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THE USE OF A BEAD MILL FOR THE PRODUCTION OF AGROCHEMICAL SUSPENSIONS

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Abstract

Plant protection products represent one of the most innovative branches of the agrochemical industry which requires considerable financial investment to adequately meet agricultural needs. The optimal agrochemicals should enable farmers to maximize yields, and their components should remain active over long periods of time regardless of weather conditions.

This article describes an innovative technology for the production of agrochemical suspensions in a bead mill. The suspension acts as a carrier of active ingredients. The parameters of the bead mill were presented, and the resulting suspensions were used in the production of fungicides.

The parameters of the substrates used in the production of agrochemicals have to comply with legal regulations. The present experiment involved liquid chromatography, and it was conducted in accordance with good practice, in line with CIPAC guidelines.

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Introduction

The main goal of plant protection products is to protect cultivated plant species against risk factors. Despite the fact that plant protection products often raise controversy, their application cannot be drastically reduced or discontinued because such measures would lead to a sudden decrease in the yield and quality of crops. High start-up costs and high product quality requirements are one of the main barriers to entering the agrochemicals market. The production of high-quality compounds and substrates with the required physical and chemical properties plays a very important role, especially in view of the fact that manufacturers often store chemical substances for further production. These substances are exposed to various external factors during storage (SZWEDZIAK et al. 2019).

Despite the fact that the modern market caters to the manufacturers' needs by offering dedicated production technologies and machines, these solutions are expensive and they do not always fulfil the consumers' expectations regarding the quality of the offered products. Therefore, in an attempt to increase their market share, local producers search for new production technologies that guarantee the high quality of plant protection products.

The quality of plant protection products is evaluated by analysing their physical and chemical parameters, including suspension stability, emulsion stability, wetting time, sieve residue, specific gravity, solution stability, and degree of solubility. The products are subjected to quality control in line with EU requirements to determine whether the quality parameters of the products present on the market are consistent with the parameters declared by the manufacturer in the registration process.

Therefore, an analysis of the problems faced by the manufacturers of plant protection products has prompted the authors to search for a generally available, easy-to-use and innovative technology that would facilitate the production of new agrochemicals that meet the expectations of both consumers and producers. Effective agrochemical production systems play an important role in industry and agriculture, and their continued development merits new research.

In the present experiment, a bead mill was used to guarantee the high quality of suspensions for the production of plant protection products. The proposed technology relies on a bead mill instead of a ball meal to obtain suspensions that act as carriers of active ingredients in plant protection products. The effectiveness of the new suspension production technology has not been investigated to date. The system has never been tested in an industrial setting in Poland. Agrochemical factories rely on dispersing and homogenizing machines to produce suspensions with the appropriate parameters for the production of plant protection products. Different types of mills cannot be compared directly, and their performance is difficult to scale. Parameters such as the efficiency and energy consumption of milling systems are critical for assessing the machines' suitability for specific applications (NAPIER-MUNN 1997). Grinding is a highly energy-consuming process, and it has been researched extensively in scientific and industrial literature around the world (GAWENDA 2009, 2010).

Fine grinding drum mills are the most widely used devices in the agrochemical industry. The material inside drum mills is ground by impact and abrasion. Industrial mills are classified into ball or rod depending on the type of grinding elements (grinding media) (TUMIDAJSKI et al. 2010). In traditional ball or rod drum mills, grinding media are set into motion by the rotation of the mill drum (cylindrical working chamber filled with grinding media) (SIDOR 2015).

The aim of this study was to develop a new technology for the production of suspensions for plant protection products in a bead mill, to obtain raw materials of the highest possible quality for the production of those agrochemicals, and to determine the content of the active ingredient in the obtained formulation.

Materials and Methods

The experiment involved a bead mill operating in a continuous system in a machine hall and a laboratory mill in a chemical laboratory (Figs. 1, 2).

The bead mill had the following parameters:

– Zirconia beads 0.8-1.0 mm, 150 kg;
– Chemical composition: ZrO_2 – 83%, CeO_2 – 17%;
– Density: 6.20 gm/cm^3 (+/-0.05);
– Bulk density: 3.75-4.05 kg/l;
– Hardness on the Mohs scale: 9.

The structure of the bead mill is shown in Figure 3. The test stand comprising a laboratory bead mill is presented in Figures 1 and 2.

