Advanced oxidation process in textile wastewater treatment using microreactor system

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Abstract. The paper analyses the possibility of treating textile wastewater contaminated with the synthetic dye Acid Violet 109 in a microreactor system using advanced oxidation process. Wastewater from textile industry pose a risk to the environment. Effluents this type could be treated on many different ways but many of them have toxic byproducts and have also high operation and maintenance costs. Advanced oxidation processes show success with acceptable operating and maintenance costs. Alternative solution for dealing with wastewater contaminated with dyes is treatment in microreactor systems. Treatment of simulated wastewater with Fenton's reagent in microreactor system was investigated. Microreactor set consisted of two plunger pump units, mixer and PTFE tube. Efficiency of decolourisation has been determined, with a focus on microreactor parameters, reactants flow and molar ratio of reaction mixture.

1 Introduction

Environmental protection has become an important topic because of the increase in industrial activity [1]. Industrial activity results in increasing water consumption and amounts of wastewater contaminated with significant amounts of pollutants. A relatively new treatment concept includes treatments in microreactor systems as an attractive alternative to standard processes. Large number of different types of microreactor systems and large number of methods for removing pollutants opens up, new possibilities for the application of different treatment types.

Treatment of textile industry wastewater with over 100,000 different commercially available dyes made with quality to be resistant to natural degradation processes is a real challenge [2-5]. Wastewater this kind, with a high content of harmful and carcinogenic dyes, requires the application of effective treatment methods. Many of the commercially used treatment methods at the end of the process have treated water but also large amounts of by-products produced during the treatment process. Then, that newly formed waste must be treated but from an economic point of view as well as from the point of view of environmental protection, such treatment methods are not desirable options.

Acid violet 109 (AV 109) is an anthraquinone dye with a violet-blue hue. It is used in dyeing and printing processes on wool, silk and polyamide materials. This dye is very stable in wastewater and treatment is not easy [6].

Advanced oxidation processes (AOP) are widely used in treatment of wastewater contaminated with various pollutants. Fenton is considered one of the most effective improved processes for the oxidation of waters containing hazardous organic pollutants [7]. It is a catalytic-oxidizing mixture of hydrogen peroxide and iron ions. In the first step of the Fenton reaction, H_2O_2 is decomposed under the divalent or trivalent iron ion. That way a reactive hydroxyl radical is formed, equation 1.

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

In this reaction, iron plays the role of a catalyst, while the hydroxyl radical is promoter of the reaction because it is continuously consumed and regenerated. The complex mechanism of decomposition of organic molecules begins with oxidation by hydroxyl radicals and continues with direct oxidation with hydrogen peroxide and oxidation of other radicals and mutual reaction of radicals. After the first step of the reaction, the oxidation of organic matter to harmless compounds, i.e. to carbon dioxide and water.

Whether if the reaction will be successful depends on the concentration and ratio of the participants in the reaction, but also to a large extent on the conditions under which the reaction is performed. The temperature and duration of the reaction are important, but the most important is the pH value of the reaction mixture. The disadvantages of the Fenton process are that the reaction is carried out in a highly acidic environment and that the process leads to the production of sludge.

Although treatment of anthraquinone dye AV 109 has not been the subject of much research, especially using Fenton's reagent or microreactor systems, there are two studies that have dealt with this topic. Stupar et al. [8] synthetized magnesium ferrite particles and used in the decolorization of the Acid Violet 109 water solutions' by combination of adsorption and heterogeneous Fenton process. Results of this experiment, for with optimal conditions, reached decolorization of 99.1%. That result was achieved 55.4% by adsorption and 43.7% by the

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Fenton process. In research of Dajic et al. AV 109 solution was treated in batch system with Fenton reagent. In this research reaction was conducted to check efficiency of Fenton reaction with different concentration of ferrous ion. Results showed that decolorisation efficiency of 90.6%; 90.5% and 98.2% can be achieved after 60 minutes, for Fe^{2+} concentration of 0.2, 0,5 and 1 mM, respectively [9].

