Research, Society and Development, v. 10, n. 10, e417101019007, 2021
(CC BY 4.0) | ISSN 2525-3409 | DOI: http://dx.doi.org/10.33448/rsd-v10i10.19007

Micronization of the pesticide chlorothalonil with different ball types

Micronização do pesticida clorotalonil em diferentes tipos de esferas

Micronización del plaguicida clorotalonil en diferentes tipos de esferas

Received: 08/03/2021 | Reviewed: 08/08/2021 | Accept: 08/11/2021 | Published: 08/15/2021

José de Freitas Rezende Neto
ORCID: https://orcid.org/0000-0002-5134-1716
Universidade de Uberaba, Brasil
E-mail: jofren28@gmail.com
Antônio Manoel Batista da Silva
ORCID: https://orcid.org/0000-0003-1082-7637
Universidade de Uberaba, Brasil
E-mail: tomanel.tamanel@gmail.com

Abstract

To achieve micronization in micro and nanoparticle agitator mills are often used. Also used are balls for the grinding step, which are: glass balls, zirconium silicate balls and zirconium oxide balls. A suspension with the active ingredient chlorothalonil at 700 g/L was prepared, being 2 liters for each type of balls. For this, a 1 liter grinding chamber with 0.7 liters of balls was used. The rotation of the mill was set at 2000 rpm and the rotation of the feed pump at 250 rpm. In addition, the temperature of the product, before grinding, was 26°C. The micronization with the glass balls during the process presented the lowest temperature 30°C, but with the lowest flow rate 0.09 L/min and the longest grinding time with 32 minutes. With zirconium silicate balls, the temperature reached was 38°C, the flow rate was 0.15 L/min and the grinding time was 20 minutes. The best result obtained was with the zirconium oxide balls, but with the highest temperature 42°C, but with the highest flow rate 0.19 L/min, and the shortest grinding time with 16 minutes, respectively. When determining the price of kWh consumed by the equipment when using the different types of balls, it was found that, with the zirconium oxide balls, a savings of up to 50% of the electricity consumption is achieved, compared to the use of glass balls. Comparing zirconium silicate balls with glass balls, a 37% savings in consumption is achieved. Finally, with zirconium oxide balls being compared to zirconium silicate, a 25% savings in electricity consumption was obtained.

Keywords: Micronization; Ball type; Microparticles and nanoparticles; Optimal particle size.

Resumo

Para alcançar a micronização em micro e nanopartículas moinhos agitadores são frequentemente utilizados. Também são utilizadas esferas para a etapa de moagem, que são: esferas de vidro, esferas de silicato de zircônio e esferas de óxido de zircônio. Uma suspenção com o ingrediente ativo clorotalonil em 700 g/L foi preparada, sendo 2 litros para cada tipo de esferas. Para isso, foi utilizada uma câmara de moagem de 1 litro, com 0,7 litros de esferas. A rotação do moinho foi setada em 2000 rpm e a rotação da bomba de alimentação a 250 rpm. Ademais, a temperatura do produto, antes da moagem, era de 26°C. A micronização com as esferas de vidro durante o processo, apresentou a menor temperatura 30°C, porém com a menor vazão 0,09 L/min e maior tempo de moagem com 32 minutos. Já com as esferas de silicato de zircônio, a temperatura atingida foi de 38°C, a vazão foi de 0,15 L/min e o tempo de moagem foi de 20 minutos. O melhor resultado obtido foi com as esferas de óxido de zircônio, porém com a maior temperatura 42°C, mas com a maior vazão 0,19 L/min, e o menor tempo de moagem com 16 minutos, respectivamente. Ao determinar o preço do kWh consumido pelo equipamento ao usar os diferentes tipos de esferas foi auferido que, com as esferas de óxido de zircônio, alcança-se uma economia de até 50% do consumo de energia elétrica, em comparação com uso das esferas de vidro. Já comparando as esferas de silicato de zircônio com as esferas de vidro consegue-se uma economia de 37% no consumo. Por fim, com as esferas de óxido de zircônio sendo confrontadas as de silicato de zircônio obteve-se uma economia de 25% no consumo de energia elétrica.

Palavras-chave: Micronização; Tipo de esferas; Micropartículas e nanopartículas; Tamanho de partícula ideal.

Resumen

Para lograr la micronización en micro y nanopartículas se utilizan a menudo molinos agitadores. También se utilizan esferas para la etapa de molienda, que son: esferas de vidrio, esferas de silicato de circonio y esferas de óxido de circonio. Se preparó una suspensión con el principio activo clorotalonil a 700 g/L, siendo de 2 litros para cada tipo de esferas. Para ello, se utilizó una cámara de molienda de 1 litro con 0,7 litros de bolas. La rotación del molino se fijó en 2000 rpm y la rotación de la bomba de alimentación en 250 rpm. Además, la temperatura del producto, antes de moler, era de 26°C. La micronización con las esferas de vidrio durante el proceso presentó la temperatura más baja 30°C, pero con el caudal más bajo 0.09 L/min y el tiempo de molienda más largo con 32 minutos. Con las esferas de silicato

de circonio, la temperatura alcanzada fue de 38°C, el caudal fue de 0,15 L/min y el tiempo de molienda fue de 20 minutos. El mejor resultado obtenido fue con las esferas de óxido de circonio, pero con la temperatura más alta 42°C, pero con el caudal más alto 0.19 L/min, y el menor tiempo de molienda con 16 minutos, respectivamente. Al determinar el precio de los kWh consumidos por los equipos al utilizar los diferentes tipos de esferas, se encontró que, con las esferas de óxido de circonio, se consigue un ahorro de hasta el 50% del consumo eléctrico, en comparación con el uso de esferas de vidrio. Comparando las esferas de silicato de circonio con las esferas de vidrio, se consigue un ahorro del 37% en el consumo. Finalmente, con la comparación de las esferas de óxido de circonio con el silicato de circonio, se obtuvo un ahorro del 25% en el consumo de electricidad.
Palabras clave: Micronización; Tipo de esferas; Micropartículas y nanopartículas; Tamaño de partícula óptimo.

