Mineralization and biodegradability enhancement of Methyl Orange dye by an effective advanced oxidation process

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ABSTRACT

An effective process for the oxidation of Methyl Orange dye (MO) was determined by comparing the mineralization efficiency between two advanced oxidation processes (AOPs) viz., ozonolysis and gamma radiolysis in presence and absence of an added inorganic salt potassium persulfate ($K_2S_2O_8$). The effects of various operating parameters such as ozone flow rate and reaction temperature were optimized to achieve the best possible mineralization extent of MO by ozonolysis. The mineralization efficiency of MO was significantly enhanced during gamma radiolysis in presence of $K_2S_2O_8$ ($\gamma + K_2S_2O_8$) compared to in absence of $K_2S_2O_8$. The presence of methyl group at the amine of phenyl ring assisted the mineralization of dye during $\gamma + K_2S_2O_8$. The oxygen-equivalent chemical-oxidation capacities (OCC) of ozonolysis and $\gamma + K_2S_2O_8$ for 75% mineralization of the dye solution were calculated as 7.008 and 0.0336 kg equiv. O_2 m^{-3}, respectively which signifies that $\gamma + K_2S_2O_8$ can be explored as an effective AOP. The non-biodegradable MO dye solution became biodegradable even after the dose of 0.5 kGy during $\gamma + K_2S_2O_8$ compared to 1 kGy in absence of $K_2S_2O_8$. The study concludes that a lower dose $\gamma + K_2S_2O_8$ could be one of the efficient pretreatment steps before undergoing biological degradation of dye solution.

1. Introduction

Textile industries are the major sources of producing highly colored dye wastewater. Synthetic dyes are extensively used in textile dyeing, paper printing, color photography, pharmaceutical, food, cosmetics and other industries (Rafi et al., 1990). The textile industries tend to intensify their efforts on producing dyes for mostly used textile fibers i.e. cotton and polyester. Along with the increase in the number of the synthetic dyes, the textile effluent creates an aquatic pollution alarm. The textile dyes as well as the dye intermediates with high aromaticity and low biodegradability have emerged as major aquatic pollutants (Arslan et al., 2000; Sauer et al., 2002). Azo dyes belong to the class of dyes most commonly employed in textile industry. These dyes pose serious environmental hazards (Mrowetz and Selli, 2004).

The majority of textile effluent treatment plants employ conventional physico-chemical treatment methods such as chemical precipitation, coagulation followed by biological treatment (RERES/7/2007; Georgiou et al., 2003). However, these physico-chemical processes need to maintain several steps and also suffer from the generation of large amount of sludge. From this point of view, microbial treatment is more eco-friendly, cost-competitive alternative, with few limitations. Firstly, many synthetic organic pollutants are toxic to the micro-organisms and

therefore, the efficiency of biodegradation depends on the molecular structure of these pollutants (Pearce et al., 2003; Kim et al., 2007). Secondly, the process efficiency of the microbial treatment plant is not very effective owing to the time span of the biodegradation process. These limitations of microbiological treatment leave a scope to develop an effective pretreatment step of the dye solution which increases the biodegradability of the same.

Advanced oxidation processes (AOPs), including high energy ionizing irradiation, involving the reaction of hydroxyl radicals (·OH), are emerging as an efficient technique for complete degradation of organic compounds with minimized generation of sludge (Andreozzi et al.,1999). We have also reported recently that sulphate ($SO_4^{\bullet-}$) radical is a better mineralizing agent than ·OH radical during radiolysis for a couple of organic compounds containing alkyl substituents Paul (Guin) et al., 2014a, 2014b). Radiation induced decolouration and degradation of individual azo dyes have been widely investigated (Suzuki et al., 1978; Paul et al., 2010, 2011). However, it is imperative to compare the efficiency of radiolysis with other AOP for the degradation of dye solution. Therefore, in the present study, two different AOPs viz. ozonolysis and gamma radiolysis in presence and absence of an added inorganic salt potassium persulfate ($K_2S_2O_8$) were employed to mineralize one of the extensively used dyes, Methyl
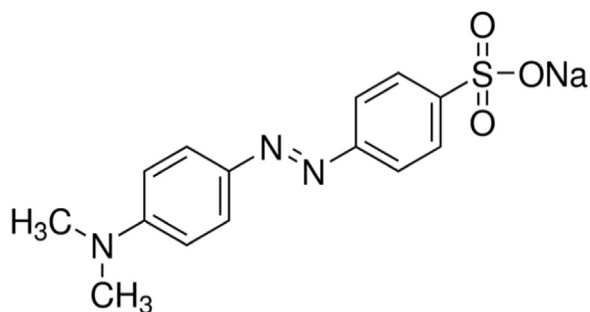
Fig. 1. Molecular structure of MO dye.

Orange (MO) in textile industries. In this maiden attempt, the mineralization efficiencies of MO by these AOPs were compared in terms of oxygen-equivalent chemical-oxidation capacities (OCCs) to find an effective oxidation process. The extent of enhancement of biodegradability of the irradiated dye solution in presence and absence of $K_2S_2O_8$ was also evaluated.

