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Experimental Assessment of the Mixing Quality in a Circular Cross-Sectional T-Shaped Mixer for the Precipitation of Sparingly Soluble Compounds

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Precipitation processes have been successfully proved to be a feasible route to extract high-value products from wastes. However, reactive crystallization is characterized by fast kinetics, especially when highly concentrated solutions are used or sparingly soluble compounds precipitate, thus requiring a fast mixing of the reactants. In this context, T-shaped mixers have been extensively investigated both experimentally and numerically as a mean to achieve a rapid reactants homogenization. Many research efforts have been focused on the analysis of rectangular cross-sectional T-shaped mixers, while less attention has been devoted to the study of circular cross-sectional ones. In the present work, mixing times in a 3 mm circular cross-sectional T-shaped mixer have been optically estimated by exploiting the extremely fast neutralization reaction between sodium hydroxide and hydrochloric acid solutions. Reynolds numbers ranging between 1,000 and 6,000 were investigated. Mixing phenomena were (i) captured by detecting the colour change of a pH indicator by means of a high frame rate camera and (ii) quantified by a suitable image analysis technique. The assessed mixing times were found in accordance with available data in the literature.

1. Introduction

In recent years, an increasing interest has been raised toward the recovery of minerals from industrial wastes. Among the others, magnesium hydroxide has been successfully extracted from seawater brines via precipitation process using alkaline reactants (Alamdari et al., 2008; Cipollina et al., 2015). However, in order to achieve suitable market product requirements (e.g. particle size, morphology, purity), reactants have to be intimately mixed before precipitation occurs. In this regard, static mixers such as confined impinging jet (CIJ) (Gavi et al., 2010; Johnson and Prud'homme, 2003), T- (Schwarzer and Peukert, 2004) and Y- (Roelands et al., 2003) mixers have been widely investigated as suitable devices to ensure higher mixing quality compared to classical stirred reactors. As far as T- and Y- mixers are concerned, they consist of two inlet channels which merge to an impinging zone connected to a vertical channel. The two inlet channels can have a certain angle of inclination, i.e. 180° for T- mixers or smaller angles for Y- mixers. Mixing of the two solutions begins at the impinging zone and further proceeds into the vertical channel, which is also typically called mixing channel. A drawing of a circular cross-sectional T-mixer is shown in the insight of Figure 1. Mixing quality in such devices has been extensively investigated mainly focusing on rectangular cross-sectional mixers (Schikarski et al., 2019), while less attention has been devoted to other cross-section types, e.g. circular (Lindenberg et al., 2008; Rahim et al., 2017) or lateral inclined walls (Mariotti et al., 2019). Roelands et al. (Roelands et al., 2003) numerically investigated the mixing phenomena in a wide angle (160°) Y- mixer with a 3 mm mixing channel diameter at a Reynolds number of 18,000. Results showed that macromixing was the rate-determining step for the homogenization of the solutions. Mixing time was of the same order of magnitude of the solutions residence time in the mixing zone. However, CFD simulations performed by the same authors indicated that perfect mixing of the two solutions was not actually achieved. Lindenberg et al. (Lindenberg et al., 2008) also investigated mixing phenomena in a circular cross-sectional Y- mixer (160° wide angle) provided with a

