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Original article

Poly-ε-caprolactone-based granules with allylisothiocyanate for controlling of golden cyst potato nematode

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Abstract. *In this study, the characteristics of extruded granules based on biodegradable poly-ε-caprolactone and montmorillonite deposited with allylisothiocyanate and their effect on Globodera rostochiensis Rol were investigated. The prepared granules were characterized using Fourier-transform infrared spectroscopy, differential scanning calorimetry, and scanning electron microscopy. It was shown that encapsulation efficiency of allylisothiocyanate in montmorillonite depends on the conditions of complex preparation and ranges from 0.76 to 29.83%, and in poly-ε-caprolactone/montmorillonite/allylisothiocyanate granules after thermal processing it decreases down to 1.06%. According to the results of Fourier-transform infrared spectroscopy it was found that allylisothiocyanate inclusion did not result in formation of new chemical bonds, but significantly affected the temperature of poly-ε-caprolactone degradation that decreased from 537 to 472 °C. In comparison with the thermogram of montmorillonite, the weight loss corresponding to dehydration at 100 °C decreased by 2.9%, which probably means that part of the intramolecular water was replaced by allylisothiocyanate molecules encapsulated in montmorillonite. In the experiment with two potato varieties infested with nematode cysts it was shown that soil treatment with allylisothiocyanate solutions allows to decrease number of cysts of Globodera rostochiensis Rol compared to positive control (non-treated infested potato) in 1.5–3.0 times depending on the variety. Moreover, in contrast to allylisothiocyanate solutions, poly-ε-caprolactone/montmorillonite/allylisothiocyanate granules are more effective that makes them promising for applications in Globodera rostochiensis Rol control.*

Keywords: *ε-polycaprolactone, organomodified clay, allylisothiocyanate, granules, gold cyst nematode, Solanum tuberosum, nematicidal effect*

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Гранулы на основе поликапролактона с аллилизотиоцианатом для борьбы с золотистой картофельной нематодой

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Аннотация. *Целью исследования являлось изучение характеристики экструдированных гранул на основе биоразлагаемого поликапролактона и монтмориллонита, депонированных аллилизотиоцианатом, и их влияния на Globodera rostochiensis Rol. Полученные гранулы были охарактеризованы с помощью инфракрасной спектроскопии с преобразованием Фурье, дифференциальной сканирующей калориметрии и сканирующей электронной микроскопии. Показано, что эффективность инкапсулирования аллилизотиоцианата в монтмориллонит зависит от условий получения комплекса и составляет от 0,76 до 29,83%, а в гранулах поликапролактона/монтмориллонита/аллилизотиоцианата после термической обработки снижается до 1,06%. По результатам инфракрасной спектроскопии с преобразованием Фурье установлено, что включение аллилизотиоцианата не приводит к образованию новых химических связей, но существенно влияет на температуру деградации поликапролактона, которая снижается с 537 до 472 °C. По сравнению с термограммой монтмориллонита на термограмме для комплекса монтмориллонита/аллилизотиоцианата было показано уменьшение содержания воды на 2,9%, связанное с вымещением части молекул воды из межмолекулярного пространства монтмориллонита молекулами аллилизотиоцианата. В ходе проведения эксперимента с двумя сортами картофеля, зараженными цистами нематод, установлено, что обработка почвы растворами аллилизотиоцианата позволяет снизить количество цист Globodera rostochiensis Rol по сравнению с положительным контролем (необработанный зараженный картофель) в 1,5–3,0 раза в зависимости от сорта. Кроме того, в отличие от растворов аллилизотиоцианата гранулы поликапролактона/монтмориллонита/аллилизотиоцианата более эффективны, что делает их перспективными для применения в борьбе с Globodera rostochiensis Rol.*

Ключевые слова: *поликапролактон, органомодифицированная глина, аллилизотиоцианат, гранулы, золотистая картофельная нематода, Solanum tuberosum, нематицидный эффект*

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INTRODUCTION

Potato is important for agriculture taking the fourth place among the most significant crops in the world[1]. The main potato producers comprising the half of the worldwide potato production are China and India[2]. As a foodstuff and a forage crop, potato is susceptible to a large number of diseases caused by various pathogens including roundworms such as potato cyst nematodes (PCN) [1]. PCN are the group of *Globodera* genera parasites including *G. rostochiensis*, *G. pallida,* and *G. ellingtonae* species. Golden potato cyst nematode *G. rostochiensis* and the pale potato cyst nematode *G. pallida* are serious pests of potatoes around the world and are targets of strict regulatory actions in many countries [2]. These species are characterized by the specific reproduction triggering. Hatching of the second stage juvenile nematodes (J2) from encysted eggs in both species of PCN is initiated by exposure of eggs to potato root leachate, containing hatching factors (HFs) [3, 4]. As the result of their activity, the PCN larvae damage the roots, which leads to a disruption in the nutrient supply of the plant, resulting in the affected crops form small, half-grown and few tubers. Control of PCNs is complicated by the fact that the environmental adaptability of PCNs makes them challenging to control, given their ability to survive without hosts for periods up to 30 years [5–7] and their tolerance to a broad range of cold/warm temperatures [7].

Among the methods of PCN control, the chemical (nematicides), biological and agrophytocenotic ones are distinguished. The modern pesticide market offers a wide range of synthetic nematicides (carbamates, organophosphates, etc.); however, they have a number of drawbacks. In particular, these are high toxicity to humans during treatment, accumulation in soil and contamination of wastewater, impact on soil microflora [8, 9]. Because of the adverse impact on the environment, organophosphate and carbamate nematicides will be increasingly restricted, which will lead to a further reduction in the number of available nematicides [10]. The efficiency of biological methods (fungal preparations) depends strongly on the scale of application and season. Among agrophytocenotic methods, there are groups of biological active substances and plant extracts with nematicidal properties [11]. Isothiocyanates (ITCs) are rather attractive among the substances of plant origin, whose nematicidal activity has long been recognized [12]. The nematicidal activity of ITCs, which are abundant in some cruciferous plants, is related to the ability of their central carbon atom to engage in rapid attachment reactions with biological nucleophiles and covalently modify proteins [13]. In particular, Wood et al. showed that allyl-, ethyl-, 2-phenylethyl-, 2-phenylethyl-, methyl-, and several other ITCs caused high mortality in *G. pallida* J2 phase nematodes [14]. Allylisothiocyanate (AITC) was found to be the most active against nematodes, as at a concentration of 12.5 ppm nematode mortality was shown to reach 87% in three days. It was also shown that at a concentration of 25 ppm mortality reaches 100% in three days, whereas at a concentration of 50 ppm the same mortality rate was observed on the first day [14].

[1]Food and agriculture data. *FAOSTAT Food and Agriculture Organization of the United Nations*. Available from: http://www.fao.org/faostat/ [Accessed 24th November 2023].

[2]Shahbandeh M. Global potato production 2020, by country. *Statista*. Available from: https://www.statista.com/statistics/382192/global-potato-production-by-country/ [Accessed 24th November 2023].

