Residence Time Distribution Study in Laboratory Scale Struvite Crystallization Reactor with Online Conductivity Measurement

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Abstract. Elimination Residence time distribution (RTD) analysis is necessary to explain the hydrodynamic behavior of a continuous stirred tank reactor. In this study, RTD was applied in a laboratory scale struvite crystallization reactor to estimate the degree on non-ideality and its effect on the reactor performance i.e. effective volume, actual hydraulic residence time (HRT), and material dispersion. An impulse-response tracer (NaCl saturated solution) approach and a conductivity meter to detect of the NaCl at the effluent of the reactor were applied. To evaluate effects on the reactor performance, variation of impeller locations, impeller speeds, and flowrates were conducted. The main findings from this study showed that the difference between actual and theoretical HRT was found around as around 10%-34% and 30%-37% for condition of the impeller location at the upper and lower part, respectively. These percentages were corresponding to the reactor’s effective volume, lower percentage means higher effective volume. This finding correlated to the value of dispersion number. It was found to be about 1.612 and 0.49 for the impeller location at the upper and lower part, respectively. Finally, it was observed that the tracer was being almost 100% recovered in the reactor due to a good flow pattern and its impeller location affects the reactor’s performance.

1. Introduction
Content of ammonia in the urea fertilizer plant wastewater is often discharged to natural water bodies without any control over the generation of eutrophication and other problems in water cycle [1]. The removal and recovery of ammonia from wastewater can be treated by biological, physical, or chemical methods, either alone or in combination [2-5]. It is of great challenge to find an appropriate technology that promotes ammonia recovery from the wastewater to produce valuable material and simultaneously polish the quality of the wastewater effluent.

Currently, ammonia content in the urea fertilizer plant wastewater can be reduced by recovering it in the forms of crystalline product called struvite [6]. Struvite is relatively easy to dry and handle and gives potential as a slow-release fertilizer [7]. The solubility of struvite (MgNH4PO4·6H2O, magnesium phosphate hexahydrate), determined in deionized water was found to be 169.2 mg/L at 25°C [8]. Shu et al. [9] reviewed that 365 kg struvite application in

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agriculture field is enough to fertilize 2.6 ha land. Potency of struvite as a fertilizer has been studied [10]. They found that struvite released less N during the first 3 to 6 weeks and more N during the last 9 weeks than that of ammonium phosphate.

The formation of struvite crystal develops in two chemical steps: nucleation or crystal birth and crystal growth which a combination of several factors such as the crystal state of initial compounds, thermodynamic of liquid-solid equilibrium, phenomena of mass transfer between solid and liquid phases, and kinetic of reaction [11-12]. In struvite crystallization process mixing shows a strong effect on the number of crystals formed and consequently, on their size [13].

The method of operation of crystallization process has an important aspect of the performance of struvite production. Many researchers have conducted experiments to get highest removal of ammonia through struvite precipitation from different types of reactors. Hutnik et al. [14] designed a continuous flow type cylindrical tank equipped with a heating/cooling jacket. The tank was also equipped with a draft type circular tube with a three-paddle propeller. Matynia et al. [15] developed jet-pump crystallizer which operates continuous reaction crystallization process. Rahman et al. [16] designed an simple reactor where feeds were continuously added. Ali and Schneider [17] designed a batch reactor with auto control of feed and temperature. Considering the above views, especially in the mixing effect in the crystallization reactor, the current study was conducted to test the effects of impeller location, impeller speed, and flow rate on reactor’s effective volume and to estimate its behavior concerning actual hydraulic retention time (HRT) and material dispersion number.

2. Methodology
2.1. Experimental setup of reactor crystallizer
The crystallizer reactor was a cylindrical tank made of Plexiglas. The schematic diagram and photograph are presented in Figure 1. The reactor was designed in two distinct portions, i.e. reaction and crystal growth section (upper part), and sedimentation section (lower part). The upper part dimension of the reactor was 40 cm in height, and 40 cm in diameter. The lower part dimension of the reactor was 40 cm in height, and 30 cm in diameter. The reactor had a total liquid volume of 90 liters. The liquid was stirred by a stainless steel propeller-type impeller (number of blades 4; blade length 15 cm; blade width 3 cm). Dosing (JCMB 45-5 AILIPU Solenoid Dosing) were used to deliver fluid to the reactor. The reactor was continuously operated at room condition. There is an internal circulator which pushed the reactants in solution downwards in a draft tube. The draft tube was installed in the upper part of the reactor. The approach of installing the draft tube in the upper part of the reactor was intended for eliminating crystal product loss at the reactor effluent. Larger-crystal products are accumulated at the bottom of the reactor, and they were discharged by opening the bottom valve.