1. Introduction

Currently, a large portion of industrialized products contain particles with a controlled size distribution in their constitution. Organic or inorganic particles and minerals are used in the formulation of concretes, polymeric composites, paints, medicines, agrochemicals and cosmetics. The desired particle size depends on the application but is usually found on the micrometric scale (Ohenoja, 2014).

In the case of pesticides, obtaining smaller and smaller particles has become crucial in the industrial process and fundamental for application because the smaller the product's particle, the better its absorption into plantations and crops. This, however, does lead to an increase in the production cost and increases the final pesticide price for the consumer (Nandi & Montedo, 2009).

Thus, the agrochemical industries are interested in these products on a nanometric scale and will continue to invest in RD&I (Research, Development and Innovation) as long as the production costs of grinding are competitive with the cost of imported material. Therefore, companies in the agrochemical sector increasingly use technological innovations to remain competitive in the market (Nandi & Montedo, 2009).

Grinding is the last stage of the fragmentation process and at this stage, particles are reduced by a combination of impact, shear stress, compression, abrasion and friction to a desired size (Rocha et al., 2020). Thus, in regard to grinding to achieve small particles, agitator mills are used (Multiesferas, 2017). In view of this, agitator mills (which are in constant technological evolution) are also used for the production of micro and nanoparticles in liquid pesticides dominated by concentrated suspension (Ullah et al., 2014).

For pesticides from the beginning of the 1980s until the year 2000, only glass balls were used. The process was slow and with a low flow, resulting in limited production. From the 2000s onwards, with the increase of agriculture in Brazil, the demand required a pesticide production far beyond what was previously necessary.

Given this need, new balls emerged on the market such as the zirconium silicate balls, which are widely used in agrochemical industries due to the gain in flow, productivity and the much higher added value when compared to the glass balls. Zirconium oxide balls also emerged. Even though they present an even more significant gain in production compared to other related balls, they are rarely used by companies in the sector because of their relatively high cost.

In this context, the objective of this article is to show the feasibility and micronization cost of the pesticide chlorothalonil (CHEBI, 2021.; Macbean, 2010), and to verify which ball, when used in the micronization process, results in better effectiveness in providing the achievement of the ideal particle size, in addition to presenting the lowest micronization cost and time, with flow gain in production and energy savings.

2. Methodology

This work was developed using practical experimentation as a basic tool, but based on theoretical aspects related to particle micronization. The type of research used can be considered quantitative, since the results are analyzed in terms of the

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size achieved for the ground particles, and qualitative, since the performances obtained from grinding, using the different ball types, are compared to each Other.

The chlorothalonil micronization process requires the execution of several subsequent stages (PUBCHEM, 2020). The process begins at the formulation stage, in which the active ingredient chlorothalonil is mixed with other raw materials so that it is dispersed into a vehicle, which in this case is water. After dispersing the active ingredient, the product is placed in a tank under agitation. This tank is fitted with a NEMO helical pump, in which the product transfer step from the tank to the ball mill takes place. This transfer is maintained with a constancy determined by the pump frequency of 250 rpm.

To start the micronization process, the agitator ball mill (ZETA model) from the German company NETZSCH *Group* was used (Netzsch, 2020), as shown in Figure 1.

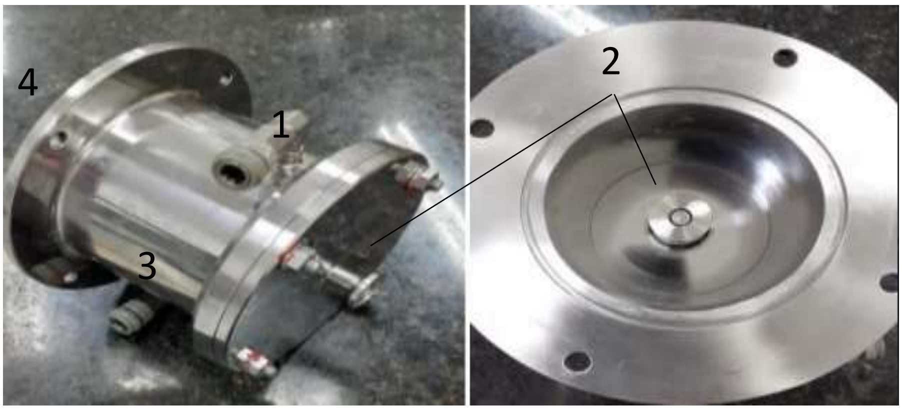
Figure 1. ZETA model of the NETZSCH agitator ball mill.

Source: Authors (2021).

The mill is composed of a control panel (1), a motor that drives the mill with a rotation speed adjustable by a frequency inverter, between 1000 and 4500 rpm. For the chlorothalonil micronization, a frequency of 2000 rpm was used (2), a 316 stainless steel grinding chamber with a volume capacity of 1 (one) liter (3), a pressure gauge for pressure control (the ideal pressure for micronization is from bar 3 to 5 (4), an agitator (in the case in question, set at an agitation frequency of approximately 600 rpm) (5), a jacketed vessel (6), and a NEMO helical pump (7).

Figure 2 illustrates the stainless steal grinding chamber (grade 316) with a volume capacity of 1 (one) liter.

Figure 2. Grinding chamber.



Source: Authors (2021).