The environmental friendliness of ITCs application is beyond doubt; however, their efficiency is not always justified due to their instability/volatility, which necessitates their constant high titer in the soil [15]. Based on the foregoing, there is a need, on the one hand, to increase the residence time of ITCs in the soil and, on the other hand, to increase their stability. A possible solution may be to deposit ITCs in a carrier matrix. The matrix based on biodegradable polymer will ensure the gradual release of ITCs in the environment without pollution or the release of harmful products, because biodegradable polymers eventually decompose into water, carbon dioxide and/or methane [16]. Shin et al. encapsulated AITC in β-cyclodextrin (β-CD) and triacetyl-β-CD (TA-β-CD) and evaluated the performance as slow releasing active compounds through low-density polyethylene (LDPE)–cyclodextrins (CDs) matrix. During the 15 days of the storage period, L-TACDs maintained more consistent AITC release and a higher concentration than L-CDs. Also, the blending of LDPE and TA-β-CD was more compatible with that of LDPE and β-CD one [17]. Bernardos et al. encapsulated allylisothiocyanate and other essential oil components in montmorillonite [18]. Among the biodegradable polymers used as agricultural carriers are polycaprolactone, polylactide, cellulose, polyhydroxyalkanoates [15–18].

There are known examples of such carriers for agriculture with proven herbicidal and fungicidal efficacy. For example, Volova et al. developed polymeric microparticle carriers based on PHA for fungicides. High herbicidal activity of the developed microparticles loaded with metribuzin and tribenuron-methyl was demonstrated in the laboratory on the *Elsholtzia ciliata* weed plant [19]. There are not so many studies specifically on the encapsulation of biologically active substances with nematicidal activity. Among them there is the study by Castillo et al. who developed controlled release formulations of rue essential oil in chitosan and alginate matrices obtained by ionic gelation for control *Melodogyne* ssp. nematodes. Encapsulated rue essential oil showed equal or superior nematicidal activity against the nematode *Melodogyne* ssp., compared to free oil and a synthetic nematicide such as carbofuran, without having a phytotoxic effect on the plant [20]. Piao et al. in their study encapsulated essential oil of flesh fingered citron in β-cyclodextrin by embedding and investigated release from the capsules compared to unembedded essential oil. The macrocapsules enabled 77% mortality of *Caenorhabditis elegans* after 4 h and 100% within an additional half-hour. Overall, microencapsulation improved stability of the essential oils and prevent product loss due to adverse environments exposed to the air, encapsulating flesh fingered citron essential oil in microcapsules has great potential as a new nematicide [21]. Since ITCs are quite volatile substances, there is a need not only to select a matrix for encapsulation, but also to select a proper encapsulation method and binder materials. Such materials (clays, CDs, collagen) may have hydrogen or carboxyl groups, or have moderate moisture absorption, which allows an ITC to be retained due to diffusion or adsorption and can then be mixed with a polymer matrix by extrusion.

Thus, the aim of this study was to obtain extruded granules based on poly-ε-caprolactone (PCL) and organomodified nanoclay montmorillonite (MMT) deposited with AITC, to study their morphological and chemical characteristics and to evaluate their nematicidal efficacy against PCNs in vitro.

MATERIALS AND METHODS

PCL was used as biodegradable material for obtaining of composite granules. The used PCL ("Sigma Aldrich", USA) had M_w = 80 kDa, C_x = 52%, T_m = 90 °C. MMT under the tradename "Monamet-101" ("Metaclei", Russia) with particle size <125 μm was used as a filler material. Allyl isothiocyanate (AITC) ("Zoranchem", China) was used as a nematicidal agent for deposition into the composite granules.

As AITC is a highly volatile compound, it was necessary to preliminary encapsulate it into the filler according to de Souza et al. [22]. AITC (50 g) and MMT (25 g) in a ratio 2:1 added in the solution, containing distilled water (150 ml) and Tween-80 (10 g). The suspension was homogenized on magnetic stirrer at 800 rpm or by ultrasonication and then dried at 110 °C for 8 hrs. Further, a modification of the conditions for preparation of the complexes was undertaken to achieve higher encapsulation efficiency. Specifically, methanol was used as a solvent instead of water to lower the drying temperature of the complexes down to 80 °C. Additionally, the ratio of AITC and MMT was changed from 2:1 to 1:2, 1:3 and 1:5 while the proportions of all other components remained unchanged.

Encapsulation efficiency was determined according the method described below. The obtained powder with encapsulated AITC was blended with PCL in ratio 1:1 and extruded on a single-screw single-zone extruder Bestruder 2v2 ("BestFilament", Russia) at 90 °C. The extruded filament was granulated manually. AITC content in the obtained granules was 0.9% (9 mg/g).

Encapsulation efficiency was determined according to the method by Shin et al. [17] using ultrasonic extraction and chromatography. 50 mg of the obtained AITC/MMT complex was suspended in distilled water (1 ml) and hexane (24 ml). The sample was then sonicated in an ultrasonic bath for 20 mins. The suspension was transferred into centrifuge tubes and centrifuged at 2500 rpm for 10 min. The content of AITC in the resulting supernatant was determined using GC. AITC content in complexes was analyzed using Agilent 6890N gas chromatograph integrated with Agilent 5975C mass spectrometer and equipped with Agilent VF-200ms column (length = 60 m, internal diameter = 250 μm, polyt rifluoropropylmethylsiloxane sorbing layer with thickness = 0.10 μm). Helium was used as a carrier gas at 1.2 ml×min^{-1} flow rate. The sample was introduced in the splitless mode. The input device and interface temperatures were set to 220 °C and 230 °C, respectively. Operating temperature of the oven: 80 °C for 3 minutes, then heating to 220 °C at 10 °C×min^{-1} rate, holding the temperature for 5 minutes. The samples were ionized by electron impact (70 eV). MSD Chemstation ver. E.02.02.1431 software was used for processing of the results. Encapsulation efficiency was determined according to the formula:

$$E_{enc}, \% = \frac{C_d}{C_T} \times 100, \quad (1)$$

where C_d – AITC content in the sample, determined by gas chromatography, g/g; C_T – theoretical maximum inclusion of AITC, g/g.

The efficiency of deposition of AITC into PCL/MMT composite granules was also determined by ultrasonication and gas chromatography, but the sample preparation differed. Approximately 10 mg of the obtained composite granules were dissolved in chloroform (1 ml). After complete dissolution, the polymer was precipitated by adding 9 ml of hexane. The resulting suspension was sonicated in an ultrasonic bath for 20 minutes, transferred into centrifuge tubes and centrifuged at 2500 rpm for 10 min. The content of AITC in the resulting supernatant was determined by gas chromatography. Deposition efficiency was determined according to the formula:

$$E_{dep}, \% = \frac{C_{gd}}{C} \times 100, \qquad (2)$$

where C_{gd} – AITC content in the sample, determined by gas chromatography, g/g; C_{gT} – theoretical maximum deposition of AITC into the granules, g/g.

Microstructure of the obtained granules was studied by scanning electron microscopy (SEM) with TM-3000 (“Hitachi”, Japan) scanning microscope (equipment of Krasnoyarsk Regional Center of Research Equipment of Federal Research Center “Krasnoyarsk Science Center SB RAS”). Previously, the samples were coated with platinum (at 10 mA, for 45 s) with Emitech K575X sputter coater. Elemental analysis was performed using BRUKER XFlash 430 H microanalysis system integrated in TM-3000. The results were processed in QUANTAX 70 software (ver.1.3).

Chemical characteristics of granules prepared and of AITC used (impurities presence, chemical bonds formation/destruction) was studied by Fourier-transform infrared spectroscopy (FTIR) using the Nicolet iS10 FT-IR spectrometer (“Thermo Scientific”, USA) and the ITX Smart prefix (“Thermo Scientific”, USA) with a diamond crystal by disturbed total internal reflection method (DTIR). The analyses were carried out with a spectral resolution of 4 cm^{-1}, averaged over 32 scans, in the range of 4000–400 cm^{-1}. The obtained IR-Fourier spectra were processed in the OMNIC software applying advanced correction of disturbed total internal reflection.

