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USE OF A PEARL MILL FOR THE PRODUCTION OF PLANT PROTECTION PRODUCTS

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Abstract:

Production of plant protection products is one of the most innovative branches of the chemical industry for agriculture requiring considerable financial outlays, which is associated with the needs of farmers. This is because the intention of farmers is to obtain higher yields and search for substances with properties independent of weather conditions and active for a longer time.

In the paper, an innovative technology for the production of suspensions, using a pearl mill, which are applied as a carrier of the active ingredient in plant protection products, has been presented. The pearl mill proposed in the research work, in which its parameters are presented, is used to prepare suspensions that are applied for the production of fungicides.

In the production of plant protection products it is important that the parameters of the substrates comply with the guidelines regulated by law. The tests were conducted in accordance with good practices according to the CIPAK method, using liquid chromatography.

Key words: suspension, pearl mill, plant protection products, liquid chromatography.

Streszczenie: Produkcja środków ochrony roślin to jeden z najbardziej innowacyjnych i wymagających wysokich nakładów finansowych działów przemysłu chemicznego dla rolnictwa. Zamiarem rolników jest uzyskiwanie wyższych plonów i poszukiwanie substancji i ich właściwości niezależnych od warunków pogodowych oraz działających w dłuższym czasie. W artykule zaproponowano innowacyjną technologię produkcji zawiesin wykorzystywanych jako nośnik substancji aktywnej w środkach ochrony roślin z wykorzystaniem młyna perełkowego. W pracy zaproponowano młyn perełkowy i przedstawiono jego parametry do przygotowania zawiesin, które wykorzystywane są do produkcji fungicydów. W produkcji środków ochrony roślin ważne jest, aby parametry substratów były zgodne z wytycznymi regulowanymi przez prawo. Do badań wykonano zgodnie z dobrymi praktykami według metody CIPAK wykorzystując chromatografię cieczową.

Słowa kluczowe: zawiesina, młyn perełkowy, środki ochrony roślin, formulacja, fungicydy, chromatografia cieczowa.

1. Introduction

The purpose of plant protection products is to protect species cultivated by humans against threatening factors. To summarize the problem of using plant protection products, it should be emphasized that it is impossible to drastically reduce or stop using plant protection products, because it will cause a sudden decrease in crop yields, as well as will reduce the quality of crops.

One of the basic barriers to entering the sector of production of plant protection products, which hinders producers from entering the market, includes high costs of starting production and producing PPP of good quality. The production of high-quality substances with appropriate physical and chemical properties is of great importance, all the more that manufacturers of plant protection products often store chemical substances that are used for further production.

Then, these substances are exposed to various external factors [Szwedziak et al., 2019].

Although the modern market meets producers' needs by offering ready production technologies and machines, these solutions are still expensive and do not fulfil the expectations of customers concerning the quality of offered products. Therefore, local producers of plant protection products who are developing, look for new production technologies to ensure the appropriate quality of plant protection products.

For this purpose, tests of the quality of plant protection products, which include: physical and chemical analyses (suspension stability, emulsion stability, wetting time, sieve residue, specific gravity, solution stability and degree of solubility), are conducted. The quality control is carried out in accordance with EU requirements in order to compare the quality parameters of plant protection products present on the market with the parameters declared by the producer in the registration process.

Therefore, the analysis of problems faced by producers of plant protection products inspires to further search for generally available, easy-to-use innovative production technology that allows for the production of new plant protection products and which meets the expectations of consumers and producers.

This issue constitutes a significant problem, and thus confirms the reasonableness of undertaking research work.

The paper presents the results of research using a new technology for the production of suspensions for the production of plant protection products using a pearl mill to ensure their appropriate quality. In the proposed new technology, a pearl mill instead of a ball mill was used to produce suspensions, and the obtained suspensions constitute a carrier for the active ingredient in plant protection products.

