"Gheorghe Asachi" Technical University of Iasi, Romania

COATING FERTILIZER GRANULES WITH BIODEGRADABLE MATERIALS FOR CONTROLLED FERTILIZER RELEASE

Krzysztof Lubkowski

West Pomeranian University of Technology, Institute of Chemical and Environment Engineering,
10 Pułaskiego Street, 70-322 Szczecin, Poland
E-mail: krzysztof.lubkowski@zut.edu.pl; Phone: +48 91 449 4730; Fax: +48 91 449 4686

Abstract

Biodegradable chitosan was used to cover fertilizer granules with an inert, impermeable layer in order to obtain a material with controlled release properties. The process was performed in a laboratory drum granulator. Prepared materials were characterized with available analytical methods (XRD, optical microscopy). The layer thickness of the obtained materials was in the range of 0.047 – 0.5425 mm. The degree of nutrients' release (0.64-0.965 within five hours) were determined with standardized method. Exponential, sigmoidal and power equations were used to describe the kinetics of nutrients' release.

Key words: biodegradable materials, controlled release fertilizers, granulation

1. Introduction

The world consumption of mineral fertilizers in 2009 was around 165.1 mLn Mg NPK (101.1 mLn Mg N, 37.5 mLn Mg P_2O_5, 26.5 mLn Mg K_2O) (IFA, 2009). An increased production of fertilizers and soil fertilization contrasts with a relatively low nutrient assimilation by crops; it is estimated that the assimilation reaches 30-50% for nitrogen, 10-25% for phosphorous and 50-60% for potassium (Finck, 1992; Hauck, 1985; Shaviv and Mikkelsen, 1993).

Low effectiveness of mineral components (mainly nitrogen) assimilation causes serious problems in view of environmental protection (Newbould, 1989; Shaviv and Mikkelsen, 1993), human (Forman, 1989; Hauck, 1985; Newbould, 1989; Shaviv and Mikkelsen, 1993) and animal (Forman, 1989; Newbould, 1989) health. It also has unfavourable effects in the economic aspect of the issue: material 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 production of mineral fertilizers, should also be pointed out.

The task of paramount importance is to increase the effectiveness of plants' nutrients assimilation and to decrease material losses, while at the same time to limit the amount of fertilizers' waste material produced by the industry. This can be achieved, among other things, through the development, production and application of the so-called "intelligent fertilizers", which release mineral components according to the nutrient requirements of the plants. The examples of such materials are slow release fertilizers (SRF) and controlled release fertilizers (CRF).

According to AAPFCO (*Association of American Plant Food Control Officials*) (AAPFCO, 1997) slow release fertilizers are chemically or biologically decomposed materials with a high molecular weight, complex structure and small solubility, whereas controlled release fertilizers are materials in case of which the release of mineral components takes place through a polymer layer or a membrane.

Among the slow release fertilizers only three groups of products of urea and aldehydes condensation are of commercial importance: urea-formaldehyde (*UF*), urea-isobutyraldehyde (*IBDU*[TM]) and urea-crotonaldehyde (*CDU*[TM]). Presently five types of urea-formaldehyde products are manufactured and have the largest share of the slow release fertilizer market. Urea-isobutyraldehyde and urea-crotonaldehyde products are less widely used because of higher costs of production.

A technology of controlled release fertilizers (CRF) production is well-established from the early sixties of the 20th century (Lunt, 1971; Lunt and Oertli, 1962; Oertli and Lunt, 1962; Oertli, 1980) and it consists in covering of fertilizer granules with an inert layer. The first technology of this type – sulphur coated urea (*SCU*) – was developed by TVA company (*Tennessee Valley Authority, USA*) in 1961. Despite of indubitable merits, nitrogen release from SCU fertilizers is relatively fast, therefore their significance gradually diminishes to the benefit of the polymer-coated fertilizers (*PC*). At present many various polymer-coated fertilizers are produced and they differ in the kind of polymer used and the manufacture technology (Trenkel, 2010), i.e.: Osmocote[TM], Multicote[TM], Plantacote[TM], Meister[TM], Nutricote[TM], Basacote[TM], Polyon[TM].

The world production of SRF/CRF is around 1 mLn Mg, and it constitutes 0.2% of overall mineral fertilizer production. 64% of SRF/CRF is consumed in USA, 21% in Japan, the rest in Europe (Trenkel, 2010). Taking into account the current pace of fertilizer industry development, the production of SRF/CRF in 2020 may amount to around 1.9-2.2 mLn Mg.