Thermal characteristics of the granules were studied by thermogravimetric analysis (TGA) and were performed under the given conditions using SDT Q600 thermal analyzer (“TA Instruments”, USA). The analyzed granules were fragmented with a sharp blade into particles of about 1 mm in size. Several dozen of such particles were used for analysis.

Nematicidal activity of the obtained granules was tested against *G. rostochiensis* pothotype Ro1 in experimental soil ecosystems in laboratory. A synthetic nematicide oxamyl (“Corteva”, USA) was used as control. Nematode infestation was performed on potato varieties “Krasnoyarskiy ranniy” (originators – Krasnoyarsk State Agrarian University (Krasnoyarsk region, Russia); Lorch Potato Research Institute (Moscow oblast, Russia)) and “Pushkinets” (originator – Tver State Agricultural Academy (Tver oblast, Russia). Soil, *G. rostochiensis* cysts (50 cysts per one pot) and a pre-germinated potato tuber were preliminary added in the experimental pots. The obtained PCL/MMT/AITC granules were introduced into the experimental pot in the amount of 50 and 100 mg per pot, based on the effective dosages for AITC according to Wood et al. [14]. For each potato variety there were seven experimental groups (in five repeats): 1 – soil treated with oxamyl (28 mg per pot); 2 – soil treated with 40 ml of AITC solution in conc. 10.9 μl/l; 3 – soil treated with 40 ml of AITC solution in conc. 21.7 μl/l; 4 – soil treated with 50 mg of PCL/MMT/AITC granules (dosage, similar to group 2); 5 – soil treated with 100 mg of PCL/MMT/AITC granules (dosage, similar to group 3), K+ – soil with cysts without the addition of the preparation (positive control), K- – intact soil without cysts and addition of the preparation (negative control).

The experiment was performed during June-July 2022. At the end of the experiment, cysts were counted on potato roots from the pot according to intra-laboratory method. Examination of the roots was carried out without removal of plants under a binocular with 3x magnification. Potato stems were also counted and measured in the end of the experiment.

RESULTS

To maintain AITC effects and to avoid thermal degradation during extrusion, AITC was first incorporated in MMT. Gas chromatography showed that encapsulation efficiency of AITC in MMT was only 1.6%. According to SEM data, MMT particles mostly have anisotropic external structure forming spherical agglomerates up to 200 μm in size (Figs. 1, *a* and 1, *b*). The surface of the particles prior the ultrasonication is well smoothed and without porosity. However, after ultrasonication of MMT and AITC encapsulation, the surface of the particles changed and became more structurally porous (Figs. 1, *c* and 1, *d*). Thus, it can be suggested that adsorption of AITC by MMT occurs by diffusion in micropores that allows AITC retention by MMT.

To confirm the inclusion of AITC in MMT, elemental analysis was also used. According to the results, in MMT prior ultrasonication O, C, Si, Na, Ca were determined in the ratio of atomic percent 41.6, 48, 5.9, 2.6, 0.6 and 0.37%, respectively. When AITC was incorporated, distinctive elements S and N appeared in the ratio of 7 and 5%, respectively. All elements can be found in the resulting complex, but their ratio changes depending on the exposure time of MMT/AITC complex, as shown in Table 1. This indicates that AITC gradually volatilizes, that requires its introduction into a more compact polymer matrix.

Table 1. Elemental atomic percentage in montmorillonite/allylisothiocyanate complex depending on the exposure time

Таблица 1. Атомное процентное содержание элементов в комплексе монтмориллонита/аллилизотиоцианата в зависимости от времени экспозиции

Elemental composition, at.%	Time, hrs		
	1.00	6.00	12.00
O	42.00	42.00	42.00
C	39.00	39.00	39.00
Si	5.90	5.90	5.90
Na	0.49	0.49	0.49
Ca	0.68	0.68	0.68
S	7.00	6.20	5.70
N	5.00	4.10	3.90

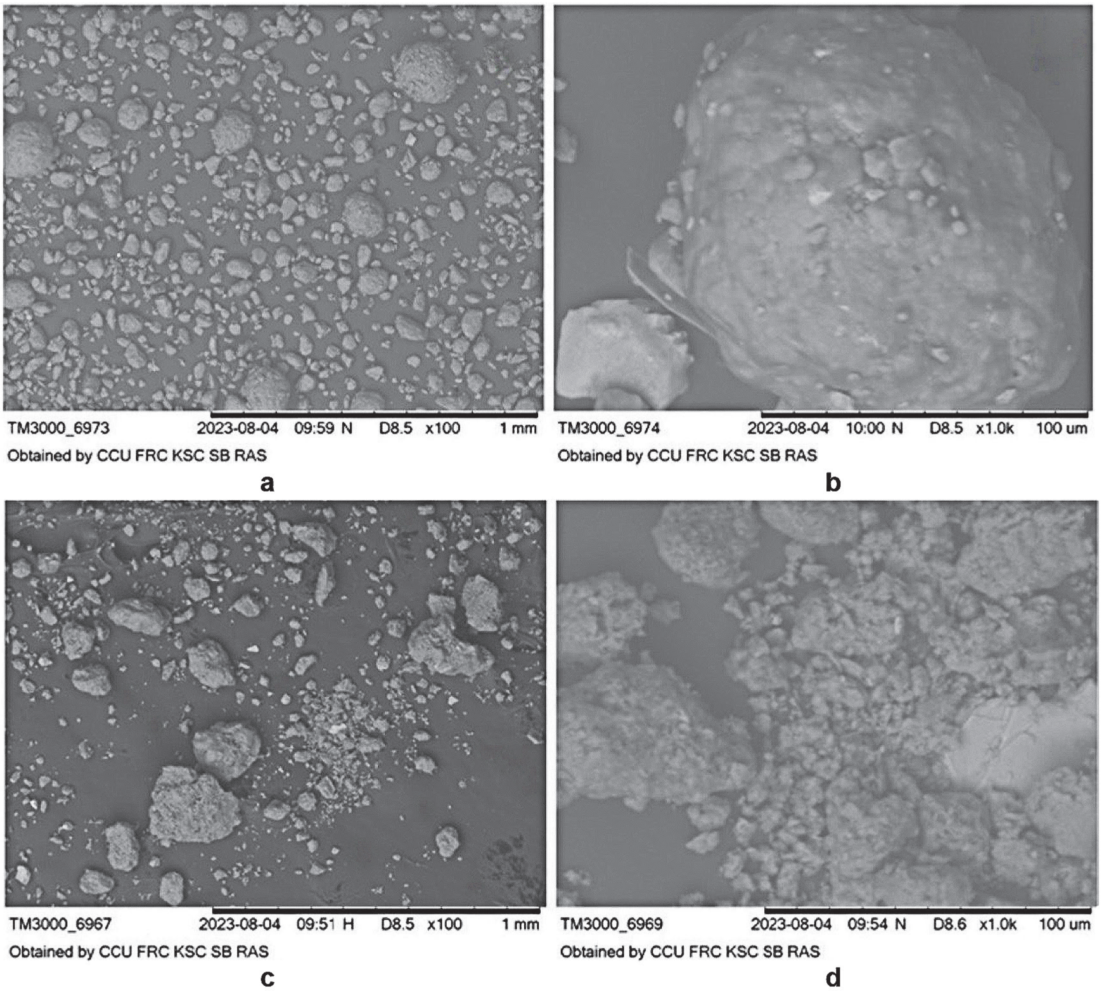


Fig. 1. Scanning electron microscopy image of montmorillonite at 100x (a) and 1000x (b) magnification and of montmorillonite/allylisothiocyanate complex at 100x (c) and 1000x (d) magnification

Рис. 1. Полученные методом сканирующей электронной микроскопии изображения монтмориллонита при увеличении 100x (a) и 1000x (b) и комплекса монтмориллонита/аллилизотиоцианата при увеличении 100x (c) и 1000x (d)

The efficiency of AITC encapsulation in MMT, depending on the conditions (Table 2), ranged from 0.76 to 29.83%. The use of methanol as the liquid phase has a significant effect on encapsulation efficiency as AITC is highly soluble in methanol, but has a low solubility in water (2 mg/ml at 20 °C). In addition, the high volatility of methanol probably allowed to reduce both the drying temperature of the complex from 110 to 80 °C and drying time compared to the case when water was used as a liquid phase, and consequently, to reduce the evaporation of AITC as the solvent evaporates.

