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Improved crystallization of ammonium sulphate using ultrasound assisted approach with comparison with the conventional approach

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ABSTRACT

In chemical processing industries, crystallization is one of the most important operations to obtain solid products with desired purity and characteristics. With distinct processing problems for the conventional approaches for crystallization, research into alternate approaches such as ultrasound assisted crystallization has been on the forefront. The present work deals with comparison of the conventional approach and ultrasound assisted approach for crystallization of ammonium sulphate followed by detailed understanding into the effect of important operating parameters (initial concentration, pH, agitation speed, depth of horn, and cooling approach) on the metastable zone width and average crystal size. Ultrasound assisted crystallization has been investigated using both ultrasonic bath and ultrasonic horn to understand the effect of type of irradiation. It has been observed that the maximum reduction in the MSZW was obtained using ultrasonic horn under conditions of optimized initial concentration. The order of average crystal size obtained for ammonium sulphate was conventional cooling crystallization > ultrasonic bath > ultrasonic horn. The average crystal size obtained was in the range of 411–450 μm for conventional approach of cooling crystallization, 350–400 μm using ultrasonic bath and 200–250 μm using ultrasonic horn. The analysis of crystal size distribution and surface characteristics using the SEM analysis was also performed under set of optimized parameters established using the particle size analysis. Overall the work has clearly established that the ultrasound assisted crystallization gave better results as compared to the conventional cooling crystallization in terms of reduced metastable zone width, better crystal characteristics and less agglomeration.

1. Introduction

Crystallization is the processing step in which solid crystals are formed from the saturated solution based on the supersaturation generated either using cooling or addition of anti-solvent. It is second most important separation process after distillation and plays a key role in deciding the final product quality in almost all the industrial sectors including the rapidly expanding areas of fine and specialty chemicals as well as pharmaceuticals. Crystallization typically consists of a solid disperse phase formation in a continuous medium, which usually is a liquid solution, in two main steps as the appearance of transition structures between solid and fluid phase described as nucleation followed by the growth of these structures into bigger crystals. For crystallization to occur, the solution concentration must be higher than the equilibrium concentration at the desired temperature which will induce nucleation and subsequent crystal growth. The difference between actual concentration and equilibrium concentration is called supersaturation, which is considered as the driving force for the crystallization. The solubility of a solute in the solvent is an important parameter which affects the supersaturation levels. Supersaturation affects the rate of nucleation and the growth of formed crystals which in turn plays a key role in deciding the final crystal size distribution. Depending on the conditions, either nucleation or growth may be predominant over the other, and as a result, crystals with different sizes and shapes are obtained making the control of crystal size and shape as one of the main challenges especially in the case of pharmaceuticals. Once the levels of supersaturation are exhausted, the solid–liquid system reaches equilibrium and the crystallization process is said to be complete, unless the operating conditions are modified to disturb the equilibrium and again supersaturate the solution [1]. Supersaturation can be achieved either by reducing temperature or evaporating the solvent or by addition of the anti-solvent. By lowering the temperature of the preheated saturated solution, the solubility of solute in the solvent can be decreased which results into crystal formation. The operation is described as cooling crystallization. Such type of crystallization is not feasible for compounds having low or no dependency of

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the solubility on temperatures. In the case of evaporative crystallization, supersaturation can be achieved by evaporating the solvent by increasing temperature, but the process is not feasible for the heat sensitive materials [2] and requires large quantum of energies for the evaporation. Due to these difficulties, antisolvent crystallization is considered to be an effective approach though the mixing of the added antisolvent needs to be properly controlled. In the present study, cooling approach has been used to induce the crystallization depending on the stronger dependency of solubility and no problems of temperature induced degradation.

Use of ultrasound for controlling the process of crystallization especially in the case of anti-solvent and cooling types has been demonstrated to be an effective approach for process intensification. Ultrasound assisted crystallization, generally known as sonocrystallization, is one of the approaches to obtain the desirable characteristics of the high-value crystalline products in an efficient manner as compared to conventional mixing based approaches. The initial studies were mainly to understand the exact mechanism by which the crystallization is affected by ultrasound and it was speculated that ultrasound improves the crystallization process based on the different effects such as pressure pulse, local cooling, segregation, evaporation, turbulence, acoustic streaming etc. all acting simultaneously in the system [3]. It has been also considered that the cavities/bubbles generated during the cavitation events provide the nuclei and hence the process of crystal formation is easier in difficult to nucleate systems [4]. In general, it is expected that the use of ultrasound provides several key benefits in terms of improving the crystal properties and process controllability, mainly by reducing *meta*-stable zone width and yielding improved particle size distribution and crystal habit. Some other advantages of ultrasound include capability of inducing nucleation at lower supersaturation than conventional agitation, secondary nucleation, reduced agglomeration, non-invasive alternative to the addition of seed crystal (seeding) in sterile environment and strategy of obtaining the desired crystal distribution by controlled application. It is important to understand that though the qualitative trends might be similar for different compounds, the quantitative effects are typically dependent on the specific compound and hence the detailed study into understanding the effect of operating parameters is always important. The present work deals with crystallization of ammonium sulphate which has been considered as the model compound based on the importance of the compound and lack of previous studies dealing with ultrasound assisted crystallization for this specific compound.

