TYPES OF POLYVINYL ALCOHOL USED FOR CONDITIONING LIQUID MIXES OF FERTILIZERS OR FOR THEIR ENCAPSULATION IN MONOLITH PARTICLES

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In this study, based on the reactions of polyvinyl alcohol with boric acid, phosphoric acid and phosphorous acid, fertilizer combinations containing the three essential macroelements (N, P and K) as well as boron (microelement and fungicidal agent) were obtained.

The products obtained by the reaction of boric acid with polyvinyl alcohol were used to obtain monolithic granules, using urea as fertilizer. In the presence of water there will be swelling of the polyvinyl alcohol network with controlled release of urea and boron from the system.

Also, the phytotoxicity of the various polyvinyl alcohol variants obtained with different degrees of hydrolysis was tested.

Keywords: polyvinyl alcohol, fertilizer, encapsulation, controlled release

1. Introduction

The demand for human food will constantly be growing due to the increase in the world population. Hence, as farmers are pressured to produce more resources it is essential to improve the crop production whilst taking in consideration the concerning environmental factors [1].

Similar to human beings, plants require several nutrients for their growth and development [2] Plants obtain their structural nutrients (carbon, hydrogen and oxygen) through the leaves and roots whilst mineral nutrients are absorbed through the soil [2]. Hence, the availability of these components in the soil determines crop quality and productivity. A regular restoration of these nutrients needs to be provided to maintain or even increase the fertility of the soil and quality of the harvest [2]. To achieve this, fertilisers are used and are essential for the healthy growth of plants. However, most of the macro elements (N, P and K) are lost in the process which leads to a decrease in valuable resources as well as

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pollution. Nowadays, urea is a widely used fertiliser due to its relatively low cost. However, it is vulnerable to losses which reduce efficiency and production. Urea can be hydrolysed to NH_3 and CO_2 by soil urease and NO_3 is formed through nitrification which can significantly contribute to environmental pollution [3]. Hence, ammonia volatilisation and ground water pollution by nitrates represent some of the main concerns which need to be addressed. The development of new and improved fertilisers with different modes of action needs to remain a priority.

Slow or controlled release fertilisers are currently emerging as they represent a more sustainable and beneficial alternative. The release of the active substance is controlled over a period of time to better meet crop demand [2]. The ideal slow-release fertiliser can be described as a conventional fertiliser coated with a natural or semi-natural environmentally friendly macromolecule [3].

Independent of the methods used for encapsulating the fertilizers, two types of fertilizer granules are obtained: granules covered by a semipermeable polymer membrane or monolithic granules where the fertilizer is embedded within a polymeric matrix. The controlled release is done in the presence of water within the soil. When the water penetrates the capsules, the swelling of this hydrophilic coating can take place which allows the controlled release of the active substance [4]. The release may also occur as a result of increased osmotic pressure due to water penetration through the semipermeable polymer membrane [5].

So far, several types of polymers such as polyethylene or polyesters have been applied but some of these classes have been reported to be poorly biodegradable or not cost effective to be pursued further [3]. Usually, polymers containing large hydrocarbon chains tend to be non-biodegradable. The introduction of heteroatoms into the chain could confer biodegradability. Hence, more efficient methods of encapsulating various fertilisers need to be developed to meet the global demand of productive and sustainable agriculture. Also, new macromolecule materials need to be investigated and analysed. Some results have already been reported in this direction. There are studies that have reported polyvinyl alcohol (PVA) used as a waterborne polymer coating [6]. Some studies have focused on improving nutrient release retardation efficiency by cross-linking PVA with carboxylic acids, which forms a new structure that confers low permeation flux [7]. Other studies have attempted to improve the water resistance and slow-release properties of PVA by masking the hydroxyl groups in PVA [8]. In this sense polyvinylpyrrolidone (PVP) can be taken into account because it can bind the hydroxyl groups in PVA improving the physical properties of the PVA film as was shown by Kamada et al. (2003) [9]. In addition to these investigations, we were interested in assessing the feasibility of using polyvinyl alcohol (PVA) with different degrees of hydrolysis as a potential encapsulating agent. PVA has hydroxyl groups with normal reactivity which can react with the functional groups

already present in the fertiliser. Hence, the fertiliser is linked through a covalent bond which is easily hydrolysable and allows the release of the active substance.

Our ultimate goal was to analyse whether polyvinyl alcohol with different degrees of hydrolysis should be considered as a potential coating agent for different fertilisers or pesticides.

