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Using Y-shaped microreactor for continuous decolorization of an Azo dye

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ABSTRACT

This study reports the decolorization of an Azo dye (DR16) in a Y-shaped microreactor using Fenton process. The effect of important operation parameters, including dye, H_2O_2, and Fe^{2+} concentrations; solution pH; and feed flow rates on the decolorization efficiency under continuous conditions, has been studied. The results showed that at pH values between 3 and 4, more DR16 vanished from feed stream. Moreover, higher decolorization efficiencies were obtained at higher Fe^{2+} and H_2O_2 concentrations as well as lower dye concentration and feed flow rate. The results indicated that it is possible to reach an efficiency of 86% for DR16 dye decolorization in just 4.2 s, as residence time, using this microreactor. This was obtained due to efficient reactants mixing in the microreactor mixing point. This study illustrates the advantage of using microreactors for continuous flow decolorization process in the comparison with conventional use of batch stirred tank reactors.

Keywords: Microreactor; Continuous decolorization; Fenton process; Azo dye; Direct red 16; Wastewater treatment

1. Introduction

Water pollution by dyes is an important global issue [1]. Industries use dyes in textile dyeing, paper production, leather tanning, and printing. Many kinds of dyes are available on the market, of which 80% of them based on Azo chromogen. The Azo dyes are chemical components containing Azo groups (–N=N–) bond to benzene or naphtha rings in their structure. Various methods have been developed to treat the dye contaminants from the textile industries' wastewater [2]. These processes are coagulation, ozonation, and adsorption by activated carbon, flocculation, and Fenton oxidation [3–6].

Some of the recent studies were focused on using Fenton process to remove several kinds of Azo dyes [7–9]. Fenton process is one of the most effective and rapid process to treat wastewater. The process is based on the generation of the highly reactive hydroxyl radicals from reagents Fe^{2+} and H_2O_2 [10]. The most important advantage of the Fenton process is its simplicity and no need of complicated equipments. Moreover, the used chemicals are available at reasonable costs [11]. In this process, ferric ions and OH radicals are formed by the reaction between hydrogen peroxide and ferrous [12,13]. The reaction equation is as follows:

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$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \quad (1)$$

The hydroxyl radical (OH), which is a well-known strong oxidant, is able to rapidly attack reactants and decompose them [14]. Hydroxyl radicals can react with ferrous or hydrogen peroxides as follows: [15,16]

$$Fe^{2+} + {}^\bullet OH \rightarrow Fe^{3+} + OH^- \quad (2)$$

$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + H_2O^\bullet \quad (3)$$

Moreover, the ferric ions and hydrogen peroxide make ferrous, OOH, and OH radicals according to the following reactions:

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe \cdots OOH^{2+} + H^+ \quad (4)$$

$$Fe \cdots OOH^{2+} \rightarrow Fe^{2+} + HO_2^\bullet \quad (5)$$

$$Fe^{2+} + H_2O^\bullet \rightarrow Fe^{3+} + H_2O^- \quad (6)$$

$$Fe^{3+} + H_2O^\bullet \rightarrow Fe^{2+} + H^+ + O_2 \quad (7)$$

Most of reported studies on using Fenton process were carried out in batch reactors [17]. However, a few works were reported in which the wastewater was decolorized in continuous processes. Merzouk et al. [18] used continuous electro-coagulation for decolorization of a synthetic textile wastewater by aluminum electrodes. They investigated the effect of some parameters such as residence time, influent of pH, and inlet dye concentration on the decolorization process. A decolorization efficiency of 85% of red dye in 14 min was reported by the authors. In another study, Li and Jia [19] designed a packed-bed bioreactor for continuous decolorization of synthetic dyes using rice hull-*Schizophyllum* sp. F17. The decolorization process was carried out in two steps and the decolorization efficiencies of 89.71 and 60.44% at dye concentrations of 142.63 and 110.7 mg/l were reported. However, the reported reaction times were 41 and 29.4 h, respectively, for these dye concentrations.

On the other hand, several studies were reported in which Fenton process was performed in continuous flow reactors. Monteagudo et al. [20] utilized a specific continuous reactor (compound parabolic collector) with air injection for photo-Fenton degradation of the non-biodegradable dye (Reactive Blue 4). In another study, Rosales et al. [21] used a combined technique of the Electro-Fenton process to remove synthetic dyes. They studied continuous decolorization of several dyes in a bubble reactor. Their experiments revealed that with a residence time of 21 h, about 80% of color removal was achieved.