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vertical channel diameter of 1 mm. Mixing was experimentally assessed using the competitive-parallel reactions between the fast neutralization of sodium hydroxide with hydrochloric acid and the slower hydrolysis of 2,2-dimethoxypropane (DMP) forming acetone and methanol. Computational Fluid Dynamics (CFD) simulations were also carried out to further study the mixing in the device. Results reported mixing times ranging from 20 to about 1 ms for a Reynolds number between 1,000 and 6,000, respectively. Literature findings have shown that such devices could provide rapid mixing, which would be suitable for precipitation processes. Therefore, mixing information is crucial for the selection of the proper mixer features, e.g. vertical channel length or channel diameter. The present paper aims at experimentally characterizing the mixing quality in a 3 mm diameter circular cross-sectional T-shaped mixer, which has been less investigated in the literature. A novel experimental methodology was adopted to gain useful information on this kind of mixing device. Specifically, mixing times were assessed at the turbulent Reynolds numbers ranging between 1,000 and 6,000 by examining the evolution of the neutralization reaction between sodium hydroxide (NaOH) and hydrochloric acid (HCl). In this regard, many other experimental techniques have been proposed in the literature. An extensive review of the most common methods was presented by Aubin et al. (Aubin et al., 2010). Among these techniques, acid-base reactions coupled with pH indicators and competing parallel reactions were largely employed providing reliable mixing information (Bertrand et al., 2006). Branebjerg et al. (Branebjerg et al., 1995) investigated the mixing in micro-channels using a solution of bromothymol-blue (BTB) as pH-indicator, which exhibits a transition between 6 (yellow colour) and 7.6 (blue colour). Mixing of the fed solutions was recorded using a video camera and the total observed time at which the pH indicator did not change its colour anymore was interpreted as the mixing time. Different pH indicators were employed in other works, such as the methyl orange or the phenolphthalein (Aubin et al., 2010). In the present work, the neutralization reaction between NaOH and HCl was visualized by means of a colorimetric technique by using the Alizarin Yellow R sodium salt pH indicator, which has a transition interval between pH of 10 (yellow colour) and 12 (red colour). A high frame rate camera was used to capture the neutralization reaction in the mixing channel. A digital image analysis technique was developed to quantitatively obtain the hydroxyl ions concentrations in the mixing channel, thus providing information on the mixing phenomena. The reason for such non-conventional pH indicator is motivated by the possible application of the same methodology also for the study of the precipitation of sparingly soluble compounds, whose precipitation process evolves by consuming hydroxyl ions. In the present investigation, detected mixing times were found in agreement with macromixing times typical of T-mixer reactors, thereby validating the experimental/digital image analysis technique here proposed.

2. Materials and methods

The heart of the test section was a circular cross-sectional T-shaped mixer made by two inlet channels 30 mm long and a mixing (vertical) channel 60 mm long. Inlet and mixing channels have the same internal diameter equal to 3 mm. The mixer device channels were excavated in a polymethyl methacrylate (PMMA) block, which guarantees high transparency. NaOH and HCl solutions were stored and collected in three glass flasks. NaOH solutions were prepared from pellets (Honeywell FlukaTM) with an assay of 98-100.5 %, while HCl ones were obtained after a dilution of a fuming 37 % HCl solution (EMSURE®). Alizarin Yellow R sodium salt powder (Thermo Fisher, Kandel, GmbH) was adopted as pH indicator. Two gear pumps (Fluid-o-Tech® FG series) were employed for solutions handling. The mixer was backlighted using halogen bulbs. A Sony® RX100-VII 20 Mpixel digital camera was used to capture the neutralization phenomenon. Figure 1 shows a schematic representation of the adopted experimental set-up. A drawing of the T-mixer is also shown in the insight of the same figure.

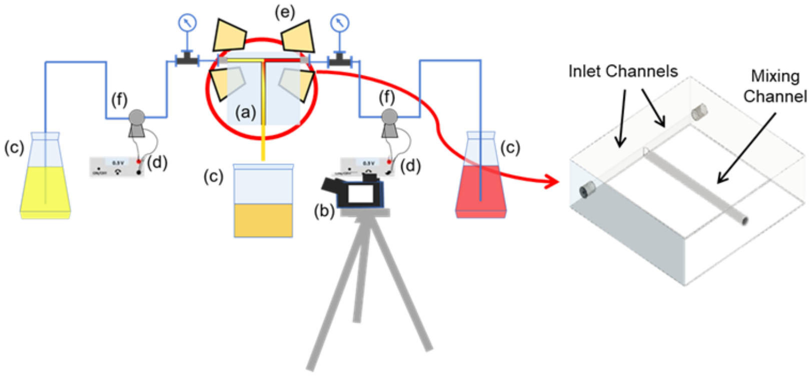

Figure 1 Experimental set-up: (a) circular cross-sectional T-shaped mixer; (b) high frame rate digital camera; (c) flasks; (d) power supply; (e) halogen bulbs; (f) gear pumps. On the right, an insight of the T-mixer.

