საქართველოს მეცნიერებათა ეროვნული აკადემიის მოამბე, ტ. 13, №4, 2019
BULLETIN OF THE GEORGIAN NATIONAL ACADEMY OF SCIENCES, vol. 13, no. 4, 2019

Biochemistry

Synthesis of Nitrogen-Containing Biodegradable Polymer Fertilizers with the Prolongation Action

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ABSTRACT. Intense growth of the population calls for the increase of production of grain crops. One of the ways to resolve the problem is application of nitrogen-containing fertilizers in increased doses. According to the current data, annually more than 200 million tons of nitrogenous fertilizer is introduced into soil, but because of its good water solubility its major part is lost due to its volatility and washing-off, which results in substantial economic losses. To elevate the yield of grain crops the ecologically pure and economically efficient bio-composites which contain linear structure polymerized nitrogenous fertilizers acting by the prolongation mechanism and microorganisms able to destruct such fertilizers were developed. The process of creation of polymerized fertilizers was studied. It was shown that in the range of 110-125^{0}C, up to deep conversion of fertilizers, reaction rate constants keep constant values, when they are computed according to the Arrhenius's second order equations. Results of I.R. spectroscopy studies showed that at the first stage of the reaction of carbamide-formaldehyde interaction, when methylol-derivatives are formed (specter wave 1030 cm^{-1}) we observe also conversion of methylol groups into dimethylene ether groups (specter wave 1085 and 1110 cm^{-1}). Rectilinear dependence of the reaction rate constant logarithm alteration on inverse absolute temperature refers to the fact that reaction rate constants undergo change according to the Arrhenius equation. At the application of polymerized nitrogenous fertilizers the fixed hectare norm of nitrogenous fertilizers decreases minimum by 40%, productivity increases by 15-20% and the environment is protected from pollution by nitrogenous fertilizers. Technology of obtaining polymerized nitrogenous fertilizers and polymer biodegradable biocomposites have been developed. *© 2019 Bull. Georg. Natl. Acad. Sci.*

Key words: prolongation mechanism, microorganisms, biocomposites, technology, fertilizers

Intense growth of the population calls for the increase of production of grain crops. Annually arable lands decrease because of intense urbanization and industry intensification. One of the ways to resolve the problem is assimilation of intense technologies, especially application of nitrogen-containing fertilizers in increased doses. According to the current data, annually more than

200 million ton nitrogenous fertilizers are introduced into soil, but because of their good water solubility the major part (more than 50%) is lost due to its volatility and washing-off, which results in substantial economic losses. At the same time, it contributes to global pollution, causing many diseases.

To resolve the problem a new type of the so-called "exchange fertilizers" was developed in the United States of America. They consist of hardly soluble ingredients, which are released in soil as a result of buffer effect of chemical reactions going on there and are assimilated by plants [1-4].

Our research aimed to receive a chemical synthesis of a polymer biodegradable in soil and containing amide and peptide groups of prolongation action to isolate its destructor from soil, inclusive urease activity microorganisms and to create nitrogen-containing biocomposites easily biodegradable in soil.

Materials and Methods

The subject of our study was the linear structure of nitrogenous fertilizer of prolongation action synthesized by us, which was obtained in the solution as well as in the melt, via carbamide and formaldehyde polycondensation [5].

To study biodegradation of nitrogenous fertilizers with prolongation effect we isolated freely residing nitrogen-fixing microorganisms (Azoto-bacter sp., Clostridium sp.) and various strains of urobacteria (Urobacillus sp.) from soil [6].

Isolation of microorganism from soil and their identification was realized according to the methods of M. Burger and T. Dobrovolskaya [7]. Nitrogen was determined by I. Kjeldal method.

