ATLANTIS PRESS
Advances in Engineering Research, volume 125
International Conference on Material Science, Energy and Environmental Engineering (MSEEE 2017)

Research of Dissolution Crystallization Process of Chlorantraniliprole

Lina Yang [a] Hui Chen [b,*] and Baochen Liang [c]

School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, China.

[a]lnyangtj@163.com,[b]Correspondingauthor:chenhui_410@163.com,[c]bcliangtj@163.com

Keywords: Chlorantraniliprole, crystallization process, purity, crystal form.

Abstract. Chlorantraniliprole is anthranilic diamides insecticide, in order to solve the chlorantraniliprole industrial crystallization problem, such as the purity of products is not high, the crystal type is not good enough, this paper proposes a new kind of chlorantraniliprole crystallization process, The influences of the parameters such as dissolution temperature, dissolution rate of dissolution agent , dissolution agent concentration and stirring speed on the purity, recovery rate and crystal shape of the sample were investigated .The experimental results show that the crystal products with high purity and better percent recovery and better crystal shape can be obtained under the optimized crystallization process.

1. Introduction

Chlorantraniliprole is a kind of anthranilic diamides insecticide. Chemical name: 3 - bromine - N - [4 a chlorine - 2 - methyl - 6 - [(methyl amino formyl) phenyl] - 1- (3 - chloro pyridine - 2 - base) - 1 - h a pyrazole - 5 - formamide. Chlorantraniliprole is adjacent formyl amine benzamide kind of broad spectrum insecticide, it has strong insecticidal activity, low toxicity and good environment to mammal's compatibility etc., suitable for a wide range of promotion [1]. In order to solve the problems of purity is not high, the crystal shape is not good enough in industrial crystallization of chlorantraniliprole, dilution crystallization process of chlorantraniliprole has been optimized.This paper proposes a new chlorantraniliprole solvent crystallization process,in this process ,the two methyl formamide is solvent, methanol solution as the dissolution agent for separation and purification chlorantraniliprole, and through analysis the influence on product purity, crystal type, yield under different process conditions to select the best process parameters, lay a foundation for process production.

2. Experiment

2.1 Reagents and Instruments.

Reagent: standard sample of chlorantraniliprole, purity 99%, chlorantraniliprole crude, two methyl formamide, analytical pure methanol, chromatographic pure methanol, deionized water

Apparatus: laser power meter, constant temperature magnetic stirrer, constant temperature crystallizer, low temperature constant temperature tank, peristaltic pump, analytical balance, high performance liquid chromatograph, scanning electron microscope

2.2 Experimental Operation

Under the condition of 20ºC, the crude chlorantraniliprole was dissolved in dimethyl formamide solvent in a 250ml crystallizer, and then added methanol as the dissolution agent to obtain crystal product which grew 24 hours after dissolution agent finished. Then, added the methanol solution to wash this crystal after filtrated and dried it in a vacuum drying oven in 55ºC.The experiment examined the effects of crystallization temperature, the leaching agent dropping rate, concentration of dissolution agent, stirring speed on chlorantraniliprole crystallization product purity, yield and the crystal type, and optimizing the process conditions of chlorantraniliprole crystallization . In the experiment, the product purity was determined by HPLC [2]. Scanning electron microscope was used to analyze the product.

3. Experimental Results

3.1 Effect of Crystallization Temperature

As shown on fig.1, the effects of crystallization temperature (0℃, 10℃, 20℃, 30℃ and 40℃) on the yield and purity of the product were investigated under the condition of the same dissolution agent, flow rate, dissolution concentration and agitation rate. With the increase of crystallization temperature, the percent recovery of crystalline products decreased, especially at 20℃. Compared with other crystallization temperature, the purest product can be obtained at 20℃. So, the optimum crystallization temperature can be considered as 20 ℃.