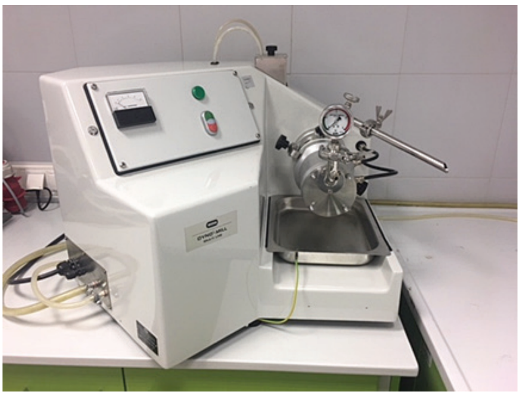

Fig. 1. Test stand – laboratory bead mill

Fig. 2. Test stand – bead mill in the machine hall

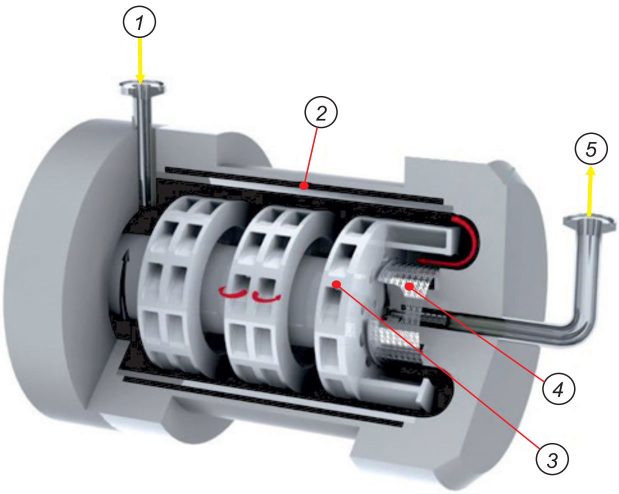

Fig. 3. Diagram of a bead mill: *1* – cooling milling container with easy-to-replace grinding cylinder made of hardened or stainless steel, silicon carbide and zirconia, *2* – agitator disks made of stainless steel, hardened steel, zirconia, tungsten carbide, polyurethane and polyamide, *3* – product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

The tested compound was metazachlor which is an active ingredient in commercially active pesticides. The Metazachlor 500 S.C. pesticide was used in the experiment.

The formulations containing metazachlor as the active ingredient were subjected to 25 series of tests that were carried out in triplicate. The tested products were subjected to qualitative analyses to determine the content of the active ingredient (metazachlor) in g/l, density at 20°C g/l, and pH. All tests were conducted in accordance with good laboratory practices based on the guidelines of the Collaborative International Pesticides Analytical Council (CIPAC). The methods developed in the industrial sector are rigorously tested in laboratories around the world. If approved, they are published in CIPAC Handbooks (refer to "CIPAC Methods" and "CIPAC Publication"). In this study, the content of the active (ingredient in the tested products was determined by liquid chromatography (IA/HPLC/10).

The content of the active ingredient was determined by preparing standard solutions of this compound and solutions of the tested samples. The eluent was 1% aqueous solution of H_3PO_4 : acetonitrile (50:50) which was used as solvent. The tests were carried out in the Agilent Technologies 1260 Infinity liquid chromatograph.

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

$$c = \mathrm{AT}/\mathrm{AS} \cdot \mathrm{MS}/\mathrm{MT} \cdot P \ [\%] \tag{1}$$

where:

c – metazachlor content of the tested products [%],
AT – surface area of metazachlor in the chromatogram of the tested solution,
AS – surface area of metazachlor in the chromatogram of the tested solution,
MS – weighed amount of the standard [mg],
P – standard purity [%].

pH was measured in 1% suspension of the product and directly in the product at 20°C by the potentiometric method (*MT 75.3 Determination of pH values* 2000, p. 131). Relative density was determined with the DMN 4100 M density meter at ambient temperature (*Test No. 109…* 2012, p. 2) All tests were carried out in accordance with the Regulation of the Minister of Health of 22 May 2013 on Good Laboratory Practice and the performance of laboratory analyses in compliance with the principles of Good Laboratory Practice and the provisions of Directive 2004/9/EC of 11 February 2004 amending Council Directive 87/18/EEC of 18 December 1986 (Official Journal of the European Union).

Results and Discussion

The results of the experiment were used to determine the content of the active ingredient, density and pH of the obtained formulation (Figs. 4-6). The results are presented in Table 1 as the means of triplicate measurements.

The results of the analysis indicate that Metazachlor 500 S.C is characterized by a stable content of the active ingredient (metazachlor) as well as stable pH and density. The formulation produced in the bead mill contained 509.1 g/l of the active ingredient on average. It had a pH of 6.7 and density of 1.13 g/ml.

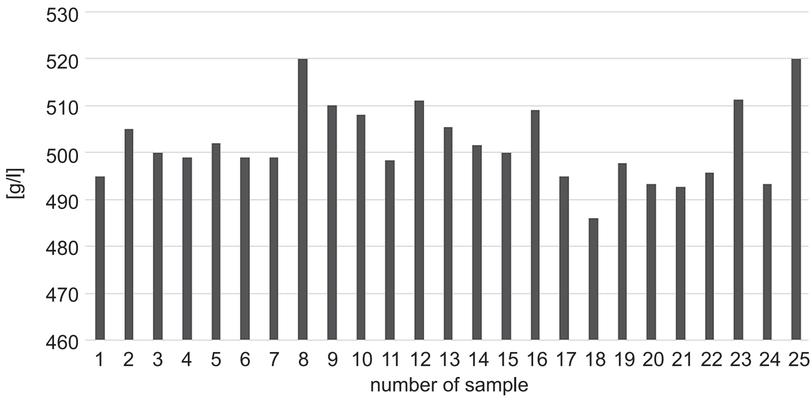

Fig. 4. The content of the active ingredient in individual samples of Metazachlor 500 S.C [g/l]

