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BIOPOLYMERS FOR SEED PRESOWING TREATMENT

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Abstract. Physico-chemical properties of specially modified forms of natural biopolymers – carboxymethyl cellulose and xanthan gum – were studied. The effectiveness and ability to film formation of water soluble polymeric compositions of these biopolymers, their influence on the growth and productivity of agricultural crops were examined. The effect of the biopolymers, mineral fertilizers and micronutrients content in the solution on its viscosity, as well as the dependence of the formed films thickness on the content of modified biopolymers and fertilizers were investigated. It was established that using natural film-forming compositions the consumption of fertilizers and micronutrients per hectare of crops reduces significantly (by 10–100 times), the yield of plants increases by 15–80 %. The compositions are characterized by high sanitary, hygienic and ecological indicators.

Keywords: biopolymer, carboxymethyl cellulose, xanthan gum, mineral fertilizers, ultrasound, modifier.

1. Introduction

The use of polymeric materials in comparison with other materials takes almost the first place in the world; in particular the use of biopolymers in different fields is very promising. Biopolymers obtained from biological renewable resources are environmentally friendly and economically beneficial. They are of considerable importance in agriculture. It is well-known that the seeds and grains quality often reduces under various negative factors, namely: biological inferiority as a result of growing conditions abnormality, injuries during sowing, harvesting and processing, as well as the damage by the pathogenic microflora. Therefore the development of polymeric compositions for the seeds pre-treatment based on such biopolymers as carboxymethylcellulose (CMC), its sodium salt (Na-CMC) and xanthan gum (XG) is a prospective way. Existing recommendations on this issue are complemented by new data, which allow using the technology of the grains surface treatment by polymeric film-forming compositions with micronutrients in the form of metal complexes [1]. Special methods of laboratory evaluation, creation and analysis of biopolymer compositions are of great importance [2].

The aim of the study was to investigate the effect of water-soluble biopolymers film formation and their compositions with fertilizers and micronutrients, as well as to explore the biopolymers film thickness and study its dissolution rate from the grain surface after application. The other aim was to examine the change of modified xanthan gum and carboxymethyl cellulose properties under the influence of inorganic fertilizers and to conduct practical tests of the biopolymer modified forms for pre-treatment of seven agricultural crops.

We proposed to use the new water-soluble polymeric compounds of natural origin with minimal concentration of substances in its aqueous solution in agriculture. Additionally it was proposed to introduce fertilizers and micronutrients into this solution in a dissolved form to improve film formation and stimulate growth of germs. For the same purpose water pretreated by the ultrasound was also used. We selected xanthan gum and sodium salt of carboxymethyl cellulose from five natural biopolymers as film-forming materials [3]. These compounds decompose in the soil, they are environmentally friendly, cheap and sometimes they are the source of plant nutrition by mono-, di- and polysaccharides which are formed during their decomposition.

2. Experimental

Polymer composition for seed pre-treatment includes fertilizers (12–12.5 %) and micronutrients (3.5–3.12 %) having a stimulating effect on germination and growth of plants. The modified polysaccharides of natural origin: xanthan gum in the amount of 0.1–1 wt % and the sodium salt of carboxymethyl cellulose in the amount of 0.5–2.5 wt % were used as water-soluble polymer film formers. Buffer solution was used to maintain pH in the range of 5.8–7. Hydrogen index of such compositions is in the range of 5.8–6.5 depending on nature of the film former. For XG based biopolymers pH is 6.15–6.16, and for polymers based on Na-CMC – 5.81–5.87. Their preparation technology consists of 2 stages *via* mixing of polymer solutions with the necessary amount of fertilizers and micronutrients. In the final stage the polymer film-forming composition contains the required amount of fertilizer and trace elements needed for plant growth and nutrition. In such a form the composition retains specified nutrients in its structure and is fixed on the surface of grains and seeds.