2. Materials and Methods

In this study, a polyvinyl acetate in methanol solution (concentration 40%) was used, obtained through in solution polymerisation of vinyl acetate in the presence of AIBN (azobisisobutyronitrile) as the initiator. The lacquer was diluted with methanol (at a concentration of 20% and 25%) and used for hydrolysis in suspension (volume ratio lacquer: paraffin oil = 1:1) using sodium hydroxide as a solution in methanol as a catalyst. The reaction was conducted at 35℃. To determine the amount of methyl acetate produced over time, samples were taken from the reaction mixture. PVA was separated from the liquid phase and introduced in hexane spiked with acetic acid, washed, filtered, dried at constant weight, and analysed to determine the degree of hydrolysis.

For testing the phytotoxic characteristics on PVA on plants, the experiments took place in greenhouse conditions and the plants were grown in plastic pots (10 x 10 cm) with 4 repetitions for each variant. The reaction of PVA (concentration of 12%) with boric acid was carried out in an aqueous medium, pH = 6.5 and a temperature of 65℃ for 3 hours. The reaction of PVA with phosphoric and phosphorous acids took place in an installation consisting of a 750 mL flask fitted with a stirrer, a descending reflux condenser and a drip funnel. Distilled water (500 mL) and PVA (44 g) were introduced into the reaction flask. After dissolution of the PVA, H_3PO_4 solution 85% (44 g) was introduced into small portions by stirring. The reaction mixture was maintained at 65℃ for 3 hours. A white gelatinous and homogenous product was obtained with a pH = 2.

Statistical analysis was performed using the one-way Analysis of Variance (ANOVA). The comparisons of means were calculated by Duncan test ($p < 0.05$).

3. Results and Discussion

3.1. Polyvinyl alcohol (PVA) synthesis and hydrolysis determination

In order to assess the feasibility of using PVA for encapsulation, we wanted to examine the synthetic process of obtaining PVA with different degrees of hydrolysis and its phytotoxic characteristics.

The polyvinyl alcohols used as surfactants were synthesised from the hydrolysis of polyvinyl acetate in suspension. The principle of polyvinyl acetate hydrolysis consists of suspending the polyvinyl acetate in an immiscible and totally inert medium in relation to the hydrolysis reaction, respectively in paraffin

oil. In this way, the hydrolysis occurs at the level of the polyvinyl alcohol pearls, with the process of forming the compact gel and blocking the hydrolysis reactor being completely eliminated. This method presents the advantage of being able to easily control the hydrolysis reaction through dosing the methyl acetate present in the system, with this analysis being able to be performed much quicker than the hydrolysis. To achieve this, the reaction was run in an autoclave equipped with an agitator and a water bath.

To determine the degree of hydrolysis, a standard method was used.[10] This also allows the comparison between the two types of measurements and can enable the determination of the reaction kinetics. The process of determining the degree of hydrolysis by analysing the amount of methyl acetate is based on the reaction equimolarity (for one mole of PVA one mole of methyl acetate is formed). Hence, equation 1 can be used where DH_τ is the degree of hydrolysis, $[A_cM_e]_\tau$ is the number of moles of methyl acetate per cm^3 determined by titrating at the time τ and $[A_cM_e]_0$ represents the number of moles of methyl acetate per cm^3 corresponding to 100% DH.

$$DH_\tau = \frac{[A_cM_e]_\tau}{[A_cM_e]_0} \times 100 \quad (1)$$

Calculating the concentration of methyl acetate in the liquid phase is not at all simple because the composition of the liquid phase is constantly changing during the alcoholysis reaction. Due to this fact, it was necessary to develop a calculation algorithm for determining the concentration of methyl acetate to which the value obtained at the moment τ by dosing the methyl acetate in the system by chemical analysis should be related [11,12].

This is determined by the continuous change in the composition of the liquid phase during the alcoholysis reaction, as part of the methanol enters the transesterification reaction and an equivalent number of moles of methyl acetate is formed in the process.