Chemical reactions with well-defined kinetics can be exploited to characterize mixing times in T-mixers. In particular, the neutralization reaction between hydrochloric acid (HCl) and sodium hydroxide (NaOH) can be considered instantaneous, as it is characterized by a reaction time of the order of the nanoseconds. Therefore, as soon as solutions meet, the reaction takes place immediately. As a consequence, solutions can be considered well mixed when reaction stops occurring in the mixing channel. In the present work, in order to visualize the neutralization reaction between HCl and NaOH, Alizarin Yellow R pH indicator was dissolved into the solutions and pictures of the mixing phenomena were captured. All the images collected were processed by using the Matlab® Image Processing Toolbox®. Digital images were imported in the software in the form of three matrices owing information regarding the Red, Green and Blue (RGB) colours detected at each pixel of the camera. The combination of RGB matrices gives the real colour of an object. In the present procedure, images were converted from RGB to Hue Saturation Value (HSV) colours space. Transformation allows the identification of the Hue of an object, which can be univocally related to the colours detected at each pixel by the camera (close to the perception of the human eye). The use of digital image analysis based on HSV colours space has already been applied in other application fields, e.g. to determine temperature polarization in spacer-filled channels for membrane distillation (Tamburini et al., 2013). A relationship between the hue component of the HSV space and the corresponding concentration/pH value is needed in order to quantitatively assess the hydroxyl ions concentration variation (and thus the pH) in the mixing channel during the neutralization reaction. Therefore, a calibration curve was derived in situ by using solutions of known pH value ranging from 8 to 13:

$$\mathrm{pH} = 6.8821 \cdot 10^{-5} \cdot \mathrm{Hue}^4 - 1.2509 \cdot 10^{-2} \cdot \mathrm{Hue}^3 + 0.8424 \cdot \mathrm{Hue}^2 - 25.051 \cdot \mathrm{Hue} + 289.17 \qquad (1)$$

For each calibration measurement at least 100 pictures were taken. Hue was assigned after averaging over all the collected Hue maps, reducing the random noise produced by the digital camera. Figure 2 presents the obtained calibration curve.

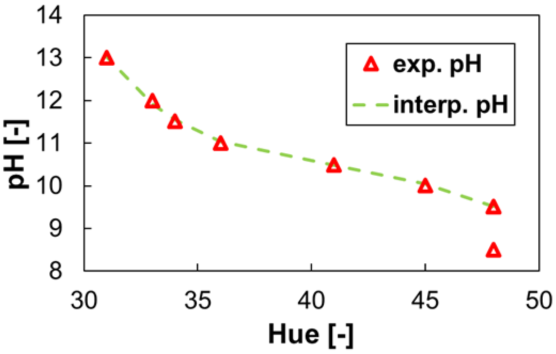

Figure 2 Calibration curve (green dashed line) between known solutions pH and detected Hue. Hollow triangles refer to experimental pH values.

As it can be seen from Figure 2, Hue does not change below pH values lower than 9.5, as those pH lay out of the Alizarin Yellow R colour transition range. Therefore, two solutions of pH of 9.5 and 8.5 (the two points at the highest Hue value in Figure 2) have the same Hue value. NaOH and HCl solutions 10.7 mM and 10.0 mM, respectively, were prepared by dissolution of pellets in order to assess the mixing in the T-mixer. Note that, these NaOH and HCl inlet concentrations correspond to 5.35 mM and 5.00 mM after the impinging due to an obvious dilution of the species in the mixing channel. No-stoichiometric solutions were prepared in order to: (i) obtain a theoretical final hydroxyl ions (OH^-) concentration of 0.35 mM, leading to a solution pH of ~10.5, which falls within the transition range of the Alizarin Yellow R; (ii) keep the resulting pH far from the titration curve, where very small variations of acid or base concentrations can sharply vary the solution pH. Three fluid velocities inside the mixing channel were investigated, namely 0.63 m/s, 1.38 m/s and 1.75 m/s, corresponding to Reynolds numbers of 1,890, 4,140 and 5,250, respectively (Table 1). Reynolds numbers were calculated with respect to the mixing channel diameter (3 mm) and considering a solutions kinematic viscosity equal to $1 \cdot 10^{-6}$ m^2/s. For each experimental test, at least 100 pictures were taken shooting at a 20 frame per second, capturing 5 seconds of the process. Hue maps were first transformed in pH maps, using the calibration curve of Eq. (1), and then into concentration maps. Note that, in the analysis, concentration maps (once calculated from Hue maps) were averaged over all the captured pictures in order to reduce (i) the digital random noise of the sensor of the camera and (ii) the turbulent fluid fluctuations.