One of the CRF drawbacks, particularly polymer-coated CRF, is that after nutrients' consumption there is still a considerable amount of useless polymer left in the soil, around 50 kg/ha per year (Trenkel, 2010). A good and possible solution, although not as yet used on a technological scale, is to produce CRF using biodegradable materials (Akelah, 1996; Perez-Garcia et al., 2007), manufactured from raw materials renewable in the process of biosynthesis. One of such materials is chitosan – poly(2-amino-1,4-β-glukane) – natural polysaccharide produced commercially by deacetylation of chitin (Monteiro and Airoldi, 1999), which is the structural component of sea 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 industry, as it might be used in the systems of controlled drugs release (Felt et al., 1998; Illum, 1998; Yao et al., 1995). For several years now, scientists have been examined the possibility of using chitosan in the agrochemical industry. The main area of research is focused on how to use chitosan as a nutrient in organic or mineral fertilizers, which can improve soil fertility, enhance plants' growth and stimulate crops'

yield (Chibu et al., 2002; Ohta et al., 2000, 2004a, 2004b; Seo et al., 2000). The interest of using chitosan as a fertilizer compound, that could be responsible for nutrients controlled release, is relatively small and merely few papers from this area of research can be found in the literature (Entry and Sojka, 2007, 2008; Jamnongkan and Kaewpirom, 2010; Wu and Liu, 2008; Wu et al., 2008).

The objective of this research was to obtain materials with controlled release properties by covering granules of mineral fertilizer with a layer of chitosan as an example of biodegradable, natural polymer, with the use of a laboratory drum granulator and spraying method. The aim of the work was also the evaluation of the nutrients release kinetics from the prepared materials. To interpretation of the release kinetics three equations (power, exponential and sigmoidal) have been applied in order to check which of them fits best the kinetic data.

2. Experimental

2.1. Materials

Purified and characterized in detail (Bartkowiak and Hunkeler, 1999a, 1999b) oligochitosan, with a molar mass M_n=5000 g/mol and the degree of deacetylation >95%, was obtained by radical degradation as previously described (Bartkowiak, 2001), where chitosan with a molar mass M_n=50000 g/mol was used as a starting material (Hutchinson/McNeil Int., Philadelphia, USA, product E-055). In the investigation 18% solution of oligochitosan in 1 M acetic acid was used. The additives used in the experiments were: glycerine $C_3H_8O_3$ (p.a., POCH, Gliwice, Poland) as a plasticizer, sodium tripolyphoshate TPP (p.a., POCH, Gliwice, Poland) as a compound with three orthophosphoric groups that increase the ability of formation gel-polyelectrolyte complexes with chitosan, a 25 wt% solution of a natural wax Candelilla (PPH Standard, Warsaw, Poland) as a modifier increasing hydrophobic properties of obtained materials.

As a source of active mineral components (N, P, K) the commercial, granulated, multicomponent fertilizer (Fosfan SA) was used in the experiment. Photometry (Spekol 11) and potentiometry (ammonium ion selective electrode, Orion) were used to determine the total content of nitrogen (5 wt% N-NH_2 + N-NH_4). The content of phosphorous (6 wt% P_2O_5) and potassium (10 wt% K_2O) were determined with photometry and flame photometry (Flapho 40), respectively. The measured contents of mineral components are consistent with the data declared by the fertilizer's manufacturer.

2.2. Method

Granules of multicomponent fertilizer were covered with a layer of biodegradable mixture of chitosan and the additives by the spraying method in

the laboratory drum granulator (capacity 20 dm^3, 10 r.p.m.). A process temperature was kept at a level of 85-105°C.

2.3. Characterization

Morphology of the prepared samples was assessed by means of photography and optical microscopy. The thickness of the covering layer was determined with the use of optical microscope Nikon Eclipse 50i (magnification 10x10). XRD experiments were performed on an X′Pert PRO (Philips) powder diffractometer with a proportional detector, computer-aided data acquisition and a copper lamp as an X-ray radiation source. The XRD patterns were recorded in the range of 2θ equal to 10-60°. The measurements of time and the degree of release of mineral components from the obtained materials were performed in water, according to the standardized method (Trenkel 2010, European Standard EN 13266, 2001). Five granules of the prepared materials (2 g with the accuracy of 0.0001 g) were placed in a glass beaker containing 100 mL of water at temperatures of 25°C. After given periods of dissolution the solution was taken for analysis.

The amount of released phosphates was measured in regular periods of time up to 5 hours. Gravimetric and photometric methods were used to determine the amount of released phosphates. It has been shown recently (Perez-Garcia et al., 2007) that the release of mineral components from slow/controlled release fertilizers in soil might be easily predicted from the release experiments performed in water. It was assumed that the release of phosphates corresponds to the release of all mineral components of the prepared materials and therefore only the release of phosphates was determined.

