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Mechanistic analysis of hybrid sono-photo-ferrioxalate system for decolorization of azo dye

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ABSTRACT

This paper has attempted to identify the physical mechanism of the hybrid advanced oxidation process (HAOP) of sono-photo-ferrioxalate for azo dye decolorization. An approach of coupling experimental results with simulations of cavitation bubble dynamics has been adopted. Concurrent analysis of simulations of cavitation bubble dynamics and experimental results have revealed interesting links between physics of ultrasound/cavitation, and chemistry of decolorization. The role of ultrasound and cavitation in HAOP is revealed to be of physical nature. Oxidizing radicals produced via photo-ferrioxalate system contribute mostly to decolorization. Physical effect of strong micro-convection induced by ultrasound/cavitation in reaction system helps effective utilization of these radicals. Among three radical species, *viz.* $O_2^{\bullet}$−,$^{\bullet}$ OH and $HO_2^{\bullet}$, produced via photo-ferrioxalate system the contribution of $O_2^{\bullet-}$ and $HO_2^{\bullet}$ radicals to decolorization is equally significant as that of $^{\bullet}$OH radical with the highest oxidation potential.

1. Introduction

The textile dyeing and finishing industries are highly water and chemical intensive, and hence, the second largest contributors to water pollution after agriculture sector. The modern textile industry has produced as many as 3600 dyes using more than 8000 chemicals. The major pollutants appearing in wastewater discharge from textile industry are dyes [1,2]. Many of these dyes (classified on the basis of their chemical structure as azo or non-azo) are bio-recalcitrant and are not easily degraded by conventional biological techniques. Effective degradation of these dyes requires advanced oxidation processes (AOPs), which are based on production of oxidizing radicals such as $^{\bullet}$OH, $^{\bullet}$O and $HO_2^{\bullet}$. The conventional AOPs applied for degradation of bio-recalcitrant pollutants are Fenton (or Fenton-like), photo-ferrioxalate, photocatalysis, ozonation, ozone/UV, H_2O_2/UV, etc. [2–13]. A relatively new AOP is sonolysis (or application of ultrasound), which employs ultrasound irradiation of the reaction mixture, for production of oxidizing radicals [3,13,14]. In sonolysis, ultrasound manifests its physical and chemical effects through phenomenon of cavitation [15–21]. In transient cavitation, the temperatures and pressures inside the bubble reach extreme ($\sim$5000 K, $\sim$500 bar) at the moment of maximum compression (or minimum radius) during radial motion [22–24]. At this moment, vapor and gas molecules present in the bubble undergo dissociation to produce numerous small chemical species – some of which are radical species [25]. These species get released into the bulk liquid medium with fragmentation of bubble, and induce the chemical reactions.

More recently, several authors have reported use of hybrid AOPs for degradation of recalcitrant pollutants, in which two or more AOPs are applied simultaneously [13,14,26,27]. Such hybrid processes have been reported to yield higher degradation than any of the individual AOP. Despite significant amount of literature published in this area, the exact physical mechanism of the hybrid AOPs has remained largely unexplored. It is not clear as how the individual mechanism of AOPs reinforces each other's effects, which is ultimately manifested in greater extent of degradation of the pollutant. One of the widely used hybrid AOPs for degradation of recalcitrant pollutants is photo-ferrioxalate system, in which the photo-sensitive ferrioxalate complex decomposes to form oxidizing radicals [28–32]. More recently, this hybrid AOP has been coupled with sonolysis [33–36]. The new hybrid AOP of sono-photo-ferrioxalate system has been revealed to be more effective in degradation of recalcitrant pollutants. For example, Katsumata et al. [33] have compared degradation of ferinitrothion under photo-ferrioxalate and sono-photo-ferrioxalate systems. The latter system has been revealed to yield much higher and faster degradation of the ferinitrothion. Zhou et al. [35] have investigated degradation of antibiotic sulfamethazine using photo-ferrioxalate as well as sono-photo-ferrioxalate system and they have also reported that later process is more efficient toward

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complete mineralization of sulfamethazine. A summary of literature on degradation/mineralization of various bio-recalcitrant pollutants through photo-ferrioxalate and sono-photo-ferrioxalate systems is given in Table S1 in supplementary material.

The present study has addressed the fundamental issue identification of physical mechanism of sono-photo-ferrioxalate system. Using the approach of coupling experimental results with simulations of cavitation bubble dynamics, we have attempted to discern the mechanistic links between sonolysis and photo-ferrioxalate system. An azo dye (*viz.* Acid Red B or C.I. 14720) has been used as the model pollutant. Concurrent analysis of experimental and simulations results has revealed interesting physical features of degradation of Acid Red B dye and has provided mechanistic insight into the process. As preamble for readers not conversant with subject matter, the basic chemistry of sonolysis and photo-ferrioxalate system has been given in supporting material provided with this paper [11,37–40].

2. Materials, experimental procedures and bubble dynamics model

2.1. Materials

Ferric sulfate anhydrous (AR Grade) and potassium oxalate (AR Grade) were procured from Loba Chemie India Ltd. Hydrogen peroxide (30% v/v), hydrochloric acid (GR Grade), NaOH (pellet form) were procured from Merck India Ltd. Acid Red B dye (an azo dye with chemical formula $C_{20}H_{12}N_2Na_2O_7S_2$; abbreviated hereafter as ARB) was obtained from local vendor (a. b. Chemicals and Instruments Pvt. Ltd., Guwahati). All chemicals were used as received without further any pre-treatment. Reaction mixtures (dye solution + reagents in photo-ferrioxalate system) in each experimental set were prepared using ultra pure water ($\geq$18 MΩ cm resistivity at 25 °C) from a MQ-Synthesis unit (Millipore, USA).

