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Mechanistic analysis of sono-photolysis degradation of carmoisine

Sankar Chakma [a,b], Vijayanand S. Moholkar [a,*]

[a] Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati 781039, Assam, India
[b] Department of Engineering Sciences, Indian Institute of Science Education and Research Bhopal, Bhopal 462066, Madhya Pradesh, India

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ABSTRACT

The hybrid advanced oxidation process (AOP) of sono-photolysis, in which sonication and photolysis (UV-C/H_2O_2) are applied simultaneously, is known to give effective degradation of several bio-recalcitrant pollutants. This study has attempted to identify the links and interactions between the mechanisms of individual AOPs of sonolysis and photolysis, when applied simultaneously. Experimental results have been analyzed concurrently with the simulations of cavitation bubble dynamics. It is revealed that oxidizing ($^{\bullet}OH$) radicals generated through photolysis contribute mostly to degradation reactions. Due to highly sporadic nature of transient cavitation, the contribution of sonolysis to degradation is rather subordinate as compared to photolysis. Nonetheless, faster degradation and higher mineralization in sono-photolysis, as compared to photolysis alone, essentially points at supportive role of ultrasound in the hybrid AOP. Addition of electrolytes (or salt) to the reaction mixture during sono-photolysis treatment causes effective partitioning of the pollutant molecules in the interfacial region of transient cavitation bubble, which results in further enhancement of degradation kinetics and mineralization. Although the present study has employed Carmoisine as model pollutant, the mechanistic principles identified in this study, and their manifestations in terms of degradation/mineralization of pollutants are applicable to any other bio-recalcitrant pollutant.

Introduction

Advanced oxidation processes (AOPs) based on production of hydroxyl radicals ($^{\bullet}OH$) with high oxidation potential of 2.8 eV have been widely investigated for effective degradation of bio-recalcitrant pollutants appearing in wastewater discharge from chemical and process industries. Combination of the AOPs or the hybrid AOPs (HAOPs) has also been attempted by many authors for faster and higher degradation of pollutants as compared to individual AOPs [1–6]. Despite significant literature on wide range of HAOPs, combining conventional AOPs such as Fenton or Fenton–like, ferrioxalate, photocatalysis, photolysis (UV/H_2O_2), ozonation, sonolysis, etc., the exact physical mechanism (or the mechanistic synergy between different AOPs when applied simultaneously) of these HAOPs has remained largely unexplored.

Among the ultraviolet irradiation based advanced oxidation techniques, the most widely employed techniques are photolysis [7–9] and photocatalysis [10–16]. A brief summary of some recently published literature using these techniques for degradation/mineralization of organic pollutants is given below.

Rasoulifard et al. [7] have assessed the performance of light emitting diodes for degradation of Direct Red 23 (DR23) dye using UV/$S_2O_8{}^{2-}$ protocol. A continuous photo-bioreactor has been used for the process. Rasoulifard et al. [7] have also assessed the effect of operational parameters like initial dye concentration, peroxydisulfate concentration, temperature and photonic efficiency. This study demonstrated that UV/LED were controllable light illumination source, which provided changing current intensity that altered the irradiation efficiency. Although 100% decolorization of the DR23 dye was obtained at 12.5 mM $S_2O_8{}^{2-}$, initial dye concentration of 20 ppm and 80% current intensity. Lin and Lee [8] have studied the effectiveness of two different homogeneous photolysis process, *viz.* UV/$S_2O_8{}^{2-}$ and UV/H_2O_2, for degrading of polyvinyl alcohol (PVA). They have reported that the acidic condition is more efficiency than the alkaline condition for both the processes for degradation of PVA. This study reported that that $SO_4^{\bullet -}$ was better for degradation of PVA than $^{\bullet}OH$ radicals. Lin and Lee [8] have also studied the photolysis processes and presence of salts (Na_2SO_4, $NaNO_3$, and NaCl) and reported that the efficiency and rate of degradation of PVA reduced in UV/$S_2O_8{}^{2-}$. However, UV/H_2O_2 process was not affected much by addition of salts. The

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* Corresponding author. Tel.: +91 3612582258; fax: +91 361 2582291.
E-mail address: vmoholkar@iitg.ernet.in (V.S. Moholkar).

