ENE 806 Project Report

Theoretical and Experimental Analysis of CSTRs in series in comparison with PFR

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1. Introduction

In water treatment, we need to add some chemicals for various purposes. For example, chlorine dioxide and ozone are used for disinfection (Limoni and Teltsch 1985; Long, Hulsey et al. 1999). Sodium hydroxide and lime are employed in waste water treatment on large scale for pH adjustment, which can be used to assist the coagulation of natural organic matter or as agent for softening water (Rautenbach, 1996). Aluminum and iron salts, such as aluminum sulfate (alum) and ferric chloride are the most common inorganic salts for coagulation (Crittenden, 2005). Polyelectrolytes have recently been used to obtain optimum coagulation (Crittenden, 2005). It is true that the selection of the optimum type and dosage of chemicals cannot be made for any water or wastewater treatment without experiments (Walter J. Weber, JR, 1972). In water treatment we currently used reactors (or tank) to process the different stages that are need for this purpose. In those tanks, the fluid flow, which is determined by reactor configuration, will have big effect on the distribution of different chemicals in the reactors.

The reactors used for water treatment can be categorized based on the operation pattern, hydraulic characteristics, unit operation occurring, and entrance/exit conditions (Crittenden and Montgomery Watson Harza (Firm) 2005).

Reactors used for carrying out chemical or physical reactions can be characterized as ideal or non ideal, according to the nature of the hydraulic and mixing conditions. In contrast with non ideal reactor, ideal reactors are assumed to have uniform mixing and hydraulic conditions, depending on the specific reactor configurations. Common reactor configurations include (1) plug flow reactors (PFRs), (2) completely mixed batch reactors (CMBRs) and (3) completely mixed flow reactors (CMFRs). In addition, a CMFR may also be referred as a complete-mix reactor (CMR), continuous stirred tank reactor (CSTR), constant flow stirred tank reactor (CFSTR), or backmix rector (Crittenden and Montgomery Watson Harza (Firm) 2005).

CSTR and PFR are probably the two most widely-accepted reactor regimes used for water treatment or analysis plants such as settling tanks, activated sludge reactor basins, aerated lagoons, oxidation ponds, and high-rate anaerobic digesters (Reynolds and Richards 1996). For example, the CSTR/PFR concepts were used in the design and performance evaluation of

waste stabilization ponds (Von Sperling 2002). Nevertheless, the choice between PFR and CSTR would be made as a function of the desired application. For example, in the mixing of coagulants, the intense mixing provide by CSTRs is desirable to disperse the reactants quickly. Flocculation, on the other hand, requires moderate agitation to increase the rate of particles collision and formation of large aggregate particles, which can be achieved by PFR regime. As for the disinfection process in water treatment, a typical reactor may be a long, narrow channel, long pipe or tubular, or a series of long channel, because it is typically carried out by the exposure time to the disinfectant of interest for a specified duration of time. So for the reactors used for contact time analysis, PFR will be preferred (Crittenden and Montgomery Watson Harza (Firm) 2005). On another hand, the efficiency between CSTR and PFR have been compared in terms of the hydrogen production from thermal decomposition of water and isothermal-type reactor with membrane. It was found that hydrogen yield of PFR-type membrane reactor is about 1.5 times larger than that of CSTR-type membrane reactor (Ohya, Yatabe et al. 2002).

The concentration distributions of chemicals in are generally not uniform throughout PFRs. The reason is that, in an ideal plug flow regime, there is no longitudinal mixing of the fluid elements as they move through the system. Therefore, each time a new plug is introduced in the inlet of the reactor, another plug of the same size should exit from the outlet. In consequence, a pulse that passes through the PFR is supposed to have exactly the same shape it had initially with a retention time (RT), which equals to the ratio of volume (V) to flow rate (Q), see Figure 1a. From the practical aspect, a plug flow regime is approached in systems that have large length-to-width ratios. For instance, if a tube has a length-to-width ratio of 50:1, the flow regime will approach plug flow if the velocity is not excessive (Reynolds and Richards 1996).

In contrast, complete mixing in a CSTR reactor produces the tracer concentration throughout the reactor to be the same as the effluent concentration. In other words, in an ideal CSTR, at any travel time, the concentration down the reactor is identical to the composition within the CSTR (Hoboken et al., 2005). The consequence of this is that the shape of the tracer curve is significantly different from that obtained with the PFR. For an impulse input, the effluent concentration of the tracer instantly reaches a maximum as this tracer is uniformly distributed throughout the CSTR. Then, this concentration gradually dissipates in an exponential manner as the tracer leaves the effluent. The shape of this tracer curve is exponential because, as the tracer leaves the reactor, its concentration is reduced with the rate at which the tracer mass

