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Precipitation of barium sulphate in a hollow fiber membrane contactor, Part I: Investigation of particulate fouling

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ABSTRACT

Particle formation by precipitation is an important unit operation for the production of fine solids such as catalysts, pigments, and pharmaceuticals. It is the decisive step for determining properties such as particle size, shape, and purity, which in turn determine the quality of the end product. In this study, we investigated the precipitation of $BaSO_4$ particles in a hollow fiber membrane device. A solution of $BaCl_2$ was passed tangentially over a membrane surface and reacted with a solution of K_2SO_4 introduced through the membrane pores. The resulting supersaturation induced nucleation and particles grew on the lumen side of the hollow fibers. Particulate fouling was observed using X-ray images with $BaSO_4$ as a radiocontrast agent. It was shown that this fouling was attributed primarily to fiber blockage by newly formed crystals rather than to pore blockage. Moreover, a larger inner diameter of hollow fiber was shown to slow down considerably the fouling of the device. A numerical simulation was developed to calculate the supersaturation inside a hollow fiber, and the results of the simulation were compared with experimental data.

1. Introduction

Particle formation by precipitation is an important unit operation for the production of fine solids, such as catalysts, pigments, and pharmaceuticals (Mersmann, 2001; Myerson, 2002). Precipitation typically consists of mixing two liquid streams to create supersaturation, which then induces nucleation, particle growth and (very often) agglomeration. Most of the time, the final product has to fulfill specific requirements in terms of particle size, shape, composition or purity. The influence of physicochemical factors (i.e. temperature, reactant concentration, additives) is generally well known. Hydrodynamic factors concerning initial contact and mixing of reaction fluids also play major roles in the control of particle quality due to their influence on the supersaturation distribution in the reactor volume. Design factors, such as feed addition mode, feed rate, feed location, feed concentration, stirring speed, and stirrer type have been shown to affect the resulting average particle size (see Franke and Mersmann, 1995; Houcine et al., 1997; Bałdyga and Orciuch, 2001).

Most of the continuous crystallizers, such as the stirred tank reactor, operate with some degree of mixing supplied by internal agitators or by pumping. However, these configurations are reported to be not very suitable because of the complexity of their internal hydrodynamics, particularly the distribution of the local power dissipation rate influencing the intensity of mixing. Other devices ensure a better control of contact mode and mixing. Simple devices such as T- or Y-tubes, or more sophisticated ones, such as Hartridge–Roughton chambers, are well known examples. These devices are very interesting from a mixing point of view and allow, under optimal operational conditions, to reach a micromixing time of the order of a millisecond (Bénet et al., 2002). However, when used for precipitation, these devices may be obstructed by solid particles, which are stuck or nucleated on the inner surfaces. Alternative devices to reduce obstruction effects have also been proposed, such as the two-impinging-jet mixing device, the sliding surface mixing device, and the vortex reactor (i.e. Mahajan and Kirwan, 1996; Rousseaux et al., 1999; Bénet et al., 2002).

The use of polymeric membranes as a means of inducing crystallization has recently attracted renewed interest. The first study reported the use of a hollow fiber reverse osmosis device as a crystallization technique (Azoury et al., 1986, 1987). Inside the hollow fibers, the concentration of precipitable ions increased during the osmosis operation from undersaturation, to saturation and finally to supersaturation, from which spontaneous precipitation occurred. The method was applied to the precipitation of calcium oxalate

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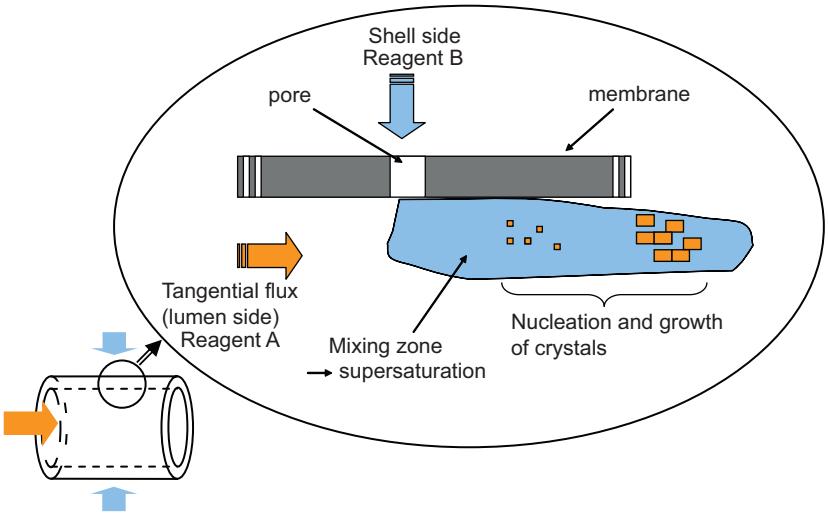

Fig. 1. Diagram of the hollow fiber membrane precipitation device.