The areas of effectiveness of the new suspension production technology covered by the research work have not been recognized yet. No studies were conducted in this direction under the conditions of production applied in Poland. For the production of plant protection products, dispersing and homogenizing machines and devices are used, which allow for obtaining suspensions with specified parameters and for the formation of plant protection products.

It is difficult to compare different types of mills directly, and their performance is difficult to scale. It is worth paying attention to such parameters as the efficiency and energy consumption of various types of milling installations, because this information is necessary for a preliminary assessment of the mill suitability for specific applications [Napier-Munn, 1997]. The grinding process is very energy-consuming, and this issue is the subject of many scientific and industrial research conducted worldwide [Gawenda, 2009, 2010].

The most common devices used in the industry, whose operation is based on impact and abrasion, are drum mills, applied for fine grinding. The division into ball or rod mills is based on the type of applied grinding elements (grinding media) [Tumidajski et al., 2010]. In classic drum mills - ball or rod ones - the movement of the grinding media is caused by the rotation of the mill drum (cylindrical working chamber filled with grinding media) [Sidor, 2015].

The aim of the study is to develop a new technology for the production of suspensions for the production of plant protection products using a pearl mill, as well as to obtain raw materials of the best possible quality for the production of plant protection products and to examine the content of the active ingredient in the obtained formulation.

2. Materials and methods

The research object was a pearl mill operating in a continuous system in the production hall and a laboratory mill located in the chemical analysis laboratory (Fig. 1, 2).

A pearl mill used for the tests had the following parameters:

- Zirconia beads 0.8-1.0 mm, 150 kg
- Chemical composition: ZrO_2 - 83%; Ce O_2 - 17%
- Density: 6.20 gm / cm^3 (+/- 0.05)

- Bulk density: 3.75-4.05 kg / l
- Hardness according to Mohs scale: 9

Figure 3 shows a construction of the pearl mill used for the research. Figures 1 and 2 present a test stand that consists of a laboratory and production pearl mill.

A chemical substance constituting the active ingredient in the commercially available product from the metazachlor pesticide group was used for the tests. The Metachlor 500 S.C. pesticide was used for the tests.

For the formulations containing the metazachlor active ingredient, 25 series of tests were carried out in triplicate. The following quality tests were performed: content of the active ingredient - metazachlor g/l, density at 20°C g/l, pH. All tests were conducted in accordance with good laboratory practices based on international CIPAK methods (Collaborative International Pesticides Analytical Council). The methods are proposed by companies and are tested by laboratories all over the world. After evaluation of the results and adoption, the methods are published in the CIPAC Handbooks (see "CIPAC Methods" and "CIPAC Publication"). In all cases the content of the active ingredient was determined by liquid chromatography [IA/HPLC/10].

In order to determine the active ingredient, standard solutions of these substances and solutions of tested samples were prepared. The eluent, which was a 1% aqueous solution of H_3PO_4: acetonitrile (ACN) 50:50 was used as a solvent. The tests were carried out using an Agilent Technologies 1260 Infinity liquid chromatograph.

The content of active ingredient in the product was calculated using the following formula:

$$c[\%] = AT/AS \times MS/MT \times P \quad (1)$$

Wherein:

c - metazachlor content in the tested products [%]

AT - metazachlor surface area in the chromatogram of the tested solution

AS - metazachlor surface area in the chromatogram of the tested solution

MS - weighed amount of the standard, mg

P - standard purity [%]

The pH measurement was conducted for a 1% suspension of the product and directly in the product at 20°C by a potentiometric method [MT 75.3 Determination of pH values, CIPAC Handbook Volume J, p. 131,2000]. The relative density was determined using a DMN

4100 M density meter at ambient temperature [Test No. 109 Density of Liquids and Solids, OECD, p. 2, 2012] All tests were carried out in accordance with: The Regulation of the Minister of Healt of 22 May 2013 on Good Laboratory Practice and Performance of Studies in Compilance with the Principces of Good Laboratory Practice and Directive 2004/9/EC of 11 February 2004 amending Council Directive 87/18/EEC, Official Journal of the Europen Union.