Microreactors are novel reactors with a channel hydraulic diameter of equal or less than 1 mm [22,23]. Microreactors have interesting characteristics such as their small size, fast responding, and their flexibility with low capital and operating cost. It is anticipated that traditional pilot plants may be replaced by these systems.

Among the reported studies in literature, Burns and Ramshaw [24] investigated the nitration of benzene in the presence of the H_2SO_4 catalyst in a T-shaped microreactor with a diameter of 127 μm. Their results showed that decreasing in the microchannel diameter led to a considerable reduction in corresponding byproduct (di-nitrobenzene) concentration due to more efficient mixing. In another study, Lindstrom et al. [25] introduced a microreactor with walls coated with TiO_2 nanoparticles. They studied photo degradation of Methlyne Blue with air-saturated in the presence of excess oxygen. The degradation rate enhanced significantly with the addition of oxygen. However, the author reported that it could operate for more than 1,000 h without any reduction in performance.

In another work, Gao et al. [26] reported ozonation of synthetic wastewater containing Azo dye Acid Red 14 (AR 14) in a high-throughput microporous tube-in-tube microchannel reactor. Their results showed that with increase in ozone gas flow rate, simultaneous decrease in the liquid flow rate, and initial AR 14 concentration, the decolorization efficiency was enhanced significantly.

In another research, Matsushita et al. [27] made a photo catalytic microreactor to reduce organic content of an aqueous solution. The microreactor was coated with a layer of TiO_2 catalyst. They reached to a yield of 92.5% in the best condition.

The aim of the present study is to introduce a novel method for using microreactors in a continuous flow decolorization process. Fenton reaction is a fast reaction. However, long process times, in order of 30 min, were reported for employed conventional batch systems for this reaction [17,28]. This time is called mixing time, which is the time needed by reactants to find each others. Decreasing the treatment time in the proposed continuous systems is the main feature of this study. For this purpose, decolorization of DR16 by Fenton process was investigated. Experiments were conducted in a continuous Y-shaped microreactor in which the Fenton degradation of Azo dye was taken place. The two streams of solution (Azo dye and ferrous sulfate) and H_2O_2 continuously were diverted to the reactor. After the feed streams passed through the microreactor, the treated effluent was analyzed using an UV/V. The influences of different parameters, including H_2O_2, Fe^{2+}, and DR16 concentrations; solution pH; and flow rates of feed streams in DR16 oxidation, were investigated.

2. Experimental

2.1. Materials

An Azo dye Direct Red 16 with a purity 99% from Alvan Sabet Company was used in the experiments. Direct Red 16 molecular structure is illustrated in Fig. 1. Material used in this work were hydrogen peroxide (35% w/w), ferrous sulfate ($FeSO_4{\cdot}7H_2O$, 99%), sulfuric acid (H_2SO_4, 98%), and sodium hydroxide, which all supplied by Merk Inc. The dye solutions were prepared by dissolving a necessary quantity of dye in deionized water. The pH of the solution was adjusted by adding suitable amount from H_2SO_4 and/or NaOH solutions.

2.2. Microreactor

The microchannel was fabricated from Plexiglas with a depth, width, and length of 0.9, 1 and 70 mm, respectively. The cover plate of microreactor was made from quartz plate. The fabricated microchannel is shown in Fig. 2.

2.3. Experimental procedures and analysis

A schematic diagram of the experimental setup illustrated in Fig. 3. A peristaltic pump (QIS©, DSP100) diverted the feeds through the Y-shaped microchannel.

The required amount of $FeSO_4{\cdot}7H_2O$ was added into the dye solution and then the solution pH was adjusted. Both feeds flow rates were measured using two separate flow meters. Samples were collected from the microreactor output stream. A UV spectrophotometer from UNIC Company was used to analyze the samples. The absorption spectrum of DR16 solution was examined to determine the wavelength of the maximum absorption. Fig. 4 shows the absorption spectrum and the maximum absorbance wavelength ($\lambda_m = 524$ nm).