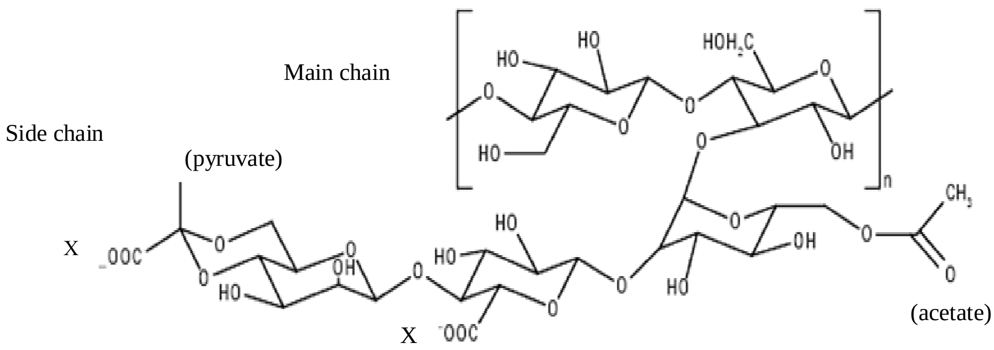
Xanthan gum (gum of corn sugar), $(C_{35}H_{49}O_{29})_n$, is a mixture of polysaccharides, which are formed as secondary metabolites during sugar enzymation by *Xanthomonas campestris* bacteria. Macromolecule of such heteropolysaccharide consists of three monothes: *β-D*-glucose, *α-D*-mannose and *α-D*-glucuronic acid with the ratio of 2:2:1. In this case *β-D*-glucose connected by 1,4-glycosidic bonds forms the XG main chain [4].

After modification we received the modified xanthan gum (XG-M) of the following structure:

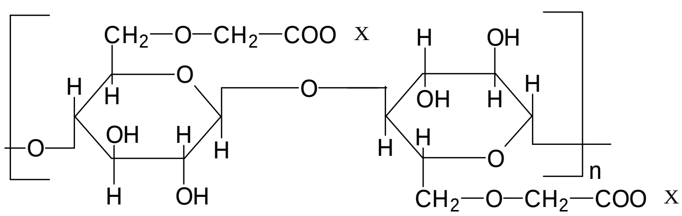
$$[C_5H_5O_2(OH)_{2x}CH_2OH(COOX)_m]_nCH_3$$

where m = 0.1–2; n = 2140–53590; mol. mass = = 2 000 000–50 000 000; X – functional group of $–NR_4^{-1}$ modifier, where R = H, CH_3, C_2H_5, which have the analytical characteristics: pH($_{1\%\ \text{aqueous solution}}$) = 6.0–7.0; $F_{p(1\%\ \text{aqueous solution})}$ 273 K, mp 543 K; $n_D^{20}{}_{(1\%\ \text{aqueous solution})}$ = = 1.333; heat of combustion 14.6 J/g;.dynamic viscosity of 1% aqueous solution at 298 K is equal to 1200–1600 mPa·s. The size of light-yellow XG-M powder particles $d \leq 180$ mm (depending on the brand) and humidity is ≤ 15 %. It is practically insoluble in ethanol and ether, but has a nice solubility in cold and hot water. Biochemical properties of xanthan gum are controlled by changing bacteria living conditions [5] and *via* chemical modification [6].

Carboxymethyl cellulose (CMC), (celluloseglycolic acid, simple ether of cellulose and glycolic acid, tylose, valotsel, edifas), $[C_6H_7O_2(OH)_{3x}\ (OCH_2COOX)_m]_n$, (where m = 0.08–1.5; n = 370–2950; mol. mass 90 000–700 000, X – functional group of $–NR_4^{-1}$ modifier, where R = H, CH_3, C_2H_5). It is a colorless amorphous substance, a weak acid ($K = 5.25\cdot10^{-7}–5.0\cdot10^{-5}$) [4]. Carboxymethylcellulose (synonyms: salt of cellulose polycarboxymethyl ether, carmellosum natricum, carmellose, carboxymethycellulose, cellulose, carboxymethyl ether, acucell, aguacorb; cellulose gum, E466) is white, odorless, granulated powder with the following characteristics: density 0.52 g/cm^3, bulk density (flowability) 780 g/l, dissociation constant in water pK_a = 4.30; $pH_{(1\%\ \text{aqueous solution})}$ = 5.0–6.0; mp ~ 500–525 K; hygroscopic (containing 10 % of water), can absorb large amounts of water at temperatures up to 310 K and relative humidity approximately 80 %; practically insoluble in acetone, alcohol (95 %), ether, toluene, easily soluble in water at any temperature forming a colloidal solution [7, 8].



Xanthan gum. Modified xanthan gum (XG-M)



Modified policarboxymethyl ester of cellulose (CMC-M)

Used biopolymers are powders from white to yellow color. While dissolved in water they can form liquid transparent colloidal solutions – sols and viscous gels. Their viscosity in water increases with the increase of their concentration and approaches to the fluid solid gel.

The thickness of the formed films of biopolymers and compositions on their basis was measured on a flat or ball-shaped solid surface of steel model by means of the electromagnetic meter thickness ("Elcometer", ©Copyriht Elcometer Instruments Ltd. 2004-2005); conditional viscosity – by the viscometer VZ-4 with a hole size of 4.3 mm.