leaves the reactor (Figure 1b). It is important to notice that the chemical (so called "tracer") concentration at the retention time (RT) is quiet reduced in comparison with the PFR model where the concentration is the same as the input concentration. This phenomenon describes well the lack of performance in the CSTR regime in comparison with the PFR model (see Figure 1).
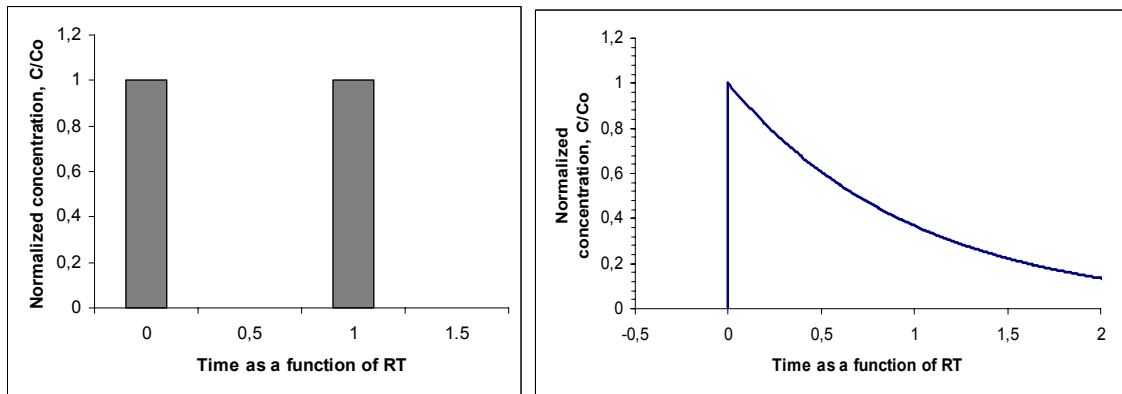
Figure 1a (left) and 1b (right): Conservative tracer curves for an ideal plug flow reactor and an ideal CSTR respectively, as a function of the retention time (RT).

It is also important to notice that the mixing degree in a CSTR is an extremely important factor (Cholette, Blanchet et al. 1960), and it is assumed that the fluid in the reactor is perfectly mixed in this case – that is, the contents are uniform throughout the reactor volume. In practice, an ideal mixing would be obtained if the mixing is sufficient and the liquid is not too viscous. If the mixing is inadequate, there will be a bulk streaming between the inlet and the outlet, and the composition of the reactor contents will not be uniform. If the liquid is too viscous, dispersion phenomena will occur and this fact will affect the mixing extent.

In environmental engineering, it is alreadyknown that the hydraulic performance of a reactor can be improved by increasing the number of CSTRs in series. As a consequence and as a fact, treatment processes are frequently staged to meet treatment objectives (e.g. ozonation may be carried in three or four consecutive stages). Staged treatment processes are currently analysed as tank in series. It has already been demonstrated that, for a same total reactor volume (V_T) it is possible to approach the performance of a PFR (in terms of retention time) by increasing the number (n) of CSTRs in series (in this case each CSTR in the series has a volume of V_T/n). See Figure 2 and compare with Figure 1a.
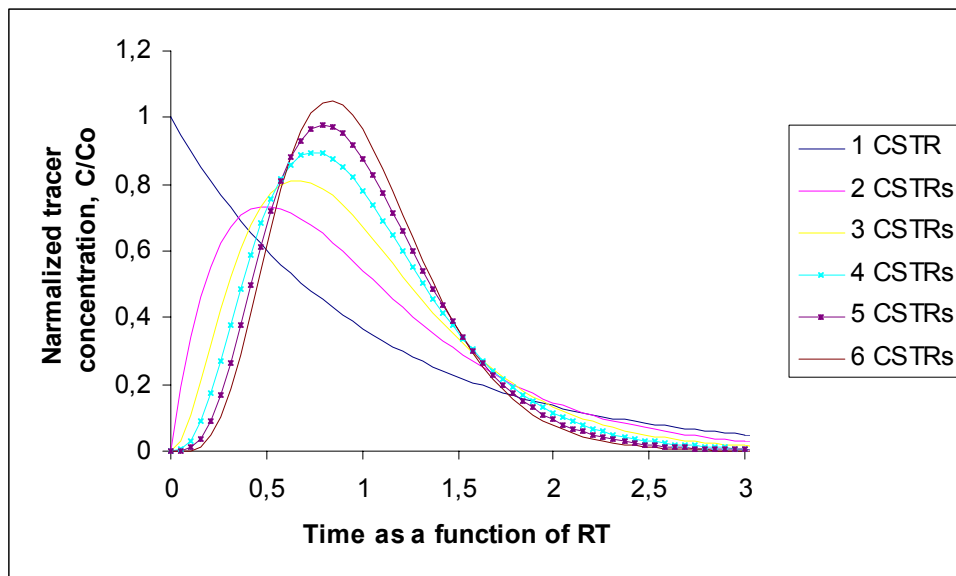
Figure 2: tracer curves for one, two, three, four, five and six CSTRs in series. Each CSTR series has the same total volume and the same total mass of tracer added. We can see easily that the maximum concentration is approaching the retention time (1) by increasing the number of CSTRs in the series. The maximum concentration tends to increase with the number of CSTR which corroborate the fact that the CSTR volume is negatively proportional to the number of CSTR in the series.

It turns out to be the goal of this project, that is, it could be interesting to see what happens if the total reactor volume V_T is increased with the number of CSTRs in the series. In other words, what will happen to the tracer curves for series of different numbers of CSTRs that all have the same volume V? (In this case, $V_T=nV$). Our first guess, and this guess turn out to be our hypothesis, we expect to see the same increasing performance (as shown on Figure 2) of the series considering the retention time but with a diminution of the maximum concentration of the tracer. Moreover, we expect the see a more homogeneous concentration of the tracer by increasing the number of CSTR in the series.

To get a way to study this subject, a home-made 6 CSTRs in series tank was built. At the same time, we decided to make both a mathematical prediction model and conduct a series of experiments. The mathematical model will allow us to make a comparison between the experimental data and the analytical model.

2. Material and Method

For this experiment, we've designed a 6 CSTRs tank made of Polyvinyl chloride (PVC). The 6 CSTRs have been designed in the way that their respective volumes are all the same (1588mL) and that each helix of the stirrer (model 7790-400, Phipps & Bird Inc., Richmond,

VA) is centred in the middle of each CSTRs. The height of each CSTR is decreasing from the first to the last one in order to overcome the hydraulic head loss and allow the liquid to flow in a homogeneous way from the first to the last CSTR. A schematic representation of this 6 CSTRs tank is shown on Figure 3. This tank has then been constructed by James C Brentan and his students. See Figure 4.