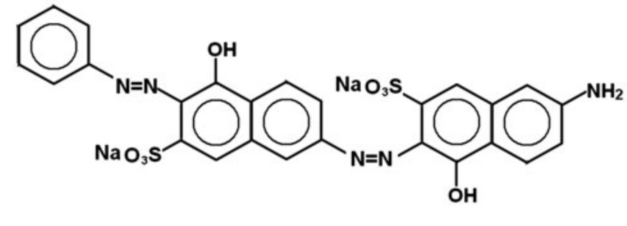

Fig. 1. Chemical structure of Direct Red 16.

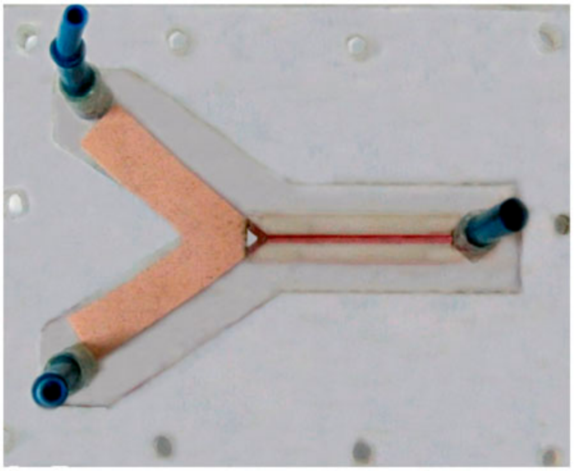

Fig. 2. The microreactor used in the experimental study.

In the next step, the decolorization efficiency was obtained by measuring the absorption intensity of the solution at 524 nm. The decolorization efficiency (%) of DR16 is defined as follows:

$$\text{Decolorization efficiency } (\%) = \frac{\text{abs}_0 - \text{abs}_1}{\text{abs}_0} \times 100 \qquad (8)$$

in which abs_0 and abs_1 are the absorbances of DR16 in aqueous solution at the initial condition and the outlet stream, respectively. It should be noticed that abs_0 is the absorbance of diluted DR 16, by considering the amount of H_2O_2 solution (water + H_2O_2) fed to the reactor. In other words, by the calculation of amount of material entered via H_2O_2 solution, the initial dye was diluted with water and its absorbance was measured and called abs_0.

In this study, the effects of different parameters over decolorization efficiency were investigated. Examined range is given in Table 1. All experiments were conducted at 25°C.

In all experiments, in order to be sure that the measured concentrations are in steady state condition, all samplings were done after 2 min as it was found that during this time, the system reached to steady state condition for all feed flow rate. The minimum and maximum residence times in the range of this study were 0.5 and 4.2 s, respectively. In order to illustrate this point, an example of unsteady state test for feed flow rate of 3 ml/min is shown in Fig. 5. It should be mentioned that the residence time of reactant for this layout in the microchannel was about 1.5 s and entire time required for analysis was almost 10 s.

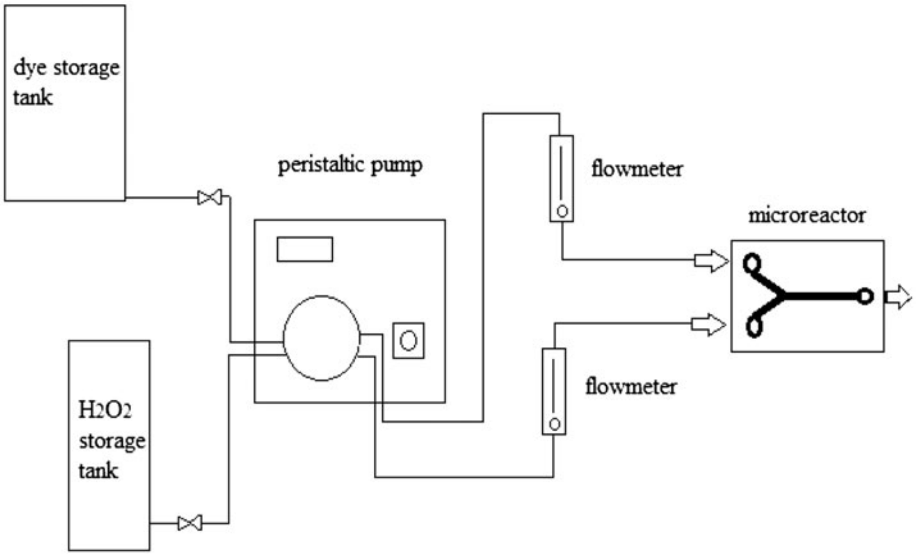

Fig. 3. A schematic diagram of the experimental setup.