3. Results and Discussion

3.1. Physico-Chemical Properties of the Compositions

At the first stage of research we studied the dependence of the conditional viscosity of aqueous colloidal solution on the concentration of CMC-M and XG-M biopolymers (Figs.1 and 2). It is almost the same for both modified biopolymers, but for XG the maximum increase of viscosity with a plastic gel formation occurs already at its 0.5 % concentration in water, when a conditional viscosity rapidly increases from 95 to 642 s, *i.e.* by seven times (Fig. 1). For CMC-M the maximum increase of viscosity with the formation of plastic gel is carried out at 0.75 % concentration in water, when the conditional viscosity rapidly increases from 488 to 3498 s, *i.e.* again by seven times (Fig. 2). This phenomenon can be explained by the molecular weight of XG-M larger in 10 times compared with CMC-M. Investigated solutions were prepared on the basis of distilled water. The viscosities of the same biopolymers based on sonicated water (dashed curves in Figs. 1 and 2) were determined for comparison. One can see from Figs. that the viscosity of solutions based on sonicated water is less compared with those based on distilled water at the same concentrations of film-forming materials.

The decrease in viscosity of solutions based on sonicated water can be explained by the following factors. If we consider water as a natural polymer, molecules of which are bounded by hydrogen bonds in macromolecules, then ultrasound (or cavitation) treatment of water destroys the hydrogen bonds formation. Thus solutions based on the treated water have a lower viscosity. One more reason may be the fact that during the ultrasonic treatment microbubbles are generated from dissolved gases. The bubbles size is less than 10^{-9} m, *i.e.* less than the size of colloidal parts. Water density decreases and its viscosity decreases as well [9].

Obviously, it is connected with the formation of intermolecular Van der Waals forces and strong hydrogen bonds between hydroxyl and carboxyl groups of both biopolymers at the concentrations higher than the above mentioned limits. The higher concentration of carboxyl groups in CMC is confirmed by partially acidic pH of its water solution (pH = 5–6). Thus the polymer viscosity for 0.75 % solution (Fig. 2) increases faster and more intensively because the molecular interaction between the functional groups (–OH and –COOX) in carboxymethyl cellulose is stronger than that in the xanthan gum.

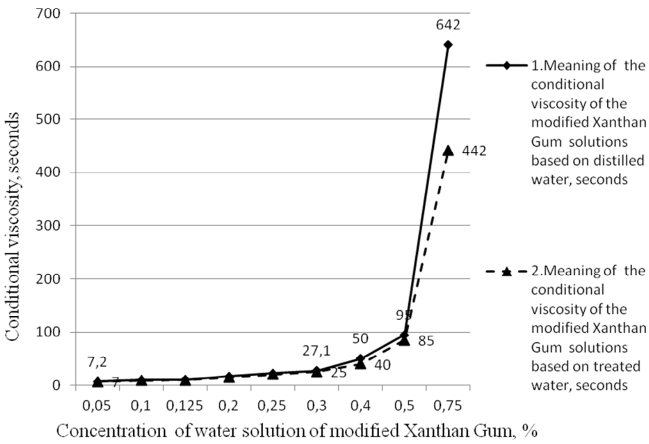


Fig. 1. The dependence of the conditional viscosity of XGM solution on its concentration in distilled water (continuous curve 1) and in sonicated water (dashed curve 2) (VZ-4, *d* = 4.3 mm)

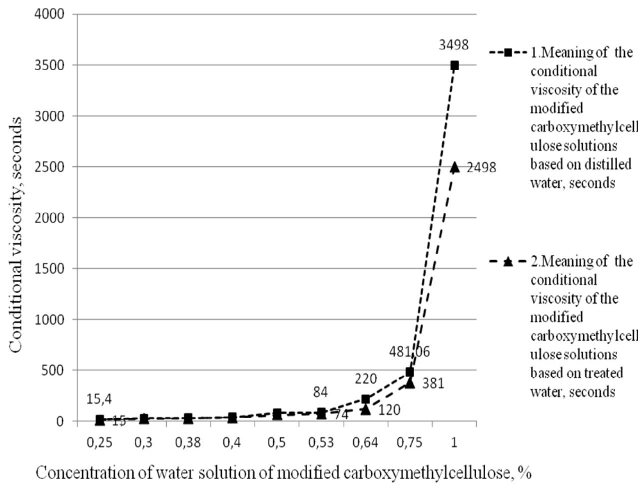


Fig. 2. The dependence of the conditional viscosity of CMC-M on its concentration in distilled water (continuous curve 1) and in sonicated water (dashed curve 2) (VZ-4, *d* = 4.3 mm)

The polymer solutions should be prepared with the concentration under which they are in a state of easy-fluid colloidal solution-sol. It is necessary to form the film of optimal thickness on the seeds surface. The optimal concentration of working water solution was found to be 0.5 % for CMC-M and 0.125 % for XG-M. Effluent time is 83 s for CMC-M and 10.6 s for XG-M respectively (Figs. 1 and 2) [10].

