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Degradation of orange-G by advanced oxidation processes

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ABSTRACT

The degradation and mineralization of orange-G (OG) in aqueous solutions by means of ultrasound irradiation at a frequency of 213 kHz and its combination with a heterogeneous photocatalyst (TiO₂) were investigated. The effects of various operational parameters such as, the concentration of the dye and solution pH on the degradation efficiency were studied. The degradation of the dye followed first-order like kinetics under the conditions examined. The sonolytic degradation of OG was relatively higher at pH 5.8 than that at pH 12. However, an alkaline pH was favoured for the photocatalytic degradation of OG using TiO₂. Total organic carbon (TOC) measurements were also carried out in order to evaluate the mineralization efficiency of OG using sonolysis, photocatalysis and sonophotocatalysis. The hybrid technique of sonophotocatalytic degradation was compared with the individual techniques of photocatalysis and sonolysis. A simple additive effect was observed during the sonophotocatalytic oxidation of OG using TiO₂ indicating that the combined treatment offers no synergistic enhancement. TOC results also support the additive effect in the dual treatment process.

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1. Introduction

Textile dyes constitute one of the largest groups of organic compounds that represent an increasing environmental concern with reference to water pollution. Of the dyes available in the market, approximately 50-70% is azo dyes followed by the anthraquinone dyes. Azo dyes can be divided into monoazo, diazo and triazo classes depending on the presence of one or more azo groups (-N=N-).

Azo dyes belong to the largest class of dyes used in textile and paper industries. They are very stable to ultraviolet and visible light irradiation. Moreover, they are resistant to aerobic degradation [1] and can be reduced to potentially carcinogenic aromatic amines under anaerobic conditions or in vivo [2,3]. About 1–20% of the total synthetic dyes in the world is lost during the dyeing process and is released in the textile effluents [4,5]. The release of this contaminated water into the environment is a considerable source of non-aesthetic pollution and eutrophication which can produce dangerous by-products through oxidation, hydrolysis, or other chemical reactions taking place in the wastewater itself [6,7]. The various methods through which the degradation and mineralization of such dye effluents can be achieved have therefore received increasing attention. Chlorination and ozonation have been used for the removal of certain dyes but they work at slow rates, as well as have high operating costs [8,9]. Therefore, in order to overcome the drawbacks of some of the conventional treatment methods, advanced oxidation processes have been pro-

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posed by many scientists and engineers. Different advanced oxidation processes (AOPs) include, electrochemical oxidation processes, sonolysis, supercritical water oxidation and homogeneous and heterogeneous photochemical processes [10-12]. Particularly, sonochemical degradation of certain organic pollutants and azo dyes were widely studied by Hoffmann and coworkers [13-15]. Sonochemical degradation often fails to achieve the complete mineralization. A few studies have focused on combined AOPs [16-18]. Ragaini et al. [16] observed a synergetic enhancement in the degradation rate for the sonophotocatalytic degradation of 2-chlorophenol using a 20 kHz ultrasound. Peller et al. [17] carried out combined high frequency (660 kHz) sonolysis/photocatalysis and achieved synergistic degradation of 2,4-dichlorophenol without making any toxic intermediates even at very low catalyst loadings. Selli [18] reported a synergy in combining sonolysis and photocatalvsis for the degradation of an azo dve. acid orange 8.

Recently, Collings et al. [19] studied the rapid degradation of polychlorinated biphenyls (PCB's) and certain organochloride pesticides present in the soil using ultrasound (20 kHz, 160 W). It was reported that 1 min of sonication was sufficient to achieve 90% destruction of the PCB's and 99% destruction was attained after 7 min. Such a rapid decomposition of the pollutants was believed to be due to the solid particles in slurry acting as foci for the nucleation and collapse of micro bubbles. These quite remarkable observations have prompted us to study the effect of solid particles on the sonolytic degradation of a textile dye, orange-G (OG).

The photocatalytic degradation of OG has been reported in several studies [20,21]. Nagaveni et al. [22] reported the degradation of OG using combustion-synthesized nano-TiO₂ under solar light,



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and found that the initial degradation rates were 1.6 times higher than that using Degussa P25 TiO_2 . Sun et al. [23] studied the degradation of OG on nitrogen doped TiO_2 and reported that the doped TiO_2 nanocatalysts demonstrated higher activity than the commercial Degussa P25 under visible light.

In the present study, sonolysis, heterogeneous photocatalysis and a combination of both (sonophotocatalysis) have been chosen for the degradation of OG, with the aim of investigating effect of solid particles in a multi-AOP to find the best possible conditions for the degradation of the dye.