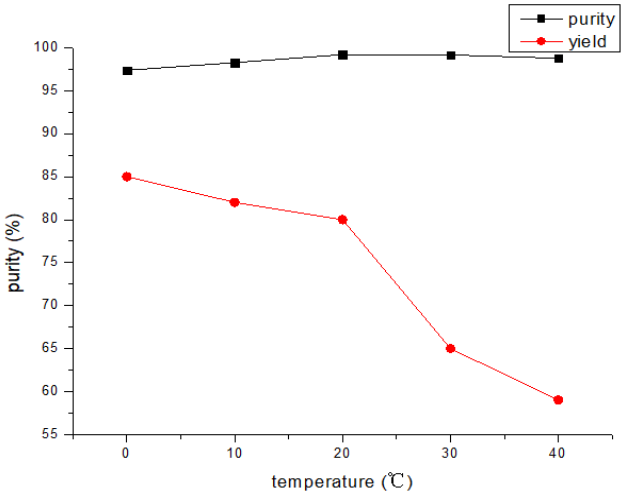

Fig. 1 Effect of crystallization temperature on the yield and purity of the product

3.2 Effect of Flow Rate of Dissolution Agent

As shown on fig. 2, the effects of constant and variable dropping speed of dissolution agent have been investigated under the same crystallization temperature, the concentration of dissolution agent and stirring speed. For dilution crystallization, when the crystal just appeared, supersaturation is generally higher. So, the dissolution agent flow rate should be controlled at a low level. With the emergence of the crystal, the supersaturation of the system is also increasing, so the dissolution agent flow rate should be increased gradually. For the constant dropping speed, the dissolving agent flow rate is too fast when the crystallization first appeared. At this time, the supersaturation is too high and easy to produce fine crystals [3]. Considering the product yield and in order to save time, the variable dropping speed of dissolution agent should be used.

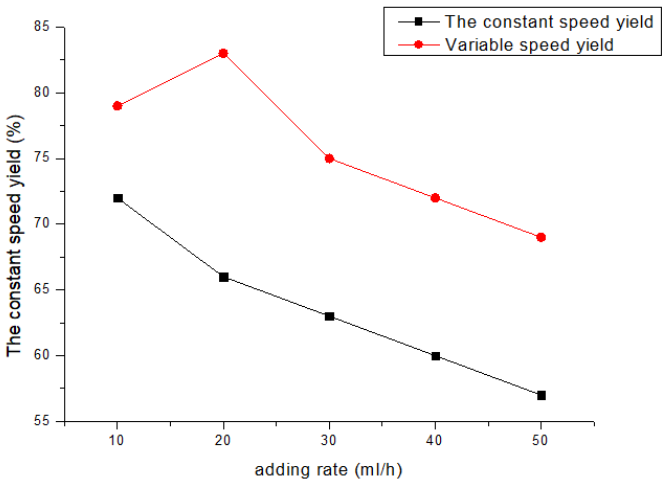

Fig. 2 Effect of flow rate of dissolution agent on recovery rate of product

3.3 Effect of Methanol Solution Concentration

The effects of the concentration of methanol solution on the purity and yield of the product were investigated under the same crystallization temperature, dissolution rate, stirring rate and agitation

intensity [4]. The result is shown in Figure 3. When the dissolution agent flow rate of acceleration is constant, with the increase of water dissolving agent, the faster of the supersaturation crystallization system is generated, the recovery rate increased, and the purity of the product also changed. Considering these factors, the concentration of the methanol solution at 0.8-0.9 can be regarded as the optimal crystallization condition.

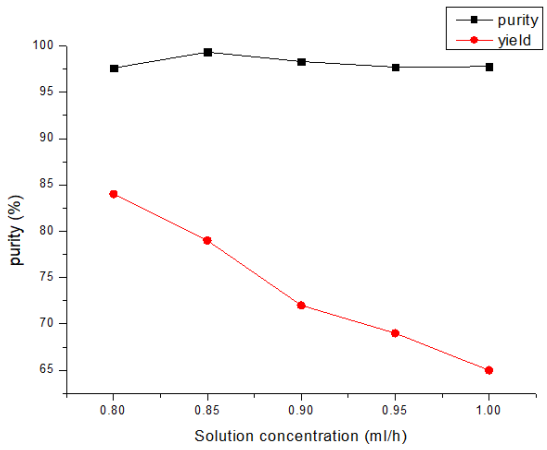

Fig. 3 Effect of concentration of methanol solution on purity and recovery rate of product

3.4 Effect of Agitation Speed

The effects of different mixing speed on the purity and recovery of the product were investigated under the same crystallization temperature, dissolution rate, and concentration of the dissolution agent. The result is shown in Figure 4. The purity of crystalline product increased with the increase of stirring speed, and reached the maximum at 90rpm, but the recovery rate changed a little. After 90rpm, the recovery rate decreased obviously. When the stirring speed is relatively low, the molecular force in the solution is light and the mass transfer is incompletely. Crystal precipitation often appeared at the bottom of the reactor, resulted in coalescence of crystals,and low purity of the products. But if the stirring speed is very high, the possibility of collision products may increase,which will lead to the crystal break, and difficult to grow large particles. Because of this, fine crystalline will loss in filtration and washing process, leading to a dropping recovery rate.

