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Sonochemical Degradation of Cationic Dye Effect of Potassium Monopersulfate and Operating Parameters

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Abstract: In this work, the sonochemical degradation of Bromocresol Green (BCG), an cationic triphenylmethane dye, in water was investigated. The effects of additives such as potassium monopersulfate (oxone) was studied. The effects of several operating parameters such as initial BCG concentration, power and solution pH on the degradation of the dye were carried out. The obtained results showed that ultrasound completely destroyed BCG (6 10^{-5}M) after 60 min of sonication. It was found that the initial rate of sonolytic degradation increased with increasing the initial BCG concentration. The degradation rate of the dye increased substantially with increasing power in the range of 20–80W. The significant degradation was achieved in acidic conditions (pH 2) where the color removal was 99% higher than those observed in higher pH aqueous solutions. The ultrasonic degradation of dye was enhanced by potassium monopersulfarte (oxone) addition. It was found that the degradation of the dye was accelerated with increased concentrations of oxone for a reaction time of 45 minutes.

Keywords: Bromocresol Green, Sonochemistry, Operational parameters, Additive, Wastewater, environment.

1. INTRODUCTION

Wastewater from textile industry impose serious environmental problems, because of their color and their potential toxicity [Brown.M.A and De Vito.S.C , 1993, Klemola.K et al,2007]. This release in natural environment, mainly in aqueous medium, is undesirable because of the potential transformation of these compounds to toxic and carcinogenic of speicies. Dye pollutants in wastewaters are the principal source of environmental aqueous contamination. However, several treatment processes are available for the removal of this type of pollutants. Many physical and chemical methods, such as coagulation, floatation, chemical oxidation, solvent extraction, hyperfiltration, etc., have been tried in order to remove color from wastewater, but they have not been very successful since dyes are stable to light and oxidizing agents, and they involve high operational cost and aerobic digestion. Alternate technologies popularly known as Advanced Oxidation Processes (AOPs) have been extensively explored for effective degradation of these compounds for the past few decades. These techniques (AOPs), which involve an in situ generation of highly oxidizing agents such

as _OH radical, have emerged as an important class of technologies to accelerate the non-selective oxidation. Over the past two decades, sonochemical degradation of organic pollutants in water has been extensively investigated as a novel AOPs [Pétrier.C et al,a1994, b2001,Hoffmann.M.R et al,1996, Hamdaoui.O and Nafferchoux.E ,2008, Merouani.S et al ,2010]. 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 [Colussi.A.J et al,1998, AdewuyiY.G ,2001, Thompson.L.H and Doraiswamy.L.K ,1999] The chemical effects are a direct result of the very high temperatures, on the order of 5000 K, and pressures, in the range of hundreds of bars, which are reached in the gaseous cavities when the cavities size is reduced many orders of magnitude within a few microseconds [Suslic .K.S ,1991]. The extremely high temperatures and pressures formed in collapsing cavitation bubbles in aqueous solutions lead to the thermal dissociation of water vapor into reactive hydroxyl radicals and hydrogen atoms [Hart.E.J and Henglein.A,a1985,b1987].

The aim of this work was to investigate the influence of various additives such as potassium monopersulfate (oxone) on the sonolytic degradation of Bromocresol Green (BCG). Additionally, the effects of some experimental parameters such as ultrasonic power and pH on the sonochemical degradation of dye was studied.

2. MATERIALS AND METHODS

Materials

The cationic acidic dye, Bromocresol Green sulfonat salt, was obtained from Sigma–Aldrich and used without further purificatio which is a highly water soluble, was used as a model solute. The structure BCG 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.

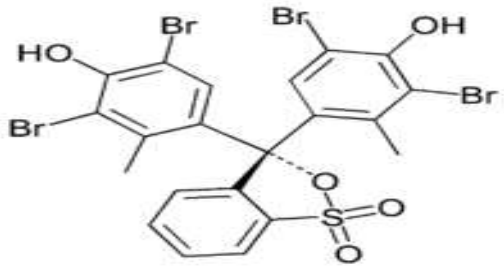

Figure. 1 Chemical structure of Bromocresol Green.