3. Results and discussion

The starting material, as granules of mineral fertilizer (*sample s0*) are of regular, spherical shape and white colour, with a slightly grey shade (Fig. 1A). They are hard, although subjected to adequate crushing force they may be easily crumbled to small
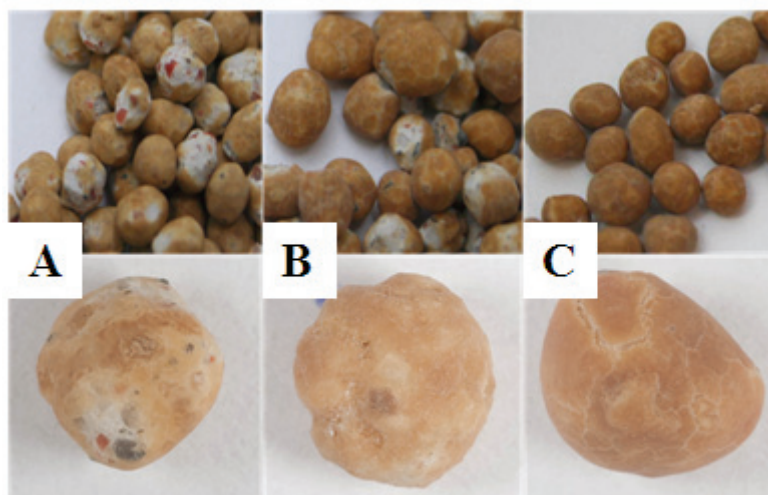
pieces and then milled to powder.

For the necessity of experiments the fraction of granules with a diameter of 3-4 mm were selected. As a result of covering of mineral fertilizer granules in the laboratory drum granulator with the mixture of chitosan and the additives the samples of materials varying in the appearance, surface layer structure and morphology have been obtained. The pictures of the material covered with the layer of chitosan (mass ratio chitosan/fertilizer equal to 8/100) are presented in Fig. 1B (*sample s1*). The granules of fertilizer are not covered completely with the polymer, the surface structure and colour of the prepared material is not uniform.

In Fig. 2 the pictures of the materials obtained as a result of covering the granules of fertilizer with higher amounts of chitosan (mass ratios of chitosan to fertilizer 10/100, 12/100 and 14/100) are shown (*samples s2, s3 and s4*). Into the solution of chitosan small amounts of natural wax (with mass ratios of wax to fertilizer 2/100, 4/100 and 6/100, respectively), enhancing the hydrophobic properties of the material, were added. Along with the increase of chitosan amount, the coverage of granules with the polymer was growing, followed by the colour unification. Nevertheless, the surface structure of the prepared samples is not homogeneous: numerous cracks, fractures and grooves can be noticed (Fig. 2C).

In order to improve the plastic properties of the material and to avoid the formation of the cracked surface, the fertilizer was covered with chitosan with an addition of natural wax and glycerine as a plasticiser (*samples s5, s6, s7 and s8*). The mass ratios of chitosan to fertilizer were as follows: 8/100, 12/100, 18/100 and 24/100, whereas the mass ratios of glycerine to fertilizer: 2/100, 3/100, 4.5/100, 6/100. The amounts of natural wax were the same as in the previous experiment.

The pictures of the prepared materials are shown in Fig. 3. All the samples are characterized by a dense and compact structure, there are no visible cracks and fractures on the surface. Along with the increase of chitosan and glycerine the colour of the samples changes from light brown to dark brown. Increasing the amount of glycerine in the samples makes their surface look glassy-like. As a modification of the covering chitosan solutions, sodium tripolyphoshate (TPP) was additionally used.

Fig. 1. A - granules of the starting material - commercial, multicomponent fertilizer (s0), B - granules of the fertilizer covered with the layer of chitosan - mass ratio chitosan/fertilizer 8/100 (s1)

Fig. 2. Granules of the fertilizer covered with the mixture of chitosan and natural wax with various mass ratios of chitosan to fertilizer: A - 10/100 (s2), B - 12/100 (s3) and C - 14/100 (s4)

Fig. 3. Granules of the fertilizer covered with the mixture of chitosan, natural wax and glycerine with various mass ratios of chitosan to fertilizer: A - 8/100 (s5), B - 12/100 (s6), C - 18/100 (s7) and D - 24/100 (s8)

Preparation of the samples was a three-step process. In the first step granules of fertilizer were covered with the solution of chitosan (mass ratio chitosan/fertilizer 30/100) containing small amounts of glycerine (mass ratio glycerine/fertilizer 6/100). In the second step the material was covered with the solution of TPP (mass ratio TPP/fertilizer 15/100).

The pictures of so prepared material are shown in Fig. 4A (*sample s9*). In the final step the granules were again covered with the same solution of chitosan and glycerine. The pictures of the material obtained in this way are presented in Fig. 4B (*sample s10*).

During the covering the colour of the granules was changing from brown (like in Fig. 3B) to white-grey with black spots shining through the outer layer (Fig. 4A), and to light brown with irregular brown spots at the end (Fig. 4B).