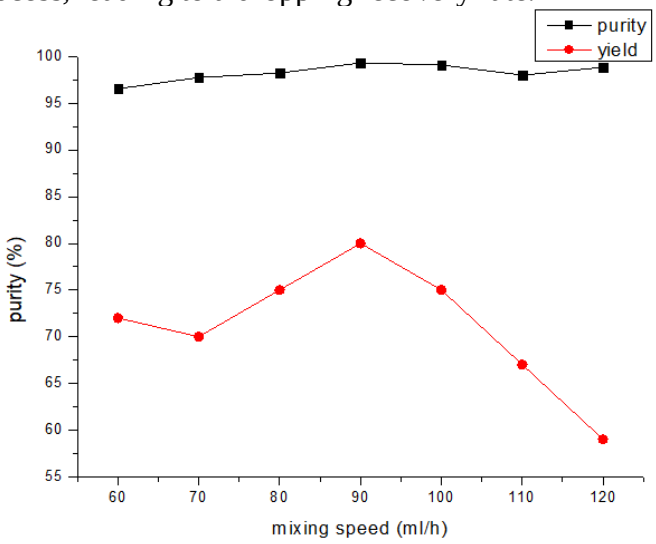

Fig. 4 Effect of agitation strength on recovery rate and purity of the product

4. Optimization of Dissolution Crystallization Process of Chlorantraniliprole

Based on the experimental result of dissolution crystallization temperature, the effect of dropping speed and concentration of dissolution agent, the stirring speed,on the chlorantraniliprole were studied. Depend on the process with optimal condition, crystallization temperature is 20℃, the drop acceleration of the dissolution agent starts at 30ml/h, and the drop acceleration is 20ml/h after the

crystal appears, Then gradually increase the rate of drop, the concentration of the dissolution agent is controlled between 0.8-0.9 , the stirring speed is 90rpm.The chlorantraniliprole crystal products as shown in the figure, compared with the original crystal structure is more regular and clear.

Fig. 5 SEM of sample as original

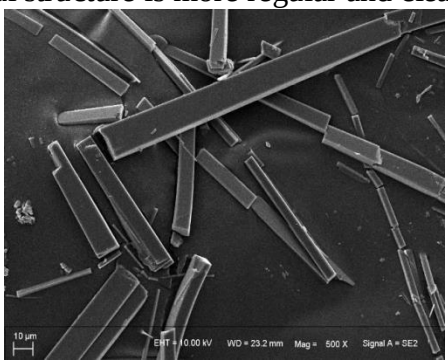

Fig. 6 SEM after dissolution analysis

5. Summary

It is a simple and effective new separation method to purify chlorantraniliprole through dissolution crystallization by using dimethylformamide as solvent, methanol solution as dissolution agent. The result shows that the crystallization method only need simple equipment, and mild reaction conditions.When the crystallization temperature is 20℃, the dropping speed of dissolution agent starts at 30ml/h, and change to 20ml/h after the crystal appeared, the dropping speed gradually increases, the concentration of the dissolution agent is controlled between 0.8-0.9, and the stirring speed is 90rpm, the purity of chlorantraniliprole can be increased from 95.21% of raw material to 99.3% through only one crystallization. And on the basic of the purity enhancement, the recovery rate can reach to 70%-85%, and the crystal form of the product compared with the raw materials is more regular and clear.

References

[1]. Caboni P,Sarais G,Angioni A,Vargiu S,Pagnozzi D,Cabras P,Casida J E. Journal of Agricultural and Food Chemistry,2008.

[2]. Guangcheng Wang,Chunxian Wu,Liming Gao,Bingkun Chen. High Performance Liquid Chromatography of Chlorantraniliprole Suspension[J]. Pesticide, 2009, (04) : 267-269.

[3]. Runyan Li,Shang Zhou,Junbo Gong. Study On The Crystallization of Ampicillin Sodium [J]. Chinese Journal of Antibiotics,2011,(09):676-679.

[4]. Yuying Han.The Crystallographic Study of Cefazone Sodium[D].Tianjin University ,2012.