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ULTRASONIC CAVITATION INDUCED DEGRADATION OF CONGO RED IN AQUEOUS SOLUTIONS

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Abstract: Ultrasonic cavitation induced degradation of Congo red in aqueous solution was investigated for a variety of operating conditions. It is found that the degradation of Congo red in aqueous solution follows pseudo-first-order reaction kinetics and the degradation rate is dependent on the initial concentration of Congo red, the temperature and pH of the aqueous medium. The effects of Fe^{2+} and Fenton reagent addition on the sonochemical degradation of Congo red were also investigated. The results obtained here indicate that the degradation rate of Congo red in aqueous solution was substantially accelerated by Fe^{2+}, NaCl or Fenton reagent addition.

Keywords: *Degradation, Congo red, cavitation, sonochemistry*

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1. Introduction

Effluents of textile dyeing processes are intensely colored and contaminated with high concentrations of chemical oxygen demand, suspended and dissolved salts and traces of recalcitrant material [1, 2]. Improper processing of these effluents not only deteriorate the aesthetics of receiving waters and may hinder the penetration of oxygen, but also pose significant threat to life forms upon hydrolysis of some dyes in the wastewater to form toxic products [3]. The reason for the presence of dye residuals in wasted effluents is that some dyes have poor exhaustion capacities such that an important fraction of them is ultimately discharged with spent dyebaths. Among such poorly exhausting dyes, those with azo bonds have the largest consumption in textile dyeing processes due to their brilliant shades. Hence, much research has been conducted on methods of azo dye destruction, many of them being centered on advanced oxidation processes (AOP) [4–8].

Over the past two decades, sonochemical degradation of organic pollutants in water has been extensively investigated [9–13]. Ultrasonic irradiation provides a way of onsite ·OH generation. By such, the dissolved vapors and gases in the liquid are entrapped by cavitation bubbles, which release very high temperatures during their adiabatic collapse [14, 15]. In sonolysis of water containing hydrophilic compounds such as textile dyes, hydroxyl radicals are generated only by water fragmentation in the collapsing bubbles, and oxidative dye destruction is possible if the radicals are effectively ejected into the solution bulk. The efficiency of ·OH diffusion into the aqueous phase is related to system parameters such as frequency, reactor geometry, presence of cavitation nuclei, and the ambient conditions [9, 10]. The mechanism and kinetics of ultrasonic azo dye degradation has been recently investigated in pure dye solutions using simple compounds such as azo benzene and methyl orange [16, 17].

Congo red [1-naphthalene sulfonic acid, 3, 30-(4, 40-biphenylenebis (azo)) bis (4-amino-)disodium salt, CR] is a benzidine-based anionic disazo dye, i.e. a dye with two azo groups. It is toxic to many organisms and is a suspected carcinogen and mutagen. Benzidine, a human carcinogen, and CR are, however, banned in many countries because of health concerns. But, it is still widely used in several countries. Synthetic dyes, such as CR, are difficult to biodegrade due to their complex aromatic structures, which provide them physicochemical, thermal and optical stability [18]. In the present paper, attempt has been made to employ ultrasonic cavitation for the degradation of azo dye Congo red that is widely used in textile dyeing plants and the effects of dye concentration, temperature, Fe^{2+} and Fenton reagent addition on the degradation rate of Congo red were also investigated.

2. Experimental

2.1. Materials and Apparatus

Congo red, is an anionic azo dye (Scheme 1) [IUPAC name - 1-napthalenesulfonic acid, 3, 3-(4, 4-biphenylenebis (azo)) bis (4-aminodisodium) salt]. Some other important chemical properties of the dye are noted in Table 1. The dye was obtained from M/s Merck. FeSO4 and H2O2 purchased from Sharad Chemicals Pune were of analytical grade and used without further purification. Concentration of the dye solutions were estimated using absorbance recorded on UV-VIS spectrophotometer CHEMITO-109 over the wavelength of 497 nm. Sonication was performed with a 20 kHz

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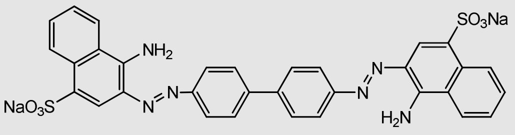

CONGO RED

Scheme 1: Structure of Congo red dye

Table 1: Physicochemical properties of the dye Congo red

Parameter	Values
Molecular weight	696.68
Molecular formula	$C_{32}H_{22}H_6Na_2O_6S_2$
Solubility in water	soluble (1g/30mL
Absorption maxima	497 nm
Synonyms	Direct red 28, Cotton red. C.I.22120

Model US2008 (Heishler Technology) Ultrasonic Reactor at a power of 150 W.