2.2. Tracer study
The experimental study was conducted in a continuous flow mode. A schematic diagram of the RTD experiments is presented in Figure 1. In the RTD studies saturated NaCl solution was used as a representative tracer in order to describe the liquid flow behavior in the reactor. A simple impulse-response method was used in this study. A conductivity probe connected to a conductivity meter (Corning Pinnacle 541, Cole-Palmer, IL, USA) was used to detect the concentration of the NaCl solution at the effluent of the reactor. Three sets of studies were conducted varying the impeller locations, impeller speeds, and flowrates to examine their effect on the liquid flow behavior. The impeller location was set at the lower (20 cm from the reactor bottom) and the upper parts (55 cm from the liquid surface). Each variation of the impeller locations was carried out by modifying the impeller speed (80, 130, and 180 rpm). Liquid flowrates used were 30, 40, and 50 L/h equivalent to HRT of 3, 2.25, and 1.8 h, respectively, corresponding to its impeller speed variations.
2.3. RTD Analysis

The residence time distributions of tracer in the reactor is explained by the $E(t)$ curve that gives the variation of tracer concentration at the effluent of the reactor. The curve is given by equation (1) [18].

$$E(t) = \frac{C(t)}{\int_0^\infty C(t) \, dt}$$  \hspace{1cm} (1)

It explains insignificant appearance how much time fluid element spent in the reactor and describes a fluid distribution (hydraulic behavior) in the reactor. The mean residence time ($t_{ave}$) can be calculated with the uses of equation (2). It is a function of $C_i$, the measured tracer concentration at time $t_i$, and $\Delta t_i$ which is the interval between two measurements. The variance of the RTD, $\sigma^2$, and the normalized variance, $\sigma_\delta^2$, can be evaluated as equations (3) and (4), respectively. A dispersion number (D/\mu L) has been formulated by Levenspiel [18] and given in equation (5).

$$t_{ave} = \frac{\sum t_i C_i \Delta t_i}{\sum t_i C_i \Delta t_i}$$  \hspace{1cm} (2)

$$\sigma^2 = \frac{\int_0^\infty t^2 C(t) \, dt}{\int_0^\infty C(t) \, dt} - t_{ave}^2$$  \hspace{1cm} (3)

$$\sigma_\delta^2 = \frac{\sigma^2}{t_{ave}^2}$$  \hspace{1cm} (4)

$$\sigma_\delta^2 = 2 \left( \frac{D}{\mu L} \right) - 2 \left( \frac{D}{\mu L} \right)^2 \left( 1 - e^{-\frac{D}{\mu L}} \right)$$  \hspace{1cm} (5)
Index distribution of the tracer or effective volume of the reactor is assumed by ratio of actual HRT to theoretical one. The calculated dispersion number (D/uL), is a parameter that measures the extent of axial dispersion [18]. The degree of fluid mixing in the reactor was estimated by the Morril dispersion index (MDI) formula as also applied in a plug flow reactor by Machdar et al. [19]. The MDI was calculated from the T_{10} and T_{90} parameters, which were estimated from the RTD curve by calculating the time interval related to 10% and 90% of the area under the curve, respectively.

3. Results and discussions

3.1. Residence time distributions (RTDs)

The RTD was enumerated using the tracer results from Figure 2 and equation (2). A tracer result summary including data analysis is presented in Table 1. Figure 2 presents the tracer concentration (conductivity values) at the effluent of the reactor versus time for the two experiments of each study. The variability between each curve for the given tracer was relatively narrow, which explained that the conducted tracer study was consistence.

All curves in Figure 2 demonstrated that two essential evidences i.e., a delay time tracer was firstly detected and tailing or extend in tracer tracking. The first condition was related to the minimum time required for the tracer reaching conductivity detector (in the outlet). The second condition likely indicated the presence of a stagnant volume of the reactor. The tailing phenomenon was probably caused by the tracer passes a stagnant (dead) volume of the reactor and slowly released by local mixing, and finally generating long tracer tracking.

As shown in Table 1, the average value of MDI under impeller location at upper and lower part were 8.10 and 6.35, respectively. A larger MDI indicates more mixing in the reactor [20].

3.2. Effect of impeller location and speed

It was observed that, the actual HRT was mainly shorter than that of the theoretical one for all being tested. The general investigation from Figure 2 is that the impeller location at the upper part is related to higher effective volume of the reactor. In other words, the impeller location affects the reactor’s performance. The effective volume of the reactor was found about 81% and 67% in average for the impeller location at the upper and lower part, respectively. As shown in Table 1, this investigation is more noticeable from the higher dispersion numbers calculated at the upper part than that of at the lower part of the impeller location. The average value of dispersion number was found to be 1.6 and 0.7 for the impeller location at the upper and lower part, respectively. As the impeller speed increases, the dispersion number rises for all flow rates tested.