According to HPLC results of the prepared complexes, the best EE value (29.8%) and, as a consequence, concentration of AITC in the complex (12.3%) was observed for AITC/MMT complex prepared in methanol with initial AITC/MMT ratio 1:2 and agitated with magnetic stirrer (no. 6 in Table 2).

Table 2. Encapsulation efficiency of montmorillonite/allylisothiocyanate complexes prepared in different conditions

Таблица 2. Эффективность инкапсуляции комплексов монтмориллонита/аллилизотиоцианата, приготовленных в различных условиях

Allylisothiocyanate/ montmorillonite ratio	Soluble phase	Agitation	Tween80	Concentration of allylisothiocyanate in the complex, %	Encapsulation efficiency, %
2:1	Water	Ultasonication	+	2.3	3.96
			-	0.5	0.76
		Magnetic stirrer	+	0.6	1.06
			-	2.1	3.09
	Methanol		+	12.3	20.89
1:2				7.8	29.83
1:3				0.6	2.55
1:5				0.3	1.90

This complex was further used for preparation of composites with PCL by extrusion. As a result, the concentration of AITC in the composite granules amounted only 1.06%, which was probably due to thermal degradation during extrusion. However, this amount of AITC was sufficient for further application in efficacy test against *G. rostochiensis*.

To confirm the theory of AITC adsorption in MMT due to diffusion, FT-IR was performed. In the IR spectrum of the initial MMT small peaks at 3656 cm^{-1}, 2945 cm^{-1} and 2867 cm^{-1}, which correspond to asymmetric and symmetric vibrations of CH_2 groups, can be observed (Fig. 2, *1*). Peaks in the area of 1640 cm^{-1}, 1540 cm^{-1}, 1500 cm^{-1} correspond to vibrations of NH- or C-N groups, which are characteristic for dialkyldimethylammonium chloride used for MMT treatment. The peaks at 1485 cm cm^{-1}, 1475 cm^{-1} are characteristic of OH- stretching and bending vibrations of free and bound water. The observed broad band with a maximum at 1004 cm^{-1} reflects stretching and bending vibrations of Si-O and Al-O bonds. Specifically, the bands in the area of 890-970 cm^{-1} are related to stretching vibrations of Si-O and Al-O bonds, while in the rest of the area up to 1200 cm^{-1} bending vibrations of Si-O bonds are present. The broad band at 1027 cm^{-1} refers to the stretching vibrations of Si-O-Si tetrahedrons of the silicon-oxygen lattice, while the bands of bending vibrations of Me-O are observed at 469 and 515 cm^{-1}. The band at 796 cm^{-1} corresponds to Si-O-Si vibrations of SiO_4 tetrahedral rings.

The IR spectrum of AITC (Fig. 2, *2*) showed the presence of characteristic peaks in the area of 2100 cm^{-1}, 2165 cm^{-1} and 700 cm^{-1} corresponding to vibrations of -NCS (isothiocyanate) group, as well as peaks in the area of 1000 cm^{-1} and 965 cm^{-1} corresponding to C-H groups and $CHCH_2$. Small peaks in the 2890 cm^{-1} and 3000 cm^{-1} area represent symmetrical vibrations of CH_2 groups.

When AITC is encapsulated in MMT (Fig. 2, *3*), the broadening of the peak in the 3656 cm^{-1} area and the change in the height of the peaks at 2945 cm^{-1} and 2867 cm^{-1} can be seen on the IR spectrum. Additionally, the appearance of extra peak in the area of 2100 cm^{-1} corresponds to the vibrations of isothiocyanatic group –NCS. A decrease in the width of the peaks in the area of 1200 cm^{-1} and 900 cm^{-1} corresponding to strain vibrations of Si-O bonds was also observed. Thus, it can be concluded that AITC encapsulation in MMT does not lead to the formation of new bonds and AITC encapsulation occurs mainly due to diffusion processes.

Finally, on the FTIR spectra of PCL/MMT/AITC granules (Fig. 2, *5*) the peaks at 975-2860 cm^{-1} and 1750-1700 cm^{-1} characteristic for PCL (Fig. 2, *4*) corresponding to strong stretching vibrations of CH_2- and C=O groups respectively were clearly visible. Vibrations of SiO and SCN groups were not observed. In general, FTIR spectrum of the obtained PCL/MMT/AITC was similar to that of PCL.

TGA data of MMT, MMT/AITC complex, AITC and PCL is presented in Figs. 3–6. On TGA spectrum of MMT (Fig. 3) in the area of 150 °C dehydration and decrease in weight on 3.9% can be observed. In the area of 200–550 °C multistage decrease in weight on 10.7% occurred which is associated with the release of heat. This process is related to alkyldimethylammonium thermolysis followed by vapor release of pelargonic acid and pelargonaldehyde in the area of 200–400 °C, as well as with release of carbon dioxide in the area of 300–550 °C as the result of oxidation of organic compounds. The described effects are probably due to the technique of MMT modification that was confirmed by FTIR-analysis. In the area of 550–780 °C release of carbon dioxide occurred with heat absorption occurred followed by decrease in weight on 4.7%. These effects are probably the result of calcium carbonate inclusion in the samples.

TGA spectrum of AITC (Fig. 4) showed the general weight loss occurring between 46 and 120 °C, that confirms the volatile nature of AITC. The complete evaporation of AITC occurs above 120 °C and the maximal evaporation rate is observed at 112 °C.

