



An inhibitory effect of self-assembled soft systems on Fenton driven degradation of xanthene dye Rhodamine B



Uzma Ashraf, Oyais Ahmad Chat, Aijaz Ahmad Dar*

Department of Chemistry, University of Kashmir, Hazratbal, Srinagar 190 006, J&K, India

HIGHLIGHTS

- Presence of surfactants in wastewaters influences the Fenton driven decay of RhB.
- Cationic surfactants retard the decay of RhB more than non-ionic surfactants.
- SDS inhibits the decay process completely.
- Mixed micelles exhibit intermediate effect on decay kinetics of RhB.

ARTICLE INFO

Article history:

Received 15 July 2013

Received in revised form 9 October 2013

Accepted 14 October 2013

Available online 25 November 2013

Keywords:

Dye
Rhodamine B
Surfactant
Kinetics

ABSTRACT

Rhodamine B (RhB) is known to be a common organic pollutant despite having various technical applications. Treatment of effluents containing such compounds is important so as to minimize their effect on environment. Advanced Oxidation Processes (Fenton and Fenton like reactions) are such methods that can oxidize the contaminants powerfully and non-selectively. This work investigates the oxidation kinetics of dye RhB by hydroxyl radical ($\cdot\text{OH}$) generated via Fenton reaction in presence of surfactant assemblies of varying architectures using spectrophotometric, spectrofluorometric and tensiometric methods. The presence of surfactants viz. cationics, non-ionics and some binary mixtures in the pre-micellar and post micellar concentration ranges were found to inhibit the degradation of RhB to a varying degree. However, the reaction was totally inhibited in anionic surfactant. The experimental data was fitted to a pseudo first order kinetic model and the kinetic parameters obtained thereof were explained on the basis of the nature and type of interaction between the cationic form of RhB and the surfactants of varying architectures. The work has a critical significance in view of the fact that degradation studied in presence of surfactant assemblies is more representative than studied in aqueous solution because such conditions compare well with the conditions prevailing in the environment.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Dyestuffs have been known to be serious organic pollutants in wastewaters for several years (Mehrddad et al., 2011). The annual production of dyes and pigments is more than 7×10^5 tons, and it has been estimated that approximately 5–15% are lost in industrial effluents. The treatment of effluents containing such compounds is, therefore, important so as to minimize their effect on the environment and also to decolourize the water. A wide range of methods (Spadaro et al., 1994; Chen et al., 2011) have been developed for the removal of synthetic dyes from the wastewaters but all having one or the other disadvantage. Thus, there is a need for developing treatment technologies that are more effective in eliminating dyes from wastewaters. Advanced Oxidation Processes

(AOP'S) are among such methods, which are based on the generation of highly reactive $\cdot\text{OH}$ that can oxidize the contaminants powerfully and non-selectively (Moumeni and Hamdaoui, 2012). Among AOP's, Fenton process is based on oxidation using Fenton reagent-an oxidative mixture of hydrogen peroxide and ferrous ions (Fe^{2+}) as catalyst. Although AOP's have attracted considerable interest in the degradation of dye components (Kusic et al., 2006; Fan et al., 2009; Xue et al., 2009; Hou et al., 2011), but no kinetic investigation has been carried out on the effect of effluent components on the dye degradation by Fenton process.

Rhodamine B (RhB) is one of the important xanthene dye with many different technical applications (Arbeloa and Ojeda, 1981; Liu et al., 2009; Sagoo and Jockush, 2011). The dye is known to exist in three forms, optically active cationic and zwitterionic forms and a colourless lactone form. The dye is also known for its good stability, hence has a comparatively high resistance to photo- and oxidative degradation (Xue et al., 2009). Owing to its stability

* Corresponding author. Tel.: +91 1942424900.