On the cross-sections of the granules various parts of the covering layer may be identified. The inner, deepest part of the layer, covering the core of the granule, is dark and was formed by the spraying with the mixture of chitosan, wax and glycerine.

The middle part of the layer is lighter and it was formed by the spraying with TPP solution. The very outer part of the layer is the effect of the repeated spraying with the mixture of chitosan. In comparison with the starting material the prepared

samples were harder, though the slightly elastic properties of the formed layer decreased the fragility of the granules and they were very difficult to crumble.

For all the samples prepared in the experiment, the measurements of the formed layer thickness have been carried out with the use of optical microscopy. The exemplary pictures of the prepared materials are presented in Fig. 5.

The structure of the formed layers is not homogeneous and their thicknesses vary in a broad spectrum. The picture shown in Fig. 5D proves that the layer of the material obtained as a result of covering the fertilizer with the mixture of chitosan, wax and glycerine, then with the TPP solution, and again with the mixture of chitosan with the additives, has a coat consisting of three sublayers.
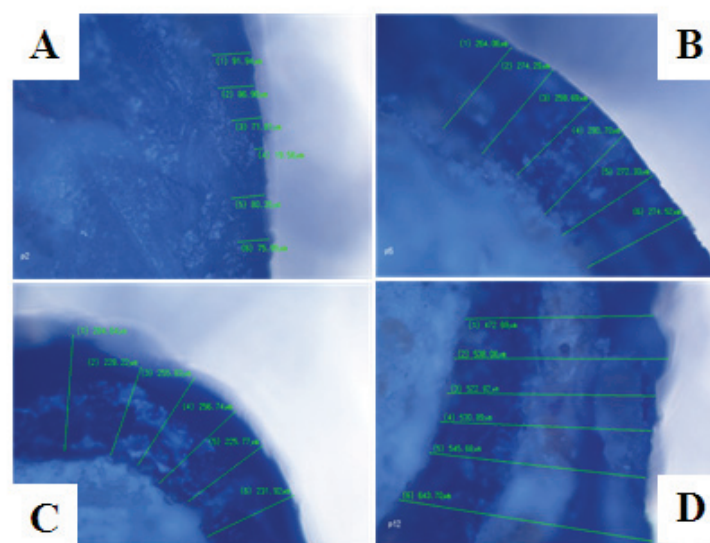
To evaluate properly the layer thickness of the prepared materials, six measurements have been carried out. The results of measurements and the statistical calculations are collected in Table 1. It can be seen that the layer thickness of the prepared samples grows along with the amounts of the covering polymer used. In order to check whether there are any interactions between the components of the fertilizer and the polymer material used to cover the granules, x-ray diffraction analysis have been performed.

Fig. 4. Granules of the fertilizer covered with the mixture of chitosan, natural wax, glycerine and sodium tripolyphoshate after two steps (A) and after the third step (B) of the process

Table 1. Results of the layer thickness measurements

	mean value, µm	standard dev.	standard error	t-value	sig. level
s1	71.17	26.09	10.65	6.68	0.001136
s2	77.33	35.07	14.32	5.40	0.002939
s3	159.17	12.98	5.30	30.03	0.000001
s4	271.00	7.69	3.14	86.28	0.000000
s5	47.00	11.38	4.65	10.11	0.000162
s6	188.67	22.83	9.32	20.25	0.000005
s7	256.17	67.23	27.45	9.33	0.000238
s8	265.83	23.80	9.72	27.36	0.000001
s9	319.83	65.89	26.90	11.89	0.000074
s10	542.50	55.99	22.86	23.73	0.000002

Fig. 5. Exemplary optical microscopy images of the prepared materials with the measured layer thickness:
A - s1, B - s6, C - s8, D - s10

The XRD spectra of the analyzed samples (*s1, s4, s8, s9, s10*) are shown in Fig. 6 and compared with the spectrum of the starting material (*s0*). All the spectra are very much alike, there are no essential differences in the position and intensity of the peaks between the spectra of prepared materials and the starting fertilizer.

All the recorded peaks may be assigned to the components of the fertilizer. Taking into account the fact that there are not any new peaks in the spectra of the prepared materials, it may be stated that no new phases are formed during the covering process. It may be concluded that the interactions between the fertilizer components and mixtures of chitosan and the additives are of physical but not chemical nature.

The prepared materials were submitted to water release experiments and the results of these tests are shown in Fig. 7. Amounts of released phosphates were determined as a function of time, at constant temperature of 25°C. The release of phosphates from commercial fertilizer (*s0*) was very fast and all phosphates were released within 50 minutes. All prepared materials reveal smaller release degree of phosphates in comparison with the starting

fertilizer. In the case of the material obtained as a result of covering the fertilizer with a solution of chitosan (*s1*), the release degree of phosphates was 0.965 after five hours. The materials obtained by covering of fertilizers with various amounts of chitosan with addition of small amounts of natural wax (*s2, s3, s4*) were found to have very similar release degrees after five hours: 0.96, 0.95 and 0.94, respectively. For the sake of simplicity, only the best of them was shown in Fig. 7.