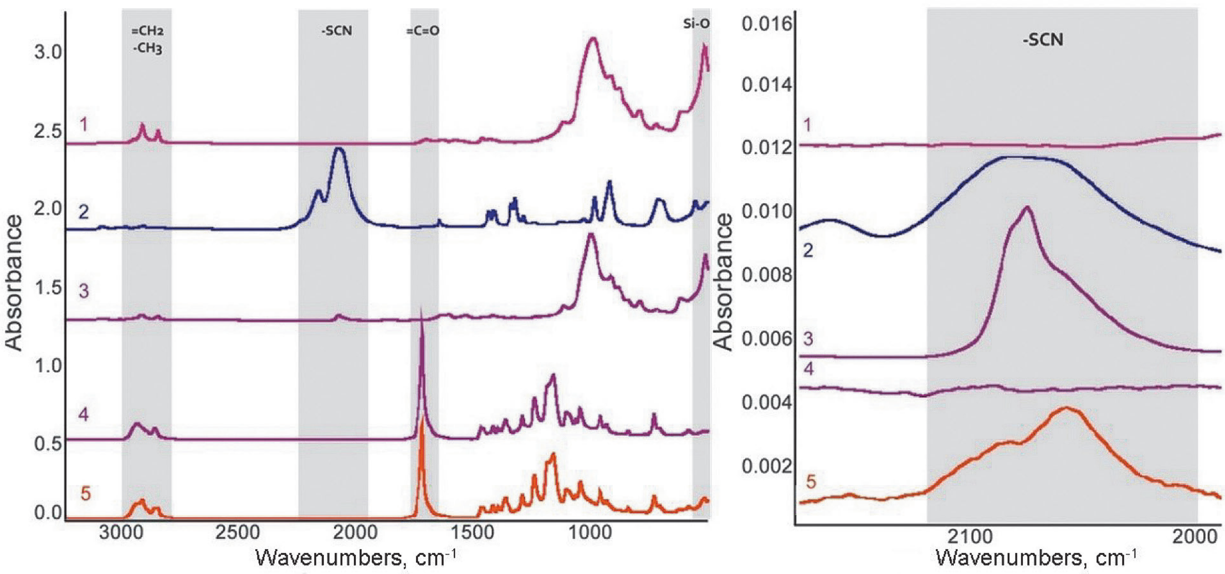
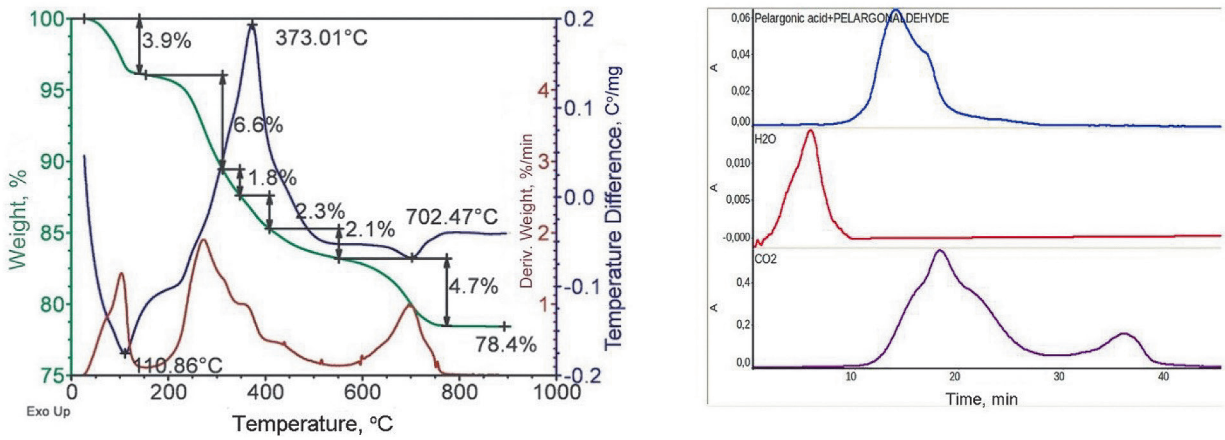


Fig. 2. FT-IR spectra of pure MMT (1), pure allylisothiocyanate (2), montmorillonite/allylisothiocyanate complex (3), poly-ε-caprolactone (4) and poly-ε-caprolactone/montmorillonite/allylisothiocyanate granules (5)

Рис. 2. ИК-Фурье спектры чистого монтмориллонита (1), чистого аллилизотиоцианата (2), комплекса монтмориллонита/аллилизотиоцианата (3), поликапролактона (4) и гранул поликапролактона/монтмориллонита/аллилизотиоцианата (5)



a b

Fig. 3. Thermogram (a) and gas release profile (b) for montmorillonite sample

Рис. 3. Термограмма (a) и профиль газовыделения (b) для образца монтмориллонита

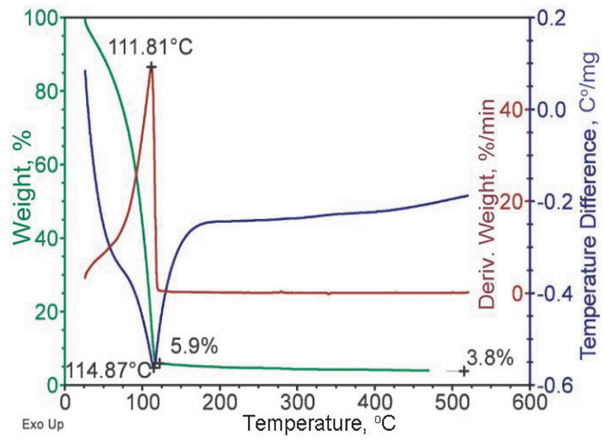


Fig. 4. Thermogram for allylisothiocyanate sample

Рис. 4. Термограмма для образца аллилизотиоцианата

On TGA spectrum of MMT/AITC complexes (Fig. 5) in the area of 100 °C dehydration can be observed followed by weight loss on 1.0%. In comparison with the thermogram of MMT, this value decreased by 2.9%, which probably means that part of the intramolecular water was replaced by AITC molecules encapsulated in MMT. In the area of 150–450 °C a multistage weight loss on 21.6% occurred which is associated with release of heat. In the area of 150–250 °C evaporation of AITC occurs and the further heating resulted in oxidative destruction of absorbed AITC with release of SO_2, CO_2, HCOH и CS_2. In the area of 550–780 °C carbon dioxide release occurred associated with heat absorption and followed by weight loss on 4.7%. As was mentioned above, the described effects are due to presence of calcium carbonate in the samples.

TGA spectrum of MMT/AITC complex slightly differed from that of MMT. The change in thermal behavior of the sample was visible. According to FTIR-analysis of the released gases, it can be suggested that after treatment of MMT with AITC, the latter replaces alkyldemethylammonium in the structure (pores, surfaces) of MMT. Comparing the temperature of evaporation of pure AITC and AITC from MMT surface it can be observed that it increased from 112 up to 200. This can be explained by AITC sorption by MMT. These effects can promote prolonged effect of AITC.

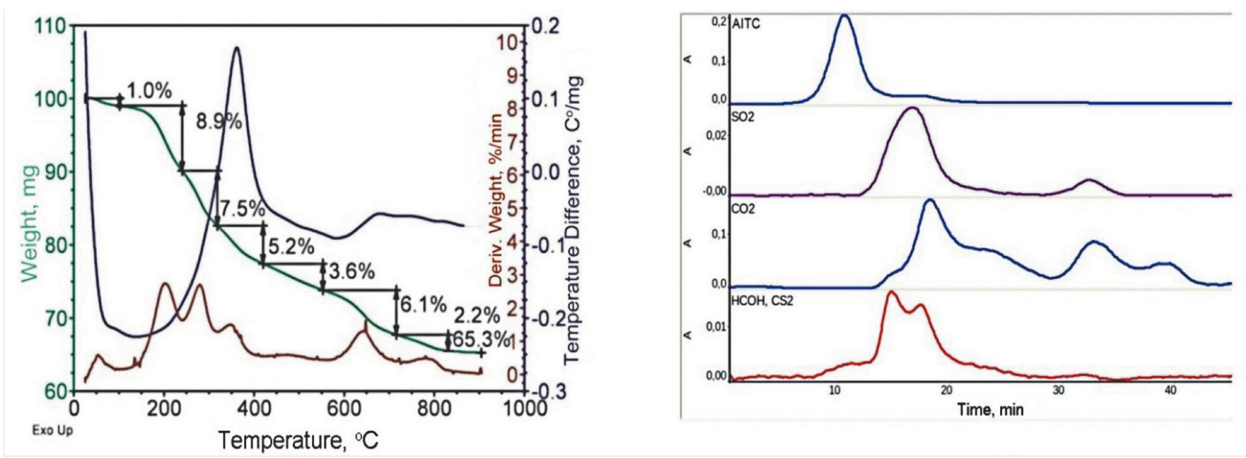
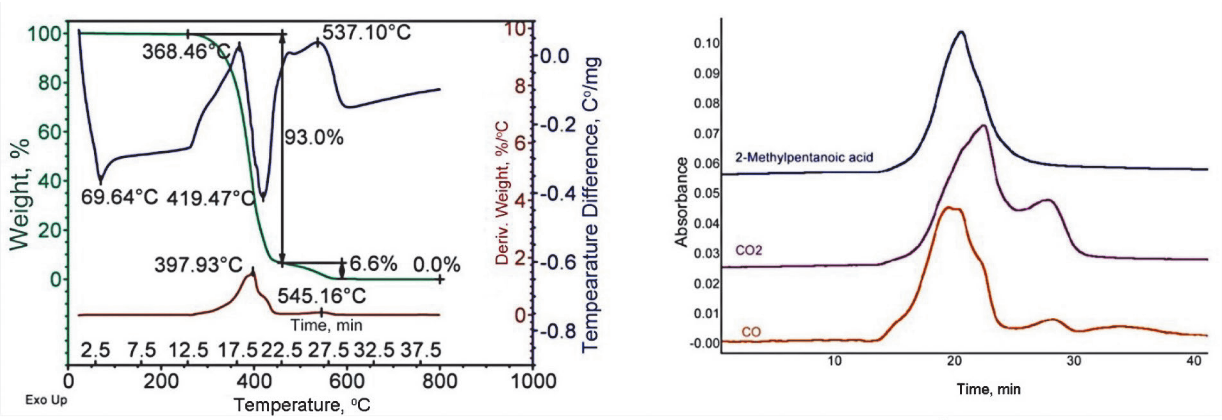