The averaging process provided a statistical steady state concentration map in the mixing channel. In addition, a hydroxyl ions concentration profile along the mixing channel (stream-wise direction) was also determined through this average concentration map by further averaging over the channel diameter. Finally, the hydroxyl ions conversion profile was calculated as:

$$conv_x = \frac{(\mathrm{OH^-conc})_{x=0} - (\mathrm{OH^-conc})_x}{(\mathrm{OH^-conc})_{x=0}} \tag{2}$$

where $(\mathrm{OH^-conc})_x$ and $conv_x$ are the hydroxyl ions concentration and conversion at a certain distance (x) along the channel length, while $(\mathrm{OH^-conc})_{x=0}$ is the hydroxyl ions concentration at the impinging zone, i.e. 5.35 mM. Conversion values can be normalized to the expected final conversion value (i.e. 93.5%) thus obtaining a variable (β) bounded between 0 and 1:

$$\beta = \frac{conv_x}{expected\ final\ conversion\ (i.e. 93.5\ \%)} \tag{3}$$

Consequently, the experimental mixing length was defined as the position into the vertical channel at which β varies of ±1% from its final value (i.e. $\beta = 1$). Then, experimental mixing times ($\mathrm{t}_m^{exp.}$) were computed as the ratio between the experimental mixing length and the fluid mean velocity in the mixing channel:

$$\mathrm{t}_m^{exp.} = \frac{\text{experimental mixing length}}{U} \tag{4}$$

where *U* is the average velocity in the mixing channel (m/s). It should be stressed that when conv_x attains its final value (i.e. β attains a value equal to 1), the corresponding hydroxyl ions concentration is of about 0.35 mM indicating that neutralization reaction completed, as all the HCl hydrogen ions reacted with NaOH hydroxyl ions. As a consequence, Alizarin Yellow R did not change its colours anymore, reaching the expected final colour.

Table 1: Investigated NaOH and HCl concentrations and velocities at the impinging zone

	Solutions	Velocities of both solutions (m/s)	Reynolds number
Case 1	NaOH 5.35mM & HCl 5.00mM	0.63	1,890
Case 2	NaOH 5.35mM & HCl 5.00mM	1.38	4,140
Case 3	NaOH 5.35mM & HCl 5.00mM	1.75	5,250

3. Results and discussion

Figure 3 shows the $\mathrm{OH^-}$ normalized conversion (β) profiles computed using Eq. (3) for all the three investigated velocities. Normalized conversion profiles were smoothed performing a moving average with a subset of 100 points.

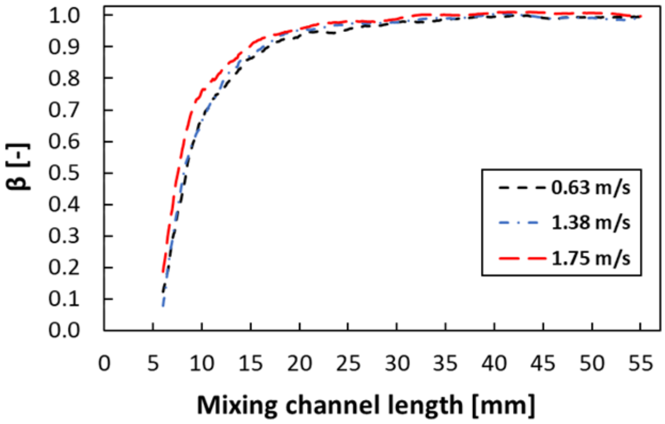

Figure 3 Normalized conversion (β) profiles along the mixing channel length for all the three investigated velocities. Profiles were calculated using Eq. (3) based on the average hydroxyl ions concentration profile obtained averaging concentration maps over 100 pictures and the mixing channel diameter. Data were smoothed by performing a moving average with a subset of 100 points.

As shown in Figure 3, for all the investigated cases the final hydroxyl ions conversion was detected at ~36 mm from the impinging zone, corresponding to a mixing time of ~57.5, 24.3, 17.1 ms for the velocities of 0.63, 1.38 and 1.75 m/s, respectively (assessed by Eq. 3). Values are in agreement with mixing times (t_m) in T-mixers, which could be estimated using the following correlation (Roelands et al., 2003):

$$t_m = \frac{12D}{U} \tag{5}$$

where D is the diameter of the mixing channel (m). Table 2 lists the theoretical mixing times evaluated using Eq. (5) and those experimentally detected, along with their relative error.

Table 2: Theoretical mixing times evaluated using Eq. (5) and those experimentally detected

	Theoretical Mixing times (Eq. 5) [ms]	Exp. mixing times [ms]	Relative error
Case 1	57.1	57.5	0.70 %
Case 2	26.1	24.3	-6.89 %
Case 3	20.6	17.1	-17.0 %

To further investigate the mixing quality in the mixer, the average OH$^-$ concentration maps for all the three investigated cases are shown in Figure 4. Note that, colour bar extremes were fixed between 0.1 and 1 mM in order to better visualize the concentration variation in the channel.