2.2. *Procedure*

100 ml aqueous solution of Congo red was sonicated. The aqueous solution was saturated with pure air before and during the sonication. The reactor was sealed and connected to a gas burette to ensure a constant pressure for 1 atm. The reactor cell was provided with cryostat in order to maintain the desired reaction temperature.

3. Results and Discussion

3.1. *Degradation kinetics*

The air saturated aqueous solutions of Congo red (20 mg/L) were sonicated for 180 min. During sonication, the dye samples were analyzed at regular interval of 30 min with UV-VIS spectrophotometer for their concentrations. It was found that the concentration of Congo red in aqueous solutions decreases with increase in sonication time (Figure 1a). In order to study the order of the ultrasonic degradation of Congo red in aqueous solution, the degradation kinetics was investigated and the regression coefficients for zero, first and second-order reaction were calculated. The result indicated that the degradation of Congo red in aqueous solution can be described by first-order kinetics (Figure 1b). The degradation rate constant is found to be 1.13×10^{-3} min^{-1} with regression coefficient R 0.99 for 20 mg/L Congo red in aqueous solution at temperature 25°C and pH 5.9.

3.2. *Effect of initial dye concentrations*

The effect of initial dye concentrations on the sonolytic degradation rate of Congo red was investigated at temperature 25°C and pH 5.9 of aqueous media. Figure 2 shows the degradation kinetics of Congo red for different initial concentrations. It was found that with increasing initial concentrations, the degradation rate constants were decreased. The ultrasonic degradation rate constants of Congo red were 11.3×10^{-4}, 8.06×10^{-4}, 6.03×10^{-4} and 4.38×10^{-4} min^{-1} at initial concentrations 20, 40, 60 and 80 mg/L, respectively. The results are correspondent closely with those reported for the sonochemical degradation of organic pollutants in aqueous solution [19, 20].

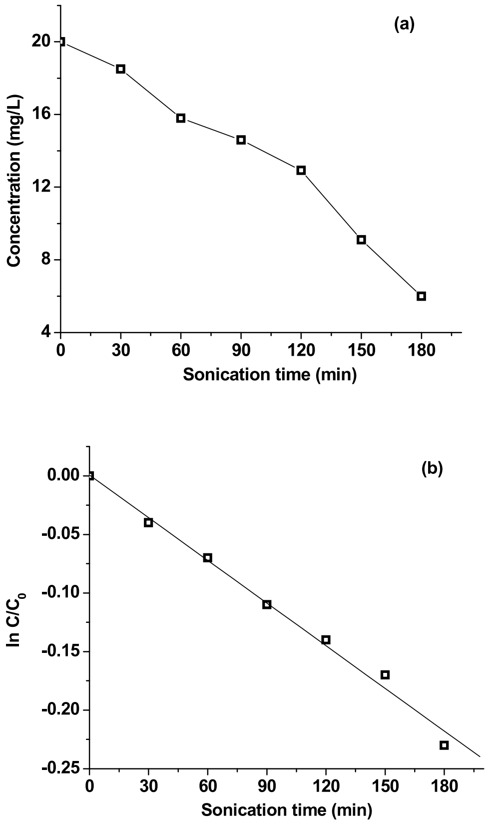

Figure 1: Degradation vs. sonication time dependency of Congo red at temperature 25°C and pH 5.9. (a) Concentration vs. sonication time profiles and (b) degradation of first-order kinetics