Also, in the case where the hydrolysis occurred in methanol the following calculation methodology was used. Knowing the amounts introduced in the reaction (gravimetric analysis), G_P^0 represents the amount of polymer in the polyvinyl acetate solution, G_M^0 is the amount of methanol from the polyacetate solution (concentration 40%) and G_M^A represents the amount of methanol required to bring the polyvinyl acetate solution from 40% to the concentration required for the experiments run. We calculated the number of moles of -OH groups equivalent to the total degree of hydrolysis of polyvinyl acetate used for the alcoholysis reaction (equation 2).

$$n_{OH}^0 = G_P^0 / M_{AcV} = G_P^0 / 86 = 1.162\ G_P^0 \times 10^{-2}\ \text{mols} \quad (2)$$

In order to determine the total amount of methanol representing the liquid phase of the reaction mixture, equation 3 was used.

$$G_M^t = G_M + G_M^A (g) \quad (3)$$

After dosing through chemical analysis of methyl acetate from a 10 mL sample of liquid phase we determined the concentration of methyl acetate (E_1). In these conditions the amount of methyl acetate formed will be determined by the relationship in equation 4.

$$G_{AcMe} = G_1 = 74 \text{ x } G_M^t / 32 \text{ x } E_1 \text{ x } 10^{-2} = 2.3125 \text{ x } G_M^t \text{ x } E_1 \text{ x } 10^{-2} \quad (4)$$

It was previously mentioned that between the amount of -OH formed and the amount of ester contained in the liquid phase there is an equimolar relationship. Based on this rationale, we calculated the number of moles of -OH groups formed in the process of methanolysis (equation 5).

$$n_{OH}^{\tau} = G_{AcMe} / M_{AcMe} = 3.125 \text{ x } G_M^t \text{ x } E_1 \text{ x } 10^{-4} \text{ mols} \quad (5)$$

As in reality the values of G_M^t within alcoholysis is constantly changing we introduced a correction factor according to equation 6.

$$\beta = n_{OH}^{\tau} (M_{AcMe} - M_M) = 42 n_{OH}^{\tau} = 1.3125 \text{ x } G_M^t \text{ x } E_1 \text{ x } 10^{-2} \quad (6)$$

Combining equations 5 and 6 we can determine the actual, real number of moles of -OH groups (equation 7).

$$n_{OH}^{\tau R} = n_{OH}^{\tau} + \beta = 1.34375 \text{ x } E_1 \text{ x } 10^{-2} \quad (7)$$

The degree of hydrolysis of polyvinyl alcohol represents the ratio $nOH^{\tau R}/nOH^0$ and taking into account formulas 2 and 7 we obtain equation 8.

$$D_H^{\tau} = \frac{1.34375 \; X \; G_M^t \; X \; E_1 \; X \; 10^{-2}}{1.162 \; X \; G_p^0 \; X \; 10^{-2}} = 1.1564 \; X \; \frac{G_M^t}{G_p^0} \; X \; E_1 \quad (8)$$

Noting the ratio $\frac{G_M^t}{G_p^0}$ with α the final relationship for determining the degree of alcoholysis will be denoted by equation 9.

$$D_H^{\tau} = 1.1564 \; X \; \alpha \; X \; E_1 \quad (9)$$

D_H^{τ}, according to formula 9 takes values from 0 to 1 and through the multiplication by 100 the values can be expressed as percentages.

The obtained results are presented in tables 1-6 and Figs. 1-5.

Tables 1 and 2 present the results obtained when determining the degree of hydrolysis through the two approaches of dosing the methyl acetate present in the

system and through analysing the solid pearls of PVA. Two different concentrations of PVA solutions were used (20% and 25%).

Table 1

The comparative results of hydrolysis degrees, determined by dosing methyl acetate (DH_τ) and through analysing the PVA pearls (DH_R)

Reaction number	Time (min)	DH_R	E_1, %	DH_τ	Correction coefficient	Observation
1	20	42.1	1.08	31.24	1.347	
2	25	51.6	1.347	38.94	1.325	
3	30	59.6	1.347	41.97	1.420	
4	35	65.8	1.7866	51.65	1.274	
5	40	71.2	1.7865	59.04	1.206	
6	45	74.6	2.310	66.79	1.117	
7	50	78.2	2.450	70.83	1.104	
8	55	81.9	2.601	75.20	1.089	
9	60	82.4	2.656	76.79	1.073	
10	65	85.7	2.742	79.28	1.081	$\overline{K}$ =1.084
11	70	87.6	2.832	81.87	1.07	
12	75	89.6	2.851	82.43	1.087	

Conditions: $[PA_cV]$=25%; volume ratio paraffin oil:lacquer = 1:1; [NaOH] = 0.4%; T = 35ºC

Table 1 emphasises that the method is applicable for the synthesis of PVA types with a DH > 75%. This is determined by the fact that under this DH value the PVA pearls did not harden, and a significant amount of methyl acetate is retained in the pearls. For DH > 75% the syneresis of the pearls occurs and this process is accompanied by the expulsion of the solvent from them and the formation of numerous pores in the PVA granules. This is emphasised by using electron microscopy (Fig. 1a, b).

