

EFFECT OF POTASSIUM MONOPERSULFATE ON SONOCHEMICAL DEGRADATION OF CATIONIC DYE IN AN AQUEOUS SOLUTION

Soumia FASSI¹, Christian PETRIER²

¹Department of Chemistry. Faculty of Sciences. University of Constantine, Algeria.

²Laboratoire de Rhéologie et Procédés, 1301 rue de la Piscine, Domaine Universitaire, BP 53, 38041 Grenoble cedex 9, France

RÉSUMÉ

In this study, removal of Cresol Red (CR), a cationic triphenylmethane dye, by 300 kHz ultrasound was investigated. The effect of additive such as potassium monopersulfate (oxone) was studied. Additionally, sonolytic degradation of CR was investigated at varying ultrasonic power. CR can be readily eliminated by the ultrasound process. The obtained results showed that. Sonochemical degradation of CR was strongly affected by ultrasonic power. The degradation rate of the dye increased substantially with increasing ultrasonic power in the range of 20W to 80 W. This improvement could be explained by the increase in the number of active cavitation bubbles. The ultrasonic degradation of dye was enhanced by potassium monopersulfate (oxone) addition. It was found that the degradation of the dye was accelerated with increased concentrations of oxone for a reaction time of 75 minutes.

Keywords: Cresol Red, Sonochemistry Degradation, Additive, Water.

1. INTRODUCTION

The release of colored wastewaters from the textile industry is a current problem encountered by developed and under developed countries over the world. This release in natural environment, mainly in aqueous medium, is undesirable because of the potential transformation of these compounds to toxic and carcinogenic of species. Organic dyes represent one of the large groups of these effluents. However, several treatment processes are available for the removal of this type of pollutants

For instance, several decontamination methods, such as precipitation, biological treatment [1], coagulation [2], adsorption on various supports [3] Many advanced oxidation processes (AOPs) were also used for the oxidation of dyes in water [4,5]. These techniques (AOPs), which involve an in situ generation of highly oxidizing agents such as $\cdot\text{OH}$ radical, have emerged as an important class of technologies to accelerate the non-selective oxidation.

Sonochemical oxidation has been investigated as a viable AOP for the destruction of various pollutants in water. In this technique, the free radicals are generated through transient collapse of cavitation bubbles driven by an ultrasound wave. Ultrasonic irradiation induces the production of cavitation bubbles in the liquid through which it is transmitted. These microbubbles grow during the subsequent compression–rarefaction cycles until they reach a critical size. Further compression leads to the collapse of the bubbles, with the concomitant release of heat and production of chemically active species during the last phase of the bubble collapse [6-8]. This collapse induces localized extreme conditions. It has been reported that the gaseous contents of a collapsing cavity reach temperatures as high as 5200 K and pressures higher than 500 atm, and about 1900 K in the interfacial region between the solution and the collapsing bubble [9]. Under such conditions, molecules trapped in the bubble (water vapor, gases and vaporized solutes) can be brought to an excited-state and dissociate [10]. The radical species produced can recombine, react with other gaseous species present in the cavity, or diffuse out of the bubble into the bulk fluid medium where they are able to react with solute molecules.

In the present work, an cationic dye, Cresol Red (CR), was chosen as a model substrate for a systematic study of the sonochemical degradation process. The aim of this work was to investigate the influence of additive such as potassium monopersulfate (oxone) on the sonolytic degradation of CR. Additionally, the effects of some experimental parameters such as ultrasonic power and pH on the sonochemical degradation of dye was studied.

2. MATERIELS AND METHODES

The cationic acidic dye, Cresol Red sulfonat salt, (molecular formula $C_{21}H_{18}O_5S$), was obtained from Sigma–Aldrich and used without further purification (molecular weight: $382.43 \text{ g mol}^{-1}$) which is a highly water soluble, was used as a model solute. The structure CR is shown in Fig. 1. Elemental iron, monopersulfate (oxone), hydrogen peroxide were commercial products of the purest grade available. All solutions were prepared with distilled water.

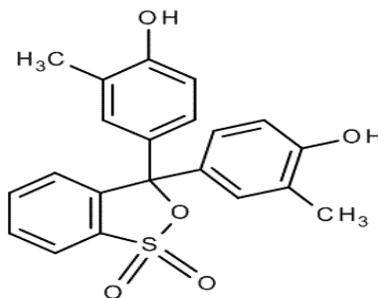


Fig. 1.Chemical structure of Cresol Red.