The stirring conditions have been kept continuous and constant (140 rotations per minute) for each CSTR in all the experiment. The flow rate was controlled with a valve installed at the last CSTR, which is used to keep the water level of the last section to be constant. The flow rate is controlled at 5.88 x 10-3 L/s for all the experiments. Under the above described conditions, 1588 mg of sodium chloride (Columbus Chemical Industries, Inc, ACS grades) was pre-dissolved with 5mL of ddH2O (Barnstead E-Pure® Laboratory Water, Barnstead-Thermolyne, Dubuque, IA) and the solution was introduced into the first CSTR as a single input with an initial concentration of 1000mg/L. NaCl has been chosen for its conservative properties. In the other word, sodium chloride ideally doesn't react or accumulate in the reactor so that the total mass should remain unchanged (Crittenden and Montgomery Watson Harza (Firm) 2005).
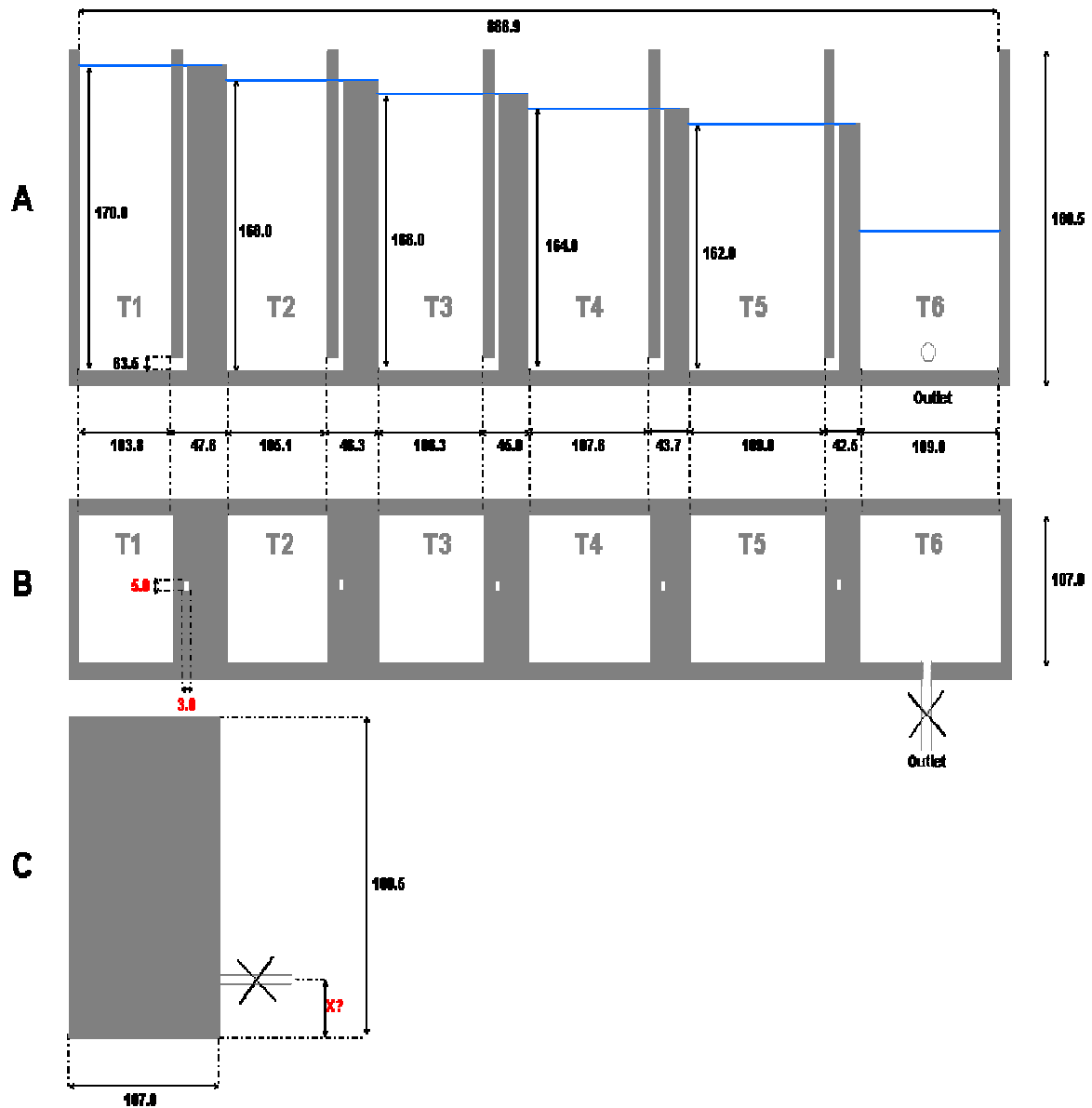
Figure 3: the design of the tank A) x-side view; B) top view; C) y-side view (all dimension is in the unit of millimeters).

The water electro conductivity has been measured in the first, second, fourth and fifth CSTR with four CON-BTA conductivity probes (Vernier, Beaverton, OR). The probes were calibrated with a standard solution of NaCl with 500 mg/L before each experiment (Conductivity = 1000 μS/cm). Those four probes have been connected to a PC computer (Dell) via a LabPro® interface (Vernier). The software used for this experiment is LabView (National Instruments Corporation, Austin, TX) in conjunction with the LabView virtual instrument (VI) furnished by Vernier for the LabPro® interface. Figure 6 and 7 display the operating and block diagram of LabView respectively.