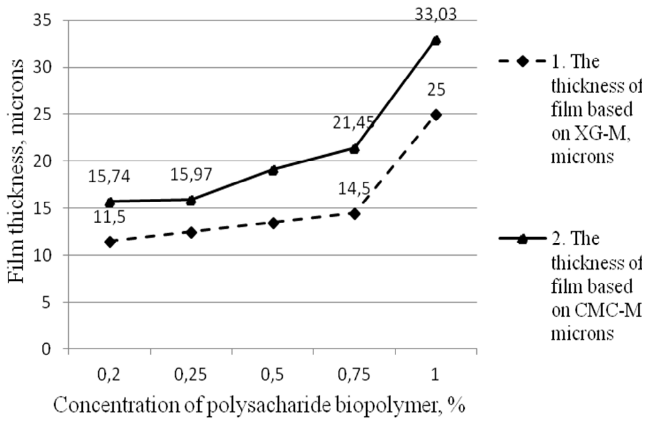


Fig. 3. Dependence of the film thickness modified by XG-M (continuous curve 1) and CMC-M (dashed curve 2) on the concentration of the biopolymers aqueous solutions on a flat steel surface

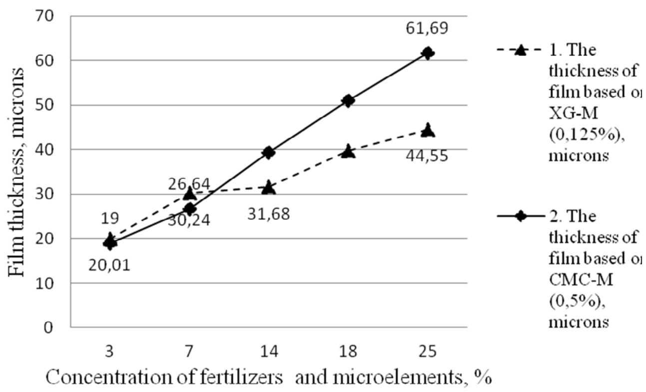


Fig. 4. Dependence of the film thickness based on XG-M (0.125 %, *continuous curve* 1) and CMC-M (0.5 %, *dashed curve* 2) on fertilizers and micronutrients concentration in the biopolymers aqueous solution on a flat steel surface

To calculate the real amount of film-forming materials, fertilizers and micronutrients we investigated the dependence between the polymer concentration and thickness of the film formed on a flat and ball-shaped solid surface of the steel model of seed and agriculture crops grain (Figs. 3 and 4). While using CMC-M the increase of this biopolymer concentration in the solution from 0.2 to 0.75 % slightly increases the film thickness to 15.74–21.45 μm. As it was mentioned above, if we exceed this limit, the viscosity rapidly increases followed by the double increase of film thickness on a flat surface (to 33.03 μm). At the same time, while using XG-M with the concentration in the solution from 0.1 to 0.5 %, the thickness of the formed film slowly increases and amounts to 11.5–25 μm. The excess of this limit sharply increases the viscosity and the film thickness to 21–25 μm (by 2 times, Fig. 3).

Hydrogen index is 5.5–5.81 for the obtained aqueous composition based on CMC-M and 6.16–6.15 – for the composition based on XG-M.

The film thickness on a flat steel surface after compositions dried at 293 K for 20–25 min also depends on the content of fertilizers and micronutrients. The following dependence between fertilizers content in the composition and the thickness of the formed film is observed: the increase of fertilizer concentration from 3 to 20 % increases the thickness of the film based on XG-M from 20.01 to 44.55 μm, while the increase of fertilizers concentration from 3 to 25 % the thickness of the film based on CMC-M increases from 19 to 61.69 μm (Fig. 4).

Thus the dependences between the viscosity, components concentration and film thickness are different for two biopolymers. XG-M aqueous solution becomes more viscous in the presence of fertilizers and inorganic salts and film thickness increases by 2 times. The increase in the salt concentration considerably affects CMC-M viscosity and the film thickness increases by 3 times.

Obviously, the solutions of salts-fertilizers influence the film-forming materials as electrolytes. The result is a partial coagulation and dense of the solutions with the simultaneous increase of film thickness. On the basis of obtained results we can assert that aqueous solutions of film-forming xanthan gum are more resistant to the action of coagulants-electrolytes.