2.2. REACTOR

Sonolysis experiments were performed in a cylindrical waterjacketed glass reactor operating at 300 kHz. Ultrasonic waves introduced from the bottom of the solution through a plate Pyrex surface (diameter 5 cm) holding the piezoelectric disk (Saint- Gobain Quartz, France) with a diameter of 4 cm. The temperature of the solution was monitored using a thermocouple immersed in the reacting medium. The temperature inside the reactor was maintained at $25 \pm 1 \text{ }^\circ\text{C}$ by circulating cooling water through a jacket surrounding the cell. Acoustic power dissipated in the reactor was estimated using standard calorimetric method [11,12]. The reactor was periodically sampled for analysis

3. RESULTATS

3.1. EFFECT OF POWER

Operating power is an important parameter affecting the cavitation activity and hence the extent of degradation. In order to investigate the influence of ultrasonic power on the sonolytic degradation of CR, experiments were conducted by varying ultrasonic power from 20 to 80W and using 300mL of $6 \cdot 10^{-5}\text{M}$ CR aqueous solution. The CR degradation rate increased with an increase in the ultrasonic power as depicted in Fig. 2.

The increase in dye degradation with an increase in ultrasonic power may be explained by the increase in the number of active cavitation bubbles. So because of the increasing acoustic amplitudes. When power is increased, transmittance of ultrasonic energy into the reactor increases. Due to this energy, the pulsation and collapse of bubble occur more rapidly, the number of cavitation bubbles increases and realizing a higher concentration of $\bullet\text{OH}$ radicals into the aqueous solution of CR [12,13]. The results of an increase in the sound power are greater sonochemical effects, resulting in higher degradation rates of CR for 30 min of sonication time .

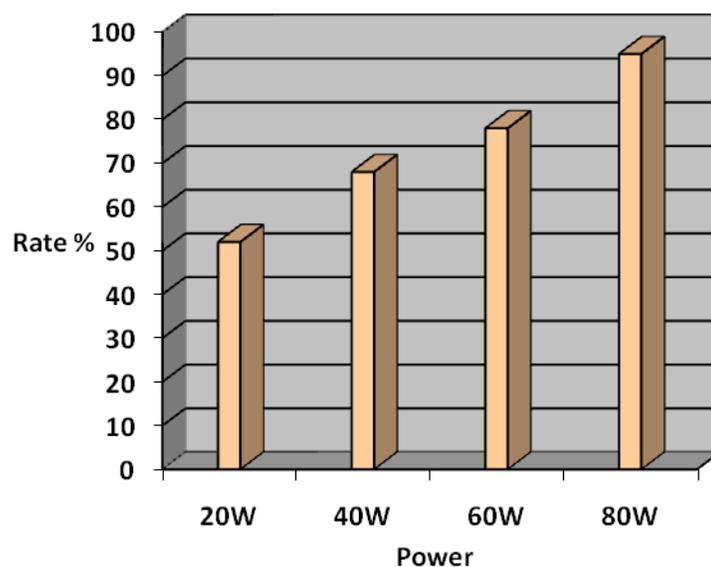


Fig.2. Effect of ultrasonic power on sonochemical degradation of CR (conditions: volume: 300 mL; initial dye concentration: 6×10^{-5} M; temperature: 25°C; pH: 4.5; frequency: 300 kHz).

3.2. EFFECT OF OXONE ADDITION

Sonochemical degradation of Cresol red was investigated in presence of potassium monopersulfate (oxone). The result obtained is shown in Fig.3. The degradation rate was enhanced by the addition of oxone. The sonolytic destruction increased with increasing oxone concentration. An initial removal rate of 90% was attained upon sonolysis of the 6×10^{-5} M CR solution alone for a reaction time of 120 min, While in the presence of oxone, the color removal increased to 96%, 97%, 98% and 99% for oxone concentrations of 10^{-4} M, 10^{-3} M, 10^{-2} M and 10^{-1} M respectively for a reaction time of 75 minutes, Besides the degradation process, the ultrasonic treatment in presence of oxone resulted in the formation of hydroxyl radical and sulphate radical anion according to the Reaction (1),