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highest degradation efficiencies were 100% with UV/$S_2O_8^{2-}$ and 58% with UV/H_2O_2 process at pH 3, oxidant dosage of 0.25 mM and an initial PVA concentration of 20 mg/L.

Mruthamani et al. [10] have investigated the heterogeneous photocatalysis process for degradation and mineralization of Rhodamine B dye using TiO_2 with enhanced photocatalytic activity with graphene oxide. The composites of reduced graphene oxide – TiO_2 were revealed to have better photocatalytic activity than TiO_2. A maximum of 93% COD reduction was obtained with 20% composites in 5 h of treatment. Khataee et al. [11] have studied degradation of an azo dye under visible light using iron rich laterite soil with mesoporous structure as iron source. The degradation reactions were Fenton–like or photo-Fenton like. Among the two, photo-Fenton like process yielded higher decolorization of 94.21% in 2 h of treatment. Chakma and Moholkar [12] have published study on degradation of Acid Red B (azo) and Methylene Blue (non-azo) dyes using mesoporous $ZrFe_2O_5$ catalyst. This catalyst possessed both Fenton-activity and photo-activity. α-Fe_2O_3 (hematite) phase in $ZrFe_2O_5$ acts as recombination center for electrons and holes, which adversely affected the photo-activity of the catalyst. However, the Fenton-activity shown by the catalyst due to this phase compensates for the reduction in photo-activity. The $ZrFe_2O_5$ catalyst demonstrated best performance for dye decolorization (90.54% for ARB and 87.62% for MB) for the protocol of sono-photo-Fenton. Habibi and Habibi [13] have reported one-pot synthesis of nanostructure composite of $ZnFe_2O_5$–$FeFe_2O_4$–ZnO and its application in photo-degradation process. This nano-composite was immobilized on glass using doctor blade method. XRD analysis revealed that the nano composite comprised of franklinite (54%), magnetite (8%) and wurtzite (48%). The photocatalytic activity of this nano-composite was tested for decolorization of azo dye of Reactive Red 195. $ZnFe_2O_5$–$FeFe_2O_4$–ZnO nano composite showed a good photocatalytic activity with 60% decolorization in 120 min. Shoabargh et al. [14] have reported hybrid photocatalytic/enzymatic process for degradation of Acid Orange 7 dye. The enzyme employed for degradation is glucose oxidase. Shoabargh et al. [14] have also assessed the relative roles of various protocols, *viz.* photo-degradation (TiO_2/polyurethane), enzymatic process (glucose oxidase/polyurethane) and photocatalytic–enzymatic (glucose oxidase/$TiO_{2/}$polyurethane), in presence and absence of UV light. The highest efficiency was obtained for the protocol of (glucose oxidase/TiO_2/polyurethane) in presence of 6 W UV source with 99% decolorization in 22 min.

More recently, the techniques of both photolysis and photocatalysis have been combined with sonolysis for enhanced efficiency of degradation/mineralization of pollutants. The principal difference between the two UV-based techniques is that photolysis is a homogeneous reaction system, while photocatalysis is a heterogeneous reaction system. Due to homogeneous nature of reaction system, sonophotolysis does not suffer from limitations of mass transfer, and it has been applied for effective treatment of several pollutants and wastewater originating from different sources [17–27]. A summary of literature on sono-photolytic degradation of different organic pollutants is given in Table 1.

Table 1
Summary of literatures on hybrid AOP of sono-photolysis for wastewater treatment.