The release degree of phosphates from materials covered with the mixture of chitosan, natural wax and glycerine (*s5, s6, s7, s8*), after five hours, were as follows: 0.90, 0.84, 0.82, 0.77, respectively. The best release degrees were achieved in the case of materials obtained as a result of two-stage and three-stage covering with the mixture of chitosan, wax, glycerine, and then with TPP solution (*s9*), and after that again with the mixture of chitosan, wax and glycerine (*s10*): 0.71 and 0.64, respectively. The standard (European Standard EN 13266, 2001) requires slow release fertilizers to liberate not more than 15% of mineral components within 24 hours. From this point of view, the prepared materials exhibited too high dissolution rate in H_2O and did not meet the standard requirements for slow release fertilizers.

The results of the layer thickness and phosphates release measurements were correlated and shown in Fig. 8. It may be concluded that the decrease of the phosphate release degrees from the obtained materials takes place with the grow of their layer thicknesses. A diffusion mechanism of the release might be pointed out as a reason of that correlation.

Along with the grow of the layer thickness, the value of diffusion coefficients decreases and the release process is more and more hindered. A slight difference between the materials covered with chitosan (*s1*), chitosan and wax (*s2, s3, s4*) and the rest of the samples should be noticed here. The samples obtained by covering with the mixture of chitosan, wax and glycerine (*s5, s6, s7, s8*), despite of the comparable layer thicknesses, reveal smaller release degrees. Probably the surface of the material may be better "sealed" when glycerine is applied in contrast to the materials covered only with chitosan and wax, where the surface is cracked and fractured.
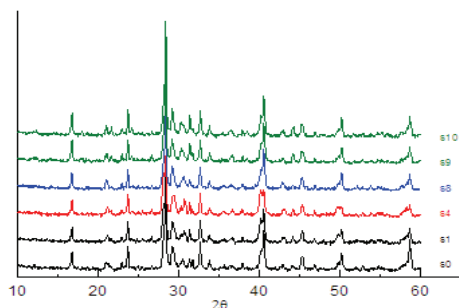
The experimental data related to release degree of mineral components from the starting fertilizer and from all prepared materials were described and interpreted with three kinetic equations: power, exponential and sigmoidal (Eqs. 1-3):

$$\frac{M_t}{M_\infty} = k_p \cdot t^n \tag{1}$$

$$\frac{M_t}{M_\infty} = 1 - exp(-k_e \cdot t) \tag{2}$$

$$\frac{M_t}{M_\infty} = \frac{a-b}{1+exp\left(\dfrac{t-d}{c}\right)} + b \tag{3}$$

where M_t/M_∞ is the fraction of nutrients released at time t, k_p and n are the power equation constants, k_e is the exponential equation constant, and a, b, c, d are the sigmoidal equation constants.

Two of the presented equations, namely power and exponential equations, have been already used in the prediction of the controlled release of drugs (Schwartz et al., 1968; Sinclair and Peppas, 1984) and mineral components of fertilizers (Al-Zachrani, 2000). The sigmoidal model has also proved its usefulness in the description of the controlled release (Jarrell et al., 1979; Jarrell and Boersma, 1979, 1980; Shaviv et al., 2003a, 2003b), although the sigmoidal equation applied in the present work differs from the equations that can be met in the literature.

The comparison between the experimental data of the phosphates release from the starting fertilizer and the predicted values calculated by the exponential and sigmoidal equations are presented in Fig. 9. Both models satisfactorily fit the experimental data. The power equation did not prove its usability in the description of these data. The comparison between the experimental data of the phosphates release from all prepared materials and the predicted values calculated by the exponential, sigmoidal and power equations are shown in Fig. 10. Based on the applied kinetic models, the constants and correlation coefficients of the equations were determined and they are placed in Table 2, along with the data related to the final release of phosphates from the prepared materials (M_t/M_∞).
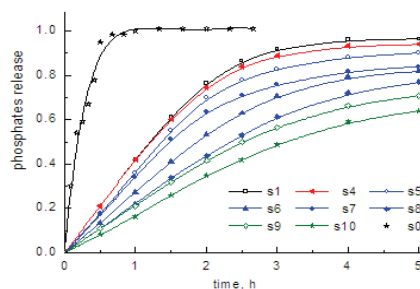

Fig. 6. XRD spectra of the prepared samples compared with the spectrum of the starting fertilizer