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±1 ◦C by circulating cooling water through a jacket surrounding the cell. Acoustic power dissipated in the reactor was estimated using standard calorimetric method. The reactor was periodically sampled for analysis

Procedures

The initial concentration of BCG solution was 610^{-5}M for all experiments. Various aqueous solutions of BCG (6 10^{-5}M) containing different additives were prepared by adding the required amount of these agents and stirring using a magnetic bar.

Sonolytic degradation of BCG was carried out at 300 kHz under different conditions using constant solution volume of 300 ml. Ultrasonic power was adjusted at 20 W, excluding runs conducted to investigate the influence of power. The pH of the solution was adjusted using NaOH or HCl

The efficiency of the proposed process was evaluated by monitoring BCG degradation by measuring absorbance at 444 nm using a UV–visible spectrophotometer.The wavelength resolution and the bandwidth were, respectively, 1 and 0.5 nm. The length of the optical path in glass cell was 1 cm. The temperature of the sonicated solution was kept at 25°C by circulating cooling water through a jacket surrounding the cell Therefore, the concentration of the BCG in the reaction mixture at different reaction times was determined by measuring the absorption intensity at 444 nm and from a calibration curve. Prior to the measurement, a calibration curve was obtained by using the standard BCG solution with known concentrations. In some cases, a proper dilution was necessary to obtain a well measurable absorption.

3. RESULTS AND DISCUSSION

Effect of operational parameters

Effect of BCG initial concentration

The effect of initial BCG concentration on the sonolytic degradation was studied by varying its concentration in the range 10^{-5}–6 10^{-5}M. The variation of both removal efficiency, calculated for 30 min of ultrasonic treatment, and initial degradation rate of BCG versus initial dye concentration is shown in Fig. 2 for an ultrasonic frequency of 300 kHz and an acoustic intensity of 20W. As shows this figure, the removal efficiency of BCG decreased with increasing initial dye concentration. The BCG elimination was completely achieved after 30 min of sonication for 6 10^{-5}M BCG, but the removal efficiency decreased to 94%, 88%, 70% ,52% and 43% when the initial concentration of BCG was increased to 210^{-5}, 310^{-5}, 410^{-5} 510^{-5} and 6 10^{-5} M, respectively.

The initial degradation rate can be expected to be dependent on the concentration of OH radicals produced and the concentration of the dye molecules at the interface of the cavitation bubble. At the surface of the collapsed bubble, the OH radical concentrationis remarkably high [Tauber.A et al ,2000]. At lower dye concentrations, a considerable part of these OH radicals will recombine yielding H_2O_2 and the degradation is carried out in the bulk of the solution where there is a lower concentration of OH radicals because only about 10% of the OH radicals generated in the bubble can diffuse into the bulk solution [Goel.M et al,2004],which conduct to lower degradation rates. On an increase in the dye concentration, the probability of OH radical attack on BCG molecules increases, thus leading to an increase in the degradation rate. However, if the dye molecules at higher concentration reach a saturation limit at the bubble surface during the persistence time of the bubble, an almost constant degradation rate at higher solute concentrations is reached. At higher dye

concentration, an increasing proportion of the OH radicals will be scavenged and the H_2O_2 yield progressively reduced and because BCG is a non-volatile compound, the sonochemical reaction with the hydroxyl radical is
expected to take place at the cavitation bubble interface where the hydroxyl radical concentration attains an upper limit. In this work, H_2O_2 analysis [Dalhatou.S et al ,2015] could not be carried out because of the colored solution of the dye.

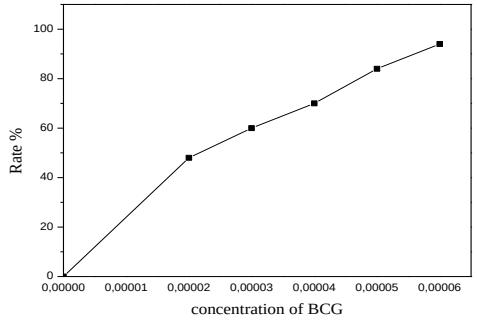

Figure. 2 Experimental and predicted initial BCG degradation rates for various dye concentrations

(conditions: volume: 300 mL; initial dye concentration: 210^{-5}–6 10^{-5}M; temperature: 25 ◦C; pH: 4.5; frequency: 300 kHz; power: 20 W).