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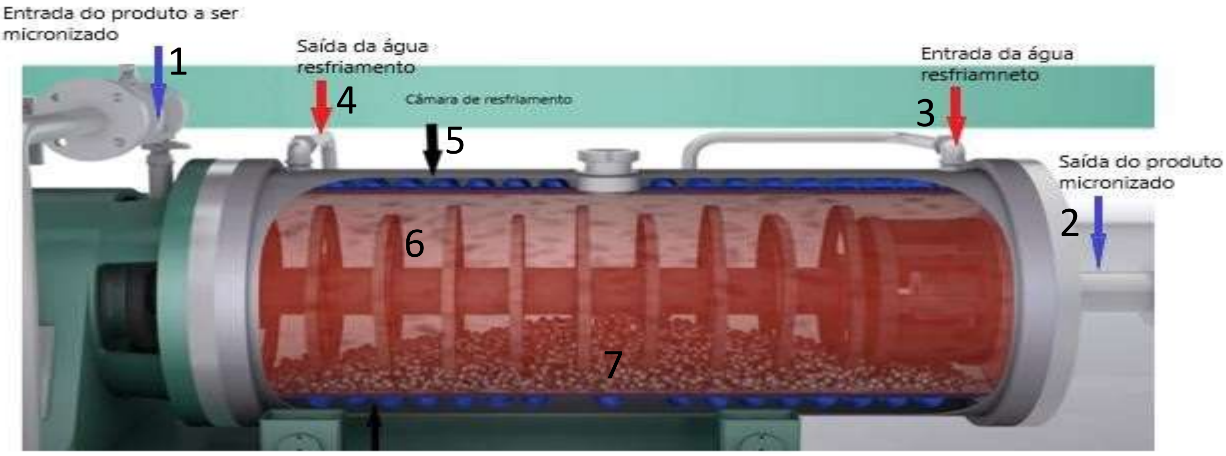
The grinding chamber, in which the cooling step is carried out, is lined with another layer of the same 316 grade stainless steel. The water enters the cooling chamber (1) at 10°C upon exiting the grinding chamber (2), from which the product exits already micronized, and where there is the highest temperature during the process. The water exit (3) is at the entry point, into the mill, for the product to be micronized (4).

Figure 3 shows the internal area of the horizontal mill, showing all its operational functionality.

Figure 3. Horizontal micronization chamber



Source: Netzsch (2021).

The entry point for the product to be micronized (1), micronized product exit (2), cooling water entry (3), cooling water exit (4), cooling chamber (5), pin rotor (6) and balls for micronization (7).

The cooling process is performed by a chiller, as shown in Figure 4, containing water and an antifreeze.

Figure 3. Horizontal micronization chamber.

Source: Authors (2021).

The industrial chiller works like a water cooler. As water passes through the chiller, its temperature is lowered.

For this work to be carried out, a 6.0 kg sample was prepared containing 700 g/L of chlorothalonil in an aqueous suspension with a density of 1.250 g/cm3. The samples were divided into three, being 2.0 kg to be micronized with the glass

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balls, 2.0 kg to be micronized with the zirconium silicate balls and 2.0 kg to be micronized with the zirconium oxide balls. In the grinding chamber, 70% of the chamber was filled with balls. A constant mill rotation was set at 2000 rpm and the feed pump rotation was set at 250 rpm. The balls were added inside the micronization chamber where the pin rotor is, as shown in Figure 5. Here the micronization tests were conducted to assess which one had the best cost-effectiveness during the process.

Figure 5. Micronization chamber with pin rotor

Source: Authors (2021).

The pin rotor is made of zirconium oxide (ZrO_2) enriched with yttrium oxide (Y_2O_3) and coated with high-resistance silicone (1).

The first test was carried out with the glass balls, the second test with the zirconium silicate balls and the third test with the zirconium oxide balls as shown in Figure 6.

Figure 6. Ball types used for micronization.

		
1st test Glass balls	2nd test Zirconium silicate balls	3rd tests Zirconium oxide balls

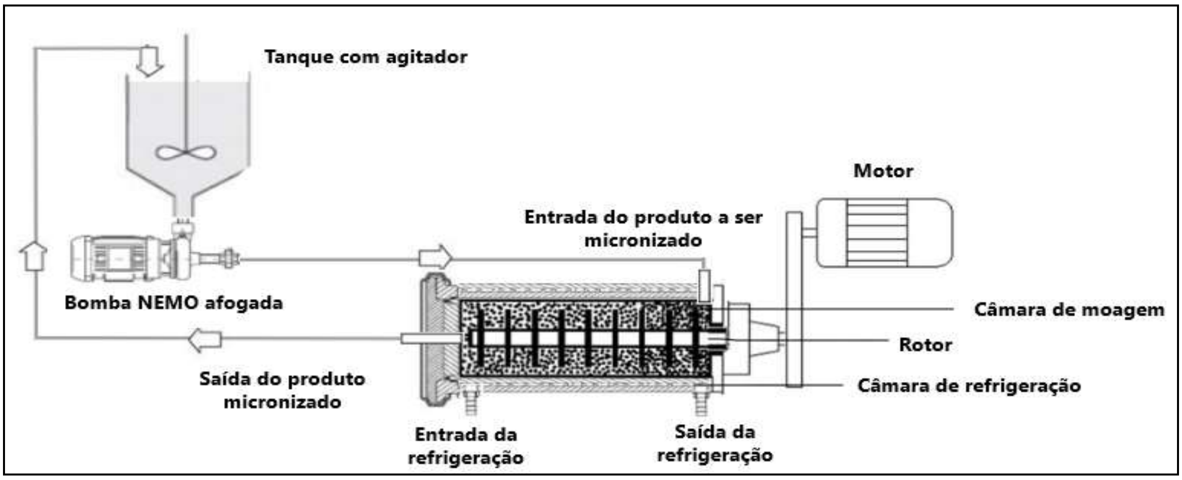
Source: Authors (2021).