Fig. 5. Thermogram (a) and gas release profile (b) for montmorillonite/allylisothiocyanate complex

Рис. 5. Термограмма (a) и профиль газовыделения (b) для комплекса монтмориллонита/аллилизотиоцианата



a b

Fig. 6. Thermogram (a) and gas release profile (b) for poly-ε-caprolactone sample

Рис. 6. Термограмма (a) и профиль газовыделения (b) для образца поликапролактона

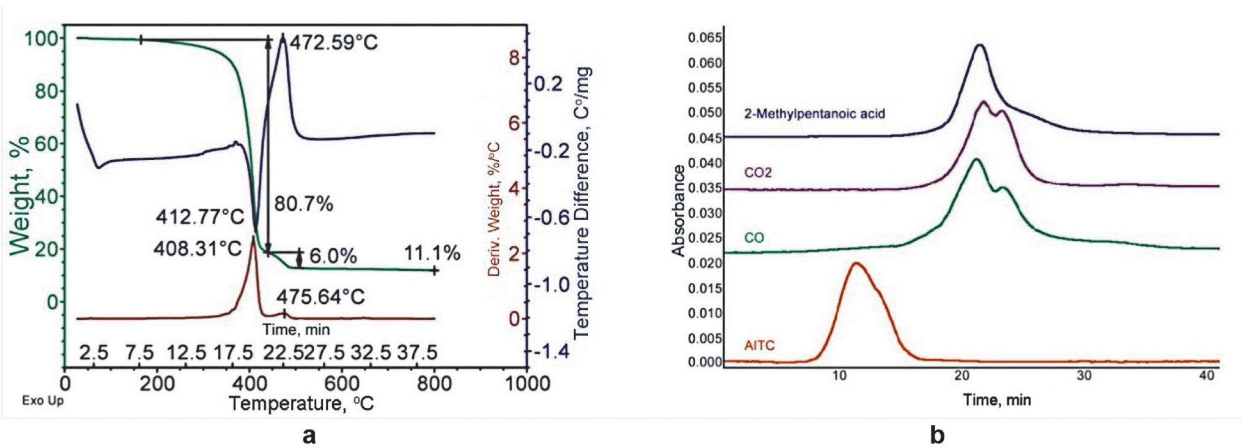
The PCL thermogram (Fig. 6) shows that polymer degradation occurs in the temperature range of 250–600 °C. The degradation of the polymer occurs with the release of 2-methylvaleric acid (or its homologue), carbon mono- and dioxide.

The thermogram of the PCL/MMT/AITC granules (Fig. 7) shows that its degradation occurs in the temperature range of 150–600 °C. Similar to AITC/MMT complexes, evaporation of AITC in the granules occurs in the temperature range of 150–250 °C (as in AITC-MMT). AITC, 2-methylvaleric acid (or its homologue), carbon mono- and dioxide were found in the gas phase of the pyrolysis products.

The effect of AITC on the growth of *G. rostochiensis* and on development of their cysts on potato roots was studied using "Krasnoyarskiy Ranniy" and "Pushkinets" potato cultivars. Regardless of the treatment and potato variety, visually the roots of all the experimental plants did not differ significantly (Figs. 8 and 9).

However, the predictably higher number of cysts was observed for positive control (Fig. 10). It was found that treatment with AITC solutions resulted in 1.5–3 times, depending on the potato variety, reduction of the number of cysts compared to the positive control. In addition, increase in AITC concentration of the solution up to 21.7 μg/l did not lead to a significant difference in the number of cysts for the variety "Krasnoyarskiy Ranniy", whereas for the variety "Pushkinets" the increase in AITC concentration resulted in a decrease in the number of cysts on the roots down to 120. In contrast to pure AITC solutions, PCL/MMT/AITC granules were more effective. When treated with 50 mg and 100 mg of the granules, the number of cysts decreased down to 125 nematodes, which is comparable to pure AITC solution and 2.4 times less than in the positive control. However, this effect was demonstrated only for the potato variety "Krasnoyarskiy Ranniy". For the potato variety "Pushkinets" regardless of the amount of granules introduced, the number of cysts was 140. It can be concluded that at such terms the amount of granules introduced did not reliably affect their efficiency.

It should be noted that the inclusion of AITC in granules intended for slow-release application and a similar effect can be achieved by increasing both the time of incubation in the soil and ITC concentration in the granules. When comparing the average number of stems and the average stem heights, for neither of these parameters any significant difference was observed. However, it should be noted that the number of stems for "Krasnoyarskiy ranniy" variety



a b

Fig. 7. Thermogram (a) and gas release profile (b) for poly-ε-caprolactone/montmorillonite/allylisothiocyanate granules

Рис. 7. Термограмма (a) и профиль газовыделения (b) для гранул поликапролактона/монтмориллонита/аллилизотиоцианата