The sulphate radical anion ($SO_4^{\bullet-}$) is a strong oxidant ($E_0 = 2.6$ eV) and engages in the following three possible modes of reactions with organic pollutants: (i) by abstracting a hydrogen atom from saturated carbon, (ii) by adding to unsaturated or aromatic carbon, and (iii) by removing an electron from the carboxylate anions and form certain neutral molecules [14]. The formation of hydroxyl radical and sulphate radical anion are powerful oxidant that can degrade dye molecules at faster rate. As with radicals OH^{\bullet} , $SO_4^{\bullet-}$ have the unique nature of attacking the dye molecule at same positions, hence, leading to a rapid fragmentation of dye molecules [28]. Reactions (2) and (3),



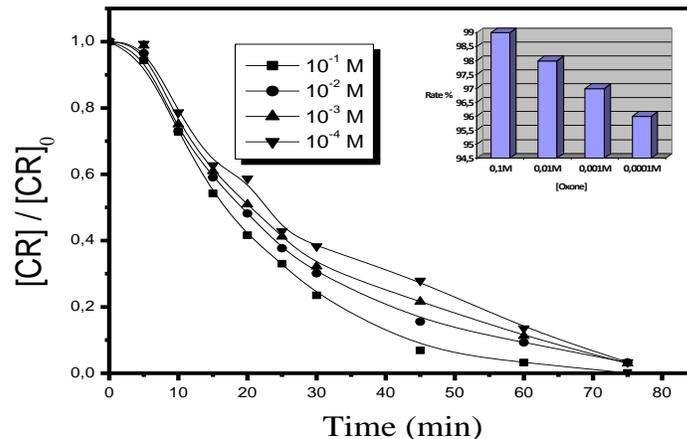


Fig.3. Effect of oxone addition on sonochemical degradation of CR (conditions: volume: 300 mL; initial dye concentration: 6×10^{-5} M; temperature: 25°C ; pH: 4.5; frequency: 300 kHz).

Moreover, the bleaching process of CR by Oxone /US is described correctly by an apparent kinetics law of order 1 Fig.4. In addition, the measure of the half time for each curve ($t_{1/2}$) allowed us to compare the performance of this process: $t_{1/2}(10^{-1} \text{ M}) < t_{1/2}(10^{-2} \text{ M}) < t_{1/2}(10^{-3} \text{ M}) < t_{1/2}(10^{-4} \text{ M})$ (a short half time means a fast rate of decolourization). The calculated rate and $t_{50\%}$ are recapitulated in Table (I).

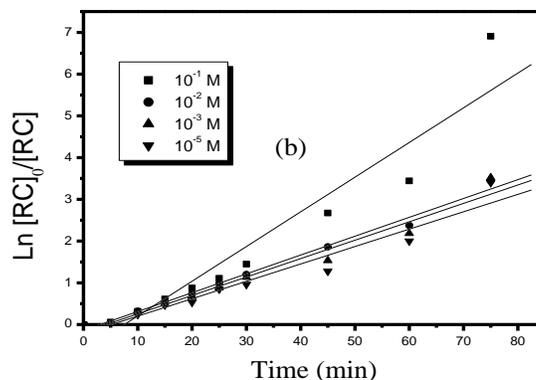


Fig.4. Kinetics of CR decolourization (linear transform $\ln(C_0/C_t)$ vs t) in US/Oxone process. (conditions: volume: 300 mL; initial dye concentration: 6×10^{-5} M; temperature: 25°C ; pH: 4.5; frequency: 300 kHz).

Table (I): Values of parameters characterizing the US /Oxone process.

[Oxone] M	$t_{50\%}$ (min)	R^2	Apparent rate constants (min^{-1})
10^{-1}	16.2	0.95586	0.08312
10^{-2}	18.8	0.99549	0.04516
10^{-3}	20.2	0.98417	0.04411
10^{-4}	22.8	0.97267	0.04168

4. CONCLUSIONS

The present work has shown that removal of the triphenylmethane dye CR can be effectively reached from water by 300 kHz ultrasound irradiation. CR sonochemical degradation in water occurs mainly through reactions with hydroxyl radicals. The degradation rate of the dye was strongly affected by the operational conditions. The degradation rate increased proportionally with increasing ultrasonic power from 20 to 80 W. The most favorable condition for the degradation was observed in acidic media. The sonolytic degradation of CR was drastically improved by the addition of potassium monopersulfate (oxone). The degradation increased with the increase of oxone concentration. Therefore, ultrasound irradiation represents a very interesting technique for the treatment of water contaminated with this pollutant. Nevertheless, further efforts should be carried out to assess the mechanism of CR degradation by analyzing the degradation by-products of the dye.

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