3.2. The Efficiency of Film Formation for Different Biopolymers

The efficiency of film formation was investigated (Figs. 5 and 6). The increase in weight of different film-forming materials on the surface of maize after drying was observed. The weight of seeds with applied biopolymeric film increases in the row (%): starch (13.4) – gelatin (12.2) – CMC-M (10) – saccharose (7) – XG-M (3.5). The results are confirmed by the histogram (Fig. 5).

The largest increase in weight of film-forming material applied on wheat is observed for gelatin and carboxymethyl cellulose (Fig. 6) and the lowest one – for starch, saccharose and XG-M. The efficiency of film formation, namely the increase in weight of film-forming materials applied on the wheat surface is: for XG-M – 2.5 %, starch – 10.2 %, saccharose – till 11.7 %, carboxymethyl cellulose – 25.1 %, and gelatin – 29.3 %. The results are confirmed by the histogram in Fig. 6.

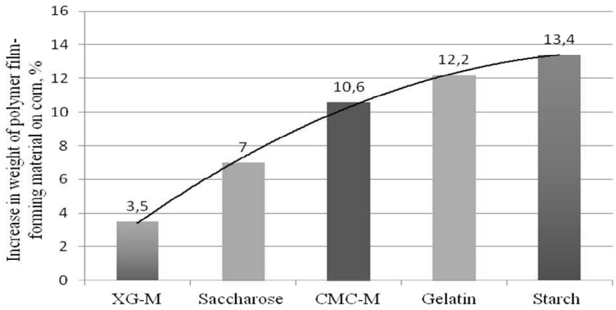


Fig. 5. The increase in weight (applying efficiency) of polymer film-forming materials applied on the surface of corn grains depending on their nature

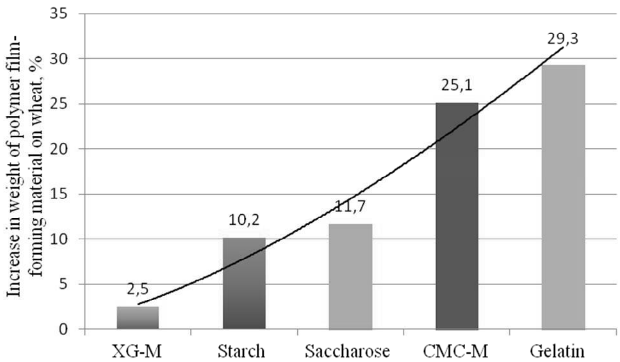


Fig. 6. The increase in weight (applying efficiency) of polymer film-forming materials applied on the surface of wheat grains depending on their nature

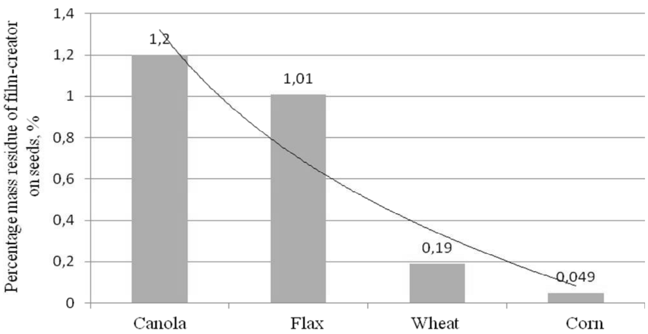


Fig. 7. Dissolution efficiency (percentage residual weight) of the starch polymer film applied on the surface of seeds depending on seeds nature

To determine the rate and efficiency of the polymer film dissolution from the surface of various seeds and for the process modeling we compared the content of starch film on the surface of treated seed after its two-hour flushing with water (1:500, v/v) at 293 K under stirring (Fig. 7). Starch from the surface of corn and wheat large grains has the best solubility. Starch from the surface of flax and canola small seeds dissolves in the worst and slowest way. The reason may be the small size of grains, the nature of their surface and the nature of its interaction with the film-forming polymer. The residual weight of polymer after dissolution is 1.2–1.01 % of the initial value. At the same time, for the larger wheat and corn grains with a more smooth surface, the dissolution rate increases and its residual weight after two-hour staying in water actually decreases to zero (0.19–0.049 %) (Fig. 7).

The investigated polymers can be placed in minorant series according to the efficiency of film formation (increase in weight of applied film-forming materials). CMC-M exhibits the best results. The average percentage value of its increase in weight for three kinds of seeds and polyethylene model granules is 25.5 %. Next polymer is gelatin; its average percentage value is 23.125 %. The increase in weight of saccharose film is 17.65 %, starch – 13.125 % and xanthan gum – only 2.5–5 % [10].