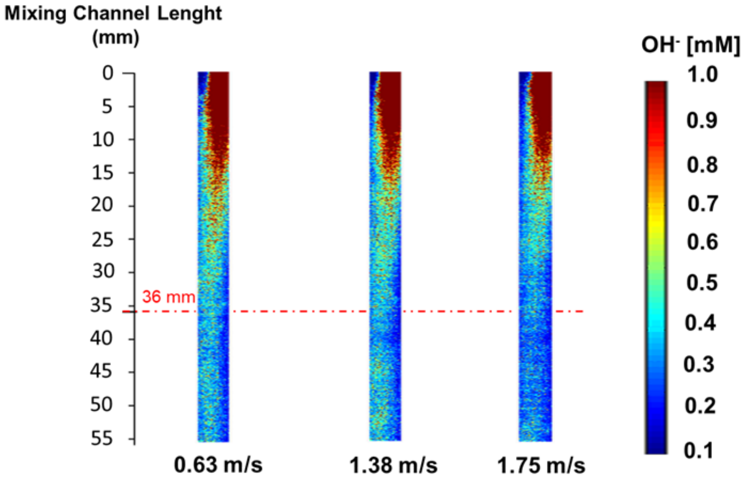

Figure 4 Average OH$^-$ concentration maps in the mixing channel for the velocities of 0.63, 1.38 and 1.75 m/s.

From Figure 4, a segregation between the two solutions can be observed up to a channel length of ~20 mm, while a good degree of mixing is reached at the channel length of 36 mm. Moreover, the higher the velocity the better the solutions homogenization degree at the outlet of the mixing channel. To quantify the solution homogenization degree, the coefficient of variation (COV) of the concentration values over the mixing channel width was evaluated at the channel length of 50 mm. Values of 0.23, 0.22 and 0.17 were obtained for the velocities of 0.63, 1.38 and 1.75 m/s, respectively. Note that, a COV of 0.17 was attained during the calibration process when a solution of known pH (uniform colour) was fed in the mixing channel. Obtained mixing results highlight the potentiality of the novel adopted experimental technique. However, on the one hand, the captured images are somehow affected by the representation of a 3D flow into a 2D plane. On the other hand, as the solution homogenization degree increases along the mixing channel length, the detected colours will not be influenced by the 3D nature of the system anymore (no overlapping of fluid structures having different colours). Therefore, the technique can allow a reliable qualitative and quantitative study of the phenomena inside the mixing channel providing information on mixing times. The technique can also be exploited for the study and the visualization of reactions, which occur with hydroxyl ions consumption. Overall, results suggest that the investigated 3 mm circular cross-sectional T-shaped mixer, at Reynolds number between 1,000 and 6,000, is suitable for the study of fast reactions, whose kinetics are slower than the mixing times here estimated. On the other hand, higher Reynolds numbers have to be investigated for the study of faster reactions.

4. Conclusions

The recovery of high-added value minerals from industrial wastes has been successfully proved via reactive crystallization. However, a fast mixing of reactants has to be ensured to achieve product-market requirements. T-shaped mixers could provide short mixing times, if suitable mixers features are selected. In the present paper, a 3 mm circular cross-sectional T-shaped mixer was investigated at three different Reynolds numbers (1,890, 4,140 and 5,250). Mixing was optically visualized using the extremely fast neutralization reaction between sodium hydroxide and hydrochloric acid solutions. The Alizarin Yellow R pH indicator was employed to detect the evolution of the neutralization reaction. The pH indicator colour change was captured by means of a high frame rate digital camera. Pictures were processed using a purposely developed digital image analysis. Mixing times ranging from 57 to 17 ms were identified. Results are in agreement with literature reported data, showing that the employed experimental/image tool technique can provide qualitative and quantitative information regarding hydroxyl ions concentration in the mixing channel. The analysis also reveals that the use of a 3 mm circular cross-sectional T-shaped mixer should be avoided if the precipitation of sparingly soluble compounds characterized by very fast kinetics (order of 1-10 ms) would be investigated at the same Reynolds numbers tested here. Higher Reynolds numbers should be considered to achieve shorter mixing times.

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