Results and Discussion

The process of creation of a polymer in the melt was investigated. To simplify the process of penetration into the polymer we synthesized linear polymers. High efficiency was achieved at definite molar ratio of starting components. Study of the process of creation of carbamide based on linear structure polymer was implemented at the following molar ratios of the initial components – carbamide and formaldehyde: 1:0.9; 1:1; 1:1.1 and 1:1.2, correspondingly. Reaction temperature was 60, 70, 80, 90, 100, 135^{0}C. Macromolecule formula is expressed as follows:

$$HOH_2C\left[-NH-CO-NH-CH_2\right]_n-NHCONH_2$$

I.R. spectral study showed that at the first stage of creation of methylol-derivatives of carbamide (specter wave 1030 cm^{-1}) we observed conversion of methylol groups to dimethylene ether groups (specter wave 1085 and 1110 cm^{-1}).

In the process of synthesis of carbamide-formaldehyde oligomers we consider expedient to study some kinetic regularities of the process within the range of 110-125^{0}C at the carbamide-formaldehyde molar ratio 1:1.2. Control over reaction progress was carried out according to the changes in formaldehyde concentration. It turned out that in the 110-125^{0}C temperature range, till deep conversion, the reaction rate constants during the reaction keep constant values, when they are computed by the second order equation.

Rectilinear dependence of the reaction rate constant of logarithm alteration to the inverse absolute temperature refers to the fact that reaction rate constants undergo change according to the Arrhenius equation.

The second order is proved also by the ratio of 1/a-x and reaction duration. In this temperature range the rectilinear relation is preserved. Activation energy computed according to the Arrhenius equation equals to 1554 kcal/mol.

The process of degradation of linear structure polymers, at the impact of bacteria is simplified because of linear structure of molecules. Urease

Table 1. Values of reaction rates and activation energy at 110–125^{0}C range at the interaction of formaldehyde and carbamide*

№	reaction duration, sec.	conversion degree,%			reaction rate constant K. 10^{-2}, l.mol $^{-1}$, sec.$^{-1}$		
		110^{0}C	120^{0}C	125^{0}C	110^{0}C	120^{0}C	125^{0}C
1	30	71.66	74.50	89.16	2.81	3.24	3.38
2	60	83.60	85.48	94.25	2.83	3.27	3.34
3	90	88.39	89.83	96.00	2.80	3.27	3.38
4	120	91.14	92.15	97.01	2.85	3.26	3.34
5	150	92.83	93.53	97.60	2.87	3.21	3.38
6	180	93.97	94.60	98.01	2.88	3.24	3.37
7	240	95.33	95.86	98.50	2.80	3.22	3.36
8	300	96.25	96.66	98.27	2.85	3.22	3.37

* carbamide and formaldehyde molar ratio 1:1.2.

ferments easily penetrate into macromolecules and biodegrade them.

Nitrogen concentration was determined in carbamide and fertilizers with prolongation action. Besides, dynamics of changes in nitrogen content was defined in soil. Transition of nitrogen into soluble form in case of the fertilizer characterized by prolongation action takes place purposively slowly.

We have studied degradation of linear structure polymer (fertilizer) by the emission of ammonia. With this in view, microorganisms apt to destruct the tested polymer were isolated from definite type soils (chestnut, alluvium-acidic, brown-carbonaceous) of east Georgia.

As a source of nitrogen, various quantities of the polymer (to adapt microorganism) were added to the medium of cultivation of microorganisms (Christiansen medium, where initially starting quantity of peptone was used as nitrogen sources); when the adapted microorganisms were obtained experiments were carried out according to the following scheme: only polymer, without inoculation (control) only with urea and polymer with inoculation (in the nutrient medium starting quantity of peptone and adapted microorganism).