3.3. *Effects of temperature*

The effect of temperature on the ultrasonic degradation rate of Congo red was also investigated at initial concentrations 20 mg/L and pH 5.9 and the results are shown in Figure 3. It was found that the ultrasonic degradation rate constants of Congo red were 10.9×10^{-4}, 8.45×10^{-4}, 6.96×10^{-4} and 5.05×10^{-4} $^{-1}$ at temperature 30°C, 40°C, 50°C, 60°C respectively. The result showed that with increasing reaction temperatures, the rate of degradation was decreased in the range of temperature in this study. It has been reported that three different regions are formed in the aqueous sonochemical process [21]: (1) The gas phase within the cavitation bubble where elevated temperature and high pressure are produced, (2) The interfacial zone between the bubble and the bulk solution where the temperature is lower than that inside the bubble but still high enough for a sonochemical reaction, (3) The bulk solution at ambient temperature where the reaction still takes place. Of the aforementioned three regions, we prefer the interfacial zone as the region where Congo red was destructured, because of the low vapor pressure of the compound. As the bulk temperature of water increased, the vapor pressure of water and volatile solutes inside the cavitation bubbles increased. The collapse

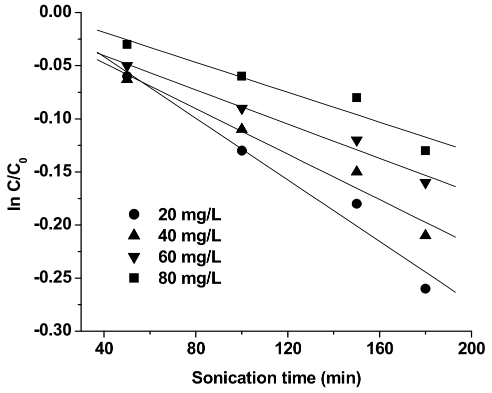

Figure 2: The effect of initial concentrations on the degradation rate of Congo red (Temperature = 25°C and pH = 5.9)

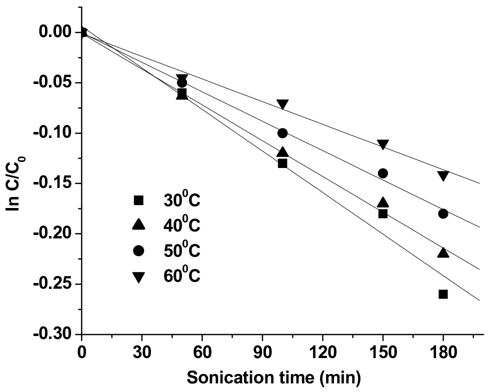

Figure 3: The effect of temperature on the degradation rate of Congo red (initial concentrations = 20 mg/L and pH= 5.9.

of cavity is thus cushioned more than that at a lower bulk temperature, this results in more moderate conditions and a lower sonochemical degradation rate.

3.4. Effect of pH

It is well known, in general, the pH values markedly influence the degradation of organic pollutants. Hence the effect of the initial pH values of the aqueous solution on the sonochemical degradation rate of Congo red was investigated at different pH in the range of 2.0 - 12.0 with initial dye concentration 20 mg/L and temperature 25±2°C and the results are shown in Figure 4. The results indicated that the ultrasonic degradation rate constants in acidic water (pH 2.0-3.0) are higher than those obtained in neutral aqueous solutions (pH 6.0- 8.0), and higher degradation rates were observed in basic medium (10.0-12.0), which indicate that both high acidic and high basic conditions are propitious to ultrasonic degradation of congo red.

3.5. Effect of Fe^{2+} and Fenton reagent addition

When an aqueous solution undergoes ultrasonic irradiation, certain chemical effect takes place due to the propagation of a pressure wave. This pressure wave leads to the occurrence of cavitation phenomenon, that is, nucleation, growth and the eventual collapse of the bubble. The split second collapse of the bubble creates localized supercritical conditions with extremely high temperature and pressure, electrical discharge and plasma effects. These extreme conditions create hydroxyl ($\cdot OH$), hydrogen ($H\cdot$), hydroperoxyl ($HO_2\cdot$) radicals and hydrogen peroxide from the aqueous solution [22]. According to the Fenton reaction, Fe^{2+} can react with H_2O_2 to produce $\cdot OH$ in weakly acidic media (pH 2-3), so Fe^{2+} can accelerate the sonolytic degradation of pollutants.