In this research, dye decomposition was caried in microreactor system. In the interest of environmental protection, it is desirable to achieve good results by minimising the use of chemicals. This research was based on analysing wastewater treatment using a new, appropriate approach that reduces the consumption of chemicals. The aim was to find the most efficient method of dye removal with minimal use of chemicals and lower material, energy and time costs, while producing as few pollutants as possible at the end of the process. The decomposition of the anthrahinone dye was carried out in a microreactor system. Microreactors are good technologies for solving various problems. These are relatively new technological processes that have only recently been utilised [10]. The treatment of wastewater from the textile industry in this way represents process intensification combined with environmental protection [11]. For real processes, microreactors need to be scaled up due to their small volume. Scaling up is not difficult as it can be done by multiplying the reactors. Short reaction time, good temperature control, security and efficiency are benefits over conventional batch treatment [12-14].

Only research than employed microreactor system in dye solution decolorisation of AV109 in microreactor was research of Svetozarevic et al. [15]. In this research biodegradation of due solution was done with soyabean and potato peroxidase. Results showed decolorisation efficiency of 95%; and 76% can be achieved after 3 minutes, for soyabean and potato peroxidaze, respectively for case when concentration of dye solution was 10 $mgdm^{-3.}$

One of problems of wastewater decomposition in microreactors are higher capital costs compering to decolourisation in batch system. The use of simple microreactor systems connected to pumps could ensure relatively low costs, and the aforementioned disadvantages would be negligible in relation to the success that could be achieved in this way.

2 Materials and methods

2.1 Materials

The investigation of decolorization of dye solution from textile industry was carried out with the Fenton's reagent under continuous conditions at room temperature. The dye solutions prepared using distilled water and Acid Violet 109, DCC colorants (Ningbo, China). Initial concentration of dye was 100 mg/dm^3. For industry wastewater with this concentration of dye is considered to be heavily polluted wastewater [16]. The pH value of the dye solution samples was set to 3, as this pH value has proven to be the most favorable in previous tests, which also corresponds to the literature data. In order to reduce clean water consumption, $FeSO_4{\bullet}7H_2O$ was added directly to dye solution. Concentration in all the samples was 0,5 $mmol/m^3$. Table 1 shows the properties of the dye used in the experiments.

Table 1. AV 109 characteristics.

Molecular formula	$C_{35}H_{34}Br_2N_3NaO_7S$
CAS number	12220-63-2
Molar mass	823.52

2.2 Method

Experiments were done in microreactor system which consisted of two pump units (LC-20AD XR, Shimadzu USA Manufacturing Inc), micromixer and microreactor tube made from PTFE.

Microreactor tubes with diameter 0.3, 0.5 and 0.8 were used in order to archive maximal possible degradation of dye. The degradation efficiency was quantified using a spectrophotometer (Shimadzu UV–Vis 1700) at 590 nm. A standard method was used comparing the absorbance to a calibration curve. The calibration gives information of the amount of dye present in decolorization product, from which the degradation efficiency of removed dye was calculated. All experiments were performed at room temperature, between 20 and 23 °C, in triplicate.

Figure 1 shows experimental set up. One pump was connected to simulated wastewater – dye solution with diluted iron and the other one with diluted solution of hydrogen peroxide. These flows mix in the micromixer and that is the moment when reaction starts.

Fig. 1. Experimental set up, PTFE microreactor tube is connected to two plunger pump units

3 Results and discussion

In this study, investigation of anthraquinone dye AV109 degradation using Fenton's reagent in a microreactor system was performed.

In this system sludge at the end of the process was not formed. That is a significant advantage because there is not by-product that should be additionally treated.

3.1 Influence of molar ratio

As the first step of the Fenton reaction, combination of H_2O_2 and Fe (II) is crucial for the generation of oxidants in this process. Molar ratio H_2O_2/Fe^{2+} was first investigated in these experiments. The degradation reaction was performed in reactors with 1, 5 and 15 m length and 0.3 mm diameter (Fig. 1).

