility of using chitosan in agrochemical industry. A review of the literature on the subject seems to suggest that the main area of research is focused on how to use chitosan as a nutrient in organic or mineral fertilizers, which can improve soil's fertility, enhance plants' growth and stimulate crops' yield. Between 2000 and 2006, 51 patents were obtained (in China, South Korea and Japan) and 8 articles were published on the subject (5 of them in English)[22 – 26]. The interest of using chitosan as a fertilizer's compound, which could be responsible for nutrients' controlled release, is relatively small. Between 2000 and 2006 nine patents were registered[27 – 35] and six articles were published (none of which was published in English) on the subject of using CRFs with chitosan. Nevertheless, in the literature available on the subject there is no data on this kind of fertilizers' functionality, rate and the effectiveness of nutrients' release, utilitarian properties, or their influence on the environment.

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