Pollutants	Process parameters	Results/max. degradation (%)	Reference
Phthalate acid esters (PAEs)	f = 400 kHz (bath), PAEs = 0.01 mM (mix. of DMP, DEP, DBP and MMP), H_2O_2 = *in-situ* generated, UV sources = 6 nos (254 nm), pH = 6.5, T = 28 °C, t = 90 min	Degradation: ~82% for MMP (0.0238 min^{-1}) and ~100% for DMP (0.0293 min^{-1}, DEP (0.0387 min^{-1}) and DBP (0.0712 min^{-1}). TOC removal of PAEs was 17%	Xu et al. [20]
Synthetic pharmaceutical wastewater (SPWW)	f = 20 kHz (bath), P = 140 W, TOC = 12 mg/L, H_2O_2 = 1200 mg/L, UV sources = 1 × 13 W (254 nm), pH = 3.9, T = ND, t = 120 min, air = 2 L/min	Max. TOC removal was 98%	Ghafoori et al. [17]
Atrazine (ATZ)	f = 20 (P = 375 W) and 400 kHz (P = 120 W) (bath), ATZ = 0.02 mM, H_2O_2 = 5.0×10^{-4} mM/min (*in-situ*), UV sources = 1 nos (254 nm), pH = 6.5, T = 28 °C, t = 60 min	~100% degradation was achieved with 60% of TOC removal	Xu et al. [19]
Synthetic pharmaceutical wastewater (SPWW)	f = 20 kHz (horn type), P = 140 W, composition of SPWW (mg/L) = 4AMP (6.25), PCM (2.5), Ph (12.5), CLP (7.5), BA (6.25), SA (28.75), DCF (0.5), NB (7.5), H_2O_2 = 1750 mg/L, UV sources = 1 × 13 W (254 nm), pH = 2, T = 33.1 °C, t = 90 min, air = 3 L/min	90% TOC after 180 min	Mowla et al. [21]
Trihalomethanes (THMs)	f = 500 kHz (PZT transducer), P = 52.55 W, THMs = 10 mg/L, *in-situ* generated H_2O_2, UV sources = 4 × 10.5 W (254 nm), pH = 4.5, T = 25 °C, t = 60 min	100% degradation and 50% TOC were achieved at optimum conditions	Park et al. [22]
Pharmaceutical wastewater (PW)	f = 24 kHz (horn), P = 200 W, PW = 125 mg/L (TOC), H_2O_2 = 6500 mg/L, UV sources = 1 × 150 W (190–280 nm), pH = 7, T = 30 °C, t = 120 min	100% TOC reduction was achieved	Monteagudo et al. [23]
Wastewater from food industry	f = 24 kHz (horn type), P = 200 W, H_2O_2 = 11,750 ppm, UV sources = 1 × 150 W (190–280 nm), pH = 8, T = 30 °C, t = 180 min	TOC removal 60% after 60 min and 98% after 180 min	Duran et al. [24]
Dimethyl phthalate (DMP)	f = 400 kHz (bath), P = 120 W, DMP = 0.05 mM, H_2O_2 = 9.75×10^{-4} mM/min (*in-situ*), UV sources = 6nos (254 nm), pH = 6.5, T = 28 °C, t = 120 min	~100% degradation	Xu et al. [18]
Diethyl phthalate (DEP)	f = 283 kHz (horn type), DEP = 45 μM, H_2O_2 = 0.32 μM/min (*in-situ*), UV sources = 4 × 10 W (254 nm, UVC) or {(2 × 10 W, 254 nm, UVC) + (2 × 10 W, 185 nm, VUV)(185 nm + 254 nm)}, pH = 6.2–6.7, T = 15–18 °C, t = 120 min	~92% (1.7×10^{-2} min^{-1}) degradation in US/UVC and ~90% (1.7×10^{-1} min^{-1}) in US/UVC/VUV TOC removal: ~30% in US/UVC and ~90% in US/UVC/VUV Positive synergy in sono-photolysis with UVC (SF = 1.68) and UVC/VUV (SF = 1.23)	Na et al. [25]