The glass balls have in their chemical composition 72% silicon dioxide (SiO_2), 14% sodium sulfate (Na_2SO_4), 9% calcium oxide (CaO), 4% magnesium oxide (MgO) and 1% inert, having a micro hardness of 400 HV (ABNT NBRNM188, 1999), modulus of elasticity in 70 GPa (Callister, 2002), a specific density of 2.5 g/cm^3. The zirconium silicate balls, which in its chemical composition consist supposition of 60% zirconium dioxide (ZrO_2), 35% silicon dioxide (SiO_2) and 5% inert and have a micro hardness of 1000 HV (ABNT NBRNM188., 1999), modulus of elasticity in 100 GPa (Callister, 2002), the specific density of 4.1 g/cm^3. The zirconium oxide balls with yttria have in their chemical composition 94.5% zirconium dioxide (ZrO_2), 5.3% yttria oxide (Y_2O_3) and 0.2% inert, having a micro hardness of 1150 HV (ABNT NBRNM188., 1999), modulus of elasticity of 210 GPa (Callister, 2002), the specific density of 6.0 g/cm^3.

The operational diagram of the grinding system serves for vertical or horizontal mills in either a pilot plant or on an industrial scale. It shows, from the beginning of the operation to the end, where the product is micronized.

The process, as illustrated in Figure 7, starts in the agitator tank, into which the raw materials are added so that the product can be dispersed.

Figure 7. Operational diagram of the grinding process.



Source: Authors (2021).

By means of a NEMO helical pump, the product is transferred to the mill, thus starting the micronization step, which can be by recycling. The mill consists of a grinding chamber with a disc or pin rotor and a cooling chamber. The process is carried out in recycling until reaching the ideal particle size and this is monitored in time intervals so that the particles get symmetrical shapes. To determine the particle size of the material to be micronized, samples were collected and a study was carried out in the Cilas 1090 particle-size-analyzer equipment, illustrated in Figure 8.

Figure 8. Cilas 1090 particle-size-analyzer equipment.

Source: Authors (2021).

The Cilas 1090 particle-size-analyzer features multiple laser technology, which works by diffraction, offering measurement of a wide range of particle sizes. According to the manufacturer, it has a wet measuring range from 0.04 µm to 2500 µm. Equipment accuracy is greater than 3% and repeatability is greater than 1%. The equipment is calibrated annually by an authorized company. To obtain the results, software from the equipment itself was used, shown in Figure 9.

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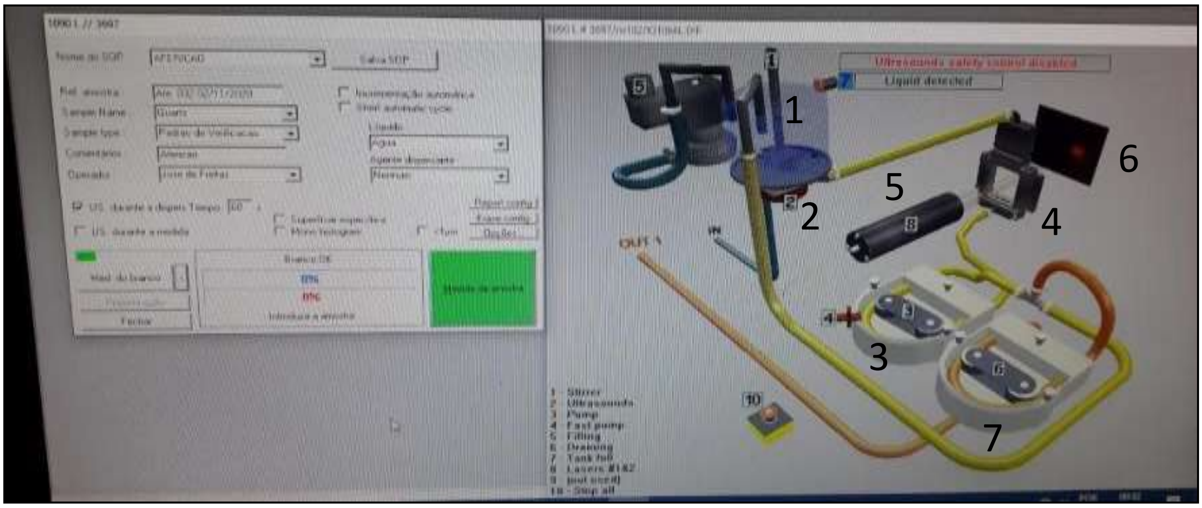
Figure 9. Cilas 1090 software equipment.



Source: Authors (2021).

The equipment has a reservior for the product's aqueous solution (1), an ultrasound for product dispersion (2), a peristaltic pump in the yellow pipe for fluid circulation (3), a crystal cell (4), a laser to capture the particles (5), box with several mirrors at different angles so that the laser can measure the entire area of the particle (6), and a peristaltic pump in the orange tube for fluid disposal.

3. Results and Discussion

To obtain the results, each process with the different ball types was monitored, covering the micronization time, the flow rate, the grinding temperature and the particle size achieved. A suspension with the active ingredient chlorothalonil 700 g/L was used. To acquire the active ingredient mass, equation 1 was used to achieve the mass balance.

$$m\,(i.a) = \frac{c\,(i.a)}{(p)}\,x\,100 \tag{1}$$

After performing the calculations, it was found that $m\,(i.a)$ = 714.29 g of the active ingredient chlorothalonil in 1 L of suspension. That is, to prepare one 1 L of a suspension at 700 g/L it is necessary to measure the mass 714.29 g of the active ingredient chlorothalonil. Using a digital densimeter, this suspension obtained a density of 1.250 g/cm^3.

Subsequently, the percentage of the active ingredient in the process is calculated, using equation 2.

$$\%\,(\,i.a) = \frac{\left(\frac{m\,(i.a)}{\rho}\,x\,100\right)}{1000} \tag{2}$$

After performing the calculations, the result found was % (i.a) = 57.143 %. Through these calculations, the percentages of the active ingredient chlorothalonil and the dispersing solution are found. Multiplying by the density, the mass is found in g to formulate 1 L of the suspension, according to the data shown in Table 1.

Table 1. Mass balance for 1 L of the suspension.

