

Covering of mineral fertilizers with chitosan

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INTRODUCTION

Production of mineral fertilizers have risen along with the increase of human population and the need for increased food production (Shaviv 1993). 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% (Hauck 1985). Low effectiveness of nitrogen assimilation causes serious problems in view of environmental protection (Shaviv 1993). The effectiveness of nitrogen absorption may be improved through developing, producing and applying the so-called *slow release fertilizers (SRFs)*. These fertilizers gradually release mineral nutrients, providing proper nutrition to plants. They were first used in 1965 (Oertli 1962). Currently, they are produced mainly in the USA, Western Europe, Japan, South Korea, Israel and China.

In a system in which a granule of fertilizer is coated with an inert layer, water penetrates through a hydrophobic membrane into the inside of a granule. 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 (Kochba 1990). Sulfur-coated urea (SCU) is an example of this kind of a fertilizer (Jarrell 1979). Other examples include (Akelah 1996): polyethylene-coated urea, polymer-coated superphosphate, natural gum, rosin, waxes, paraffins, various kinds of ester copolymers, urethane composites, epoxy and alkide resins, polyolefines, polyacrylic acid, polyvinyl alcohol, epoxidized soybean oil or butadiene-methylstyrene block copolymers. The second kind of fertilizers is a system where the active component is dispersed in a polymer matrix. The first study into a matrix system was published in 1987 (Hepburn 1987), but the system has not been thoroughly studied (Al-Zachrani 1999), nor has it been used in industrial applications.

SRFs's drawback 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 in a technological scale, is to produce SRFs using biodegradable materials (Al-Zachrani 1999). Chitosan is one of such materials. Owing to its unique polycationic properties and other features it is being intensively investigated in the pharmaceutical field, as it might be used in systems of controlled drugs release (Illum 1998, Felt 1998). The interest in the agrochemical industry is mainly focused on how to use chitosan as a nutrient in organic or mineral fertilizers (Ohta 2000, Chibu 2002). The interest of using chitosan as a fertilizer's compound which could be responsible for nutrients' slow/controlled release is relatively small. In the literature available on the subject there is no data on this kind of fertilizers' functionality, rate and effectiveness of nutrients' release, utilitarian properties, or their influence on the environment.

MATERIALS AND METHODS

We used purified and characterized (Bartkowiak 1999) oligochitosan with a $M_n = 10000$ g/mol and a degree of deacetylation > 95%. Oligochitosan was obtained from chitosan with a $M_n = 50000$ g/mol by previously described radical degradation (Mullagaliev 1995). In the experiments 14% solution of oligochitosan in 1 M acetic acid was used. Two commercial NPK fertilizers (F1 and F2)

of different producers were dissolved in distilled water (100 g/l dm³). The solutions of oligochitosan and fertilizers were mixed to obtained the weight ratios of oligochitosan/fertilizer: 1/10 and 1/1. In the resulted mixtures more or less distinct gel structures were observed. The solutions of oligochitosan and fertilizers and the obtained mixtures of them were spray dried (BUCHI Mini Spray Dryer B-290) with inlet/outlet temperature 170°C/80°C, aspirator set at 80%, pump setting of 10%. The resulted powders were characterized with X-ray diffraction (X'Pert PRO, Philips), infra-red spectroscopy (FT/IR-430, Jasco) and scanning electron microscopy (DSM 962, Zeiss). Time and degree of release of mineral components was measured according to the standard method (PN-EN 13266). The phosphates content was determined with the colorimetric method (Spekol 11).

RESULTS AND DISCUSSION

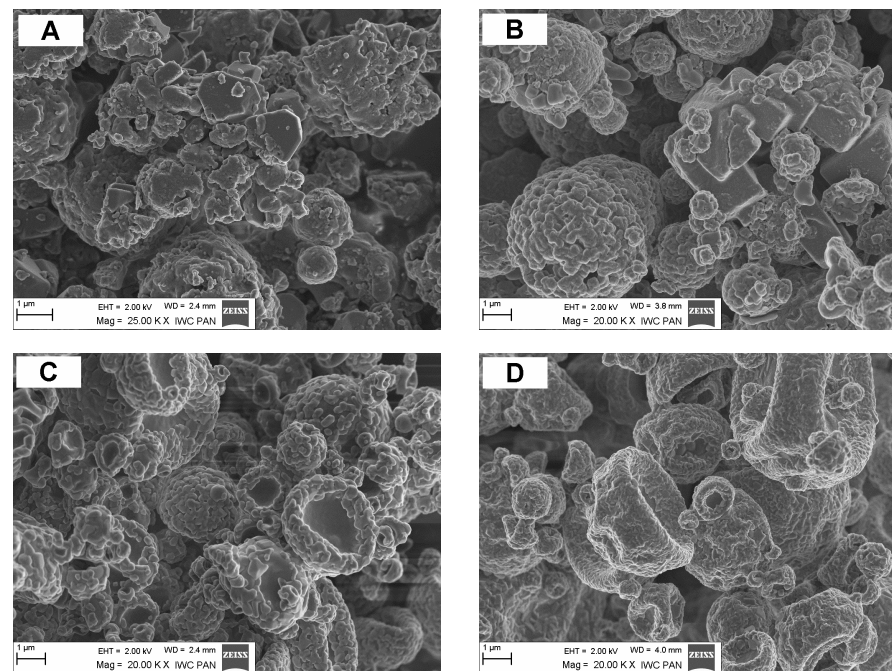


Figure 1: SEM images of spray dried fertilizers F1 (A), F2 (B) and mixtures of oligochitosan and fertilizers F1 (C) and F2 (D).