Fig. 7. The release of phosphates from the prepared materials compared with the starting fertilizer
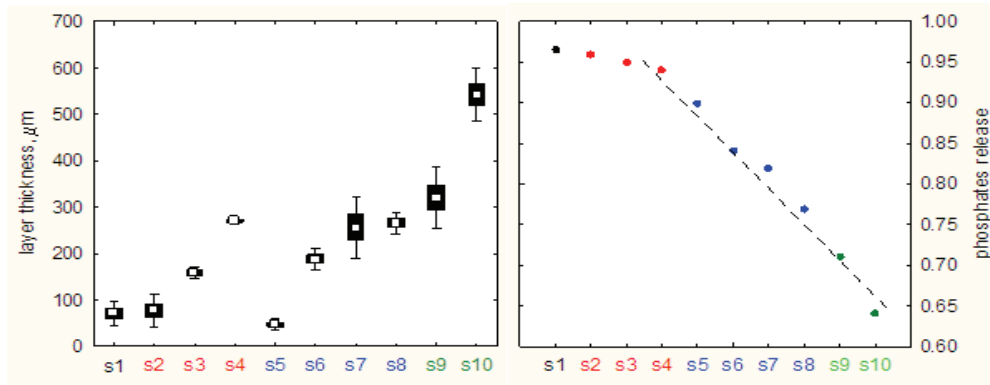
Fig. 8. Correlation between the layer thicknesses and phosphates release (after five hours) from the prepared materials
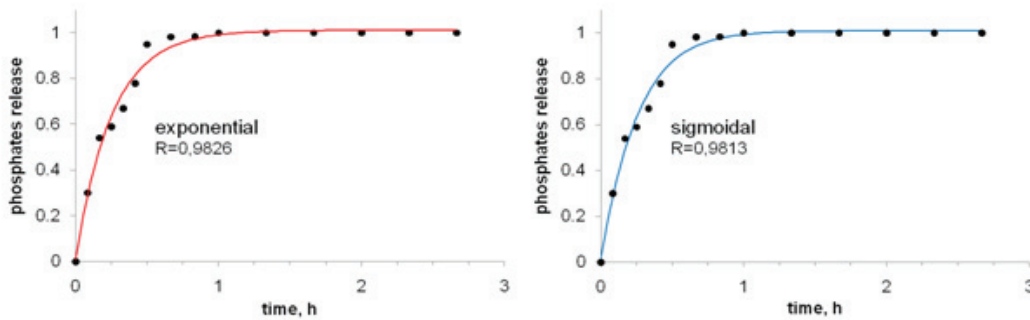

Fig. 9. Comparison between the experimental data of the phosphates release for the starting fertilizer and the predicted values calculated by Eqs. 2 and 3

Table 2. Constants of the empirical, kinetic equations after fitting to release data

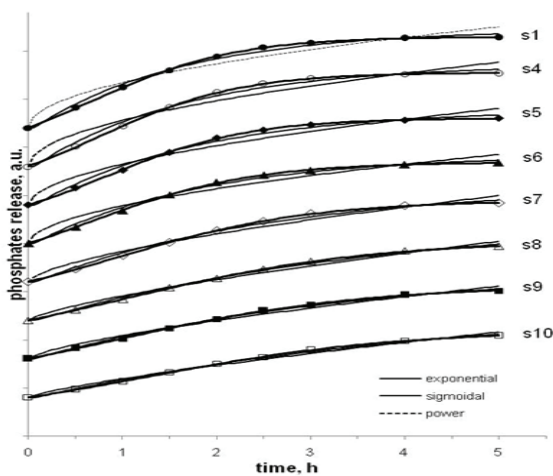| No	M_t/M_∞	sigmoidal					exponential		power	
		a	*b*	*c*	*d*	*r*	k_e	*r*	k_p	*r*
s0	1	-6.270	1.009	0.434	0.235	0.9813	3.9218	0.9826	-	-
s1	0.965	-0.399	0.949	0.663	0.774	0.9997	0.6207	0.9878	0.4742	0.8779
s4	0.94	-0.352	0.977	0.753	0.749	0.9995	0.6086	0.9853	0.5033	0.8740
s5	0.90	-0.295	0.902	0.839	0.754	0.9997	0.5661	0.9847	0.5317	0.8843
s6	0.84	-0.409	0.845	0.635	0.873	0.9996	0.5525	0.9905	0.5323	0.9048
s7	0.82	-0.339	0.848	0.937	1.033	0.9998	0.3890	0.9907	0.6400	0.9417
s8	0.77	-0.381	0.829	1.013	1.313	0.9997	0.2752	0.9945	0.7260	0.9702
s9	0.71	-0.405	0.763	0.842	1.346	0.9998	0.2950	0.9955	0.7034	0.9701
s10	0.64	-0.273	0.697	1.250	1.333	0.9997	0.2265	0.9942	0.7787	0.9752