The residual of film forming material does not exceed 0.1–1.0 % after two-hour staying in water. It means that under natural conditions, particularly in the Carpathian region with sufficient humidity during the season (on average 750–800 mm precipitates per year), the film-forming biopolymer (starch) and other polysaccharides (CMC-M and XG-M) are completely dissolved and do not affect the growth and yield of crops. They are environmentally friendly and do not pollute the soil [10].

3.3. Composition Influence on the Growth and Yield of Crops

The influence of obtained compositions on the growth and yield of plants was investigated under field conditions on the example of seven agricultural crops: canola, corn, soybean, rice, flax, wheat and sunflower.

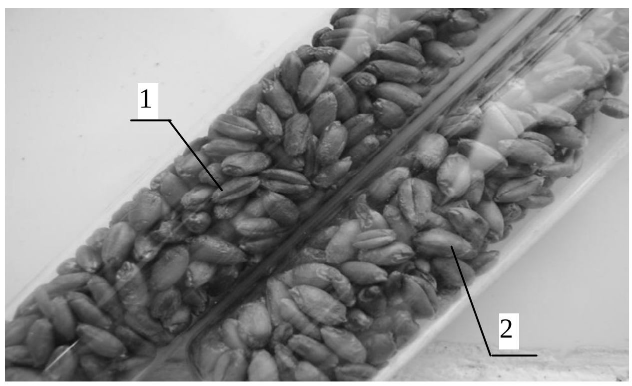


Fig. 8. Seeds of spring wheat, coated with the film-forming compositions based on XG-M (1) and CMC-M (2) with fertilizers and micronutrients (scale 1:1)

The wheat grains are depicted in Fig. 8. Their surface was treated before sowing by films of fertilizers and micronutrients based on two best film-forming materials (CMC-M and XG-M). We added food dyes to the solutions to mark the size of the area covered by the biopolymer. Polymeric film is applied uniformly and completely coats the grain surface area [11].

Use of the solutions with XG-M and CMC-M, compared with the control samples without seeds pre-treatment, can reduce the overall costs of fertilizers and micronutrients by 9–107 times, particularly for spring wheat (by 9 times), for rice and soybeans (by 15 times), for corn (by 41 times), for flax (by 45 times), for sunflowers (by 57 times), and for spring canola (by 107 times). Histograms in Fig. 9 confirm this fact.

The comparison of real costs (in UAH/ha) of mineral fertilizers applied on the seeds surface and directly introduced into the soil is represented in Fig. 10. One can see that while using the pre-treated samples the costs were less by 7.5 times for spring wheat, by 9 times for rice, by 15 times for soybeans, by 40 times for flax, by 64 times for sunflower, by 72 times for corn and by 150 times for spring canola.

Using the solutions with XG-M and CMC-M on the control areas allows to get a higher yield of all 7 crops compared with that obtained while using untreated seeds. The histograms of percentage increase in yield of these crops are shown in Figs. 11 and 12.

Stimulation of five from seven tested agricultural crops (except wheat and canola) results in weight and percentage increase in yielding compared with that of control untreated seeds [11]. Weight increase is 15–25 % per hectare for sunflower, rice and flax, and 50–80 % for soybean and corn, compared with an average yield of these crops in Ukraine in 2012 [12].

The economic profit from the implementation of the developed presowing treatment agrochemical technology may be achieved due to the significant reduction of fertilizers and micronutrients consumption. Compared with traditional nutrition technology the total economic profit is approximately 456 UAH\ha for soybean, 560 UAH\ha for wheat, 724 UAH\ha for rice, 816 UAH\ha for flax, 1057 UAH/ha for sunflower and 1100 UAH\ha for corn. Thus 1 kg of biopolymeric compositions based on XG-M and CMC-M with the price of 1–3 UAH/kg would be enough to treat up to 50–100 kg of seeds or grains [12].