Analysis of the obtained results showed that at the 4th hour of cultivation of microorganisms, ammonia content in the medium was approximately 0.6 mg/ml and by the 10th hour of the cultivation it fell to 0. At this period, source of ammonia in cultivation medium is peptone (starting dose); by the 10th hour of cultivation, peptone reserve is exhausted and microorganism starts to use carbamide as nitrogen sources (it destructs lication of nitrogen fixers on the seed material (Azospirillum Brazilense) together with fertilizer characterized by the prolongation action, showed that hectare norms of nitrogen compared with the control (obtained by agro-rules) were reduced by more than 40-45%, while productivity was increased by 15-20%, correspondingly. This effect was achieved by joint application of fertilizers of prolongation action and nitrogen-fixers. Such technology practically ensures reduction of nitrogenous fertilizers wash-off and evaporation to the minimum, while the plant is provided with nitrogen along the whole vegetation period, which ensures growth of productivity and environment protection from pollution. Finally, it will give substantial economy and ecological effect.

Conclusion

New nitrogenous fertilizer of linear polymer structure was synthesized and kinetic regularities of its creation were studied.

Active strains of urobacteria able to destruct nitrogen-containing polymer of linear structure were isolated from soil.

Biocomposites containing polymerized carbamide and its destructor microorganisms were obtained.

Biodegradable nitrogenous fertilizer of linear polymer structure increases production of grain crops by 15-20% and decreases hectare norms of nitrogenous fertilizers by 40-45%.

Technology of obtaining the polymerized nitrogenous fertilizers and polymer biodegradable biocomposites is developed.

The work was prepared within the frame-work of the project #2016-36/STCU#6309 “Biodegradable polymers synthesis and application in environment protection from pollution” funded by the Shota Rustaveli National Science Foundation Science & Technology Center in Ukraine.

ბიოქიმია

აზოტშემცველი პროლონგირებული მოქმედების ბიოდეგრადირებადი პოლიმერული სასუქების სინთეზი

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მარცვლეული კულტურების მოსავლის ასამაღლებლად შემუშავებულია ეკოლოგიურად სუფთა და ეკონომიკურად ეფექტური პროლონგირებული მექანიზმით მოქმედი, ხაზოვანი სტრუქტურის მქონე პოლიმერიზებული აზოტოვანი სასუქებისა და მათი დამშლელი მიკროორგანიზმების შემცველი ბიოკომპოზიციები. შესწავლილია პოლიმერიზებული სასუქის წარმოქმნის პროცესი. ნაჩვენებია, რომ 110–125^{0}C ტემპერატურის ინტერვალში, ღრმა გარდაქმნამდე, რეაქციის სიჩქარის მუდმივები პროცესის მიმდინარეობისას, ინარჩუნებს მუდმივ მნიშვნელობებს, როდესაც ისინი გამოთვლილია არენიუსის მეორე რიგის განტოლების

მიხედვით. ი.წ. სპექტროსკოპიული გამოკვლევის შედეგად დადგენილია, რომ კარბამიდისა და ფორმალდეჰიდის ურთიერთქმედებისას, რეაქციის პირველ ეტაპზე, კარბამიდის მეთილოლწარმოებულების წარმოქმნის დროს (სპექტრის ტალღა 1030 სმ$^{-1}$), ადგილი აქვს აგრეთვე მეთილოლის ჯგუფების დიმეთილენეთერულ ჯგუფებად გარდაქმნას (სპექტრის ტალღა 1085 და 1110 სმ$^{-1}$). რეაქციის სიჩქარის მუდმივას ლოგარითმის ცვლილების სწორხაზობრივი დამოკიდებულება შებრუნებული აბსოლუტური ტემპერატურისაგან იმაზე მიუთითებს, რომ რეაქციების სიჩქარის მუდმივები იცვლება არენიუსის განტოლების მიხედვით. პოლიმერიზებული აზოტოვანი სასუქების გამოყენებით, აზოტოვანი სასუქის საჰექტარო ნორმა მცირდება 40%-ზე მეტად, მოსავლიანობა იზრდება 15-20%-ით, ხოლო გარემო დაცულია აზოტოვანი სასუქებით დაბინძურებისაგან.

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Received July, 2019