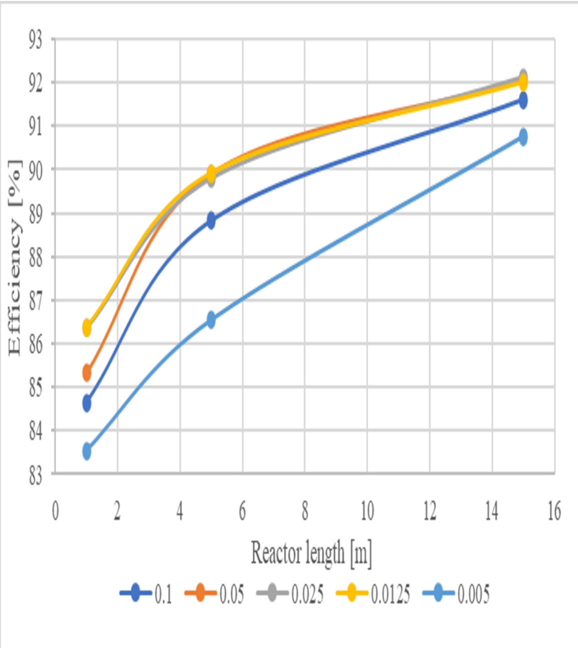

Fig. 2. Influence of molar ratio on decomposition of AV109

From Fig. 1, it can be concluded that reactor with 15 m length had shown best performance with efficiency of dye removal for reaction mixture with molar ratio 0.0125 and 0.025. As these results showed almost same efficiency it is better to use reaction mixture with molar ration of 0.025 because in this case larger quantity of wastewater would be treated with the same quantity of additionally added chemicals.

3.2 Influence of reactor diameter and length

3.2.1 Reactor diameter

The degradation reaction was performed in reactors with 0.3, 0.5 and 0.8 mm diameter and the length of 1 m. (Fig. 3).

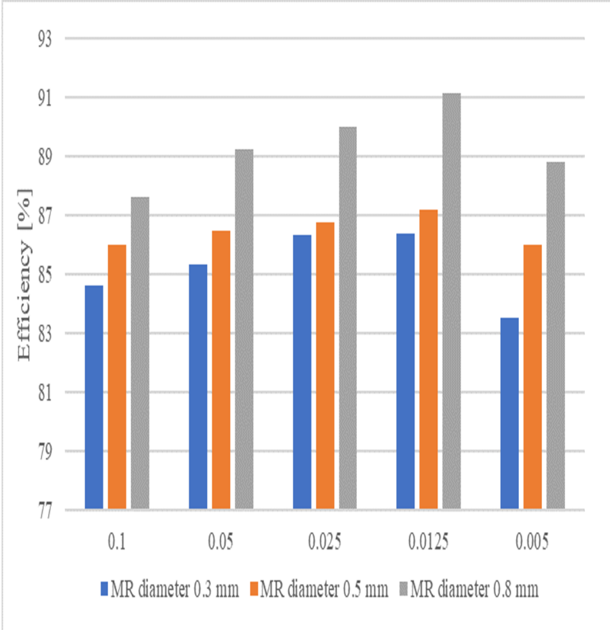

Fig. 3. Influence of reactor diameter on decomposition of AV109

It could be concluded that decomposition of dye AV 109 in Fenton's reaction in microreactor is successful but the reactor with 0.8 diameter sowed highest dye removal. The results in reactor with diameter of 0.8 are with efficiency greater than reactor with diameter of 0.5 and 0.3 mm in average 2.88 and 4.12 % respectively.

3.2.1 Reactor length

After influence of reactor diameter, the influence of the microreactor's length was investigated. Figure 4 shows influence of reactor (length diameter 0.8 mm) length on decomposition of textile dye in wastewater.

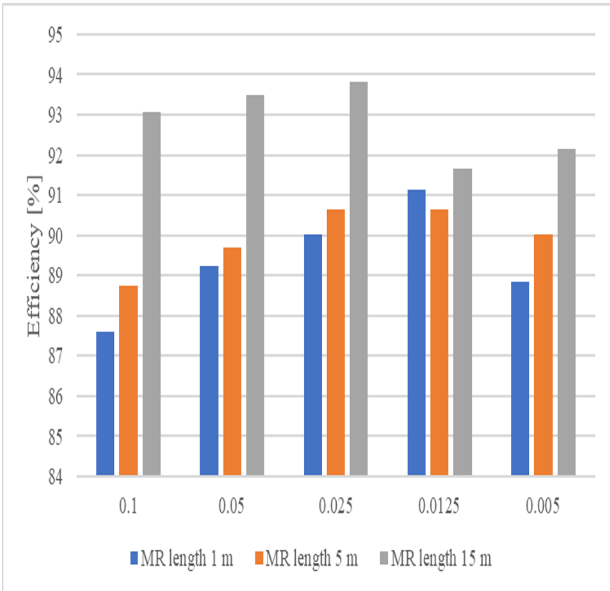

Fig. 4. Influence of reactor (with diameter 0.8mm) length on decomposition of AV 109 in simulated wastewater

The degradation reaction was performed in reactors with 1, 5 and 15 m length and 0.8 mm diameter (Fig. 4).