(Azoury et al., 1986, 1987), and later to the controlled crystallization of biological macromolecules and organic compounds (Todd et al., 1991).

Membrane distillation, which is a solvent removal method similar to reverse osmosis, has recently been used for crystallization (Curcio et al., 2001). A hydrophobic porous hollow fiber membrane device was used to create uniform supersaturation, while crystallization took place in a circulating crystallizer. The transport mechanism was broken down into three steps: evaporation at the membrane interface, migration of the vaporized solvent through the membrane pores, and condensation on the opposite side. NaCl was used as a model compound and relatively low variation coefficients for the crystal size distribution (CSD) were obtained (between 42% and 57%) (Curcio et al., 2001). The same technique was applied to the preparation of fumaric acid crystals in aqueous L-malic acid solutions (Curcio et al., 2003a), single lysozyme crystals suitable for X-ray diffraction analysis with sodium chloride as precipitating agent (Curcio et al., 2002, 2003b), and trypsin crystals with ammonium sulphate as the precipitant agent (Di Profio et al., 2005a,b).

Membrane reactors have also been used for precipitation reactions (Jia and Liu, 2002; Jia et al., 2003; Chen et al., 2004). Precipitation was studied with ultrafiltration hollow fiber devices of various molecular weight cut-off (MWCO) for the preparation of barium sulphate and calcium carbonate particles. In this configuration, one reactant was introduced from the shell side, which was kept at a higher pressure, to the lumen side, where it reacted with another reactant to form particles. Nanosized particles of primarily about 70 nm were produced with the smaller MWCO membranes. However, no quantitative information on the CSD was given, while particle aggregation was found to increase with MWCO due to transmembrane flux increases caused by the larger pores (Jia and Liu, 2002; Jia et al., 2003; Chen et al., 2004). Particulate fouling problems were also reported, which, due to the low reactant concentrations used, must be more pronounced at higher concentrations. $BaSO_4$ crystals were also synthesized within a stainless steel membrane minireactor by precipitation (Chen et al., 2005; Li et al., 2007). The coexistence of different crystal morphologies was observed for different supersaturation ratios and flow rates. However, crystal nucleation and growth did not stop immediately at the outlet of the device.

Recently, antisolvent crystallization of L-asparagine was investigated in porous hollow fiber devices (Zarkadas and Sirkar, 2006). Two configurations were investigated: the first involved the addition of antisolvent to a crystallizing solution flowing on the lumen side of a microporous hollow fiber membrane, the second used the permeation of fluid from the tube side to the shell side of the membrane device by keeping the lumen side pressure higher. The experimental results showed that the CSD obtained shifted to smaller sizes compared to literature data in batch stirred crystallizers. However, a decrease in antisolvent flux was measured with the first configuration, which was attributed primarily to fiber blockage by newly formed crystals. It was pointed out that the optimization of operating conditions and design of the device would increase the performance of this membrane crystallization process. The same authors also proposed solid hollow fiber cooling precipitation in non-porous hollow fiber devices for aqueous potassium nitrate and ethanolic salicylic acid solutions (Zarkadas and Sirkar, 2004). A solid hollow fiber crystallizer and completely stirred tank, operating in series, proved successful in yielding a narrow and reproducible CSD.

The study presented here is the first of two papers dealing with $BaSO_4$ precipitation in a hollow fiber membrane device. This first part presents the investigation of particulate fouling in the hollow fiber membrane device. The process principle is summarized in Fig. 1. Solution **A** ($BaCl_2$) flowed tangentially to the membrane surface and reacted with solution **B** (KSO_4) introduced through the membrane pores. The resulting supersaturation induced nucleation and particles grew on the lumen side of the hollow fibers. An original method using X-ray imaging was developed to characterize the position of particulate fouling inside the device. Hollow fiber devices of different inner radii were tested. Moreover, a numerical simulation was developed to calculate the supersaturation inside a hollow fiber, and the results of the simulation were compared with the experimental data.

2. Theory

2.1. Model

A theoretical model was developed for the purpose of understanding what happens in a hollow fiber in terms of the supersaturation created (which induces nucleation and crystal growth). An understanding of the phenomenon is aimed for, rather than an exact prediction of the properties of the crystals obtained.

Fig. 2 shows a hollow fiber of length L and radius R (2-D geometry) in a cylindrical coordinate system. The real 3-D geometry can be obtained from the 2-D geometry assuming axial symmetry. The $BaCl_2$ (**A**) solution is introduced at the inlet of the lumen side, with