Ammonium sulphate is used extensively as chemical fertilizer. In industry, it is produced using the reaction of sulphuric acid and ammonia or based on the extraction from lactam, a typical by-product. Due to the requirement of desired particle characteristics, it is important to study the crystallization of ammonium sulphate in greater details. An overview of earlier work related to crystallization of ammonium sulphate has been now presented to establish the novelty of the current work. Meadhra et al. [5] developed a mathematical model to simulate the crystal growth rate of ammonium sulphate in the conventional stirring based approach. It has been reported that the pH and temperature played an important role in deciding the mean crystal size and shape of crystal with pH as 5.0–5.5 and temperature as 70–90 °C being the best conditions. Dougle et al. [6] performed the studies of crystallization of ammonium sulphate mixed with ammonium nitrate and soot. It was concluded that ambient aerosol particles consisted of internal mixtures of ammonium nitrate and sulphate. It was also reported that crystallization of ammonium nitrate is not promoted by soot but only by the ammonium sulphate. Rauls et al. [7] reported studies related to understanding the influence of impurities on crystallization of ammonium sulphate. It was reported that presence of impurities affects the supersaturation increasing the MSZW for the ammonium sulphate crystallization and also leads to formation of larger crystals as compared to the pure solution. Li et al. [8] studied the effect of major influencing factors on the crystal characteristics for the evaporative crystallization of ammonium sulphate. It was reported that seeding, agitation speed, evaporation temperature and pH of the solution affects the crystal size and their distribution. Also, it was demonstrated that optimizing these parameters improves the size, color and purity. The analysis of the literature revealed that none of the earlier studies dealt with the use of ultrasound assisted crystallization for improving the ammonium sulphate crystal characteristics and hence the novelty of the current work dealing with ammonium sulphate crystallization is clearly established.

The objective of this work was to study the crystallization of ammonium sulphate using the ultrasound assisted approach with comparison with the conventional (i.e. cooling) approach. Also the influence of direct or indirect sonication on the improvement benefits has been established considering the lack of such comparison studies (most of the works focus on use of one type of ultrasonic reactor). Initially, the effect of different operating parameters such as initial concentration, stirring speed and pH has been studied using conventional as well as ultrasound assisted crystallization approaches. The effect of cooling temperature and type of cooling media in the case of conventional crystallization as well as the effect of horn immersion depth, volume and sonication time has also been investigated in the case of ultrasonic horn and bath as per the suitability of the operating parameter to the specific configuration. The key parameters used for comparison of the different approaches include the crystal size distribution (CSD) and the metastable zone width (MSZW) which enables clear understanding of the process intensification benefits as well as the final product characteristics. These parameters are important factors describing the crystallization operation and generally used for establishing the efficacy of the operation.

2. Materials and methodology

2.1. Materials

Anhydrous ammonium sulphate was procured from Merck Pvt. Ltd., Mumbai, India. Distilled water was used as solvent and was prepared freshly in the laboratory. Digital thermometer, pH meter and optical microscope with digital camera connected to a computer were used to monitor the progress of crystallization.

2.2. Experimental setup

For conventional cooling as well as ultrasound assisted crystallization, the setup used for experiment consists of a flat bottom cylindrical glass beaker with a capacity of 150 ml. A pitched blade impeller having a diameter of 10 mm was used to ensure uniform bulk mixing in the case of conventional approach and ultrasonic bath. For the case of ultrasonic horn, additional stirring was not used and the liquid streaming induced by horn was found to be sufficient to ensure adequate mixing. The temperature of the solution was maintained using an ice cooling bath. Ultrasonic horn obtained from M/s Dakshin, Mumbai operating at 36 kHz and a rated power dissipation of 120 W has been used. The tip of the horn is 2 cm in diameter and immersion of tip directly into the solution gives a direct mode of irradiation. Ultrasonic bath obtained from Raheja Chemicals, Pune, India operating at 50 kHz and a rated power dissipation of 80 W has been used as the second ultrasound source. In this case, the glass reactor was suspended in coupling fluid, which was water, giving an indirect mode of irradiation.

2.3. Experimental methodology

Initially, a known quantity of ammonium sulphate was dissolved in distilled water and heated to higher temperature to ensure that the crystals are completely dissolved in water. The pH of the solution was varied using Ammonia water solution or concentrated sulphuric acid as