Components	% (m/m)	Density	Mass (g)
Chlorothalonil	57.143	1.250	714.29
Dispersing solution	42.857	1.250	535.71
	100.00		1.250

Source: Authors (2021).

For the production of 6.0 liters of the suspension, the mass balance in presented in Table 2.

Table 2. Mass balance for 6 L of the suspension.

Components	Mass (g)	Liters	Total mass (g)
Chlorothalonil	714.29	6.0	4285.74
Dispersing solution	535.71	6.0	3214.26
	1.250		7500.00

Source: Authors (2021).

In other words, to produce 6.0 liters of the pesticide Chlorothalonil 700 g/L, 4285.74 g of technical chlorothalonil and 3214.26 g of the dispersant solution, the masses were measured and placed in the agitator tank for total dispersion. The product was then divided into three parts: 2.0 liters for each micronization process, as shown in Table 3.

Table 3. Micronization process.

Test	Balls used	Litro
1	Glass	2.0
2	Zirconium Silicate	2.0
3	Zirconium Oxide	2.0

Source: Authors (2021).

The mill conditions for micronization are the same for the three types of balls. That is, there is a constant metric in the process, as shown in Table 4.

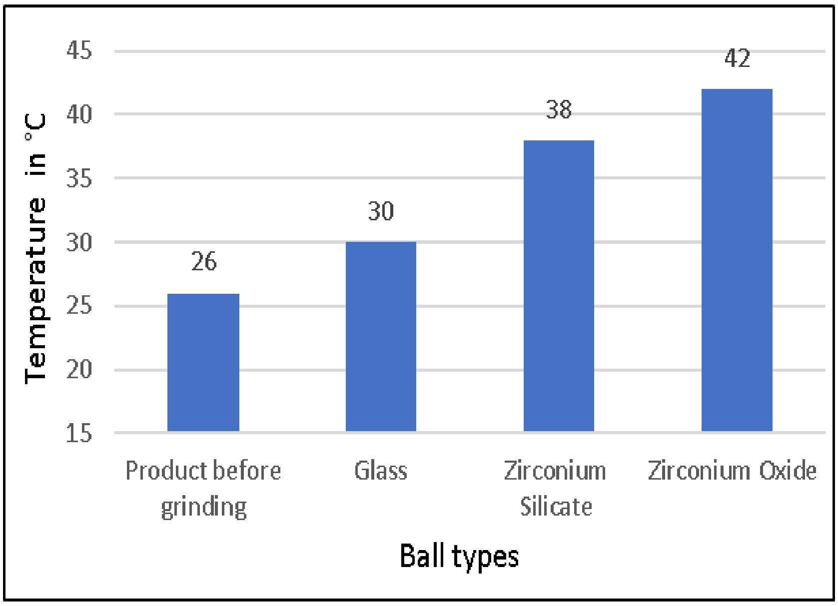
Table 4. Constant metric in the process.

	Balls	Grinding chamber (L)	Amount of balls (L)	Mill Rotation (rpm)	Feed pump (rpm)
Test 1	Glass	1.0	0.7	2000	250
Test 2	Zirconium Silicate	1.0	0.7	2000	250
Test 3	Zirconium Oxide	1.0	0.7	2000	250

Source: Authors (2021).

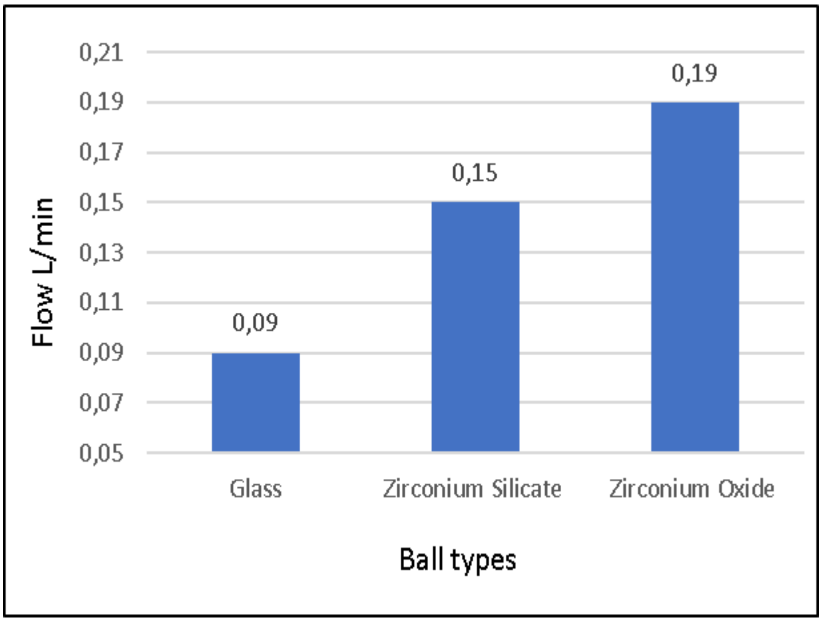
The process variables are temperature, flow rate and grinding time, though there are changes in the results obtained for each type of ball tested. The product has a temperature of 26°C before grinding. Micronization with glass balls obtained the lowest temperature during grinding at 30°C, the lowest flow rate at 0.09 L/min, and the longest grinding time at 32 minutes. With the use of zirconium silicate balls, the grinding temperature was 38°C, the flow rate was 0.15 L/min and the grinding time was 20 minutes. The most interesting result was obtained with the use of zirconium oxide balls. For this situation, the highest temperature was 42°C, the highest flow rate was 0.19 L/min and the lowest grinding time 16 minutes. All values for the different ball types are shown in Figures 10 11, 12.

Figure 10. Grinding temperature for the product before micronization and for the different ball types.