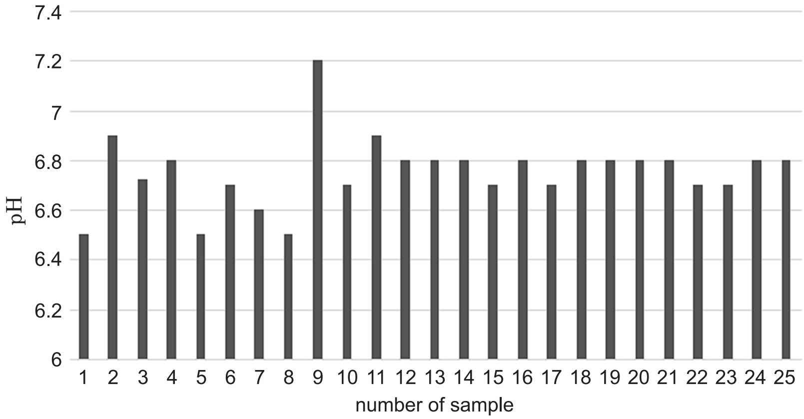

Fig. 5. pH in individual samples of the tested pesticide containing metazachlor as the active ingredient

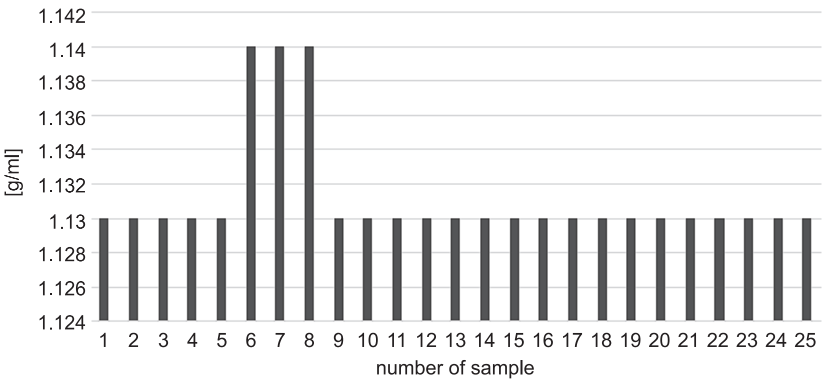

Fig. 6. Density [g/ml] of individual samples of the tested pesticide containing metazachlor as the active ingredient

Table 1

Results of the analysis of the tested product containing metazachlor as the active ingredient

No. of sample	Content of the active ingredient [g/l]	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

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

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).

Table 2

Descriptive statistics for the tested product containing the metazachlor active ingredient

Statistical quantity	METAZACHLOR 500SC		
	content of the substance	pH	density
Number of samples	25	25	25
Mean	501.90	6.75	1.130
Median	500.0	6.8	1.129
Minimum	486.1	6.5	1.13
Maximum	520.0	7.2	1.14
Lower quartile	495.8	6.7	1.13
Upper quartile	508.0	6.8	1.13
Variance	70.270	0.021	0.000
Standard deviation	8.38	0.14	0.00

Table 3

Results of a statistical analysis of the tested product containing metazachlor as the active ingredient for individual confidence intervals

Product	pH 95% confidence interval	pH 99% confidence interval	Density [g/ml] 95% confidence interval	Density [g/ml] 99% confidence interval	Content of the active ingredient [g/l] 95% confidence interval	Content of the active ingredient [g/l] 99% confidence interval
METAZA-CHLOR 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

The results obtained in all 25 tests were within the calculated limits. The content of the active ingredient (70.270 g/l) was the only parameter characterized by a greater scatter of values, which resulted in higher variance. Selected quality parameters of Metazachlor 500 S.C. had been previously analysed in our earlier study which revealed that the content of the active ingredient, pH and density were within the accepted standards, whereas the average metazachlor content varied across products from different batches (SZWEDZIAK et al. 2019).

The calculated confidence intervals indicate that despite higher variance, the content of the active ingredient was within the acceptable limits (Tab. 2). These results suggest that a bead mill is a reasonably efficient solution for manufacturing agrochemical suspensions.

Conclusions

The results of the present study indicate that the tested formulations of plant protection products containing metazachlor as the active ingredient, produced in a bead mill, fulfil the required quality standards. The recommended standards for the manufacture of plant protection products were not exceeded in the formulation produced in a bead mill. This observation was confirmed in an analysis of variance.

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

1. The use of a bead mill filled with zirconia beads (0.8-1.0 mm in size, density – 6.20 gm/cm^3) enabled the production of agrochemicals containing metazachlor as the active ingredient whose parameters were within the acceptable limits. The quality of the manufactured formulation was consistent with the relevant standards.

2. The use of a bead mill ensures that the formulations of plant protection products containing metazachlor as the active ingredient will conform to the applicable standards at a 99% confidence level. These results were confirmed statistically.

3. The use of a bead mill guarantees that metazachlor-based formulations will conform to the required standards in the production of fungicides where metazachlor is the active ingredient.

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