3.3. Effect of flowrate or HRT

Figure 2 also presents the experimental RTD curves at flow or HRT. After each RTD experiment, the tracer concentration in the effluent stream became zero. This means that the tracer was being almost 100% recovered in the reactor due to a good flow pattern. An increase of flowrate or reduce of HRT from 30 L/h (HRT = 3 h) to 50 L/h (HRT = 1.8 h) results in a increasing effective volume, but it was not significant difference in impeller speed of 80 rpm.

From the tracer data analysis, at condition of the impeller location at the upper part, the difference between the actual and the theoretical HRT was found as 34%, 14%, and 10% in average for the flowrate of 30 L/h, 40 L/h, and 50 L/h, respectively. Concurrently, at condition of the impeller location at the lower part, the difference was found as 37%, 33%, and 30% on average.

Percentage of the difference between the actual and the theoretical HRT were comparable to the stagnant (dead) volume in the reactor. In this study, lower flowrate or higher HRT decreased reactor’s effective volume. This effect was likely due to the lower water turbulence, leading to fluid short-circuiting or channeling in the internal body of the reactor. This phenomenon of short-circuiting in the stirred tank reactor were also reported by other researchers as a well [21, 22]. These drawbacks can primary be improved through a better agitation.
Figure 2. RTD curves. a to i: impeller location at the upper part. j to r: impeller location at the lower part. a to c: impeller speed 80 rpm, flowrate 30, 40, 50 L/h. d to f: impeller speed 130 rpm, flowrate 30, 40, 50 L/h. g to i: impeller speed 180 rpm, flowrate 30, 40, 50 L/h. j to l: impeller speed 80 rpm, flowrate 30, 40, 50 L/h. m to o: impeller speed 130 rpm, flowrate 30, 40, 50 L/h. p to r: impeller speed 180 rpm, flowrate 30, 40, 50 L/h.
Table 1. Summary calculation of RTD analysis.

| Impeller location | Impeller speed (rpm) | Flowrate (L/h) – (HRT) | Average Actual HRT (h) | Average Effective volume (%) | Average Dispersion number (D/μL) | Average MDI (-) |
|-------------------|----------------------|------------------------|------------------------|-----------------------------|----------------------------------|----------------|
|                   | 80                   | 30 (3)                 | 1.92                  | 64                          | 1.6                              | 7.22            |
|                   | 40 (2.25)            | 1.94                  | 86                    | 1.2                         | 7.65                             |
|                   | 50 (1.8)             | 1.59                  | 88                    | 1.5                         | 7.04                             |
| The upper part    | 130                  | 30 (3)                 | 2.03                  | 68                          | 1.9                              | 8.14            |
|                   | 40 (2.25)            | 2.18                  | 97                    | 1.1                         | 8.90                             |
|                   | 50 (1.8)             | 1.72                  | 96                    | 2.1                         | 7.67                             |
|                   | 180                  | 30 (3)                 | 2.02                  | 67                          | 2.1                              | 10.16           |
|                   | 40 (2.25)            | 1.70                  | 75                    | 1.3                         | 5.88                             |
|                   | 50 (1.8)             | 1.55                  | 86                    | 1.4                         | 11.11                            |
| Average           |                      |                       |                       | 81                          | 1.6                              | 8.10            |
| The lower part    | 80                   | 30 (3)                 | 2.64                  | 82                          | 0.7                              | 6.03            |
|                   | 40 (2.25)            | 1.80                  | 80                    | 0.5                         | 5.25                             |
|                   | 50 (1.8)             | 1.43                  | 79                    | 0.4                         | 5.07                             |
|                   | 130                  | 30 (3)                 | 1.49                  | 50                          | 0.3                              | 4.71            |
|                   | 40 (2.25)            | 1.39                  | 62                    | 0.3                         | 5.12                             |
|                   | 50 (1.8)             | 1.12                  | 62                    | 0.3                         | 5.00                             |
|                   | 180                  | 30 (3)                 | 1.74                  | 58                          | 2.6                              | 9.38            |
|                   | 40 (2.25)            | 1.37                  | 61                    | 0.8                         | 7.96                             |
|                   | 50 (1.8)             | 1.24                  | 69                    | 0.8                         | 8.66                             |
| Average           |                      |                       |                       | 67                          | 0.7                              | 6.35            |

4. Conclusions
The experimental results led to three main conclusions: (1) impeller location and impeller speed have significant effect on actual HRT and effective volume of the reactor; (2) material tracer do not travel completely inside of the reactor due to fluid short-circuiting or channeling; and (3) the results further indicated that in order to increase reactor’s effective volume, mixing system and impeller speed must be considered.

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