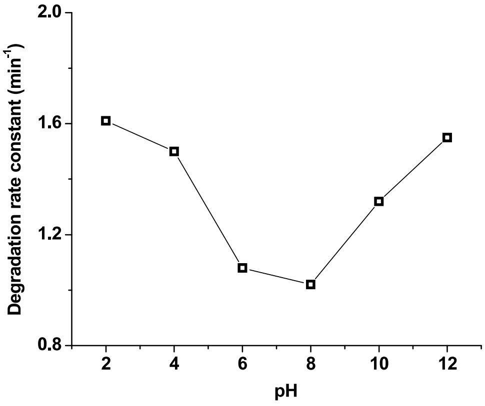

Figure 4: . The effect of the initial pH of the aqueous solution on the degradation rate of Congo red (initial concentration = 20 mg/L and temperature=25°C)

$$H_2O \longrightarrow \cdot OH + H\cdot \tag{1}$$

$$\cdot OH + \cdot OH \longrightarrow H_2O_2 \tag{2}$$

$$Fe^{2+} + H_2O_2 \longrightarrow FeOH^{2+} + \cdot OH \tag{3}$$

$$FeOH^{2+} + H_2O_2 \longrightarrow Fe(OH_2)^{2+} \tag{4}$$

It has been reported that the sonochemical degradation of phenols can be enhanced by the addition of Fe^{2+} [23, 24]. Here, the effect of Fe2+ addition on the sonochemical degradation of Congo red (initial concentration 20 mg/L, pH 3.0, temperature 25°C) was investigated and the result is shown in Figure 5. The results reveal that much higher degradation rate was observed when Fe^{2+} was added in the dye aqueous solution during sonication. The pseudo-first-order rate constants of Congo red degradation in aqueous solution increased to 2.69×10^{-3} min^{-1} and 3.74×10^{-3} min^{-1} from 1.43×10^{-3} min^{-1} with 2.5 μmol/L and 5 μmol/L Fe^{2+} addition, respectively. This increment was mainly due to the higher OH radical concentration produced from the Reaction (3).

Similarly, the addition of Fenton reagent can increase the yield of OH radical and accelerate the sonochemical reactions. Many researchers have reported the improved efficiency of sonolysis processes by employing sonolysis coupled Fenton reagent [25, 26]. Here, the enhancement effect of Fenton reagent on the sonochemical degradation of Congo red was also examined. Figure 6 shows the degradation results of Congo red in aqueous solution at pH 3.0 with H_2O_2 oxidation, Fenton reagent oxidation, sonication only and sonication coupled Fenton reagent. It was found that the oxidation of Congo red with 20 μmol/L H_2O_2 (25°C, pH 3.0) for 180 min is less than 2%, so the degradation of the

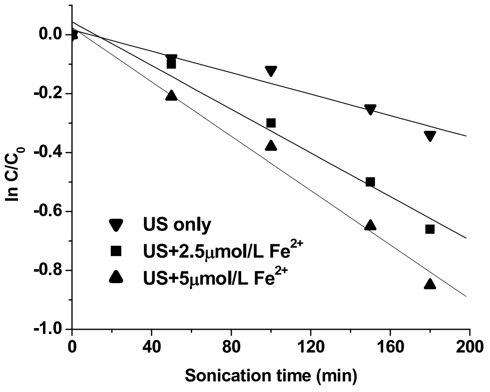

Figure 5: The effect of Fe^{2+} addition on the degradation rate of Congo red (Initial dye concentration = 20 mg/L, temperature = 25°C and pH = 3.0)

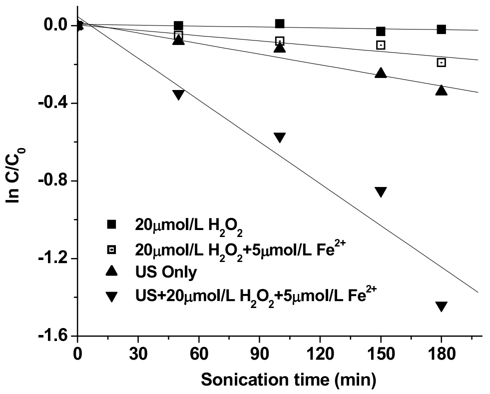

Figure 6: The effect of Fenton reagent addition on the degradation rate of Congo red (Initial concentration 20 mg/L, temperature 25°C and pH 3.0)

dye by H_2O_2 oxidation can be neglected. From the result it can be seen that the degradation rate of Congo red was substantially enhanced by the addition of Fenton reagent to the ultrasound system. The degradation rate constants are found to be 6.99×10^{-3} min^{-1} with 5 μmol/L Fe^{2+} and 20 μmol/L H_2O_2 addition, but the degradation rate constants are only 1.43×10^{-3} min^{-1} and 1.10×10^{-3} min^{-1} with sonication and Fenton reagent (5 μmol/L Fe^{2+} and 20 μmol/L H_2O_2) oxidation, respectively. The sonolysis of the dye with a lower dosage Fenton reagent (5 μmol/L Fe^{2+} and 20 μmol/L H_2O_2) can improve the degradation rate by about 4 and 5 times compared to that of direct sonication or Fenton reagent oxidation. The enhancement in the degradation rate constant of Congo red could be mainly due to the contribution of additional OH radicals produced from the Fenton reagent.