2. Materials and methods

2.1. Experimental conditions

Sonolysis experiments were performed at an ultrasound frequency of 213 kHz in a continuous wave mode. The ultrasound unit used was ELAC LVG-60 RF generator coupled with ELAC Allied signal transducer with a plate diameter of 54.5 mm [12]. The power output on the RF generator for all experiments was 35% which corresponds to a calorimetric power of about 20 W. All reagents used were of AR grade and were used without further purification. Aqueous solutions of OG (Sigma-Aldrich) were prepared using Milli-O water. All experiments were performed at natural solution pH, which was left uncontrolled during the reaction. For those runs carried out at alkaline or acidic conditions, the initial pH was adjusted by adding appropriate amounts of NaOH or H₂SO₄. Experiments were carried out under atmospheric conditions and at room temperature. The temperature was maintained $(20 \pm 2 \circ C)$ by circulating water through a jacket surrounding the cell. The volume of the solutions sonicated was 250 mL. Photoirradiation was carried out by means of a Xe-arc lamp (450 W, Oriel).

All sonolytic, photocatalytic and sonophotocatalytic experiments were performed in the same experimental assembly. A typical experimental procedure adopted for the heterogeneous photocatalytic degradation of dyes is described below. By dissolving appropriate amounts of the dye in 250 mL of Milli-Q water within the reaction cell, the desired concentrations of the dye were prepared. A known amount of the photocatalyst, viz., Degussa P25 TiO_2 (particle size 20 nm, surface area 55 m²/g) was then added to the dye solution. The sonication at higher frequencies is not expected to affect the particle size since the physical effects generated are relatively weaker. Prior to irradiation, the aqueous suspension was mixed continuously in the dark for 45 min to ensure adsorption equilibrium of OG on the catalyst surface was reached. Continuous stirring in this case is essential for maintaining the photocatalyst in the illuminated part of the suspension. During irradiation, 3 mL aliquots were withdrawn at appropriate time intervals and the photocatalyst was removed immediately by filtration through a 0.45 µm syringe filter (Pall Corporation).

2.2. Analytical determinations

The solute concentration was monitored over time using electrospray mass spectrometry (ESMS). The mass spectrometer used was a Micromass QUATTRO 11 coupled to a Hewlett Packard series 1100 degasser. The instrument was calibrated using the automatic tuning procedure with respective to the parent compound as the standard. The mass range scanned was m/z 50–500 and several spectra were obtained across each chromatographic peak. All mass spectra were the averages of 3–4 spectra obtained across the top of each chromatographic peak with background noise subtracted. The analysis was carried out in positive electrospray ionization mode at cone voltages of 30 V, 50 V and 80 V, respectively. The mobile

phase consisted of 50/50 (acetonitrile/water). The flow rate of the solvent was 0.03 mL/min and the capillary voltage was set at 3.5 kV. The degradation intermediates were identified by comparing the chromatograms to those of known compounds using mass spectrometry and HPLC. The concentration of OG was determined by a high-performance liquid chromatograph, Shimadzu LC-10 AT VP system with a Shimadzu SPD-10 AVP UV-vis absorbance detector with an Altech reversed phase column (C18, 150 mm × 4.6 mm inner diameter, 5 μ m beads); a mobile phase of acetonitrile/water = 90/10; flow rate of 1.0 mL/min; detection wavelength of 480 nm. For intermediate separation, an acetate buffer (0.1 M ammonium acetate in acetic acid) was used as the mobile phase with a flow rate of 1 mL/min and the detection wavelength of 280 nm.

TOC was determined using a total organic carbon analyser, which utilizes oxidative combustion followed by infrared detection. The instrument used was a TOC-V_{CSH} (Shimadzu) programmed by TOC-control V Software. The instrument was calibrated before each use with standardized TOC solutions of 1000 mg/L. The absorption spectrum of OG was recorded with a "Cary Varian 50 Bio" UV–vis spectrophotometer at 25 °C. The spectrophotometer was coupled to a computer, which measured the absorption spectrum using Scan 2 software. The samples were placed in a sample compartment made of quartz and were scanned in the wavelength range of 200–600 nm. The surface tension of the aqueous solutions was measured using a McVan Analite surface tension meter (Model 2141) with a glass Wilhelmy plate. All measurements were done at room temperature.

3. Results and discussion

The degradation of OG was performed under different experimental conditions that include, (i) photoirradiation alone (UV-"control"), (ii) ultrasound alone (US), (iii) photoirradiation in the presence of TiO_2 (UV + TiO_2) and (iv) a combination of photocatalysis and ultrasound (US + UV + TiO_2) and the results are shown in Fig. 1. The preliminary experiments revealed no significant degradation of OG occurred either in the absence of US or UV. However, under the presence of US with 35% amplitude at the frequency of 213 kHz, about 43% degradation of OG occurred within 75 min.

It is known that sonolysis of aqueous solutions produces 'OH created by the implosion of cavitation bubbles (Reaction (1)) [24].

$$H_2 O \to \cdot H + \cdot O H \tag{1}$$



Fig. 1. The degradation of orange-G (0.09 mM) using various advanced oxidation processes (TiO_2 (1 g/L) was used for photocatalytic and sonophotocatalytic runs).