Effect of pH

The effect of initial pH was investigated by sonication of 6 10^{-5}M of BCG at different initial pH ranging from 2 to 9. The pH play an important role in the analysis of BCG. Thus, pH affects the structural stability of BCG and, therefore, its color intensity. It was found that the color is stable in the pH range 2–9.Fig. 3 shows the effect of initial pH on the sonochemical degradation of BCG.The presence of many functional groups (sulfonates, bromide and hydroxyl) in BCG molecule and the information about its pKa , make the prediction of its structure form (protonated or ionic), which depends on the pH of the medium .

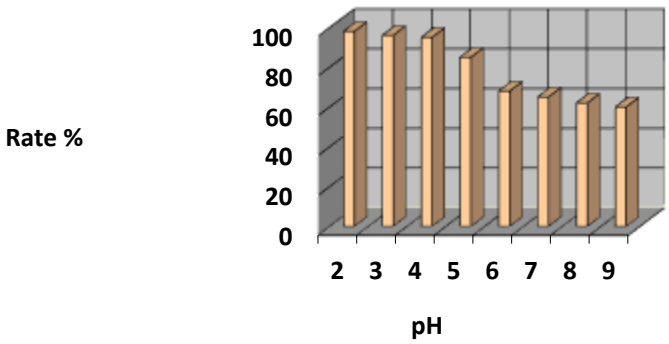

Figure. 3 Effect of pH on sonochemical degradation of BCG

(conditions: volume: 300 mL; initial dye concentration: 6 10^{-5}M; temperature: 25 °C; frequency: 300 kHz; power: 20 W).
BCG is known to exist in two principal forms, in cationic (BCG^+) or in anionic form (BCG^-), as indicated in Fig. 4 At pH values higher than pKa of BCG (4.9), the hydroxyl group of

cationic form is deprotonated and the dye is transformed into anionic form. As the protonated form is more hydrophobic than the deprotonated form [Okitsu.Ket al ,2005, Chiha.M et al 2011], the degradation of BCG in acidic medium would take place more rapidly at the bubble solution interface where the concentration of OH radicals attained their upper limit and this favors higher conversion rate. At pH ≥5, BCG molecule takes a deprotonated form, and thus, the hydrophobicity character of the molecule becomes lesser and this yield a less degradation rate than in acidic medium.

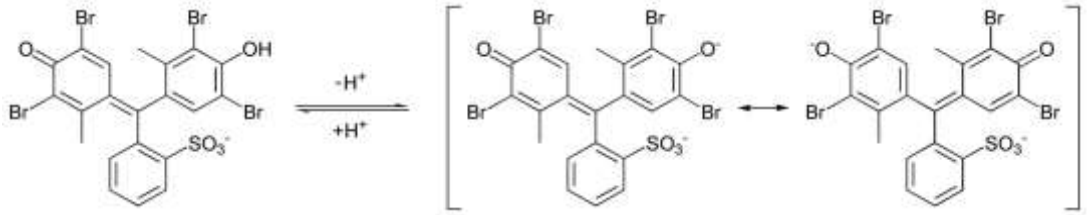

Figure. 4 Forms of Bromocresol Green in water.

Effect of power

In order to investigate the influence of ultrasonic power on the sonolytic degradation of BCG, experiments were conducted by varying ultrasonic power from 20 to 80Wand using 300mL of 6 10^{-5}M BCG aqueous solution. Fig. 5 shows the effect of ultrasonic power on sonochemical degradation of BCG. The obtained results clearly demonstrate that an increase in ultrasonic power results in an increase in sonochemical reactivity. 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, degradation of dye increased.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 increase and realizing a higher concentration of OH radicals into the dye solution [Emery.R et al 2005, Lim.M.H et al 2007]. The results of an increase in the sound power are greater sonochemical effects, resulting in higher degradation rates of BCG for 30 min of sonication time