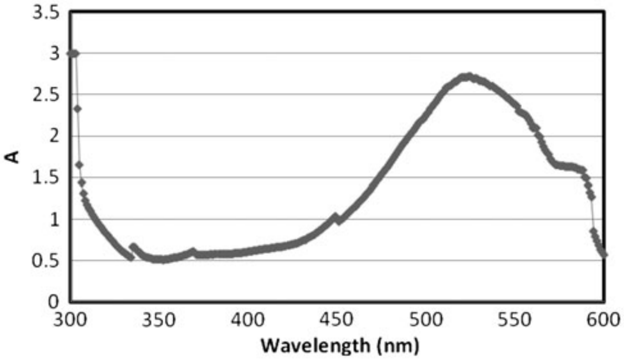

Fig. 4. UV–Visible spectrum of DR16; [DR16] = 30 mg/l and $T = 25$ °C.

Table 1
The range of operating conditions

Parameter	Range
pH	2–5.5
$[Fe^{2+}]$ (mg/l)	0.5–4
$[H_2O_2]$ (mg/l)	150–500
[DR16] (mg/l)	10–40
Flow rate (ml/min)	1–8

3. Results and discussion

3.1. Effect of pH

In Fig. 6, the effect of pH on the decolorization efficiency of DR16 by Fenton process is illustrated. As shown in this figure, the value of proper pH is about 3.5 and by changing this value, the decolorization efficiency decreased. The results clearly indicated that at low pH (less than 3), the decolorization efficiency is between 22 and 26% at various flow rates.

From these results, it can be seen that at pH higher than efficient value, the decolorization efficiency decreased again for all examined flow rates. In the reported studies in literature [29–31], pH close to 3 is usually suggested as the best condition for Fenton oxidation process. The obtained results from this study are also in agreement with this suggestion.

This can be interpreted that at lower pH values (higher H^+ concentrations), the excessive H^+ reacts with H_2O_2 and produces oxonium ion, $H_3O_2^+$. The oxonium ion is stable, and does not react with Fe^{2+} and consequently no more $OH^\bullet$ will be produced. This condition will reduce the decolorization efficiency of DR16. In addition, at pH values higher than 4.0, the formation of ferrous and ferric oxyhydroxides causes a reduction in the reaction rate between Fe^{2+} and H_2O_2 and decreases atin the decolorization efficiency of DR16.

3.2. Effect of different H_2O_2 concentration

Fig. 7 shows the relationship between the decolorization efficiency and H_2O_2 concentrations in Fenton process. The results reveal that by increasing H_2O_2 concentration from 150 to 500 ppm, a favor effect on the decolorization of DR16 was happened. The results show the decolorization efficiency improved from 62.5 to 73% at the lowest flow rate of 1 ml/min. This may indicate that by increasing H_2O_2 concentration, which

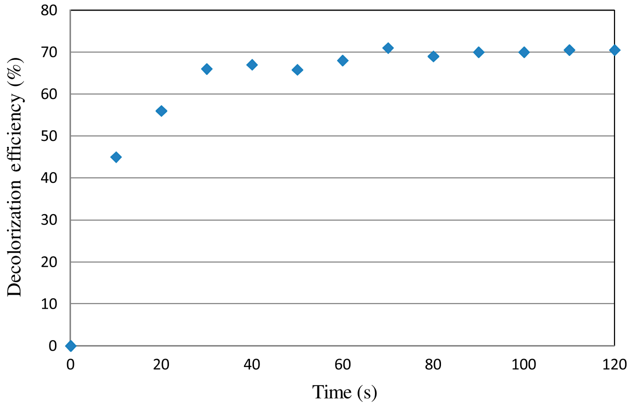

Fig. 5. An example of unsteady decolorization progress in the studied microreactor (pH = 3.5; [DR16] = 30 mg/l; $[H_2O_2]$ = 150 mg/l; $[Fe^{2+}]$ = 0.5 mg/l; and temperature = 25˚C).