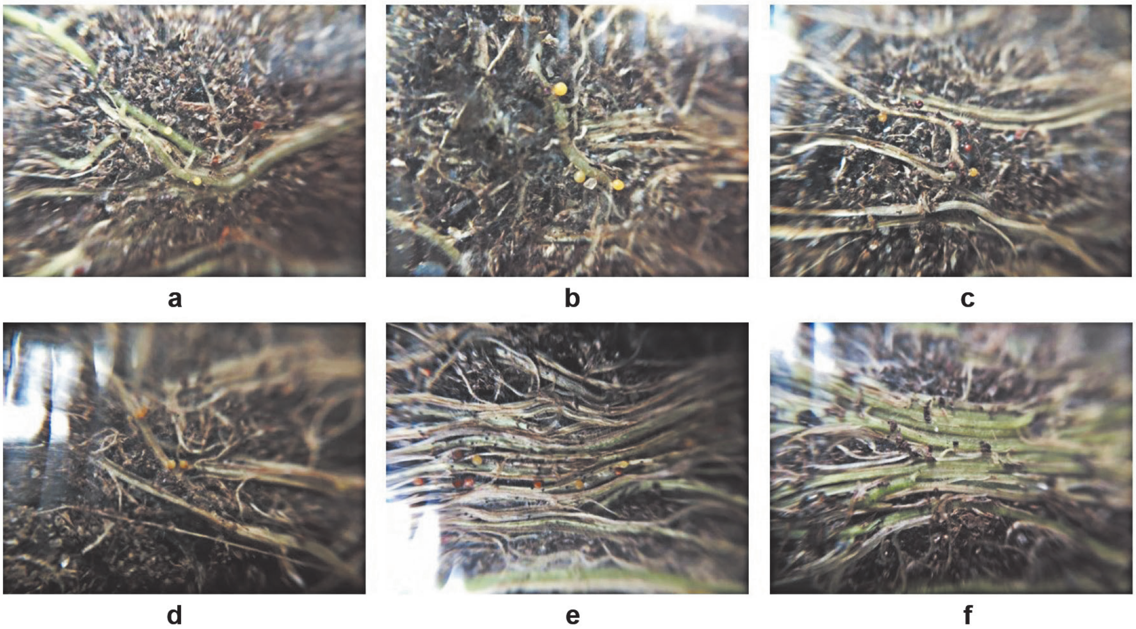


Fig. 8. Roots of potato Krasnoyarskiy ranniy, infested with *Globodera rostochiensis* cysts, two months after treatment with: a – allylisothiocyanate solution conc. 10.87 mcg/l; b – allylisothiocyanate solution conc. 21.75 mcg/l; c – 50 mg of poly-ε-caprolactone/montmorillonite/allylisothiocyanate granules; d – 100 mg of poly-ε-caprolactone/montmorillonite/allylisothiocyanate granules; e – positive control; f – negative control

Рис. 8. Корни картофеля сорта Красноярский ранний, зараженные цистами *Globodera rostochiensis*, через два месяца после обработки: a – раствором аллилизотиоцианата в концентрации 10,87 мкг/л; b – раствором аллилизотиоцианата в концентрации 21,75 мкг/л; c – 50 мг гранул поликапролактона/монтмориллонита/аллилизотиоцианата; d – 100 мг гранул поликапролактона/монтмориллонита/аллилизотиоцианата; e – положительный контроль; f – отрицательный контроль

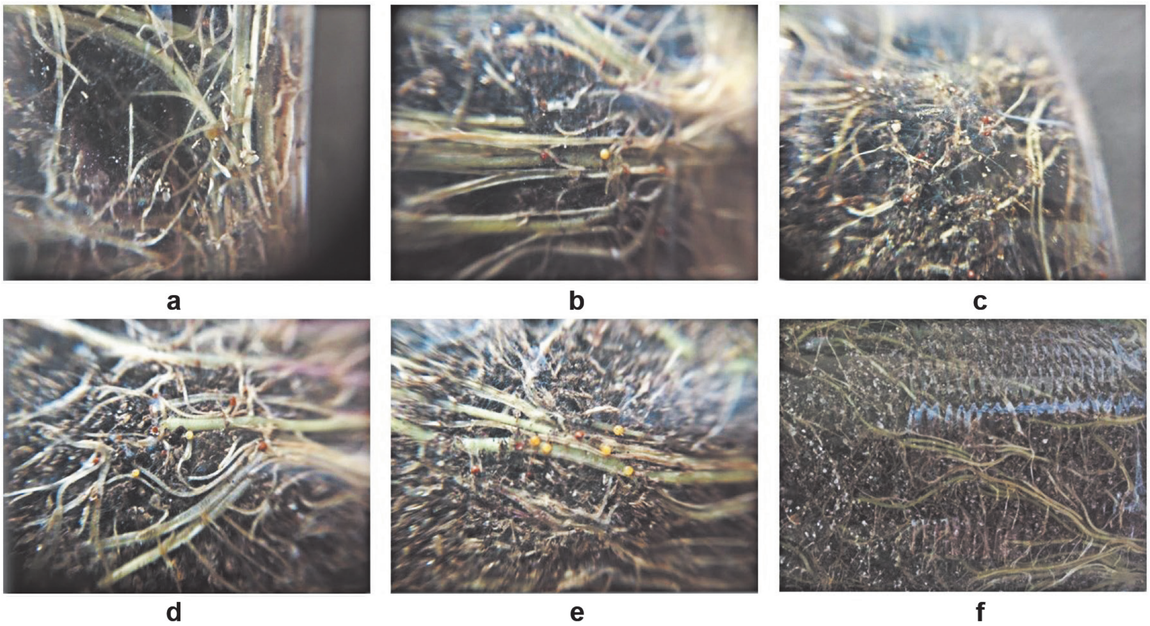


Fig. 9. Roots of potato Pushkinets, infested with *Globodera rostochiensis* cysts, two months after treatment with: a – allylisothiocyanate solution conc. 10.87 mcg/l; b – allylisothiocyanate solution conc. 21.75 mcg/l; c – 50 mg of poly-ε-caprolactone/montmorillonite/allylisothiocyanate granules; d – 100 mg of poly-ε-caprolactone/montmorillonite/allylisothiocyanate granules; e – positive control; f – negative control

Рис. 9. Корни картофеля Пушкинец, зараженные цистами *Globodera rostochiensis*, через два месяца после обработки: a – раствором аллилизотиоцианата в концентрации 10,87 мкг/л; b – раствором аллилизотиоцианата в концентрации 21,75 мкг/л; c – 50 мг гранул поликапролактона/монтмориллонита/аллилизотиоцианата; d – 100 мг гранул поликапролактона/монтмориллонита/аллилизотиоцианата; e – положительный контроль; f – отрицательный контроль