3. Results and discussion

Based on the obtained results, charts regarding the content of the active ingredient, density and pH of the obtained formulation (Fig. 4-6) was prepared. All the obtained results are presented in a table (Tab. 1). The results are the means of triplicates.

Analysing the above results, it can be concluded that the product under the trade name of Metazachlor 500 S.C, whose active ingredient is metazachlor, shows stable parameters in terms of the content of the active ingredient, pH and density. The formulation produced in the pearl mill contains on average 509.1 g/l of the active ingredient. It is characterised by a pH of 6.7 and a density of 1.13 g/ml.

The obtained descriptive statistics are presented in Tables 2 and 3. The normality of distribution was investigated using the Shapiro-Wilk test for the content of the active ingredient in the product:

- Maksymus 040 S.C (Shapiro-Wilk test W=0.877; n= 24; p=0.007)

and for pH:

- Maksymus 040 S.C (Shapiro-Wilk test W=0.717; n= 24; p=0.05)

All results obtained in 25 tests are within limits. The only quantity characterized by a large dispersion of results resulting in the amount of variance (70.270 [g/l]) is the content of the active ingredient. Tests of selected quality parameters of the Metazachlor 500 S.C. product used in the study have already been carried out in previous research. It was found that such indicators as the content of the active ingredient, pH and density of the product fulfilled the assumptions within the accepted standards, while the mean metazachlor content differed depending on the production batch [Szwedziak, Tukiendorf et al., 2019].

Based on the determined confidence levels, it can be concluded that, despite the greater value of variance of the active ingredient content, it is within limits (Tab. 2). Therefore, the use of a pearl mill is considered to be reasonable efficient.

4. Conclusions

To summarize the analysis of the obtained results, it was noted that the tested formulations of plant protection products containing the metazachlor active ingredient, produced in a pearl mill, fulfil the required standards in terms of quality parameters. In the investigated product manufactured in a pearl mill, the recommended standards for the production of plant protection products were not exceeded. This is confirmed by the performed analysis of variance.

Based on the presented study results, the following conclusions were drawn:

1. The use of a pearl mill in which 0.8-1.0 mm zirconia beads having a density of 6.20 gm/cm^3 were applied, allowed for the production of plant protection products containing the metazachlor active ingredient with parameters not exceeding the limits.

The quality of the manufactured formulation complies with the standards.

2. The use of a pearl mill ensures, with a 99% confidence threshold, that the standards set for formulations of plant protection products containing the metazachlor active ingredient are achieved, which has been confirmed statistically.
3. The use of a pearl mill for the production of a formulation containing the metazachlor active ingredient allowed for obtaining appropriate characteristics parameters for the production of plant protection products in the form of fungicides that fall within the standards.

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Fig. 1 Test stand - a laboratory pearl mill