2. Experimental

MO and $K_2S_2O_8$ were purchased from Sigma-Aldrich and used without any pretreatment. All other chemicals used were of high purity and used as received. The molecular structure of MO dye was shown in the Fig. 1. Gamma radiolysis of MO was carried out using ^{60}Co gamma chamber at a dose rate of 0.75 kGy h^{-1}. Ozone (O_3) was generated from pure oxygen using an ozone generator L10G. The rate of flow of ozone through the solution was determined as 6.7×10^{-3} mol dm^{-3} min^{-1} by the iodometric method. All the experiments were performed at pH 6.5. The absorbance values of the dye solutions were measured spectrophotometrically by using U-2800 spectrophotometer and the decolouration extent (% decolouration) of the dye solutions were calculated by using the following Eq. (1).

$$\% \ decolouration = \frac{A_0 - A}{A_0} \times 100 \qquad (1)$$

A_0 = initial absorbance of the dye solution; A = final absorbance of the dye solution at different time of treatment.

The chemical oxygen demand (COD) is a measure of the amount of oxygen required to oxidize organic matter and inorganic chemicals such as nitrite and ammonia. The COD values of the dye solutions were determined by incubating the dye solutions with strong chemical oxidant ($K_2Cr_2O_7/H_2SO_4$) under specific temperature condition for a predetermined time period by using Spectroquant®Pharo 300 COD analyzer. Mineralization extents (% mineralization) of the dye solutions were calculated by using the following Eq. (2).

$$\% \ mineralization = \frac{COD_0 - COD}{COD_0} \times 100 \qquad (2)$$

COD_0 = initial COD of the dye solution; COD = final COD of the dye solution at different time of treatment.

The 5 day biochemical oxygen demand (BOD_5) of the dye solutions were measured by using WTW OxiTop Control BOD Measurement System and the enhancement of biodegradability of the dye solutions were determined by measuring the biodegradability index BOD_5/COD ratio of the dye solutions.

3. Results and discussions

3.1. Effect of O_3 flow rate on the mineralization of aqueous MO dye solution

Mineralization of aqueous 3×10^{-4} M MO dye solution was studied by 5 min of ozonolysis with varying O_3 flow rates of 0.5–5 L/min at pH
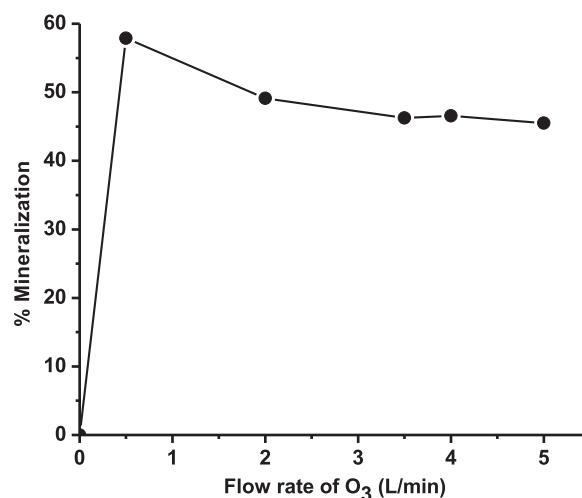

Fig. 2. Mineralization of aqueous 3×10^{-4} M MO dye solution for 6 min of ozonolysis with varying O_3 flow rates.

6.5 as shown in the Fig. 2. It was observed that ~58% mineralization of MO was achieved for 6 min of ozonolysis at a flow rate of 0.5 L/min and thereafter decreased and remained almost constant with further increase in flow rate of O_3. Although the increase in the flow rate rapidly reaches the saturation concentration of O_3, but at the same time residence time of O_3 decreases in the solution. Therefore, it leads to the fast discharge of O_3 by decreasing the time of interaction of O_3 with organic fragments which otherwise decreases the extent of mineralization. Thus in order to reduce the loss and to get maximum efficiency of O_3, flow rate of O_3 was optimized at 0.5 L/min.

3.2. Decolouration and mineralization of aqueous MO dye solution at an O_3 flow rate of 0.5 L/min

Ozonolytic mineralization and decolouration of aqueous 3×10^{-4} M MO dye solution were investigated for different time intervals with O_3 flow rate of 0.5 L/min at pH 6.5 and were shown in the Fig. 3 and inset of Fig. 3, respectively. It is clear from the figure that ~20% and 75% mineralizations were achieved after 2 min and 20 min of ozonolysis, respectively, whereas, ~90% decolouration was achieved after 2 min of ozonolysis. O_3 is a strong chemical oxidant and it can also directly react with the unsaturations present in the organic molecules (Hoigne and Bader, 1976). Moreover, O_3 reacts with the hydroxide ions of water molecules to generate stronger oxidant ·OH radical, though the rate of decomposition of O_3 increases with increase in alkalinity of the solution
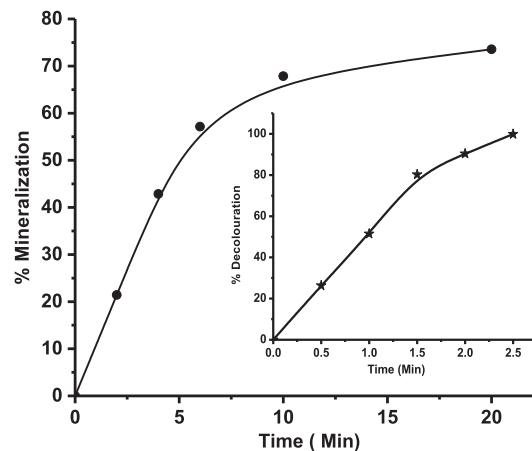

Fig. 3. Mineralization of aqueous 3×10^{-4} M MO dye solution by ozonolysis for different time intervals with O_3 flow rate of 0.5 L/min; Inset: Decolouration of aqueous 3×10^{-4} M MO dye solution by ozonolysis for different time intervals with O_3 flow rate of 0.5 L/min.