3.6. *Effect of NaCl addition*

Degradation of dyes is also effected by the presence of additives in solution matrix [27–31]. These additives are generally present as ions which are initially added to the dye solution as ionic compounds in order to improve the industrial process. However on release of wastewater, the ions become an integral part of the effluent. Many common ions present in dye wastewater are Fe^{2+}, Zn^{2+}, Ag^{+}, Na^{+}, Cl^{-}, PO_4^{3-}, SO_4^{2-}, BrO^{3-},CO_3^{2-}, HCO_3^{-} and persulphate ions. Each of these added ions causes a certain increase or decrease in percentage degradation of the dye solution. It is expected that the sonochemical degradation of non-volatile pollutants in aqueous solution takes place in the bubble-bulk interface area due to the exposure to free radicals and high temperature and pressure. Since Congo red dye molecules have polar functional groups, these compounds are soluble in water. The degree of hydrophobicity of the substrate is one of the most important factors to predict the sonochemical reaction pathway. In the sonolysis of Congo red, however, it is very difficult to estimate the degree of the hydrophobicities from chemical structure because they have a relatively large molecular size and weight. Therefore, it is unpredictable whether these compounds accumulate toward the interface region of the cavitation bubbles or not. The aim of NaCl addition to the aqueous solution is to push dye molecules from the bulk aqueous phase to the interface [24, 32]. Addition of NaCl can increase the hydrophilicity, the surface tension and ionic strength of the aqueous phase and decrease the vapor pressure [34]. The effects of the addition of NaCl with different concentrations (0.6, 1.2 and 1.8 mol/L) on the degradation rate were investigated with 20 mg/L Congo red aqueous solution at 25°C and pH 5.9 and the results are shown in Figure 7. It can be seen from the results that the degradation rates of Congo red in aqueous solution with the addition of NaCl at different concentrations are higher than that without NaCl and the degradation rates increase with increasing concentrations of NaCl. The sonochemical degradation rate constants of Congo red were 1.14×10^{-3}, 1.54×10^{-3} and 1.79×10^{-3} min^{-1} at NaCl concentration 0.6, 1.2 and 1.8 mol/L, respectively.

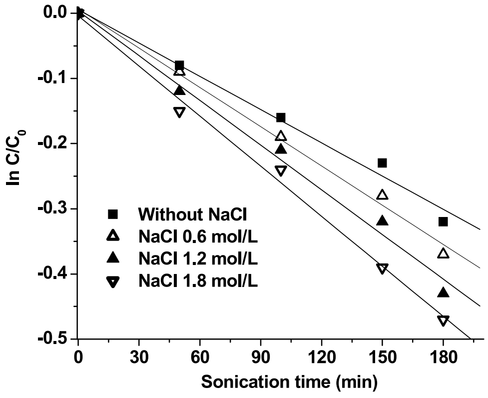

Figure 7: The effects of NaCl addition on the degradation rate of Congo red (initial concentration 20 mg/L, temperature 25±2°C and pH 5.9)

4. Conclusion

Present study investigates the ultrasound induced degradation of Congo red in aqueous solution operated at various parameters. It is found that the degradation of Congo red in aqueous solution follows pseudo-first-order reaction kinetics and the degradation rate constant is found to be 1.13×10^{-3} min^{-1} for 20 mg/L Congo red in aqueous solution at temperature 25°C and pH 5.9. The effects of some parameters on the degradation were discussed and found that the degradation rate of Congo red is strongly dependent on the initial concentration of the dye, the temperature and pH of the aqueous medium. The effects of Fe^{2+}, NaCl and Fenton reagent addition on the sonochemical degradation of Congo red were also investigated. The results obtained here indicate that the degradation rate of Congo red in aqueous solution was substantially accelerated by Fe^{2+}, NaCl or Fenton reagent addition.

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