Fig. 2 Test stand - a pearl mill in the production hall

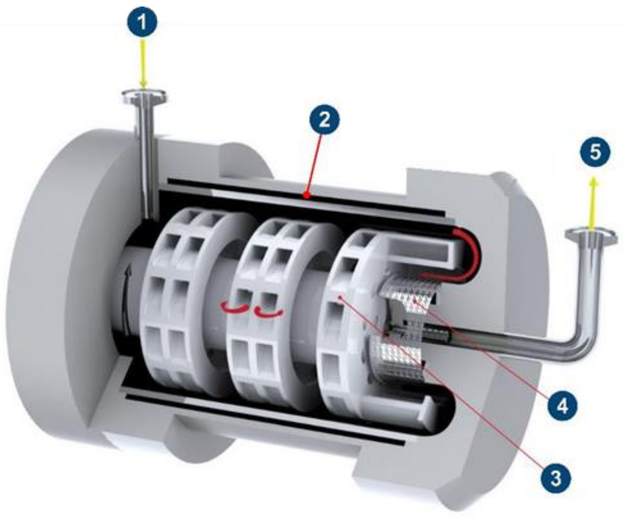


Fig. 3 Construction of a pearl mill: 1 - cooling milling container with easy-to-replace grinding cylinder made of hardened or stainless steel, silicon carbide, zirconia, 2- agitator disks made of stainless steel, hardened steel, zirconia, tungsten carbide, polyurethane, polyamide, 3 - product inlet, 4 - dynamic gap separator, 5 - product outlet, 6 - accelerators made of hardened chromium alloy, polyethylene oxide or zirconia

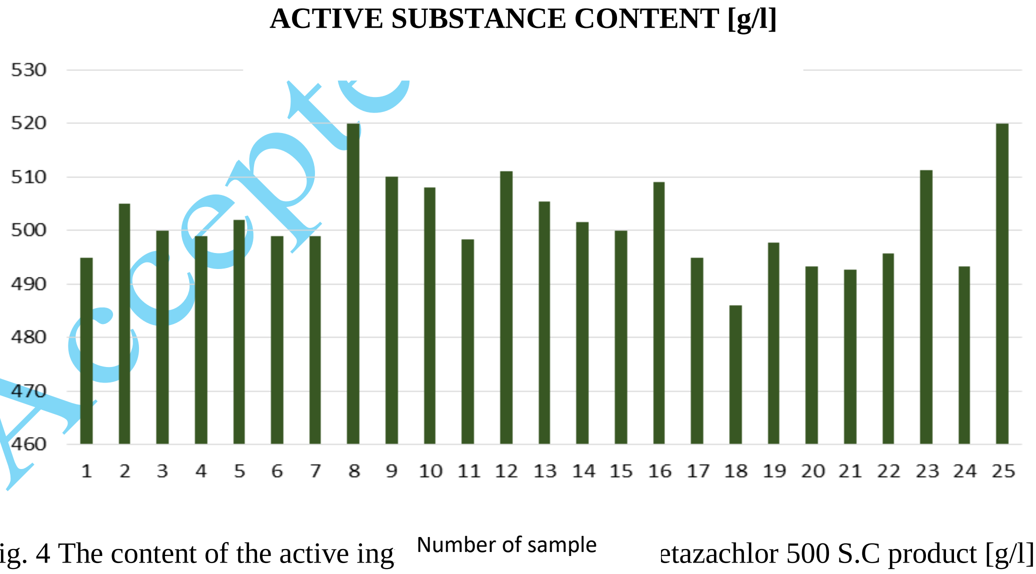
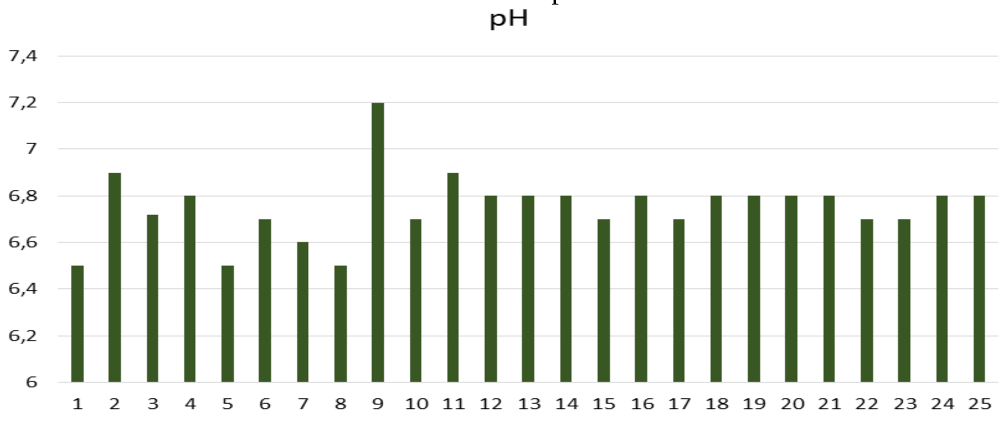


Fig. 4 The content of the active ing etazachlor 500 S.C product [g/l] in individual samples.