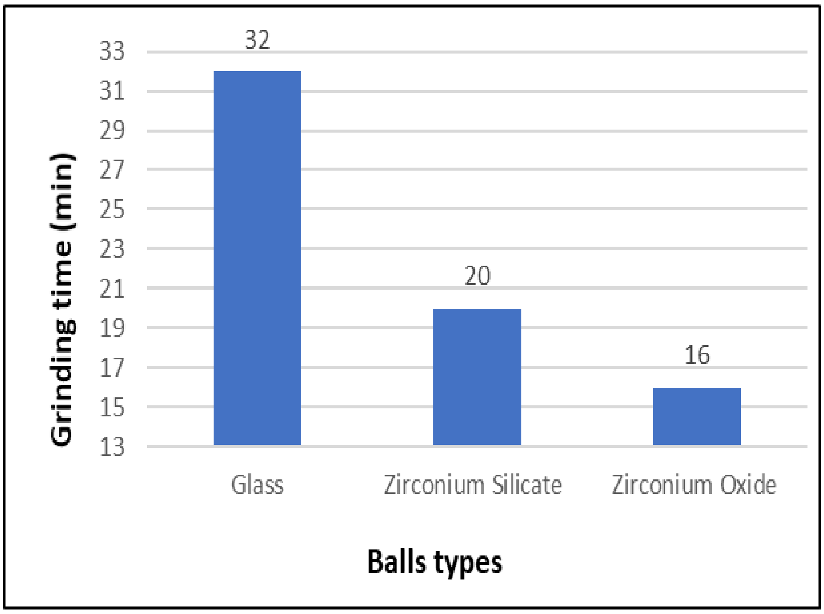
Source: Authors (2021).

Figure 11. Grinding flow rate for the different ball types.



Source: Authors (2021).

Figure 12. Grinding time for the different ball types.



Source: Authors (2021).

Before starting the grinding operation, it was necessary to analyze the pesticide particle size in order to have a product parameter to be introduced to the ball mill. To determine the particle size using the Cilas 1090 particle-size-analyzer equipment, samples of the concentrated suspension were collected and analyzed. It was measured according to the percentage of particle diameter shown in Table 5, according to the particle size distribution performed in the product before grinding, where *X* refers to the diameter (μm), Q3 to the cumulative value of the sample's mass fraction in (%), and q3 is the individual value of the sample's mass fraction in (%).

Table 5. Product particle size distribution and detailed particle size distribution - before grinding.

Measure	Result
D50	11,22 µm
D90	36,62 µm
D95	44,28 µm

X (μm)	0,50	1,50	2,00	3,00	4,00	5,00	7,00	9,00	11,00	15,00
Q3 (%)	2,79	8,73	11,45	16,31	20,58	24,65	32,79	41,14	49,16	62,14
q3 (%)	2,79	5,94	2,72	4,86	4,27	4,07	8,14	8,35	8,02	12,98
X (μm)	20,00	25,00	30,00	40,00	45,00	50,00	75,00	100,00	300,00	500,00
Q3 (%)	72,46	79,02	84,14	92,47	95,37	97,42	100,00	0,00	0,00	0,00
q3 (%)	10,32	6,56	5,12	8,33	2,90	2,05	2,58	0,00	0,00	0,00

Source: Authors (2021).

The sum of *Q3* is 100%, but in the first column *q3* is 2.79 and *X* equals 0.5. This means that 2.79% of the particles have a maximum size of 0.50 µm and the maximum diameter found was 75 μm, which refers to the *q3* of 2.58% of the particles. The diameter D90 has a value of 36.62 μm, that is, 90% of the particles have 36.62 μm. From this result, the grinding process for each ball type begins (Massarani. G, 2001).

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Considering that the ideal particle size is less than 5 *µm*, described as X (*µm*), it is verified that the sum of the *Q3* percentage distribution (%) of each ball type presents the approximate results shown in Tables 6, 7 and 8.

Table 6. Product particle size distribution and detailed particle size distribution - glass balls.

Measure	Result
D50	1,78 µm
D90	4,73 µm
D95	5,93 µm

X (*µm*)	0,50	1,50	2,00	3,00	4,00	5,00	7,00	9,00	11,00	15,00
Q3 (%)	17,93	43,58	54,90	73,31	84,90	91,46	97,37	99,36	99,93	100,00
q3 (%)	17,93	25,65	11,32	18,41	11,59	6,56	5,91	1,99	0,57	0,07

Source: Authors (2021).

Table 7. Product particle size distribution and detailed particle size distribution – zirconium silicate balls.

Measure	Result
D50	1,90 µm
D90	4,52 µm
D95	5,38 µm

X (*µm*)	0,50	1,50	2,00	3,00	4,00	5,00	7,00	9,00	11,00	15,00
Q3 (%)	11,67	39,87	52,19	72,06	85,46	93,14	98,98	99,94	100,00	100,00
q3 (%)	11,67	28,20	12,32	19,87	13,40	7,68	5,84	0,96	0,06	0,00

Source: Authors (2021).

Table 8. Product particle size distribution and detailed particle size distribution – zirconium oxide balls.

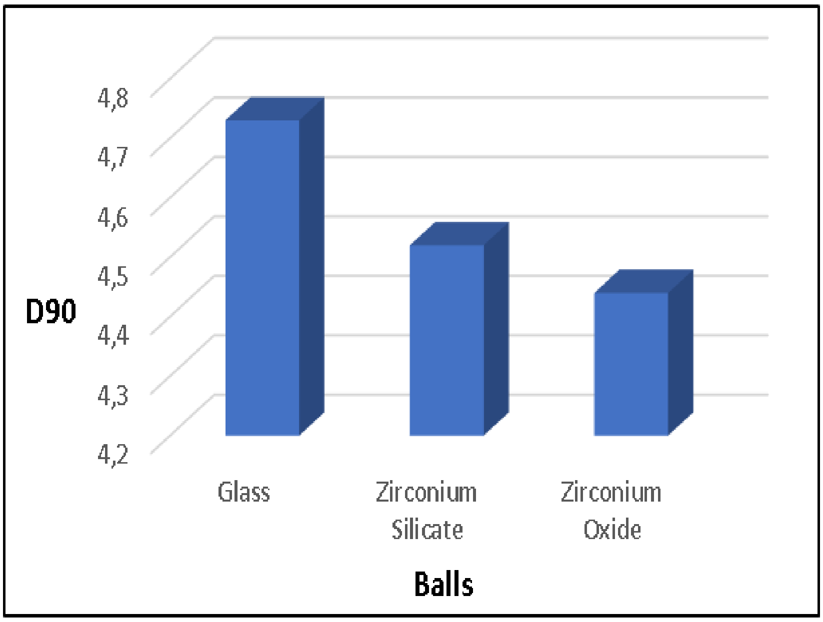
Measure	Result
D50	1,85 µm
D90	4,44 µm
D95	5,29 µm