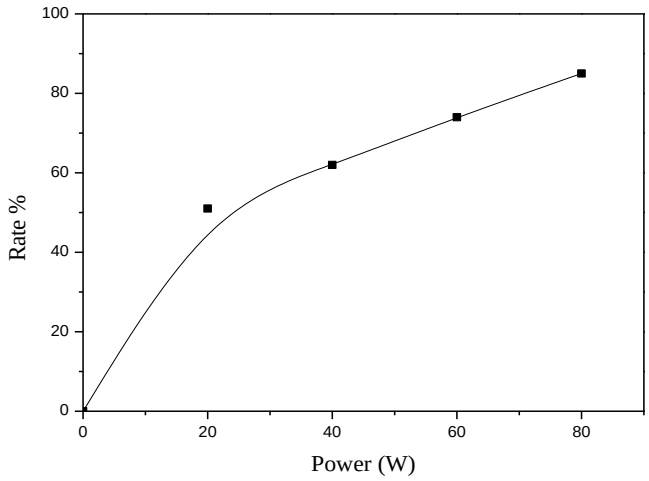

Figure. 5 Effect of ultrasonic power on sonochemical degradation of BCG

(conditions:volume: 300 mL; initial dye concentration: 6 10^{-5}M; temperature: 25°C; pH: 4.5; frequency: 300 kHz).

Effect of oxone addition

The effect of potassium monopersulfate (oxone) addition on the sonolytic degradation of BCG was investigated and the results are shown in Fig. 6. It can be observed that the degradation of BCG increases with increasing oxone concentration. An initial removal rate of 94% was attained upon sonolysis of the 6 10^{-5}M BCG solution alone for a reaction time of 60 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 45 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),

$$HSO_5^- +)))) \rightarrow SO_4^{\bullet -} + OH^{\bullet} \quad (1)$$

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 [Nasr.C et al,1997].

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 [Neppoliana.B et al 2002].Reactions (2) and (3),

$$SO_4^{\bullet -} + dye \rightarrow SO_4^{2-} + dye^{\bullet +}(\text{int}\, ermediated) \quad (2)$$

$$SO_4^{\bullet -} + dye^{\bullet +}(\text{int}\, ermediate) \rightarrow SO_4^{2-} + CO_2 + HNO_3 + other - inorganics \quad (3)$$

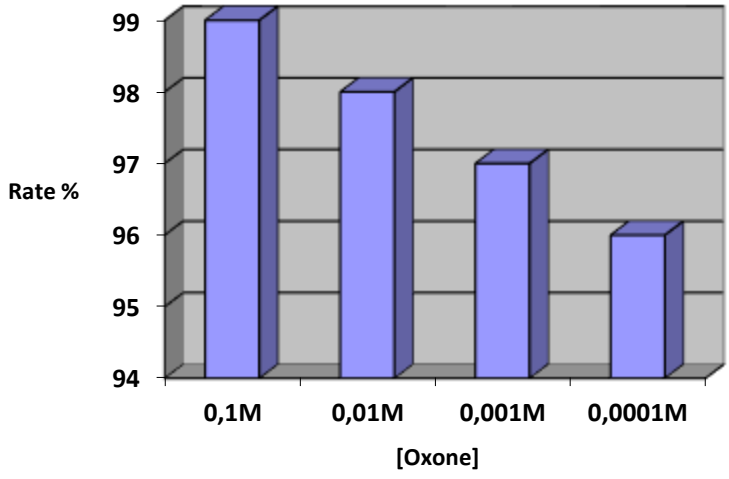

Figure. 6 Effect of oxone addition on sonochemical degradation of BCG

(conditions:volume: 300 mL; initial dye concentration: 6 10^{-5}M; temperature: 25°C; pH: 4.5; frequency: 300 kHz).

4. CONCLUSION

The results presented in this work prove the potential of ultrasound to treat water contaminated with organic dyes such as Bromocresol Green (BCG). This study demonstrates that BCG sonochemical degradation occurs mainly through reactions with hydroxyl radicals. The degradation rate of the dye was strongly affected by the operational conditions. It was found that the initial degradation rate increased with an increase in the initial dye concentration. Reaction rates are strongly affected by ultrasonic power and pH. The sonolytic degradation of BCG 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

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