Figure 4: the 6 CSTRs in series reactor with stirrers and conductivity probes inside the series. Those probes have respectively been placed in the first, the second, the fourth and the fifth reactor
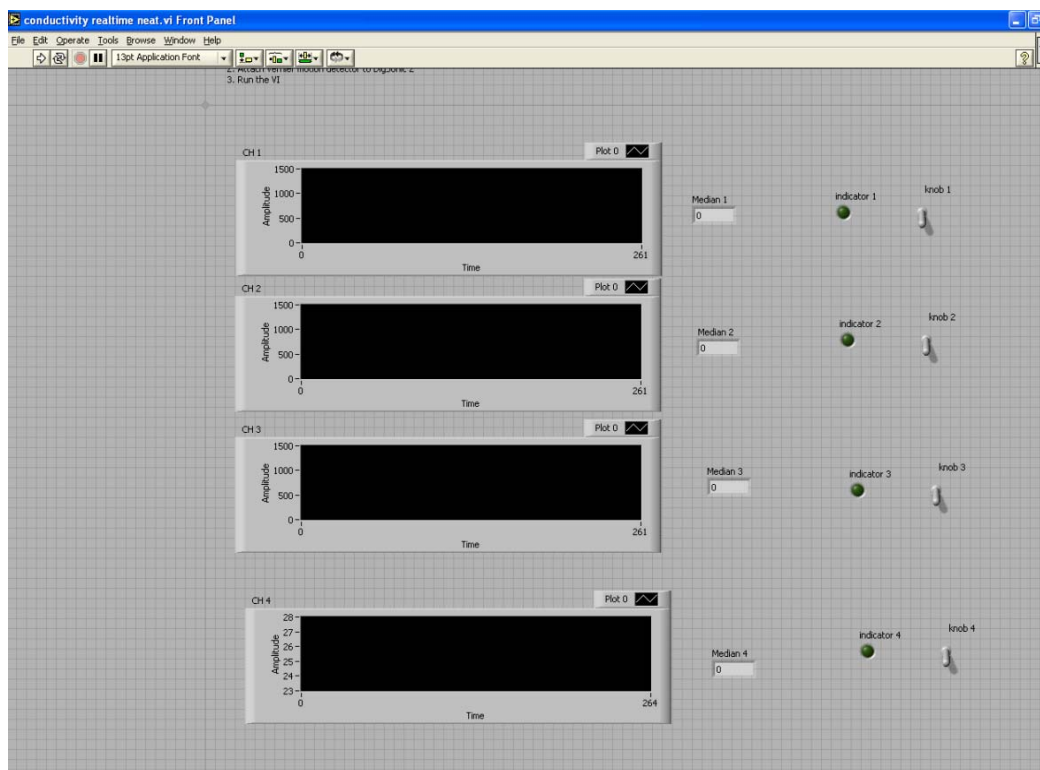
Figure 5: LabView operating diagram: The four plot areas are respectively showing the data collected with the four conductivity probes (no data collected on this picture) as a function of time (x axis) and of the electroconductivity amplitude (y axis). Knobs has been added in order to control the link between the LabView program and the Microsoft-EXEL software that has been used to store and analyze the collected data.
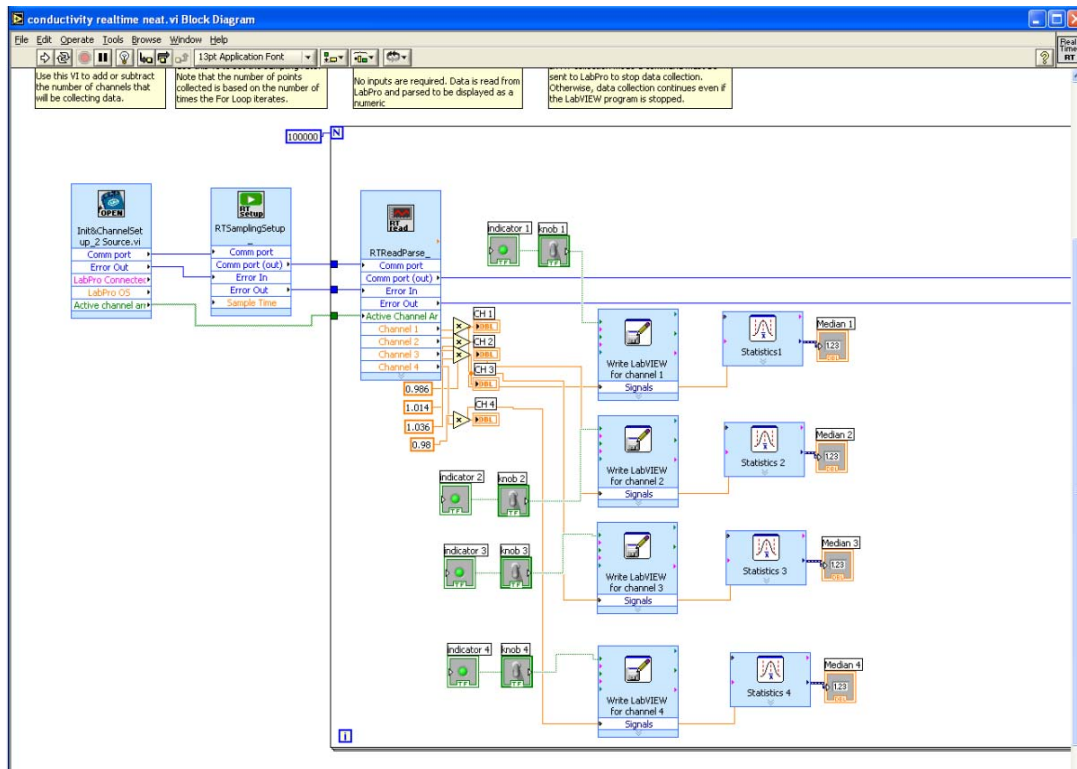
Figure 6: LabView block diagram: This block diagram shows how LabView is configured for this experiments. Note that the calibration of the probes is done directly with LabView by adding a multiplier. This multiplier is used to calibrate the probes with a 1000μS/cm NaCl solution.