Fig. 10. Comparison between the experimental data of the phosphates release for the prepared materials and the predicted values calculated by Eqs. 1-3

In the case of the sigmoidal equation the fitting of the model lines to the experimental data, expressed with the correlation coefficients, reaches very high values and is significantly better in comparison with the power and exponential models. Keeping in mind the fact that the nutrients uptake by plants is of sigmoidal character (Shaviv and Mikkelsen, 1993) and that the sigmoidal model has been already applied to the description of the controlled release (Jarrell et al., 1979; Jarrell and Boersma, 1979, 1980; Shaviv et al., 2003a, 2003b), it may be concluded that the sigmoidal equation used in the present work in the best way predicts the release of phosphates from the prepared materials.

4. Conclusions

Materials with controlled release properties can be obtained as a result of covering the

multicomponent, granular fertilizer with the solutions of biodegradable chitosan and the additives, performed in a drum granulator, with the use of a spraying method.

Depending on the amount of used chitosan and the kind of additive, the obtained materials differed from each other with respect of colour, layer thickness and homogeneity.

The layer thickness of the obtained materials was in the range of 0.047 – 0.5425 mm. The release degree of phosphates was in the range of 0.64-0.965 within five hours and it was smaller in comparison with the starting fertilizer. The decrease of the release degrees from the obtained materials proceeded with the grow of their layer thicknesses.

A diffusion mechanism of the release was pointed out as a reason for that correlation. The best correlation between the experimental data of phosphates release and the predicted values was achieved in the case of the sigmoidal model equation.

Acknowledgement

References

AAPFCO, (1997), Association of American Plant Food Control Officials (AAPFCO), Official Publication No. 50, T-29, AAPFCO Inc., West Lafayette, Indiana, USA.

Akelah A., (1996), Novel utilizations of conventional agrochemicals by controlled release formulations, *Materials Science and Engineering C*, **4**, 83-98.

Al-Zachrani S.M., (2000), Utilization of polyethylene and paraffin waxes as controlled delivery systems for different fertilizers, *Industrial and Engineering Chemistry Research*, **39**, 367-371.

Bartkowiak A., Hunkeler D., (1999), New microcapsules based on oligoelectrolyte complexation, *Annals of the New York Academy of Sciences*, **875**, 36-45.

Bartkowiak A., Hunkeler D., (1999), Alginate-oligochitosan microcapsules: a mechanistic study relating membrane and capsule properties to reaction conditions, *Chemistry of Materials*, **11**, 2486-2492.

Bartkowiak A., (2001), *Binary polyelectrolyte microcapsules based on natural polysacharides*, PhD Thesis, Technical University of Szczecin, Poland.

Chibu H., Shibayama H., Mitsutomi M., (2002), Effects of chitosan application on shoot growth and chitinase activity in rice, *Advances in Chitin Science*, **6**, 231-235.

Entry J.A., Sojka R.E., (2007), Matrix based fertilizers reduce nitrogen and phosphorous leaching in greenhouse column studies, *Water, Air and Soil Pollution*, **180**, 283-292.

Entry J.A., Sojka R.E., (2008), Matrix based fertilizers reduce nitrogen and phosphorous leaching in three soils, *Journal of Environmental Management*, **87**, 364-372.

European Standard EN 13266, (2001), Slow release fertilizers – Determination of the release of the nutrients – Methods for coated fertilizers, European Committee for Standardization, Brussels.

Felt O., Buri P., Gurny R., (1998), Chitosan: a unique polysaccharide for drug delivery, *Drug Development and Industrial Pharmacy*, **24**, 979-993.

Finck A., (1992), *Fertilizers and their efficient use*, In: *World Fertilizer Use Manual*, Halliday D.J., Trenkel M.E., Wichmann W. (Eds.), International Fertilizer Industry Association, Paris.

Forman D., (1989), Are the nitrates a significant risk factor in human cancer?, *Cancer Survey*, **8**, 443-458.

Hauck R.D., (1985), *Slow Release and Bio-inhibitor-Amended Nitrogen Fertilizers*, In: *Fertilizer Technology and Use*, Engelstad O.P. (Ed.), SSSA, Madison, 293-322.

Illum L., (1998), Chitosan and its use as a pharmaceutical excipient, *Pharmaceutical Research*, **15**, 1326-1331.

Jamnongkan T., Kaewprom S., (2010), Potassium release kinetics and water retention of controlled-release fertilizers based on chitosan hydrogels, *Journal of Polymers and the Environment*, **18**, 413-421.

IFA, (2009), World agricultural and fertilizer demand, Global fertilizer supply and trade 2008-2009, International Fertilizer Industry Association, Paris.