Number of sample

Fig. 5 Acidity pH of the tested pesticide containing the metazachlor active ingredient in individual samples.

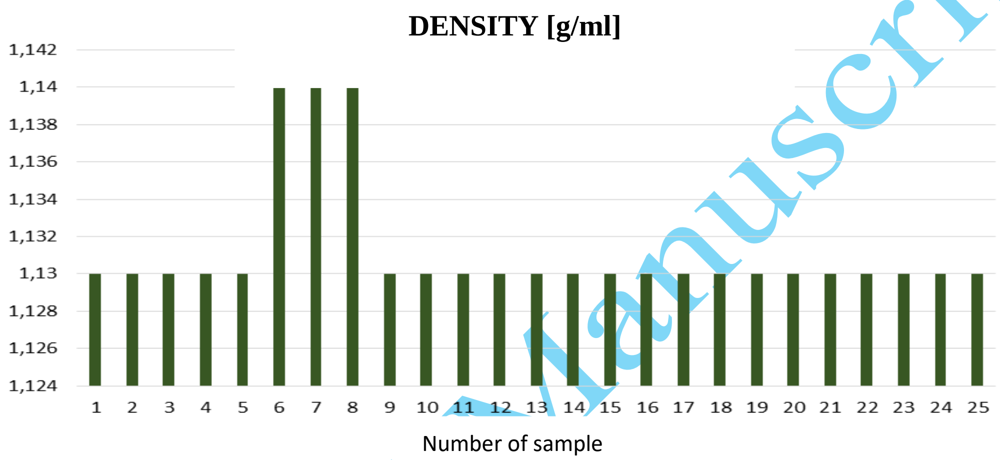


Fig. 6 Density [g/ml] of the tested pesticide containing the metazachlor active ingredient in individual samples.

Tab. 1 Summary of test results for a product containing the metazachlor active ingredient.

No. of sample	Content of the active ingredient [g/l]	Acidity pH	Density [g/ml]
1	495	6.5	1.13
2	505	6.9	1.13
3	500	6.72	1.13
4	499	6.8	1.13
5	502	6.5	1.13
6	499	6.7	1.14
7	499	6.6	1.14
8	520	6.5	1.14

9	510.1	7.2	1.13
10	508	6.7	1.13
11	498.4	6.9	1.13
12	511.1	6.8	1.13
13	505.4	6.8	1.13
14	501.6	6.8	1.13
15	500	6.7	1.13
16	509	6.8	1.13
17	495	6.7	1.13
18	486.1	6.8	1.13
19	497.8	6.8	1.13
20	493.2	6.8	1.13
21	492.6	6.8	1.13
22	495.8	6.7	1.13
23	511.3	6.7	1.13
24	493.2	6.8	1.13
25	520	6.8	1.13
Standard deviation	**± 8.38**	**± 0.14**	**± 0.00**
Variance	**70.270**	**0,021**	**0.00**

Tab. 2 A summary report of the obtained results on the basis of calculated statistics for the tested product containing the metazachlor active ingredient for individual confidence intervals.

Product	Acidity pH 95% confidence threshold	Acidity pH 99% confidence threshold	Density [g/ml] 95% confidence threshold	Density [g/ml] 99% confidence threshold	Content of the active ingredient [g/l] 95% confidence threshold	Content of the active ingredient [g/l] 99% confidence threshold
METAZACHLOR 500SC	6.69 – 6.81	6.67 – 6.83	1.130 – 1.133	1.129 – 1.133	498.44 – 505.36	497.21 – 506.59