3. Results

3.1. Modelling

We decided to modelize what would happen in theory with an ideal series of CSTRs (see Figure 7), to predict the experimental results.
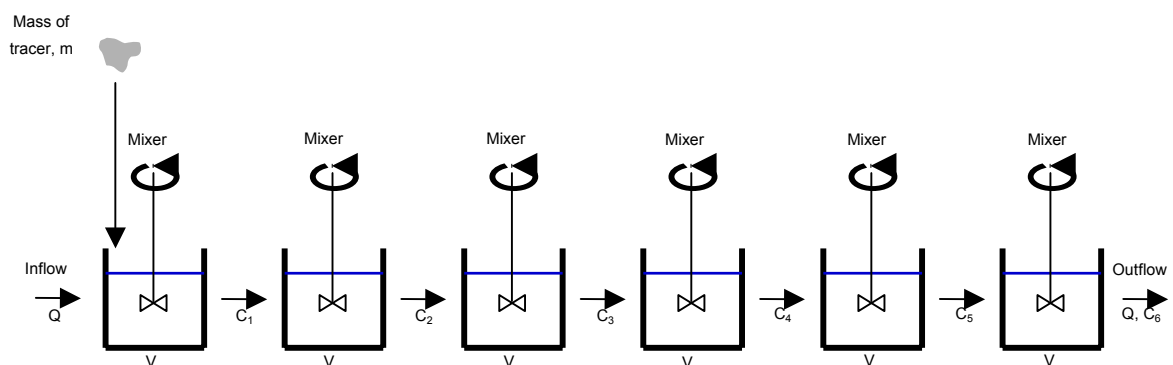
Figure 7: 6 CSTRs in series: Q (flow rate), C_{1-6} (concentration of tracer in CSTR from 1 to 6), V (volume of each CSTR). In this ideal 6 CSTRs tank, all the reactors have the same volume V.

3.1.1. First reactor in the series

Because the entire tracer is added only to the first reactor, the initial concentration would be given by the expression

$$C_0^* = \frac{m}{V} \qquad \text{(Eq. 1)}$$

Where m = mass of tracer added, g

$\qquad C_0^*$ = Initial concentration, g/m3

The mass balance expression for any control volume analysis can be expresses as:

$$\text{In} - \text{out} - \text{Loss} + \text{Generation} = \text{Accumulation} \qquad \text{(Eq. 2)}$$

Where In = mass of constituent entering system

$\qquad$ Out = mass of constituent leaving system

$\qquad$ Loss = mass of constituent disappearing

$\qquad$ Generation = mass of constituent appearing within system due to reaction

$\qquad$ Accumulation = mass of constituent accumulating in system

Because the tracer is added as a pulse input (single event), the influent concentration could be assumed as zero after the initial injection of the tracer. At the same time, because the tracer substance is considered as conservative (no reaction occurs during the experiment), the generation term could be assumed as zero too. Then equation (2) becomes:

$$0 - QC_1 + 0 = V\frac{dC_1}{dt} \qquad \text{(Eq. 3)}$$

Where C1 = Effluent concentration exiting first reactor of the series.

$\qquad$ Q = Flow rate, m3/s (this flow rate is assumed as the same for all the CSTRs in the series

Equation (3) can be rearranged as follow:

$$\frac{dC_1}{C_1} = -\frac{Q}{V}dt \qquad \text{(Eq. 4)}$$

Equation (6) can then be integrated as follow:

$$\int_{C_0}^{C_1} \frac{dC_1}{C_1} = -\int_0^t \frac{Q}{V}dt$$

$$\Leftrightarrow \ln\frac{C_1}{C_0} = -\frac{Q}{V}t$$

$$\Leftrightarrow \frac{C_1}{C_0} = -e^{-(Q/V)t} \quad \text{(Eq. 5)}$$

Considering equation (1), equation (5) can be rewrite as follow:

$$\frac{C_1}{C_0^*} = -e^{-(Q/V)t}$$

$$\boxed{\Leftrightarrow C_1 = -C_0^* e^{-(Q/V)t}} \quad \text{(Eq. 6)}$$

3.1.2. Second reactor in the series

For this second reactor, the generation term (in equation (2)) is still assumed as null, but the influent concentration changes with time and is equal to the effluent concentration from the first CSTR in the series, thus:

$$QC_1 - QC_2 + 0 = V\frac{dC_2}{dt}$$

$$\Leftrightarrow \frac{dC_2}{dt} + \frac{Q}{V}C_2 = \frac{Q}{V}C_1 \quad \text{(7)}$$