From fig. 4 it can be concluded that reactor with 15 m length had shown best performance with for any molar ratio while slightly worse are decomposition results for reactor with length of 5 and 1 meter. Differences in efficiency of decomposition between reactor with length 1 m and 5 m are 3.48±1.97 %.

3.3 Influence of flow rate

In this set of experiments, the flow rate was manipulated, resulting in different residence time and mixing intensities. That was the way to find out whether mixing intensity or residence time have greater influence on decomposition process. The degradation was performed in reactor with diameter 0.3 mm with length of 15 m. Flow rate was set to be 1 and 5 μl/min. Results are shown in figure 5.

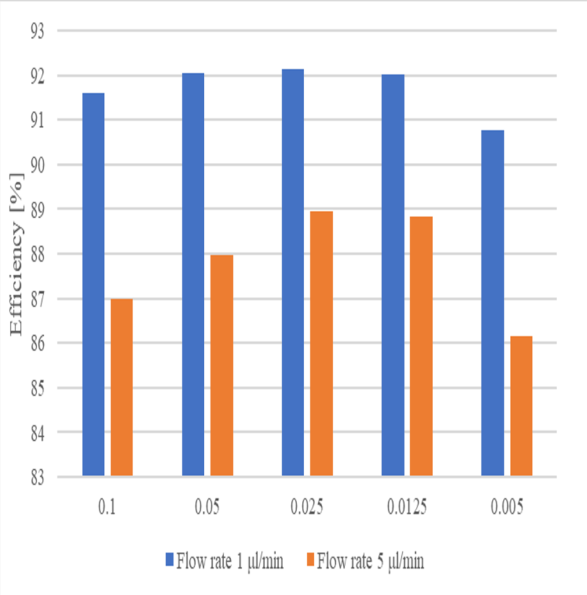

Fig. 5. Influence of flow rate on decomposition of AV 109 for different molar ratios and flow rate

At a flow rate of 1 μl/min, the reaction mixture remains in the system for 1.06 minutes and at a flow rate of 5 μl/min, the mixture remains in the reactor for 0.22 minutes. Figure 4 shows that satisfactory results are obtained when the reaction lasts 0.22 minutes, but much better results are obtained when the mixture remains in the reactor for 1.06 minutes. Difference between results od these two flows are between 3 and 5 %.

3.4 Influence of different reactor set

Results of decomposition of anthraquinone dye in different microreactor sets by Fenton's reagent are shown in figures 5- 7.

Figure 6 shows results achieved in Fenton's process in microreactors long 1 m with different diameter for various reaction mixture with flows 1 and 5 μl/min.

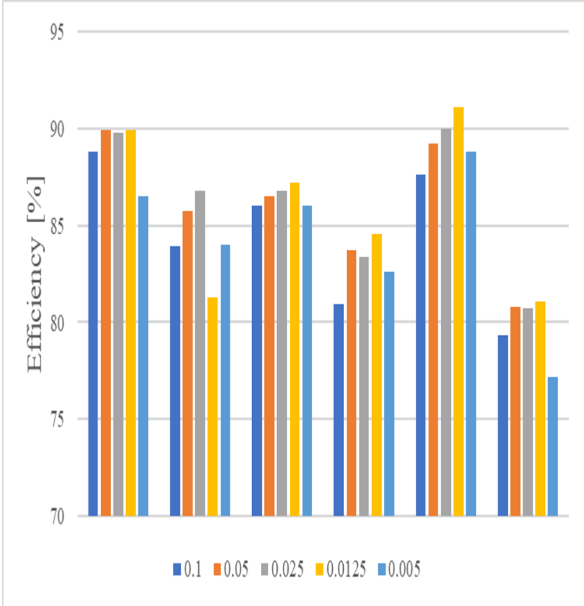

Fig. 6. Summary results of decomposition of AV 109 in microreactor system in reactors 1 m long with different diameter and for deferent molar ratios

Figure 7 shows results of Fenton's degradation process in microreactors long 5 m with different diameter for various reaction mixture with flows 1 and 5 μl/min.