Because of this, we have performed determinations of the degree of hydrolysis through the two procedures at the concentration of the lacquer of polyvinyl acetate of 20%, with the samples being taken after overcoming the gel phase (Table 2).

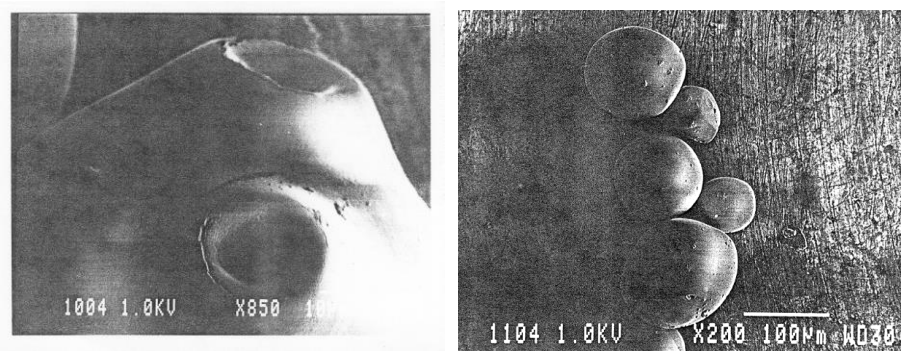

Fig. 1. a - The image of PVA pearls (after the process of syneresis) obtained using the electron microscope (10 µm); b - Structure of the final polyvinyl alcohol pearls

Within the pores formed, small amounts of a mixture of methanol-methyl acetate are retained which explains the small differences which occur between the degrees of hydrolysis determined by the PVA pearls and through dosing methyl acetate. To this we can also add the solubility of methyl acetate in the paraffin oil which has a value of 1.82%. Because of these two aspects, there is a systematic deviation which is translated as a difference between the degree of hydrolysis determined through analysing methyl acetate DH_t and the real degree of hydrolysis DH_R.

The value of the DH_R/DH_t ratio represents the correction factor K which was experimentally determined based on the data in tables 1 and 2. The value for the lacquer at the concentration of 25% is 1.084 and 1.15 for concentration of 20%.

Table 2

The comparative results of hydrolysis degrees, determined by dosing methyl acetate (DH_T) and through analysing the PVA pearls (DH_R)

Experiment	Sample	Time (min)	V_2 (mL)	V_1*(25 mL)-V_2 (mL)	E_1, %	DH_t, %	DH_R, %	K	Observation
1	1	40	15.4	9.6	1.88	72.5	83.4	1.15	$\bar{K}$ =1.15
	2	50	14.95	10.1	1.958	75.5	86.0	1.149	
	3	60	14.6	10.4	2.023	78.0	89.2	1.148	
	4	70	14.5	10.5	2.023	78.5	80.4	1.152	
	5	80	14.3	10.7	2.088	80.5	92.5	1.150	
	6	90	14.2	10.8	2.11	81.3	93.5	1.150	
2	1	50	14.3	10.2	1.979	76.3	87.4	1.150	$\bar{K}$ =1.15
	2	60	14.05	10.7	2.075	80.0	92.0	1.150	
	3	70	13.8	10.95	2.127	82.0	94.3	1.150	
	4	80	13.7	11.2	2.174	83.8	96.3	1.153	
	5	90	13.5	11.3	2.197	84.7	97.0	1.148	
	6	100	13.45	11.5	2.231	86.0	98.9	1.150	
	7	110	13.25	11.55	2.241	86.4	99.3	1.148	
	8	120	13.3	11.75	2.280	87.9	99.9	1.158	
3	1	50	15.1	9.9	1.920	74.0	85.2	1.151	$\bar{K}$ =1.15

	2	60	14.35	10.05	1.971	76.0	87.2	1.151	
	3	70	14.25	10.2	1.982	76.4	88.0	1.152	

Conditions: [PAcV]=20%; volume ratio paraffin oil:lacquer =1:1; [NaOH]=0.4%; T = 35ºC

The experimental results presented in these tables show values extremely similar to K which proves that through the entire process of hydrolysis the formation of PVA does not change the solubility of methyl acetate and methanol in paraffin oil.

Amplifying the degree of hydrolysis determined analytically (DH_t) with this correction coefficient leads to determining the real, experimental degree of hydrolysis (DH_R) with excellent results. For obtaining different PVA types with DH>75%, controlling the hydrolysis reaction in suspension can be achieved only through stopping it based on a preliminary calibration curve. This implies conducting the process at moderate reaction speeds which can allow its ending at established times based on these curves. To trace these calibration curves we studied the influence of the main parameters on the hydrolysis reaction: catalyst concentration and temperature. Figs. 2 and 3 show the time-conversion dependence for these parameters.