On Figure 1 SEM images of spray dried fertilizers F1, F2 and mixtures of oligochitosan with the fertilizers solutions (weight ratio 1/1) are presented. Observed product particles (C and D) have characteristic, ring shapes and they differ either from the particles of pure fertilizers (A and B) or the particles of oligochitosan (Lubkowski 2009). It cannot be said whether the particles of oligochitosan are coated with the particles of fertilizers or the fertilizers stuck to oligochitosan.

On Figure 2 the infrared spectra of spray dried fertilizer F1 (A), mixtures of oligochitosan and fertilizer F1 (weight ratio 1/10 (B), weight ratio 1/1 (C)) and oligochitosan (D) are presented. On Figure 3 the infrared spectra of spray dried fertilizer F2 (A), mixtures of oligochitosan and fertilizer F2 (weight ratio 1/10 (B), weight ratio 1/1 (C)) and oligochitosan (D) are presented. The spectra of drying products (B and C) does not differ essentially from the spectrum of pure fertilizers (A) and from the spectrum of oligochitosan (D). Along with the growth of the oligochitosan content the intensity of broad, shoulder band at 2895 cm^{-1} (due to C-H stretching vibrations) is observed to increase. The spectrum of native oligochitosan exhibited the characteristic band at 1656 cm^{-1} (due to N-H stretching vibrations). This band can also be noticed especially in the sample C. A broad band at $3200\text{-}3500\text{ cm}^{-1}$ in all the samples can be assigned to O-H stretching vibrations. It indicates considerable hydration of all the samples.

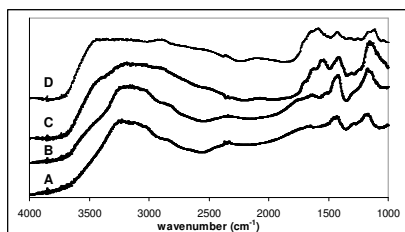


Figure 2: Infrared spectra of spray dried materials

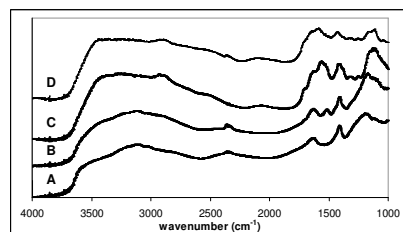


Figure 3: Infrared spectra of spray dried materials

On Figure 4 the XRD patterns of spray dried fertilizer F1 (A), mixtures of oligochitosan and fertilizer F1 (weight ratio 1/10 (B), weight ratio 1/1 (C)) are presented. On Figure 5 the XRD patterns of spray dried fertilizer F2 (A), mixtures of oligochitosan and fertilizer F2 (weight ratio 1/10 (B), weight ratio 1/1 (C)) are presented. Despite the content of oligochitosan, XRD patterns exhibited the characteristic peaks of pure fertilizers. The intensity of peaks is the smallest for the sample with the biggest amount of oligochitosan.

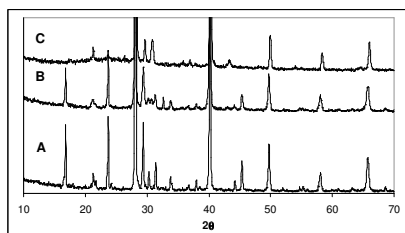


Figure 4: XRD patterns of spray dried materials

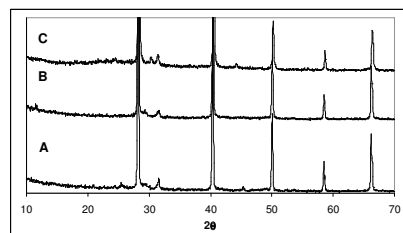


Figure 5: XRD patterns of spray dried materials

The XRD patterns of chitosan exhibited two characteristic crystalline peaks at 10.4° and 19.8° (Wang 2005, Lubkowski 2009). In the XRD patterns of oligochitosan-fertilizers complexes the characteristic peaks of chitosan are weakened or even completely disappeared. Instead some new peaks can be found. It could indicate the formation of a new regular crystalline phase. The

diffraction peaks of chitosan disappeared because the hydrogen bond within chitosan were destroyed by ions from fertilizers that chelate with $-\text{NH}_2$ and $-\text{OH}$ groups. The decrease of hydrogen bonds makes aggregated chitosan chain extend and disaggregate (Wang 2005).

The release measurements showed that about 50% of phosphorus contained in the prepared samples dissolves in water within one hour. The standard requires slow release fertilizers to liberate not more than 15% of mineral components within one day.

CONCLUSIONS

The powdered materials obtained as a result of spray drying of oligochitosan-fertilizer complexes or mixtures exhibited too high dissolution rate in H_2O and did not meet the standard requirements for slow release fertilizers.

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