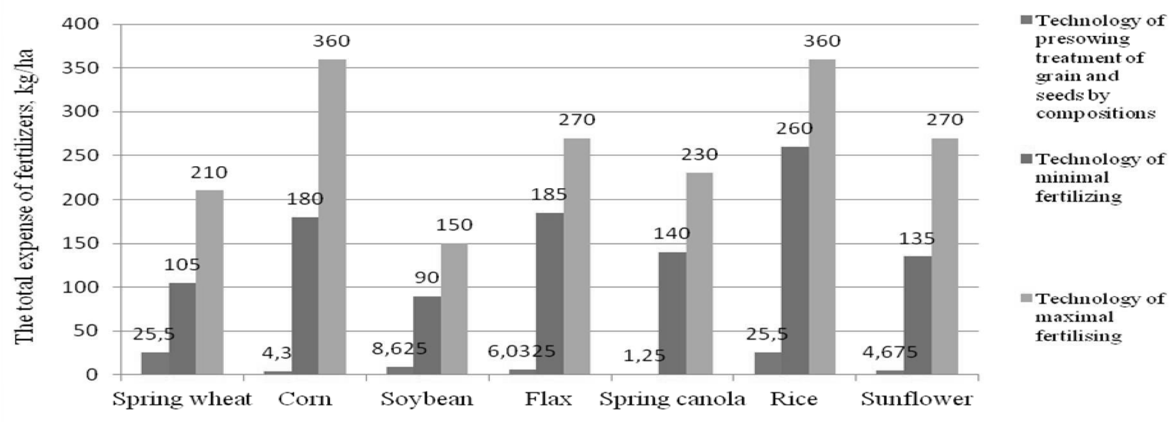


Fig. 9. The total consumption of mineral fertilizers under different nutrition technologies of seven agricultural crops

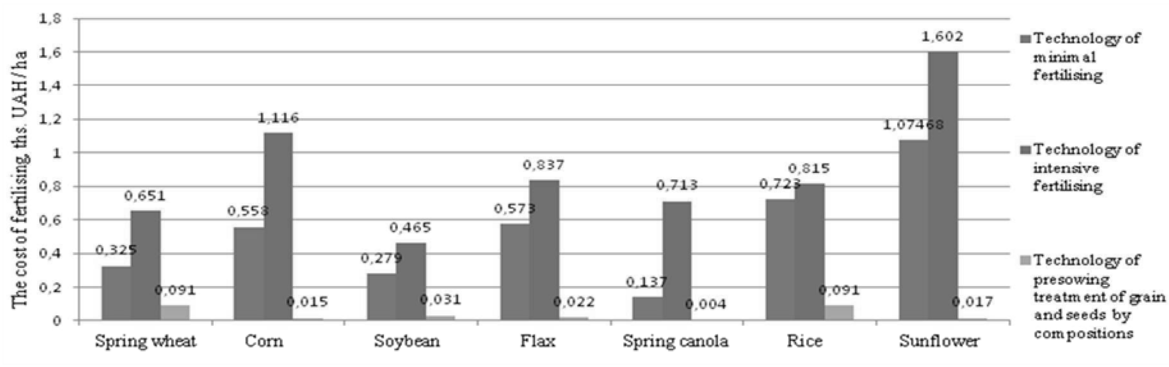


Fig. 10. Costs of introduced mineral fertilizers under different nutrition technologies of seven agricultural crops

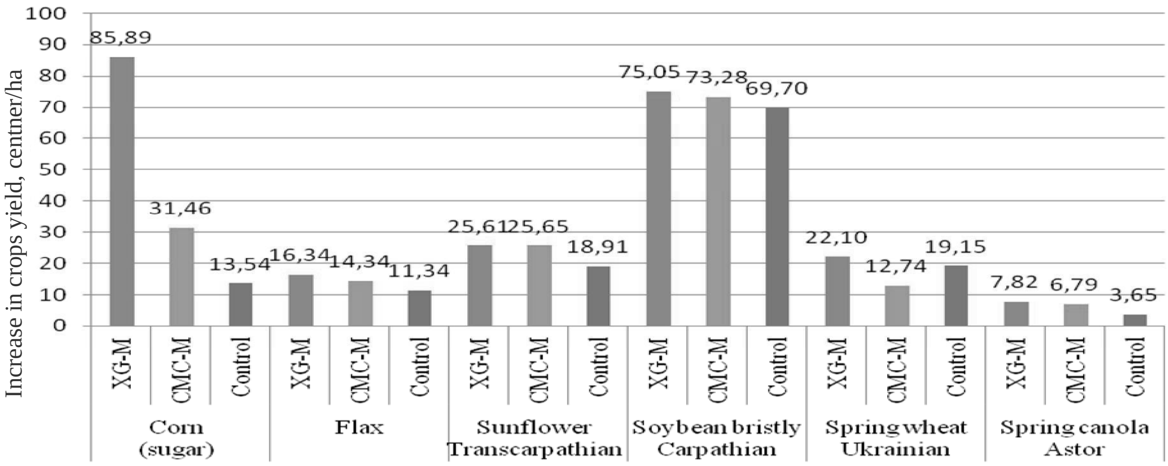


Fig. 11. Comparative histograms of increase in yielding seven agricultural crops for the seeds treated by biopolymer compositions based on XG-M and CMC-M and for the control crops when fertilizers were introduced directly in the soil *via* traditional technology on experimental plots of Botanical garden of Precarpathian University in 2012