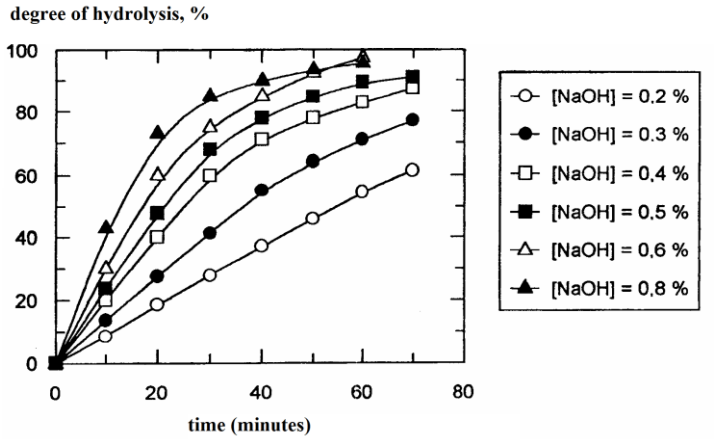

Fig. 2. Influence of catalyst concentration on the alcoholysis reaction in suspension ([polyvinyl acetate] = 40%; T = 35ºC; ratio paraffin oil:polyvinyl acetate solution = 2/1)

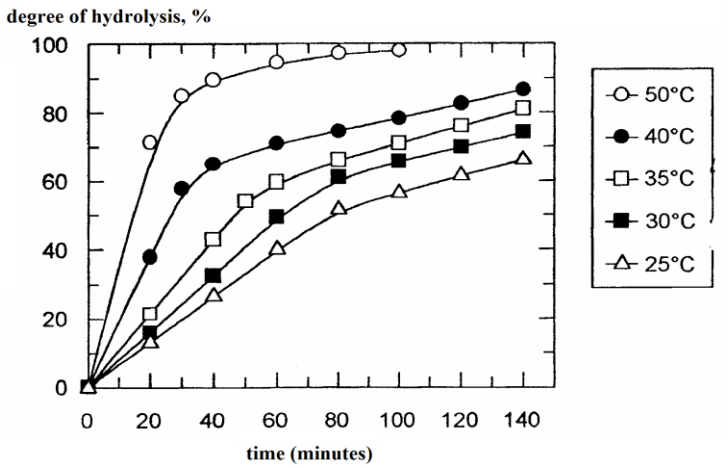

Fig. 3. Influence of temperature on the alcoholysis reaction in suspension ([polyvinyl acetate] = 40%; [NaOH] = 0.4 %; ratio paraffin oil:polyvinyl acetate solution = 2/1)

These graphs show that the hydrolysis reaction needs to be conducted with the catalyst concentration being 0.3% and at 30-35°C. These conditions allow facile control of the process.

It is worth mentioning that for using this method it is required to rigorously maintain all parameters which influence the hydrolysis constant. These parameters are the concentration of the polyvinyl acetate solution, the amount of water in the polyvinyl acetate and methanol used for dilution, the catalyst concentration and the temperature.

Experimental determinations showed that for the types of PVA with a DH < 75% a great influence is represented by the way in which the catalyst is added into the system. For the hydrolysis in suspension of the polyvinyl acetate with the catalyst there are two ways of introducing the catalyst. The first way is represented by premixing the polyvinyl acetate solution with the catalyst followed by its dispersion in paraffin oil. The second method implies dispersing the polyvinyl acetate solution in the paraffin oil followed by the addition of the catalyst. For comparison, hydrolysis tests in a homogenous solution without mixing were also performed. The results obtained can be seen in Table 3.

Table 3

Results obtained for the alcoholysis of polyvinyl acetate in suspension and homogenous solution

Sample	Hydrolysis prodedure	Mode of introducing the catalyst	M of $\overline{\text{PAcV}}$	Reaction time (min)	Overall degree of hydrolysis, %	Hydrolysis degree after extraction, %	Amount of PVA oleosoluble	Blockiness
1	Suspension	Premixing (5 min)	160,000	21	72.13	80.10	15.9	0.540

2	Suspension	Introduced in reactor after dispersion	160,000	20	69.55	84.93	27.4	0.350
3	Suspension	Premixing (10 min)	80,000	60	73.60	74.51	1.9	0.590
4	Suspension	Introduced in reactor after dispersion	80,000	54	81.43	81.48	0.116	0.520
5	Homogenous solution	Premixing	80,000	25	74.45	76.05	3.3	0.710