Where C2 = Effluent concentration exiting from second reactor

Substituting equation (6) to equation (7) yields:

$$\frac{dC_2}{dt} + \frac{Q}{V}C_2 = \frac{Q}{V}C_0^* e^{-(Q/V)t}$$

$$\Leftrightarrow \frac{dC_2}{dt}e^{(Q/V)t} + \frac{Q}{V}C_2 e^{(Q/V)t} = \frac{Q}{V}C_0^* e^{-(Q/V)t}e^{(Q/V)t}$$

$$\Leftrightarrow \frac{d[C_2 e^{(Q/V)t}]}{dt} = \frac{Q}{V}C_0^*$$

$$\Leftrightarrow d[C_2 e^{(Q/V)t}] = \frac{Q}{V}C_0^* dt \quad \text{(8)}$$

Integrating equation (8) yields the following expression:

$$\boxed{C_2 = C_0^* \frac{Qt}{V}e^{-(Q/V)t}} \quad \text{(9)}$$

3.1.3. Third reactor in the series

For this third reactor, the generation term (in equation (2)) is still assumed as null, but the influent concentration changes with time and is equal to the effluent concentration from the second CSTR in the series, thus:

$$QC_2 - QC_3 + 0 = V\frac{dC_3}{dt}$$

$$\Leftrightarrow \frac{dC_3}{dt} + \frac{Q}{V}C_3 = \frac{Q}{V}C_2 \qquad (10)$$

Where C3 = Effluent concentration exiting from third reactor

Substituting equation (9) to equation (10) yields:

$$\frac{dC_3}{dt} + \frac{Q}{V}C_3 = \frac{Q}{V}C_0^{\star}\frac{Qt}{V}e^{-(Q/V)t}$$

$$\Leftrightarrow \frac{dC_3}{dt}e^{(Q/V)t} + \frac{Q}{V}C_3 e^{(Q/V)t} = \frac{Q}{V}C_0^{\star}\frac{Qt}{V}e^{-(Q/V)t}e^{(Q/V)t}$$

$$\Leftrightarrow d\left[C_3 e^{(Q/V)t}\right] = \frac{Q}{V}C_0^{\star}\frac{Qt}{V}dt$$

$$\boxed{\Leftrightarrow C_3 = \frac{C_0^{\star}\left(\dfrac{Qt}{V}\right)^2 e^{-(Q/V)t}}{2}} \qquad (11)$$

3.1.4. Next reactors in the series

Using exactly the same approach as shown above, the effluent concentration for any number of reactors in series can be obtained. Thus, the corresponding effluent concentration for the fourth, the fifth, the twentieth and the hundredth reactor is given respectively by equations (12), (13), (14) and (15):

$$\boxed{\Leftrightarrow C_4 = \frac{C_0^{\star}\left(\dfrac{Qt}{V}\right)^3 e^{-(Q/V)t}}{6}} \qquad (12)$$

$$\Leftrightarrow C_5 = \frac{C_0^* \left(\dfrac{Qt}{V}\right)^4 e^{-(Q/V)t}}{24} \qquad (13)$$

$$\Leftrightarrow C_{20} = \frac{C_0^* \left(\dfrac{Qt}{V}\right)^{19} e^{-(Q/V)t}}{1.22 \times 10^{17}} \qquad (14)$$

$$\Leftrightarrow C_{100} = \frac{C_0^* \left(\dfrac{Qt}{V}\right)^{99} e^{-(Q/V)t}}{9.3 \times 10^{155}} \qquad (15)$$

The above mentioned formulas have been plotted in Figure 8. In order to have comparable results, the same values of flow rate, initial concentration and volume as the experiment have been used:

-Volume of each tank: V = 1.588 L

-Flow rate: Q = 5.5 mL/s

-Amount of tracer (NaCl) added: m= 1588 mg

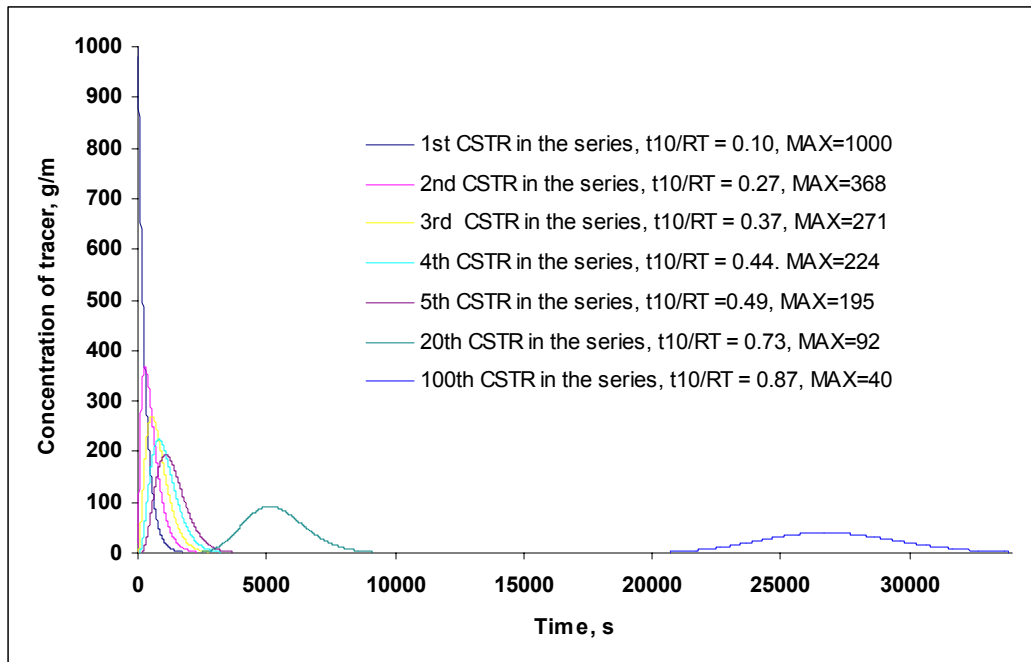-Initial concentration of the tracer in the 1st CSTR: $C_0^* = \dfrac{m}{V} = 1000 mg/L$

Figure 8: The modeling tracer curves of CSTR in series under the same conditions of our experiments (flow rate,CSTR volume).