E-mail address: aijaz_n5@yahoo.co.in (A.A. Dar).

and non-volatility it is considered as a common organic pollutant in wastewaters with carcinogenicity, mutagenicity, reproductive and developmental toxicity as its major effects (Mirsalis et al., 1989; McGregor et al., 1991). In this direction, significant amount of research has been conducted with regard to the degradation of RhB. For example, photo catalytic degradation (Yu et al., 2004; Asilturk et al., 2006; Li et al., 2006; Barka et al., 2008; Yang et al., 2008; Mehrdad et al., 2011), ultrasonic degradation (Sivakumar and Pandit, 2001; Behnajady et al., 2008; Wang et al., 2008a,b) and, sonocatalytic degradation (Wang et al., 2008a,b; Mehrdad and Hashemzadeh, 2010) of RhB has been investigated. All such investigations have been done in pure solvent conditions without considering any effect arising due to presence of various natural/ anthropogenic amphiphilic molecules.

Wastewaters containing such residual dyestuffs mostly contain auxiliary chemicals such as surfactants, salts, greases, and oils. Surfactants, the amphiphilic molecules having both hydrophilic head and a hydrophobic tail, self-assemble in aqueous solution forming colloidal sized aggregates called micelles above critical micelle concentration (Rosen, 2004). It has been vastly reported that presence of surfactants in the reaction media can either have catalytic or inhibitory effect (Fendler and Fendler, 1975; Fendler, 1982; Rodriguez et al., 2003; Hassan et al., 2011; Singh et al., 2011). Surfactant-dye interaction like interaction of surfactants with xan-thene dyes (Rhodamine B, Rhodamine 6G) (Tajalli et al., 2009), triphenylmethane dye (crystal violet) (Ghosh et al., 2012), benzidinedye (Congo red), Safranin T (Ray et al., 1997), methylene blue, and acridine orange (Park and Chung, 1986), has been a subject of extensive investigation since they are important in a variety of dyeing processes as well as in chemical research such as biochemistry, analytical chemistry and photosensitization (Alavijeh et al., 2011). To the best of our knowledge there has been no report on the effect of surfactants of varying architectures on the oxidation kinetics of RhB by $\cdot\text{OH}$ generated by Fenton reaction. Therefore, the focus of this work was to investigate the effect of surfactants in single and mixed states on $\cdot\text{OH}$ induced oxidation of RhB. The work has a critical significance in view of the fact that degradation behavior observed in presence of surfactant assemblies is more representative than studied in pure aqueous solution because the conditions of reaction media compares well with the conditions prevailing in the environment. Also, this study investigates quantitatively the feasibility of Fenton reagent as oxidizing agent to degrade dye compounds under such natural conditions.

2. Experimental

2.1. Materials

The non-ionic amphiphiles Polyoxyethylene(4) lauryl ether (Brij 30), Polyoxyethylene(23) lauryl ether (Brij35), Polyoxyethylene(20) cetyl ether (Brij58), cationic amphiphiles cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium bromide (DTAB), and anionic amphiphile sodium dodecylsulfate (SDS) were all Aldrich products and were used without further purification. The dye Rhodamine B (95%) was obtained from Sigma Aldrich. FeSO_4 , H_2O_2 , KBr, H_2SO_4 were of analytical grade. All the solutions were prepared in triple distilled water. The structure of the surfactants and dye used are presented in Scheme 1.

2.2. Procedure

2.2.1. Optimization of experimental conditions

Selection of RhB Concentration: RhB absorption increases linearly in aqueous media with increase in concentration upto 0.025 mM beyond which it shows deviation from Beer law

(Fig. S1). The deviation is attributed to the formation of aggregates of dye species at higher concentrations. These aggregates are held together by dispersion forces which exist between π -systems of the dye and forces resulting from hydrophobic effects (Tajalli et al., 2009). Thus, the concentration of 0.02 mM of RhB was selected for the kinetic experiments to overcome the deviation effects.