There are three potential sites for sonochemical reactions in aqueous solutions, namely, (i) the gaseous region of the cavitation bubble where volatile and hydrophobic species are easily degraded through pyrolytic reactions as well as reactions involving the participation of hydroxyl radicals (ii) the bubble–liquid interface where hydroxyl radicals are localized and therefore, radical reactions may predominate although pyrolytic reactions occur to a lesser extent, and (iii) the liquid bulk where sonochemical activity may take place mainly due to free radicals that have escaped from the interface and migrated into the bulk liquid. We speculate that the degradation of OG takes place mainly in the bubble–liquid interface and further discussion on this issue is provided later.

It is observed in Fig. 1 that photoirradiation in the presence of TiO₂ leads to 59% degradation in 75 min. Bandgap excitation of the TiO₂ leads to the formation of electrons in the conduction band and holes in the valence band [25]. As a consequence of such photoinduced charge separation on the semiconductor surface, electron transfer reactions occur at the semiconductor–water interface. The superoxide radical anion $'O_2^{-}$ is formed by interaction of conduction band electrons with adsorbed oxygen molecules, while the oxidation of adsorbed organic substrates simultaneously occurs either via their direct interaction with valence band holes or via valence band hole oxidation of adsorbed water or hydroxyl anions.

However, when both the US and UV are combined (sonophotocatalysis), a significant enhancement in the degradation (85% in 75 min) of OG was observed, suggesting the involvement of hydroxyl radicals formed by both bandgap excitation of the photocatalyst as well as by the water sonolysis route.

OG has a pK_a value of 11.5 hence it is in its –OH form below its pK_a and –O⁻ form above its pK_a. It was also found that the UV-vis spectrum of OG above and below its pK_a changed significantly. Therefore, it was anticipated that different degradation rates would be observed at different pH values above and below its pK_a. Hence, the sonolytic, photocatalytic and sonophotocatalytic degradation of OG at pH values well below (5.8) and above (12) its pK_a were examined.

3.1. Sonolytic degradation of orange-G

To study the effect of pH on the sonolytic degradation of OG, experiments were carried out with OG at various initial concentrations and the result is shown in Fig. 2a and b. The sonochemical degradation of OG followed first-order like kinetics, which was confirmed from the plot of $\ln C_0/C$ vs. time. Note that this cannot be strictly considered as a first-order reaction since the rate constant changes with the initial concentration of OG. We have observed similar behavior in our earlier work on the sonochemical degradation of benzoic acid [26]. This anomaly was explained based on the changes in bubble temperatures affecting the amount of OH radicals generated during cavitation and detailed discussion on this issue is provided in our previous report [26]. The only reason we use this kinetic data is to compare the rate of degradation under various experimental conditions. As can be seen in Fig. 2, the concentration of OG decreased with an increase in the sonication time at both pH values. In Fig. 2a, it is shown that the extent of degradation was significantly affected by the initial concentration of OG. For example, with an initial concentration of 0.12 mM at pH 5.8. about 33% of OG was degraded after 75 min. whereas about 54% degradation was achieved at 0.05 mM concentration. The initial reaction rate ($[OG]_i \times$ corresponding slopes from ln plots) was found to increase with increasing initial concentration of OG.

The effect of pH on the sonochemical degradation rate of OG is shown in Fig. 3. Singla et al. [26] studied the sonolytic degradation of benzoic acid at both acidic and alkaline pH and reported that with an increase in the concentration of benzoic acid in the bulk



Fig. 2. (a) Effect of orange-G concentration on the sonolytic degradation kinetics at pH 5.8. (b) Effect of orange-G concentration on the sonolytic degradation kinetics at pH 12.



Fig. 3. Effect of orange-G concentration on the sonolytic degradation rate at pH 5.8 and 12.

solution, the bubble/solution interfacial concentration was also increased at low pH. This occurs because the neutral form of benzoic acid is more hydrophobic than the ionized form and therefore more surface active. The consequence of this effect is that the reaction between OH radicals (generated within the bubbles) and OG is enhanced thereby leading to an increase in the degradation rate.

In present study, the rate of OG degradation was relatively slow at higher solution pH than at lower pH. Since the OG degradation rate showed a similar trend with pH to that observed for benzoic acid, the same explanation holds for OG. Surface tension measurements (data not shown) indicate that OG is slightly more surface active in acidic pH consistent with the slightly higher sonolytic degradation at pH 5.8 compared with that at pH 12.