First of all, we can see on this graph that the maximum outlet concentration of the tracer is decreasing with the number of CSTRs in the series. Moreover, we can see that the shape of tracer curve changes dramatically as the number of CSTRs increases. In fact the curves shape tends to be flattened as the number of CSTRs increases. From mass balance aspect, the sum of all the concentration values for each curve gives the same results, which is consistent with the fact that the same amount of tracer passes through each CSTR. As predicted the maximum concentration decreases progressively with the number of CSTRs in the series. Suprisingly, the sum (integration) of those different curves is a bit variable and the variation is in a range of 10% (this sum varies from 240,000 to 300,000). In comparison, the sum of the values for each theoretical tracer curve was constant (around 270,000) wich was consistant with the fact that the same amount of tracer pass through each CSTR in the series. This experiment has been reproduced 3 times and gives always the same kind of results (data not shown).

In order to have a comparison between this model and the plug flow reactor, the values of t10/RT has been measured as follow. By definition, t10 is the time at which 10% of the tracer has passed trough the effluent outlet. RT is the retention time (Volume/Flow rate). The values of t10/RT obtained from model have been plotted as a function of the position of the CSTR (first, second…) in series. Because the entire tracer is supposed to pass through the outlet of a PFR at the same time, the theoretical value of t10/RT is supposed to be equal to one for this kind of tank. Hence, the more the value of t10/RT is approaching 1, the more the analysed series of CSTRs is approaching the performance of a PFR. The values of t10/RT have then been ploted as a function of the number of CSTRs in the series (see Figure 9).
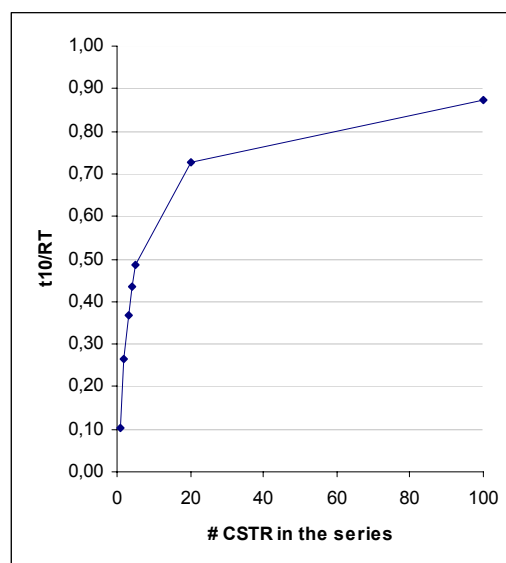
Figure 9: Evolution of t10/RT as a function of the number of CSTRs in the series

As we can see on figure 9, the value of t10/RT approaches progressively to 1 when the number of CSTR is approaching 100 by modelling.

3.2. Experimental results and its comparison with theoretical results

As a second part of this work we try to confirm the predicted results with the experiment.
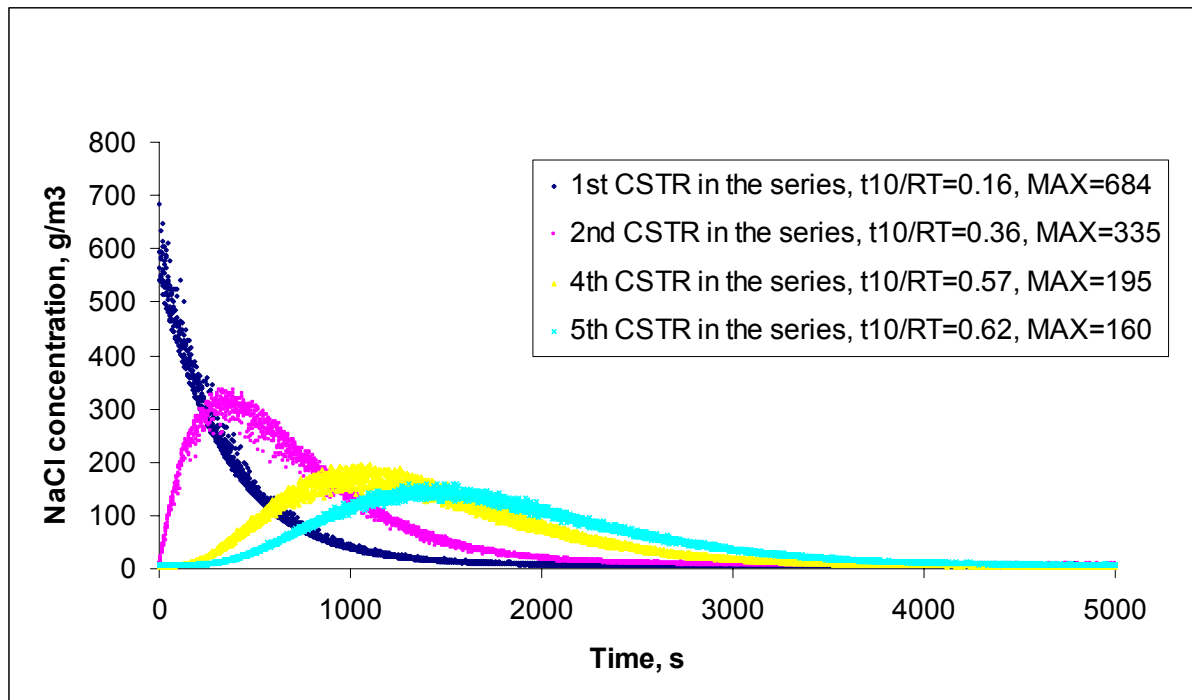

Figure 10 : the experimental concentration curves with the same hydraulic condition such as flow rate, initial concentration, etc.