Conditions: [NaOH] = 0.4% and T = 35ºC

The analysis of these results shows that the most pronounced character of block-copolymer of PVA obtained is reached when the catalyst is uniformly distributed in polyvinyl acetate through premixing. For alcoholysis degrees > 80% the block-copolymer character is becoming similar, with the catalyst being added through the wanted method. Also, the amount of oleosoluble PVA (DH<50%) from the final product is more reduced when the catalyst is introduced in the polyvinyl acetate solution before its dispersion in the paraffin oil. The big differences between the alcoholysis degrees and blockiness determined by the way the catalyst is introduced can be explained by the fact that when the catalyst is added over the lacquer dispersion in paraffin oil the catalyst enters between the lacquer pearls through certain positions. Because the reaction is stopped immediately after the gel phase, the catalyst does not have time to diffuse itself uniformly within the reaction mass. This is the reason why we recorded differences when it comes to alcoholysis degree and blockiness (block-copolymer character). For alcoholysis degrees >80% the catalyst diffuses within the entire mass and the results are extremely close which suggests that the way the catalyst is introduced is negligible.

Hence, for the types of PVA with DH<75% the way the catalyst is introduced plays an important role and can be ignored for DH>80%

3.2. Phytotoxicity of PVA tested on plants

The next goal of our work was to determine the phytotoxic characteristics of PVA on plants. Two PVA types were chosen for these assays and labelled ‘Batch 1’ (DH = 88-92%) and ‘Batch 2’ (DH = 98.5%). The tested plants were monocotyledonous species: wheat, corn, sunflower, rapeseed and tomatoes. Soil treatments were carried out before the plants sprouted and foliar when the plants had 3-4 leaves. For both types of PVA, three concentrations were tested: 1, 2 and 4%. For comparison, a variant treated with tap water was introduced into the experimental scheme. The results obtained are presented in tables 4 and 5.

Table 4

The action of polyvinyl alcohol - "batch I" - on plants

Ground treatment - percentage of emergence					
Variant	Wheat	Corn	Sunflower	Rapeseed	Tomatoes
A.p. I 1%	90±6.1	92±5.0	87±7.1	78±6.1	88±6.1
A.p. I 2%	87±5.0	95±2.0	85±4.0	75±5.1	92±5.0
A.p. I 4%	88±4.0	94±4.0	88±6.1	75±3.0	85±8.1
Control	87±4.0	96±1.0	87±2.1	76±3.0	89±4.0
Foliar treatment - phytotoxicity					
Variant	Wheat	Corn	Sunflower	Rapeseed	Tomatoes
A.p. I 1%	0	0	0	0	0
A.p. I 2%	0	0	0	0	0
A.p. I 4%	0	0	0	0	0
Control	0	0	0	0	0

Note: values are mean ± SD of 3 experiments in each group.

Table 5

The action of polyvinyl alcohol - "batch II" - on plants

Ground treatment - percentage of emergence					
Variant	Wheat	Corn	Sunflower	Rapeseed	Tomatoes
A.p. I 1%	90±4.1	95±3.0	82±6.0	77±6.0	83±7.1
A.p. I 2%	89±3.0	92±5.0	85±5.1	74±4.0	81±8.1
A.p. I 4%	88±4.0	95±2.0	83±5.0	72±1.1	84±6.1
Control	87±5.0	96±1.0	87±2.1	76±3.0	89±3.0
Foliar treatment - phytotoxicity					
Variant	Wheat	Corn	Sunflower	Rapeseed	Tomatoes
A.p. I 1%	0	0	0	0	0
A.p. I 2%	0	0	0	0	0
A.p. I 4%	0	0	0	0	0
Control	0	0	0	0	0

Note: values are mean ± SD of 3 experiments in each group.

The analysis of the results revealed no significant differences in emergence percentage between the control variant and the variants utilizing the two types of PVA. The germination percentage was not influenced by the presence of polyvinyl alcohol with different degrees of hydrolysis. The concentration of PVA (ranging 1% and 4%) did not appear to play a significant role in this regard. The analysis of the results shows that the types of PVA tested do not induce phytotoxicity in plants which was a promising result.

Alonso-Lopez et al. [13] found that the phytotoxicity of pure PVA was negligible under marine conditions. Kaur et al. [14] evaluated the phytotoxicity of

six PVA-based polymers use as media for seed germination of wheat and moong bean seedlings. The results suggested that all the prepared PVA-based hydrogels efficiently meet the moisture requirements for seed germination, without causing any toxicity.