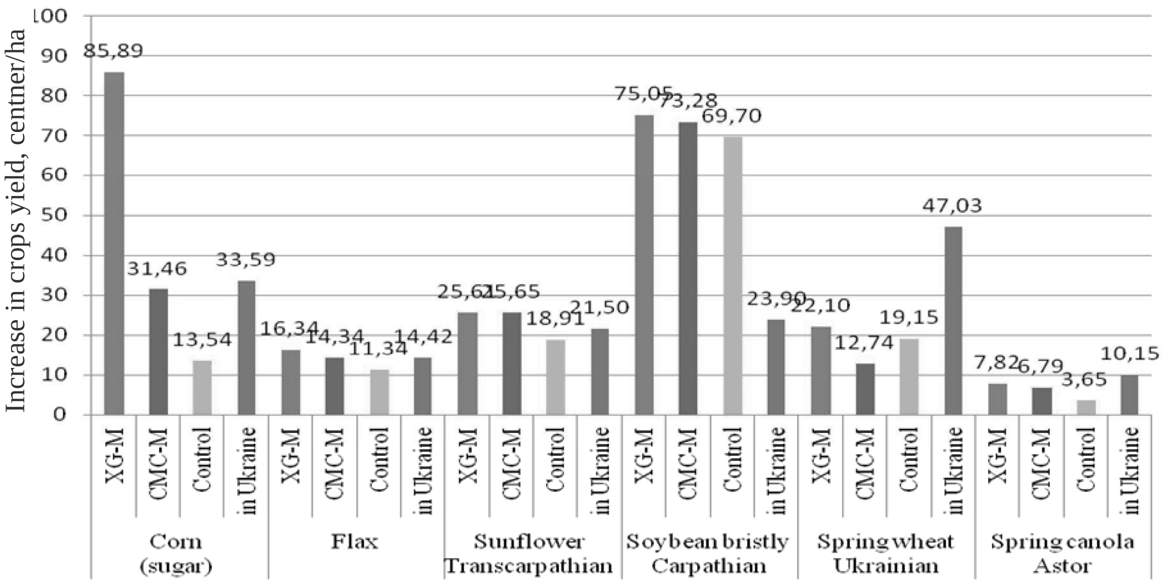


Fig. 12. Comparative histograms of increase in yielding seven agricultural crops for the seeds treated by biopolymer compositions based on XG-M and CMC-M and for the control crops when fertilizers were introduced directly in the soil *via* traditional technology throughout Ukraine

4. Conclusions

The properties of modified biopolymers – xanthan gum and modified carboxymethyl cellulose, as well as properties of their polymeric compositions with fertilizers and micronutrients have been investigated. Aqueous solutions of such biopolymers are changed under the influence of fertilizers and micronutrients. The dependences between fertilizers and biopolymers content in the solution and its viscosity have been studied. The thickness of the formed film depends on the content of modified biopolymers and inorganic substances.

The effect of biopolymer compositions based on the modified CMC and XG on the growth and yield of seven crops has been determined. Estimated economic profit from the developed technology implementation is 456–1100 UAH/ha per year. Owing to the reduction of the amount of developed fertilizers by 10–100 times (compared with the amount of traditional fertilizers and micronutrients), the pollution of soils, rivers and lakes may be reduced by 85–90 %.

Acknowledgments

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БІОПОЛІМЕРИ ДЛЯ ПЕРЕДПОСІВНОГО ОБРОБЛЕННЯ НАСІННЯ

Анотація. *Розглянуто фізико-хімічні властивості спеціально модифікованих форм природних біополімерів – карбоксиметилцелюлози та ксантанової смоли. Проведено дослідження ефективності та здатності до плівкоутворення водорозчинних композицій цих біополімерів, їх впливу на ріст і продуктивність сільськогосподарських культур. Досліджено залежності між зміною вмісту біополімерів, мінеральних добрив і мікроелементів у розчині та його в'язкістю, а також залежність товщини утворених плівок від вмісту модифікованих біополімерів та мінеральних добрив. Встановлено, що застосовування природних плівкоутворюючих композицій значно, у 10–100 раз, знижує розхід мінеральних добрив та мікроелементів на гектар посівів та підвищує на 15–80 % врожайність сільськогосподарських культур. Композиції характеризуються високими санітарно-гігієнічними та екологічними показниками.*

Ключові слова: *біополімер, карбоксиметилцелюлоза, ксантанова смола, мінеральні добрива, ультразвук, модифікатор.*