X (*µm*)	0,50	1,50	2,00	3,00	4,00	5,00	7,00	9,00	11,00	15,00
Q3 (%)	12,51	41,34	53,58	73,11	86,18	93,61	99,11	99,95	100,00	100,00
q3 (%)	12,51	28,83	12,24	19,53	13,07	7,43	5,50	0,84	0,05	0,00

Source: Authors (2021).

As illustrated in Figure 13, the D90 results for each ball type are expressed.

Figure 13. D90 for each ball type.

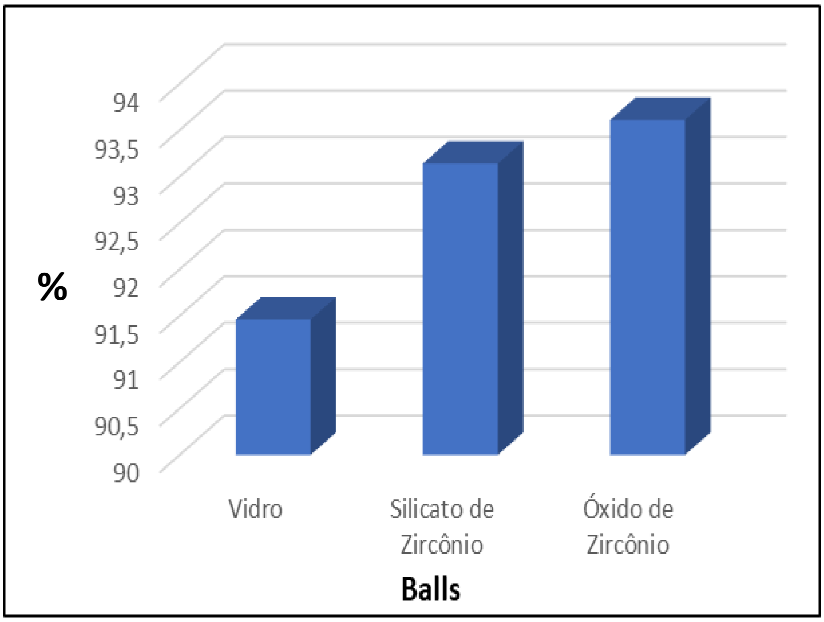


Source: Authors (2021).

The D90 of the glass balls obtained a result of 4.73 μm and the zirconium silicate balls a result of 4.52 μm. The best result of 4.44 μm, however, was obtained with the zirconium oxide balls.

The data presented in Figure 14 show the sum of Q3 (%) as a function of the ideal particle size X (μm) of 5.00. The sum of grinding with glass results in a value equal to 91.46% and the sum of grinding with zirconium oxide a value equal to 93.14%. Finally, with the best performance, the zirconium oxide had 93.61% of micronized particles smaller than 5.00 µm.

Figure 14. Sum of the *Q3* percentage distribution (%) as a function of the ideal particle size of 5 µm.



Source: Authors (2021).

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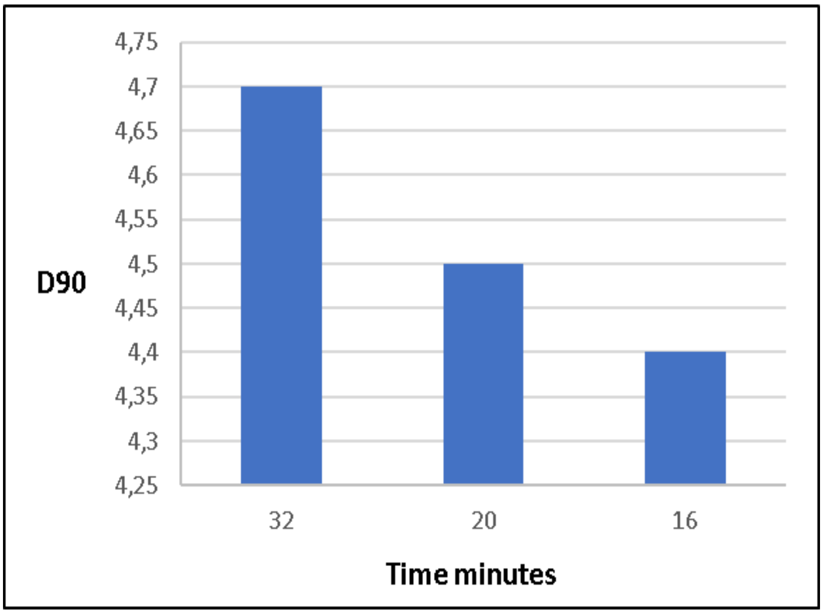
Figure 15 shows the comparison of D90 to the grinding times.