Selection of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ ratio: The ratio of Fe^{2+} and H_2O_2 is a key parameter in Fenton driven oxidation process. Many studies reveal that use of higher concentration of Fe^{2+} leads to self-scavenging of $\cdot\text{OH}$ by Fe^{2+} and hence reduces its efficiency to degrade pollutants. Also, high dose of H_2O_2 hinders the dye degradation as the highly reactive $\cdot\text{OH}$ can be consumed by H_2O_2 leading to the formation of less reactive HO_2 radicals (Lin and Gurol, 1998; Laat and Gallard, 1999). Thus for kinetic measurements, $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ ratio of 2:5 (0.2 mM Fe^{2+} , 0.5 mM H_2O_2) was selected as the optimum ratio.

Selection of reaction pH: For the effective oxidation of organic contaminants by Fenton reagent, the solution pH must be in acidic range. At higher pH values the rate of oxidative degradation is reduced due to the formation of $\text{Fe}(\text{OH})_3$ having lower catalytic activity in the decomposition of H_2O_2 (Fan et al., 2009). Lu et al. also reported that the optimum pH for the oxidation of dichlorvos by Fenton's reagent was between 3 and 4. They also found that the rate of dichlorvos oxidation by Fenton reagent decreased when the solution pH was 2.5 (Lu et al., 1999). The lower efficiency at pH 2.5 is probably due to the formation of the complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ which reacts more slowly with H_2O_2 than $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^+$ and therefore produces fewer $\cdot\text{OH}$ (Gallard et al., 1999). Thus to ensure the effective oxidation by Fenton reagent, FeSO_4 stock solution was prepared in 2 mM H_2SO_4 to have the pH of 4 in the reaction medium. It is pertinent to mention that the dye exists in its cationic form under the prevailing experimental conditions.

2.2.2. Determination of cmc

The cmc values of all the surfactant solutions under prevailing reaction conditions were determined from the plot of surface tension (γ) vs logarithm of surfactant concentration (Fig. 1). Surface tension measurements were made by the Platinum ring detachment method with the Kruss K9 tensiometer equipped with a thermostable vessel holder. The surfactant concentration was varied by adding concentrated stock surfactant solution prepared in 0.04 mM H_2SO_4 and 0.02 mM RhB of known concentration in small installments using a Hamilton Syringe to 20 mL solution containing 0.04 mM H_2SO_4 and 0.02 mM RhB in the sample vessel placed in a vessel holder. Readings were taken after thorough mixing and temperature equilibration at 25 °C (± 0.1 °C) by circulating water from a Brook field TC-102 thermostat through the vessel holder.

2.2.3. Determination of kinetics of RhB degradation

0.2 mM RhB, 10 mM FeSO_4 in 2 mM H_2SO_4 , 100 mM H_2O_2 were prepared as stock solutions for the Fenton reaction. λ_{max} of RhB was obtained at 554 nm by recording its absorption spectra using Shimadzu spectrophotometer (UV-1650PC) with matched pair of quartz cuvettes (path length = 1 cm). Kinetic experiments for the degradation of RhB by Fenton reagent were studied spectrophotometrically at the absorption maximum of RhB. 0.3 mL of 0.2 mM RhB, 0.06 mL of 10 mM FeSO_4 in 2 mM H_2SO_4 , 0.015 mL of 100 mM H_2O_2 were transferred to a cuvette and final volume was made upto 3 mL with triple distilled water alongwith the reaction initiator H_2O_2 which was added at the end. The decrease in absorbance of RhB was recorded at 25 °C for a period of 1000 s. Since the kinetic experiments were performed under pseudo first order conditions with Fenton reagent in excess, the experimental results were fitted to a pseudo first order kinetic model (Alshamsi et al., 2007) to calculate rate constant (k) of RhB degradation.

Download English Version:

<https://daneshyari.com/en/article/4408944>

Download Persian Version:

<https://daneshyari.com/article/4408944>

[Daneshyari.com](https://daneshyari.com)