At the same time, there are studies on the degradability of PVA that reveal its complete biodegradability in the ecological environment under the action of various intracellular and extracellular enzymes produced by bacterial strains [15].

3.3. PVA mixing with H_3BO_3

As PVA contains hydroxyl groups, they can participate in a series of analogous polymer reactions which are important in obtaining hydrogels. Such gels were obtained by the interaction of PVA with boric acid (Fig. 4).

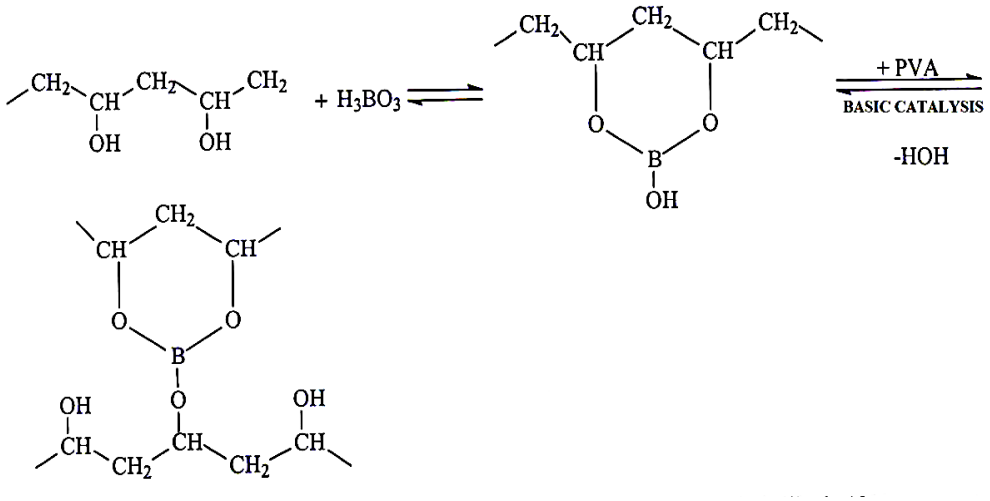

Fig. 4. Interaction of PVA with H_3BO_3

In Table 6, we present the molar ratios of PVA:boric acid and observations regarding the formed gel. It was found that the gel with the highest consistency has a pasty, pearly appearance and is insoluble in water. The products obtained from this reaction were used to obtain urea-containing monolithic granules as a fertiliser. It should be noted that in sample 5 the urea granules were introduced at the same time as boric acid due to the formation of a very consistent gel. The gels obtained together with the fertiliser were subjected to vacuum drying at 53°C after which they were ground to obtain solid granules in which urea is also introduced. In the presence of water, swelling of the PVA network and the hydrolysis of the ester groups will take place with the controlled release of urea. This will determine boron being released from the system and this process is crucial as B is an essential microelement as well as a fungicide.

Table 6

Influence of molar ratio polyvinyl alcohol / boric acid on gel consistency

No.	APV, moles US	H_3BO_3, moles	Molar ratio APV/ H_3BO_3	Remarks
1	3	$9.7 \cdot 10^{-2}$	31	very fluid gel, milky white colour
2	3	0.16	18.75	fluid colour gel, milky white
3	3	0.2	15	Semi-consistent gel, milky white colour
4	3	0.5	6	gel consisting, pearly colour
5	3	1	3	very consistent gel, pearly colour

Conditions: [APV] = 12%; pH = 6.5; T = 65°C; reaction time 3 hours

Lum et al. [16] also used boric acid with crosslinked PVA and starch as a matrix to prepare a slow-release urea fertilizer. They found out that matrix with higher swelling powers exhibited lower slow-release efficiency of urea. According to their study the optimum concentration of boric acid is 4%, reaction time is 4 h, and reaction temperature 90°C, respectively. At higher concentrations of boric acid, there is a greater likelihood of crosslinking with polyvinyl alcohol and starch as well.

3.4. PVA mixing with H_3PO_4 and H_3PO_3

The interaction of phosphoric and phosphorous acids with PVA is particularly interesting given that phosphorous is one of the basic macro-elements in chemical fertilizers (Fig. 5). Hence, the purpose of this experiment was the release of this important element.