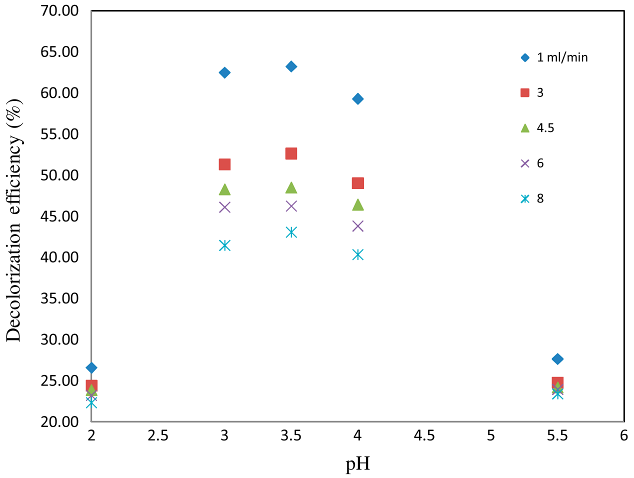

Fig. 6. The effect of pH on the decolorization of DR16 by Fenton process at [DR16] = 30 mg/l; $[H_2O_2]$ = 150 mg/l; $[Fe^{2+}]$ = 1 mg/l; and temperature = 25˚C at various flow rates (ml/min).

is the source of active OH generation, the concentration of OH increased and therefore the decolorization efficiency improved. With regard to the above reasons, in this study the efficient H_2O_2 concentration of 150 mg/l was found.

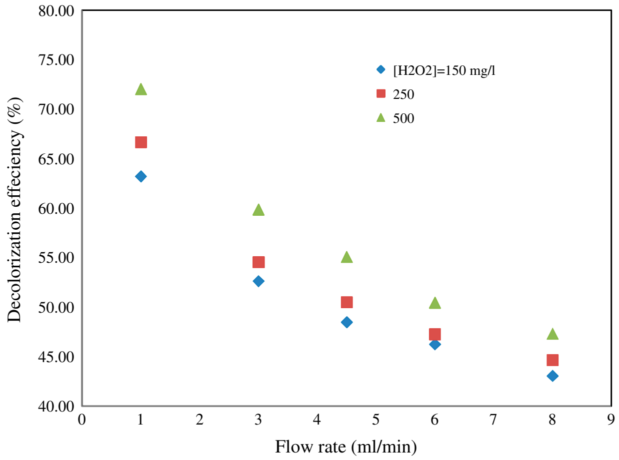

Fig 7. The effect of the H_2O_2 concentration on the decolorization of DR16 by Fenton process at pH = 3.5; [DR16] = 30 mg/l; $[Fe^{2+}]$ = 1 mg/l; and temperature = 25˚C at various flow rates (ml/min).

3.3. Effect of dye concentration

In order to study the effect of dye concentration on the decolorization efficiency, a series of experiments were carried out at various dye concentrations between 10 and 40 ppm. Fig. 8 illustrates the decolorization efficiency at various dye concentrations. From this figure, it is possible to find that the decolorization efficiency declines with increase in the dye concentration. The results show that increasing the dye concentration from 10 to 40 ppm did not have any favorable effect on the decolorization of DR16 and the efficiency values reduced from 74 to 54%. This might indicate at higher dye concentration, the OH radical was not enough for degradation of all dye molecules. Therefore, the decolorization efficiencies decreased.

3.4. Effect of the ferrous concentration

The results in Fig. 9 reveal that at a constant flow rate, the decolorization efficiency was improved with increase in ferrous concentration. From this figure, it can be seen that at the lowest flow rate, increase in ferrous concentration from 0.5 to 2 ppm caused a significant improvement in the decolorization efficiency from 42 to 79%. However, at the same condition, an extra addition of this agent from 2 to 4 ppm improved the color removal only by 6% (from 79 to 85%). Therefore, the ferrous concentration of 1 mg/l was treated as the best value in the range of studied concentrations.

It can be seen from Fig. 9 that increase in ferrous concentration increases decolorization efficiency. However, there is no direct proportionality between ferrous concentration and the decolorization efficiency. The results show that the decolorization efficiency became almost double with eight-time increase in the ferrous concentration. This can be explained by Fenton reaction and rapid H_2O_2 to OH conversion, described in Eq. (1). However, it can be seen that rate of increase in decolorization efficiency decreases gradually at higher Ferrous concentration.