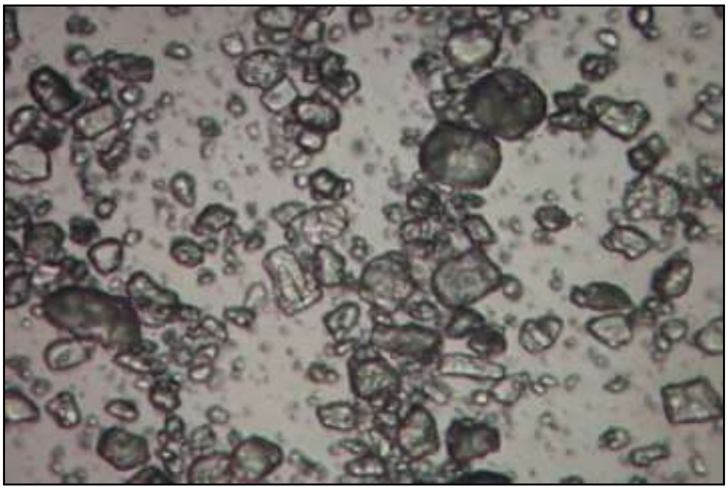
Figure 15. D90 and grinding times.



Source: Authors (2021).

In the image in Figure 16, obtained by electron microscopy at a 40X magnification of the lens and in an aqueous solution with 1% of the product, it is possible to observe the size the particles before grinding.

Figure 16. Chlorothalonil particles before grinding. 40X magnification.



Source: Authors (2021).

In the image in Figure 17, also obtained by electron microscopy with a 40X magnification of the lens and in an aqueous solution with 1% of the product, it is possible to observe the homogeneity of the particles obtained after the micronization process. Here, samples of the different ball types have similar particle shapes.

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Figure 17. Chlorothalonil particles after grinding with the different ball types. 40X magnification.

Esferas de Vidro **D90 =** 4,7µm

Esferas de Silicato de Zircônio **D90 =** 4,5µm

Esferas de Óxido de Zircônio **D90 =** 4,4µm

Source: Authors (2021).

As for the cost of the various ball types used in the micronization process of the pesticide Chlorothalonil 700 g/L, it is necessary to consider the respective prices per kilogram, as shown in table 13. The price difference between the glass balls and the zirconium silicate balls is 37.5%, between the zirconium silicate balls and the zirconium oxide balls 81.82% and between the glass balls and zirconium oxide balls 150%, which is the greatest variation.

For the micronization process, 70% of the mill chamber capacity was used for the balls. Considering the density shown in Table 1, the quantity in kilograms and the price per kilogram were obtained for each ball type. The cost was obtained in Reais R$ for each ball type used in its respective volume of 0.7 L as listed in Table 9.

Table 9. Price per kg of balls.

Balls	kg – R$
Glass	92,80
Zirconium Silicate	127,60
Zirconium Oxide	232,00

Source: Authors (2021).

Table 10. Ball cost for 70% of grinding chamber volume.

Balls	Density kg/l	Vol. L	Amount kg	Cost R$
Glass	1.500	0.7	1.050	97.44
Zirconium Silicate	2.700	0.7	1.890	241.16
Zirconium Oxide	3.800	0.7	2.660	617.12

Source: Authors (2021).

Regarding the cost, the prices of the balls were R$ 92.80 for glass, R$ 127.60 for zirconium silicate and R$ 232.00 for zirconium oxide. This fact must be seen as an investment, and not as an expense, as the balls are reusable. Only the glass balls wear out due to friction, having 4% loss for every 100 kg. The zirconium silicate and zirconium oxide balls experience no loss as these materials are much more resistant to friction.

Regarding the electrical energy consumption, the feed pump or NEMO pump has a consumption of 1.47 kWh, the micronizing ball mill has a consumption of 2.94 kWh and the chiller, a consumption of 15.44 kWh. The sum results in total consumption equal to 19.85 kWh as shown in Table 11.

Table 11. kWh of the electrical equipment.

Electric Equipment	kWh
NEMO Pump	1,47
Ball Mill	2,94
Chiller	15,44
Total	19,85

Source: Authors (2021).

Converting kWh sum using the data shown in Table 11, with the grinding time as shown in Figure 39, and taking into account the average kWh cost being equal to R$ 0.80, the final cost was found in R$ according to Table 12 for each ball type used in the micronization process.

Table 12. Average kWh with grinding time.

Balls	Grinding time "min"	kWh	kWh R$	Cost in R$ /Balls
Glass	32	10.587	0.8	8.47
Zirconium Silicate	20	6.617	0.8	5.29
Zirconium Oxide	16	5.293	0.8	4.23

Source: Authors (2021).

Analyzing these results, it can be observed that if zirconium silicate balls are used for grinding, instead of glass spheres, a reduction of 37.54% in energy consumption is obtained. Furthermore, if zirconium oxide balls are used for grinding instead of the glass, even better performance is obtained with a reduction of 50.06% in electrical energy consumption.

4. Conclusion

The micronization process using ball mills and each of the three ball types: glass, zirconium silicate and zirconium oxide, ensures that the ideal particle size is obtained for the pesticide Chlorothalonil 700 g/L, with more than ninety percent of its particles smaller than 5.0 µm.

Considering the flow rate, grinding time and energy consumption, which are the main variables that make agrochemical production more expensive, it can be inferred that even though using zirconium oxide balls requires a greater investment due to their acquisition cost, this high cost pays off as this micronization process doubles the flow rate, reduces grinding time by half and saves of up to fifty percent in energy consumption when compared to using glass balls.

Correlating the use of zirconium oxide with that of zirconium silicate, it is can also be inferred that a good performance is obtained with this micronization process, since there is a twenty-seven percent increase in the flow rate, a twenty-five percent reduction in grinding time and an equal savings percentage in energy consumption.

Suggestions for future research and work and this process of micronization in different types of balls applies not only in agricultural pesticides, but also in the pharmaceutical and veterinary field in the case of medicines in concentrated suspensions SC, and also in the food industry in the micronization of cocoa for chocolate production, the smaller the particle size of the tastiest and more expensive cocoa it is.

Acknowledgments

The authors sincerely thank the Minas Gerais State Agency for Research and Development (FAPEMIG) and the University of Uberaba (UNIUBE) for their support during the preparation of this work.

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