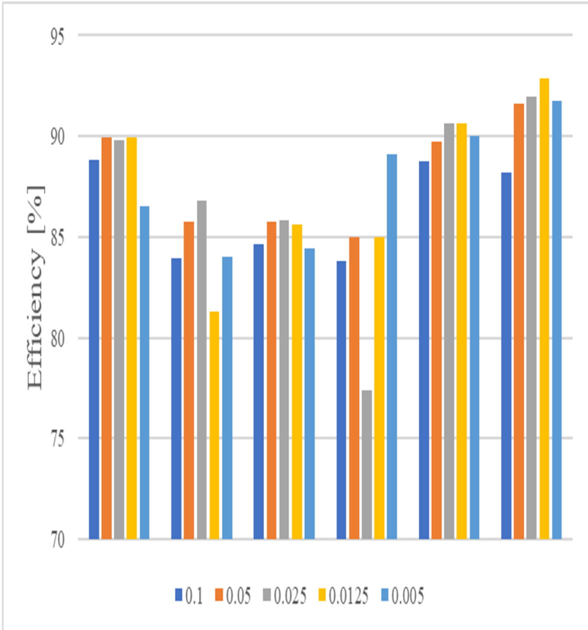

Fig. 7. Summary results of decomposition of AV 109 in microreactor system in reactors 5 m long with different diameter and for deferent molar ratios

Figure 8 shows results achieved in Fenton's process in microreactors long 15 m with different diameter for various reaction mixture and with flows 1 and 5 μl/min.

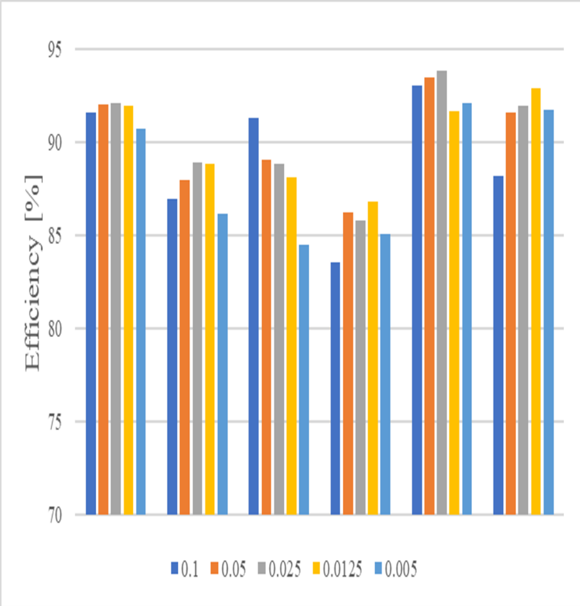

Fig. 8. Summary results of decomposition of AV 109 in microreactor system in reactors 15 m long with different diameter and for deferent molar ratios

From these figures it is obvious that Fenton's reaction is successful is microreactor systems even with relatively small amounts of chemical agents. Efficiency is highest in reactor with 15 m length but success in 5 m reactor is also at an enviable level. This kind of treatment is considered to be modern and environmentally friendly with no nus-product which is charactered for Fenton's reaction in batch systems.

4 Conclusion

In this research, the degradation of the anthraquinone dye Acid Violet by Fenton's reagent in a microreactor was investigated. First experiments were done to analyse influence of molar ratio on degradation efficiency. Next experiments were done to investigate influence of microreactor characteristic: diameter and length and at the end, influence of process parameter-flow rate on efficiency was tested.

The results showed success in comparison with this type of treatment that is normally used. Such a high level of decolorization efficiency achieved in high concentration dye solutions could be considered a success.

This type of treatment is modern, environment friendly with no toxic nus-product and wastewater treated this way could be directly released in water recipient. For all these reasons, treatment in microreactor systems should be considered for wide industry application. The obtained results and the achieved removal efficiency show that this process has a great potential for commercial use, given the fact that by numbering up the microreactor, scale-up can be easily done.

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