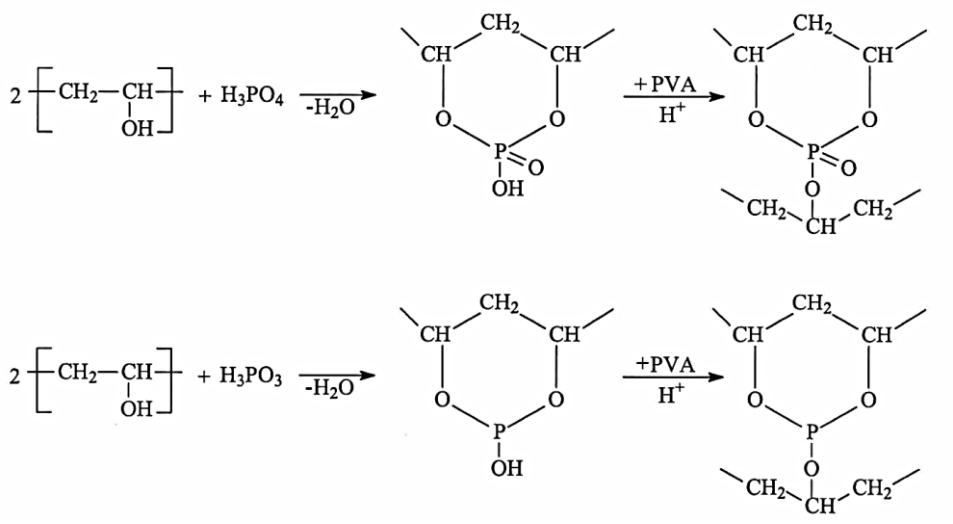

Fig. 5. Interaction of PVA with H_3PO_4 and H_3PO_3

During the research, the possibilities of making gels containing the three fertilizing macro-elements were studied: N, P and K. For this purpose, different amounts of urea were added to the gel obtained from the reaction of PVA with H_3PO_4. The pH remained unchanged, and the reaction was maintained as a gel. To change the pH value, and also to introduce the third macro-element, various amounts of KOH (as aqueous solution) were added to the gel mass containing urea. The reaction mass remained in gel form. Finally, using the KOH solution, the gel pH was brought to 6.5-7.5. These values are usually set for fertilizer solutions. The pH value was further corrected from 2 to 6.5-7.5 with the aqueous ammonia solution. The reaction was also maintained as a gel. A gel composition was thus made by adding calculated amounts of urea to the gel formed by the reaction of PVA with H_3PO_4, and finally the pH was brought to 6.5-7.5 with ammonia in aqueous solution.

In this way a fertilizer was obtained which contains only two macroelements: N and P. PVA reactions with H_3PO_3 were performed similarly to those between PVA and H_3PO_4. And in this case, gels containing the three macro-elements were obtained by similar working techniques: N, P, K, or only N and P.

Research on the interaction of phosphoric and phosphorous acids with PVA has also been reported by other authors [17-18]. Zhan et al. [18] synthesized PVA with H_3PO_4 through esterification. In this case, the obtained gel had the ability not only to absorb and hold water, but also to release phosphate fertilizer.

4. Conclusions

Polyvinyl alcohol with different degrees of hydrolysis has been synthesised and tested in terms of phytotoxicity in laboratory conditions to test its potential as an encapsulating agent for fertilisers. The results showed that this polymer presents no phytotoxicity and can be safely used in this scope. The potential for safely utilizing polyvinyl alcohol with various degrees of hydrolysis in agriculture, particularly as a surfactant in liquid compositions of foliar fertilizers, offers significant advantages. It creates a protective film on the plant's surface, thereby extending the duration of fertilizer effectiveness.

Additionally, all products obtained within this study can be considered eco-friendly: they are metabolized in plant and animal biological systems into non-toxic compounds, and they also degrade under environmental conditions. Studies performed on the biological activity in greenhouse conditions of the encapsulated urea granules showed that there are no phytotoxicity phenomena in the studied plants and the samples examined in greenhouse conditions stimulate the growth and development of wheat, corn, sunflower and tomato plants, with the effect being more obvious for tomatoes.

The gels obtained by the interaction of polyvinyl alcohol with boric acid, phosphoric acid and phosphorus have the ability to react with urea, KOH or NH_3, which leads to the production of compounds that can be used as generators of macro- and trace elements with boron plays a dual role: micronutrient and fungicide. Using these methods, we can obtain mixtures of fertilisers with gels which contain only nitrogen and phosphorous and can be used for certain cultures that require these conditions.

Our research also showed that polyvinyl alcohol has the potential for being used for encapsulation and further experiments need to be performed to allow a controlled release of the active substances over time.

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