As we can see in Figure 10, the shape of tracer curves tends to be the same as the theoretical results. Nevertheless, we can see some little differences. The maximum measured concentration for the first CSTR is around 680mg/m^3 instead of 1000mg/m^3 in the theoretical results. Moreover, the maximum concentration of the other CSTRs tends to be always a bit smaller than the theoretical results. The reason for the discrepancy in terms of maximum concentration between the modelling and experimental results is presumed to be either the diffusion nature of salt or the insufficient mixing extent in those CSTRs in series.

Figure 11 shows that the experimental value of t10/RT is a bit higher than the theoretical model, however, this value is still increasing with the number of CSTR and the curve has the same shape as the theoretical model. On this graph we can also see that the error bars for the

three repeated experiments are small demonstrating the high reproducibility of these experiments.
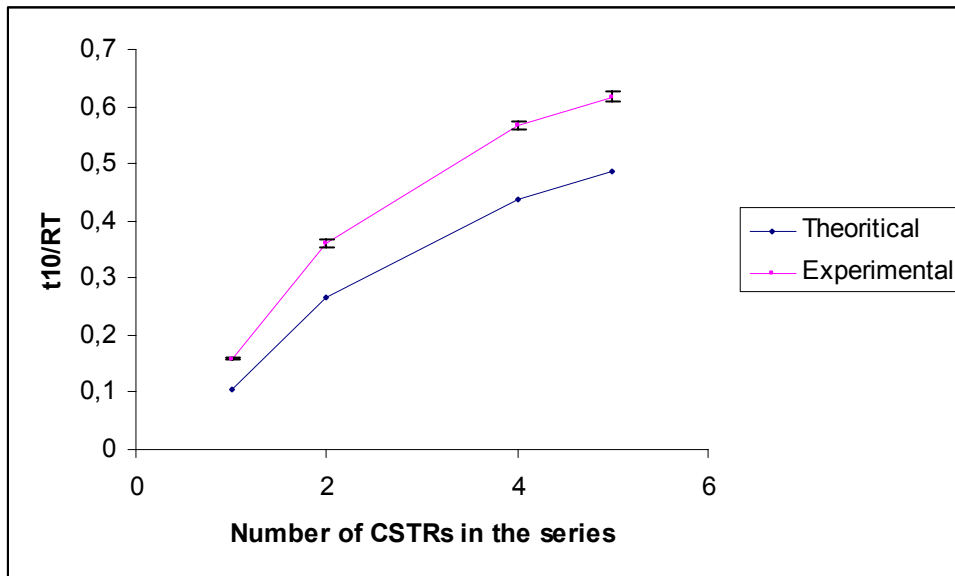

Figure 11: the change in the ratio of t10/RT with the change in number of CSTRs in series theoretically and experimentally.

4. Discussions

Things like the shape of tracer curve, the ratio of t10/RT getting from the experiments show the similar trend as the analytical modelling. To some extent, it confirms that the design of our CSTRs in series is eligible to help us find the correlation of CSTRs in series and PFR.

As expected, the analysis of the modelized and the experimental results allow us to confirm that the efficienty of CSTRs in series approach progressively the performance of a plug flow reactor by increasing the number of the CSTR in the series. In fact the value of t10/RT approaches progressively the PFR t10/RT characteristic value of one.

The theority confirmed by the experiment also showed that the salt concentration curves become flatten and the curve peak becomes wider by using 5 CSTRs in series rather than just 1 CSTR. In consequences, the concentration that passes through a series of CSTR will be more homogeneous than in a single CSTR. From application prospect, the chemical can stay in these tanks for a longer period of time so that it will have long-term efficiency if this effect is required for some particular chemicals (e.g. antimicrobial treatment).

It should be admitted that the experimental results is not exactly the same as what we predicted by modelling analysis. There are several reasons can be attributed to:

1) The dispersion and diffusion of sodium chloride can eventually explain the reduced maximum concentration of salts in the experiment.

2) Insufficient mixing extent required for complete stirring condition as well as the tracer injection method could explain the impossibility we had to have the maximum concentration of a 1000mg/L for the first CSTR in the series. Moreover, the time response of the probes or the LabView software could also been involved in this phenomenon.

3) Another fact that should be considered is the volume of the channel between each cstr. In the theoretical model there is no channel between the CSTRs in the series. The channel may eventually has a impact of the following CSTR. In fact, even if there is no mixing in this channel, it still acts as a CSTR which is just reduced in size. This channel could eventually explain why the maximum concentration of the tracer in the 2nd and the following CSTR is a bit smaller than the predicted results.

4) The water level in each CSTR is a bit higher than the height of the block between each CSTR, which is supposed to be the same as designed. Therefore, the volume of each reactor is a little bigger than that calculated from the design. Hence, this will cause the concentration to be a bit lower than predicted.

Finally, it should be realized that plug flow and completely mixed flow reactors are limiting cases and that actual flow regimes will range in a broad spectrum between these ideal models. The intermediate case is usually referred to as plug flow with dispersion, dispersed plug flow, plug flow with longitudinal mixing, intermediate-mixed flow, or arbitrary flow (Reynolds and Richards 1996).

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Appendix
List of Price for experimental setup

Tank: Material ~ $200.00

       Labor~$150.00

Jar test module: $1000.00

Conductivity meter: Interface: $220.00

             Probes: $92.00×4