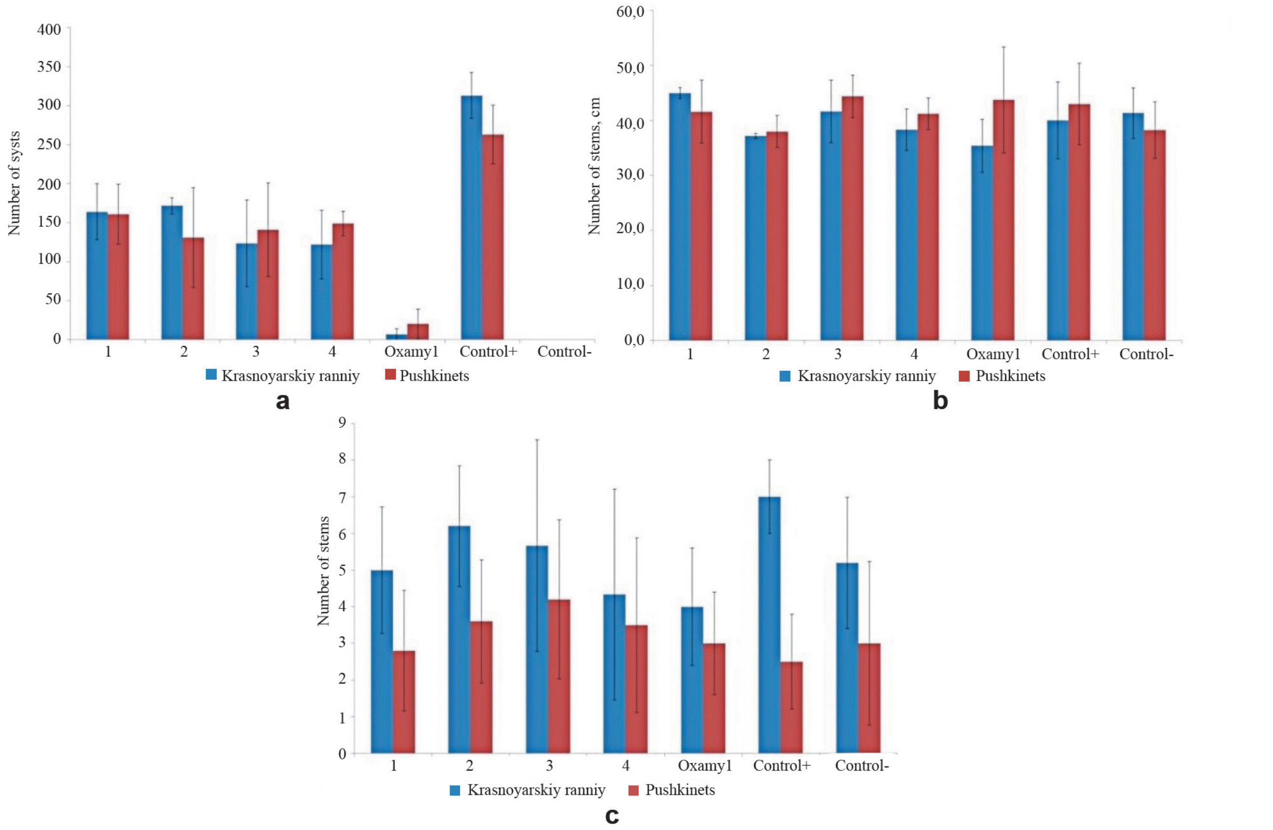


Fig. 10. Nematicidal and growth effects of poly-ε-caprolactone/montmorillonite/allylisothiocyanate granules on potato varieties Krasnoyarskiy Ranniy and Pushkinets two months after the treatment: a – number of cysts; b – height of potato stems; c – number of stems

Рис. 10. Нематицидный и ростовой эффекты гранул поликапролактона/монтмориллонита/аллилизотиоцианата на сортах картофеля Красноярский ранний и Пушкинец через два месяца после обработки: a – количество цист; b – высота стеблей картофеля; c – количество стеблей

was higher than for “Pushkinets” variety, which is probably due to the physiological differences of plants. Treatment with 50 mg of PCL/MMT/AITC granules and with 21.7 µg/L AITC solution resulted in an insignificant increase in the number of stems.

DISCUSSION

This study demonstrates the nematicidal effect of AITC deposited in a biodegradable polymer matrix. The need for encapsulation caused by the volatility of isothiocyanates and their ability to degradate in soil has been repeatedly demonstrated in previous studies [14, 23, 24]. Typically, the nematicidal activity of isothiocyanates is determined by the method of their preparation and by their chemical nature (e.g., aliphatic, aromatic, etc.) [25–29]. It was also shown that AITC can cause oxidative damage of nematodes DNA and the accumulation of toxic metabolites in their cells [30].

According to numerous studies, AITC and benzyl isothiocyanate (BITC) are considered to be the most potent nematicidal ITCs in vitro [26, 31, 32]. As Wood et al. showed, among eight isothiocyanates tested (BITC, MITC, EITC, PITC, etc.), the highest mortality rate of *G. pallida* 2nd stage juveniles was observed for AITC at an exposure concentration of 25 µl/l. In addition, a dose-response analysis by Ren et al. showed that AITC is high effective against not only root-knot nematodes (LD_{50} = 18.046 mg/kg), but also has a moderate effectiveness against fungal pathogens (LC_{50} = 27.999–29.497 mg/kg) and weeds (LC_{50} = 17.300–47.660 mg/kg) [32]. AITC is also known to have higher toxicity against root-knot nematodes (*Meloidogyne* spp.) compared to phenyl isothiocyanate [30, 31].

Encapsulation of AITC in MMT and its deposition in the polymer granules allows to prolong its biological activity and to use soil application in solid form instead of biofumigation. In this study, we assume that the encapsulation of AITC in MMT occurred mainly due to diffusion and surface adsorption of the isothiocyanate. Despite the fact that according to the FTIR spectra of the AITC/MMT complex the disappearance of several peaks in the area from 2500 cm^{-1} was observed, which is most likely due to the washout of the MMT treatment (dialkyldimethyl ammonium chloride), no qualitatively new bonds were formed. However, the possibility of the appearance of hydrogen bonds should not be excluded. Encapsulating AITC in an intermediate product (MMT, β-cyclodextrin, etc.) allows the isothiocyanate to be retained and uniformly blended with the polymer. In the study by Frankova et al., volatility tests showed that encapsulation of AITC in MMT allowed to maintain its content in MMT at the level of 60% and extend its release up to 7 days at 25 °C, and up to 1 day at 37 °C. Meanwhile, pure AITC evaporated almost immediately, regardless of temperature [18]. Concerning this, temperature plays a significant role in the method of obtaining PCL based granules. Since the boiling point of AITC is around 151–152 °C and the melting point of PCL is around 90 °C, it can be assumed that AITC undergoes partial thermal degradation during the extrusion. Thus, after extrusion concentration of AITC in the granules drops in 20 times form the predicted, which was resulted by the temperature impact and its duration in the process of extrusion. A solution to the further application of this approach may be the use of stabilizers for AITC and an increase in its concentration in MMT and, accordingly, in the granules.

It is known that the controlled release of AITC can be affected by ambient humidity and temperature. In the study on the prolonged release of AITC from mustard flour which was added to PLA matrices obtained by electrospinning, it was shown that rehydration of mustard flour activated the hydrolysis reaction, which led to release of AITC. The release at 20 °C varied from 2 to 17 mg/g within 200 hours and depended on the load of the matrices and on the PLA/polyethylene oxide ratio [33].

In the potato experiment, AITC/MMT/PCL granules were introduced in the cyst infested soil with potato tubers "Krasnoyarskiy Ranniy" and "Pushkinets". Soil moisture was maintained at 60% and soil temperature was 18–20 °C. These potato varieties were chosen as test crops due to their approval for use in 11 regions of Russia according to the State Register of Selection Achievements Admitted for Usage (National list)[3]. Both varieties lack the resistance to *G. rostochiensis*. However, there are more than 80 PCN-resistant varieties and hybrids, 15 of which are of domestic selection. PCN-resistance is determined by the presence of the H1 and Gro1-4 genes in the plant genome [11, 34, 35].

In contrast to commercial pesticide Vydate 5G® (control; the active ingredient oxamyl), the developed nematicidal granules did not completely suppress the viability of nematode cysts. Oxamyl is a well-known nematicide whose effectiveness has been proven against *G. rostochiensis* [11]. One reason for its continuous use is its short half-life in soil that ranges from a few hours to several days and depends on soil pH. Because of its rapid degradation in soil, oxamyl is considered to be relatively safe, but this affects its long-term efficacy [36]. However, the use of such nematicides is primarily limited by high toxicity (including carcinogenicity) to humans and other non-target organisms [37].

In contrast to the negative control, in the experimental groups a certain number of cysts on plant roots were observed by the end of the experiment. However, as described above, these studies require more time or an increase in the concentration of AITC in the granules. Although research on encapsulation of biologically active substances in a polymer matrix against nematodes is at its early stage of development, the use of the presented technique can be expected to increase the efficiency of isothiocyanates and reduce environmental pollution. The main challenge associated with the development of such slow-release formulations is to match and outperform the existing pesticides both in terms of field efficiency and cost.

CONCLUSION

The study demonstrated the efficiency of a slow-release nematicide formulation prepared by coextrusion of AITC/MMT complex and a low-melting biodegradable polymer. The appropriate conditions allowing a high degree of AITC encapsulation (up to 30%) and preservation of its biological activity during the extrusion process were chosen. The prepared formulation has been shown to be effective against *G. rostochiensis* RoI, which allows its practical use in agriculture. The obtained results demonstrate the promise of using the coextrusion principle for the development of slow-release formulations for agriculture.

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