2.2. Experimental procedures

Experiments have been conducted in five categories with application of the following techniques: (1) sonication alone, (2) mechanical stirring + H_2O_2 or sonication + H_2O_2, (3) sonolysis + photo-ferrioxalate, (4) sonolysis + photo-ferrioxalate + sparge gas, (5) sonolysis + photo-ferrioxalate + alcohol as radical scavenger (methanol and 2-propanol). Each of these techniques alters the predominant physical and chemical mechanisms of the textile dye decolorization system. The rationale underlying these experimental techniques will be explained in subsequent sections.

In a typical experiment, 50 mL of ARB dye solution with an initial concentration of 20 ppm (or 0.04 mM) was taken in a 200 mL borosilicate glass beaker. The desired quantities of ferrioxalate reagents, *viz.* Fe^{3+}, oxalate salts (Ox) and H_2O_2, were added to reaction solution prior to treatment. All experiments were carried out in an ultrasound bath (JeioTech, South Korea, Model: UC-10, Capacity: 10 L, frequency: 40 kHz, theoretical power: 200 W). The bath was filled with ordinary (tap) water that formed medium for propagation of ultrasound. The reaction beaker was placed at the center of the ultrasound bath. This position of the beaker was carefully maintained same in all experiments to avoid any artifact that might occur due to spatial variation in ultrasound intensity [41]. In order to control the temperature rise during sonication, water in the bath was circulated using a cooling water circulating bath (Amkette Analytics, Model: WB2000). This procedure maintained the reaction temperature at 25 ± 1 °C. A high pressure mercury UV lamp (Starlite, 160 W) was used as UV source, which emits the light in UVA range with maximum peak emission at 365 nm. The UVA lamp was located exactly above the mouth of reaction beaker. The experimental set-up was kept in a black box to avoid light radiation diffusion (greater detail of the experimental set-up is given elsewhere [42]). Before each experiment, the UVA lamp was switched on for 15 min to obtain proper diffusion of ultraviolet irradiation. Experiments were also conducted under ambient light source and it has been confirmed that the effect of ambient light is negligible. The kinetics of dye decolorization was monitored by drawing aliquots of reaction mixture at regular time interval. After withdrawal of the sample, the reactions leading to decolorization were quenched by adjusting the pH to 7.5–8 with NaOH (4N) solution. This results in formation of Fe(III) floc, which was removed by centrifugation (Tarsons, Model: SPINWIN MC-00) at 6000 rpm for 20 min. The residual concentration of the dye in the supernatant of the sample was analyzed (after filtration) using absorption at 512 nm using UV–vis spectrophotometer (Perkin Elmer, Model: Lambda 35). All experiments were carried out in triplicate to assess reproducibility of the results. As per conclusions of Gao et al. [43] the decolorization profile of ARB dye was fitted to pseudo first order model.

2.3. Cavitation bubble dynamics model

As noted earlier, the two experimental techniques employed in present study are: (1) sparging of gas through the reaction mixture, and (2) addition of alcohols to reaction mixture. Both of these techniques have implication on the cavitation phenomenon. For occurrence of cavitation phenomenon in liquid, nuclei are needed. These nuclei could be the gas pockets trapped in the crevices of solid boundaries in the medium or they could be tiny gas bubbles freely floating in the liquid. With sparging of gas through reaction mixture during treatment, additional nuclei get seeded in the medium, which increase the cavitation intensity. Sparging of gas also leaves the reaction mixture saturated with the gas – stripping away the dissolved oxygen in the medium. Depletion of dissolved oxygen in the medium affects the photo-ferrioxalate pathway, in which the $CO_2^{\bullet-}$ radical reacts with dissolved oxygen to yield $O_2^{\bullet-}$ and $HO_2^{\bullet}$ radical species, which lead to formation of H_2O_2 and Fenton-reaction.

Alcohol molecules are efficient radical scavenger. As far as sonolysis is concerned, addition of alcohol in the system can also affect production of radicals. Alcohol molecules can adversely affect generation as well as of utilization of $^{\bullet}OH$ radicals, in the reaction mixture. As shown by Ashokkumar et al. [44], alcohol molecules have tendency to adsorb onto the gas/liquid interface of the bubble. These interfacially adsorbed molecules are able to evaporate into the bubble core during collapse. During the compression phase of radial bubble motion, lateral interaction between the adsorbed alcohol molecules causes expulsion of some molecules in the bulk solution, while some molecules get evaporated into the bubble core. This phenomenon causes “quenching” effect in the transient collapse of bubble that reduces the intensity of the temperature and pressure peak reached in the bubble. Addition of alcohols in the reaction mixture thus gives a means of discriminating between the relative influence of physical and chemical effects of cavitation on the reaction.

In the present study, the diffusion limited model for cavitation bubble dynamics has been used [45]. This model is based on the hypothesis that solvent vapor transport across bubble interface and vapor entrapment in the bubble during transient collapse (leading to formation of radicals) is essentially a diffusion-limited process [46].

The diffusion limited bubble dynamics model comprises of 4 equations that take into account essential physics and chemistry of bubble dynamics using boundary layer approximation [46], *viz.* (1) Keller–Miksis equation for the radial motion of the bubble; (2) Equation for the diffusive flux of water vapor through bubble wall; (3) Equation for heat conduction through bubble wall; and (4) Overall energy balance treating the cavitation bubble as an open system. The essential equations (along with relevant boundary conditions) and thermodynamic data of this model are given in Tables 1A and B. Equations for diffusive flux and conductive heat transfer require thermal conductivity and diffusion coefficient (*i.e.* transport parameters). These are determined at the bulk temperature of the liquid