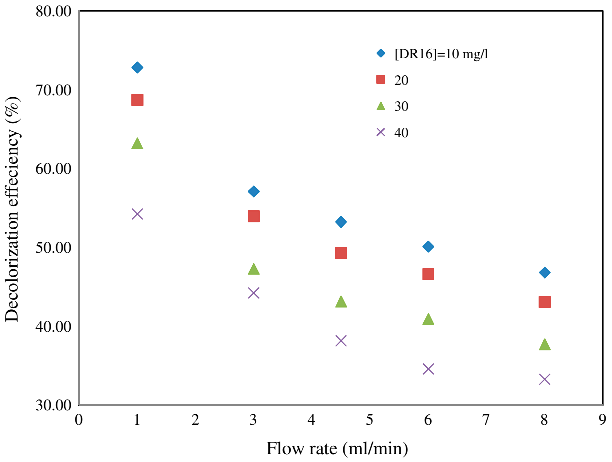

Fig 8. The effect of the dye concentration on the decolorization of DR16 by Fenton process at pH = 3.5; $[Fe^{2+}] = 1$ mg/l; $[H_2O_2] = 150$ mg/l; and temperature = 25˚C at various flow rates (ml/min).

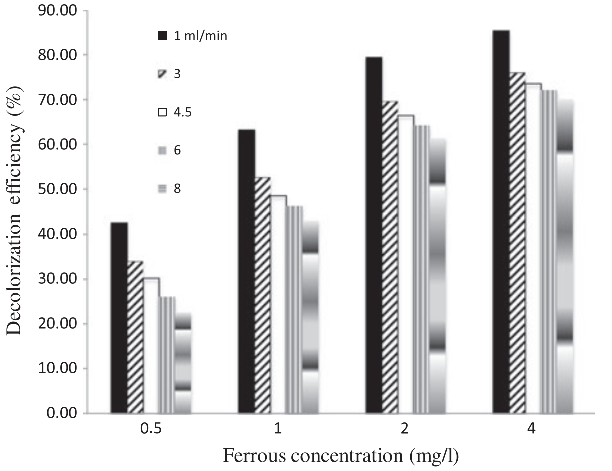

Fig. 9. The effect of the flow rate on the decolorization of DR16 by Fenton process at pH = 3.5; [DR16] = 30 mg/l; $[H_2O_2] = 150$ mg/l; and temperature = 25˚C at various Fe^{2+} concentration (mg/l).

3.5. Effect of flow rate

In the peresent work, the effect of the influent flow rate on decolorization of DR16 was investigated. The revealed results in Fig. 9 indicate that at a fixed concentration of Fe^{2+}, increase in the feed flow rate led to a significant reduction in the decolorization effiecency. This may be explained by a decrease in the reactor residence time. In other words, with increase in feed flow rate, less time is available for ferrous ions to react with hydrogen peroxide to produce hydroxyl radicals and consequent dye/hydroxyl radical reaction. For instance, at Fe^{2+} concentration of 1 ppm, increase in feed flow rate from 1 to 8 ml/min reduced the decolorization efficiency from 64 to 44%. The flow rate of 1 ml/min was obtained as the best value for this purpose.

4. Conclusions

This work represents the decolorization of Direct Red 16 dye in an aqueous medium in a continuous microreactor. This work aims to connect the well-known Fenton process with the novel microreactor technology. The results revealed that the decolorization efficiency was considerably increased compared with conventional proposed reactors such as stirred tank reactors. This is mainly due to efficient micro- and macro-mixing that took place in these types of reactors.

Based on experimental outcomes from this study, increase in the H_2O_2 and Fe^{2+} concentrations had a positive effect on dye decolorization. The results show that the decolorization efficiency reduced when the concentration of dye and/or flow rate of reactants increased.

In general, it can be concluded that the Fenton process in microchannel is quite useful to promote decolorization of DR16. High decolorization efficiency, about 86%, was obtained in the studied microreactor, which promises a new technique with high decolorization efficiency for wastewater treatment. One of the main advantages of the proposed system is reputability in scale-up for industrial purposes. For higher treatment load, the proposed microreactor can be used in a parallel cascade layout.

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