Jarrell W.M., Pettygrove G.S., Boersma L., (1979), Characterization of the thickness and uniformity of the coatings of sulfur-coated urea, *Soil Science Society of America Journal*, **43**, 602-605.

Jarrell W.M., Boersma L., (1979), Model for the release of urea by granules of sulfur-coated urea applied to soil, *Soil Science Society of America Journal*, **43**, 1044-1050.

Jarrell W.M., Boersma L., (1980), Release of urea by granules of sulfur-coated urea, *Soil Science Society of America Journal*, **44**, 418-422.

Lunt O.R., (1971), Controlled-release fertilizers: achievements and potential, *Journal of Agricultural and Food Chemistry*, **19**, 797-800.

Lunt O.R., Oertli J.J., (1962), Controlled release of fertilizer minerals by encapsulating membranes: II. Efficiency of recovery, influence of soil moisture, mode of application, and other considerations related to use, *Soil Science Society of America Proceedings*, **26**, 584–587.

Monteiro O.A.C., Airoldi C., (1999), Some studies of crosslinking chitosan - glutaraldehyde interaction in a homogeneous system, *International Journal of Biological Macromolecules*, **26**, 119-128.

Newbould P., (1989), The use of nitrogen fertilizer in agriculture. Where do we go practically and ecologically?, *Plant and Soil*, **115**, 297-311.

Oertli J.J., (1980), Controlled-release fertilizers, *Fertilizer Research*, **1**, 103-123.

Oertli J.J., Lunt O.R., (1962), Controlled release of fertilizer minerals by encapsulating membranes: I. Factors influencing the rate of release, *Soil Science Society America Proceedings*, **26**, 579-583.

Ohta K., Atarashi H., Shimatani Y., Matsumoto S., Asao T., Hosoki T., (2000), Effects of chitosan with or without nitrogen treatment on seedling growth in Eustoma grandiflorum, *Journal of the Japan Society of Horticulture Science*, **69**, 63-65.

Ohta K., Morishita S., Kobayashi N., Hosoki T., (2004), Effects of chitosan soil mixture treatment in the seedling stage on the growth and flowering of several ornamental plants, *Journal of the Japan Society of Horticulture Science*, **73**, 66-68.

Ohta K., Suzuki M., Matsumoto S., Kobayashi N., (2004), Effects of nitrogenous organic compounds on growth

and flowering in Eustoma grandiflorum*, Horticulture Science*, **39**, 1438-1440.

Perez-Garcia S., Fernandez-Perez M., Villafranca-Sanchez M., Gonzales-Pradas E., Flores-Cespedes F., (2007), Controlled release of ammonium nitrate from ethylcellulose coated formulations, *Industrial and Engineering Chemistry Research*, **46**, 3304-3311.

Schwartz J.B., Simonelli A.P., Higuchi W.I., (1968), Drug release from wax matrices. I. Analysis of data with first-order kinetics and with the diffusion controlled model, *Journal of Pharmaceutical Sciences*, **57**, 107-119.

Seo K.W., Choi D.S., Han K.S., Choi W.G., Oh S.H., (2000), Effects of chitosan fertilizer on the growth of cabbage and GABA contents in the cabbage, *Journal of Korean Society of Agriculture Chemistry and Biotechnology*, **43**, 34-38.

Shaviv A., Mikkelsen R.I., (1993), Controlled-release fertilizers to increase efficiency of nutrient use and minimize environmental degradation – a review, *Fertilizer Research*, **35**, 1-12.

Shaviv A., Raban S., Zaidel E., (2003), Modeling controlled nutrient release from polymer coated fertilizers: diffusion release from single granules, *Environmental Science and Technology*, **37**, 2251-2256.

Shaviv A., Raban S., Zaidel E., (2003), Modeling controlled nutrient release from a population of polymer coated fertilizers: statistically based model for diffusion release, *Environmental Science and Technology*, **37**, 2257-2261.

Sinclair G.W., Peppas N.A., (1984), Analysis of non-fickian transport in polymers using simplified exponential expressions, *Journal of Membrane Science*, **17**, 329-331.

Trenkel M.E., (2010), *Slow- and controlled-release and stabilized fertilizers: an option for enhancing nutrient use efficiency in agriculture*, International Fertilizer Industry Association, Paris.

Wu L., Liu M., (2008), Preparation and properties of chitosan-coated NPK compound fertilizer with controlled-release and water-retention, *Carbohydrate Polymers*, **72**, 240-247.

Wu L., Liu M., Liang R., (2008), Preparation and properties of a double-coated slow-release NPK compound fertilizer with superabsorbent and water-retention, *Bioresource Technology*, **99**, 547-554.

Yao K.D., Peng T., Yin Y.J., Xu M., (1995), Microcapsules–microspheres related to chitosan, *Polymer Reviews*, **35**, 155–180.