3.2. Photocatalytic degradation of orange-G

The pH of the solution is an important parameter for the photocatalytic degradation since it controls the surface charge properties of the photocatalyst and the size of aggregates that it forms. The influence of pH on the photocatalyzed degradation of OG at pH 5.8 and 12.0 was investigated with constant dye concentration (0.09 mM) and photocatalyst amount (1 mg/mL). Fig. 4 shows that the photocatalytic degradation rate at pH 5.8 is comparatively lower than that at pH 12. The rate of photocatalytic degradation of OG by Degussa P25 TiO₂ was observed to be 17.1×10^{-7} M min⁻¹ at pH 12 which is 1.3 times higher than that of at pH 5.8 $(12.6 \times 10^{-7} \text{ M min}^{-1})$. The higher photocatalytic activity at alkaline condition seems to be a characteristic feature for many photocatalytic systems and similar results have been obtained for the photodegradation of methyl orange [27] and phenoxyacetic acid [28]. Hung et al. [29] also monitored the effect of pH on the photocatalytic degradation of OG and detected that the OG degradation was high when the pH was greater than 9 and slowest under neutral conditions.

The effect of pH on the photocatalytic degradation rate can be explained by considering the surface charge of TiO₂ (zero point charge $(pH_{ZPC}) \sim 6.5$) and its relation to the acid dissociation constants of sulfonic acid in OG. Since the pK_a value of the sulfonic acid group is low, it will exist in an anionic form at the pH studied. As the TiO₂ surface is positively charged below its pH_{ZPC} and negatively charged above its pH_{ZPC}, it can be expected that the titanium dioxide particles would repel the dye at pH 12 and attract the same at pH 5.8. Therefore, based on a simple adsorption density basis higher photocatalytic degradation should occur at acidic pH than at alkaline pH. Contrary to this explanation, in the present investigation, it was observed that the rate reached a maximum at alkaline pH. The enhancement in the degradation rate at pH 12 may be due to formation of 'OH from the excess OH⁻ anions adsorbed on the catalyst surface. Moreover, at sufficiently higher pH values, the formation of oxidizing species such as the superoxide radical anion (O_2^{-}) could also be responsible for the rate enhancement [30].

3.3. Sonophotocatalytic degradation of OG

Suspended solids may also influence the level of cavitation generated in solution and hence the sonochemical degradation rate.



Fig. 4. Comparison of degradation rates for different processes for the degradation of orange-G (0.09 mM) in the presence of TiO_2 (1 mg/mL) with and without ultrasound.

The presence of particles under an ultrasound field (called sonocatalysis) may enhance degradation by providing additional nuclei for bubble generation. Therefore, in order to monitor the effect of suspended solids (TiO₂) on cavitation, the following experiment was conducted under the experimental conditions of (OG) = 0.09 mM and TiO₂ amount of 1 mg/mL, and the results obtained are shown in Fig. 4. From Fig. 4, it can be deduced that within experimental error, there is no significant enhancement in the degradation rate by the addition of TiO₂ during sonolysis, and that the sonocatalytic degradation follows the degradation trend of sonolytic degradation at both acidic and alkaline pH.

In order to explore ways to enhance the OG degradation rate experiments combining photocatalysis and sonolysis were carried out [31,32]. For any hybrid technology, it is obviously expected that the efficiency of the hybrid system (AB) should be higher than the sum of the efficiencies of the two single technologies (A and B), comprising the hybrid technology, that is, AB > A + B.

Synergy index =
$$\frac{R_{(\text{US}+\text{UV}+\text{TiO}_2)}}{R_{\text{US}} + R_{(\text{UV}+\text{TiO}_2)}}$$
(2)

where R_{US} , $R_{(\text{UV+TiO}_2)}$ and $R_{(\text{US+UV+TiO}_2)}$ are sonolytic, photocatalytic and sonophotocatalytic degradation rates.

The sonophotocatalytic degradation experiments at pH 5.8 and 12 were carried out using Degusa P25 and the data is shown in Fig. 4. As can be seen that, at pH 5.8, OG underwent relatively slow degradation under ultrasound irradiation in the presence of titanium dioxide (US + TiO₂) while, under photocatalysis (UV + TiO₂) the degradation occurred at a higher rate. A further significant increase in the reaction rate was observed when the illuminated suspensions were simultaneously sonicated, i.e., under sonophotocatalysis (UV + US + TiO_2), where the degradation rate was higher than that of the individual sonolysis or photocatalysis rates. For example, the degradation rates at pH 5.8 with sonolysis, sonocatalysis and photocatalysis are, $R_{\rm US} = 6.2 \times 10^{-7}$ M min⁻¹, $R_{(US+TiO_2)} = 6.1 \times 10^{-7}$ M min⁻¹ and $R_{(UV+TiO_2)} = 12.6 \times 10^{-7}$ 10^{-7} M min⁻¹, respectively. A sonophotocatalytic degradation rate of $R_{(UV+TiO_2)} = 22.3 \times 10^{-7}$ M min⁻¹ was observed, giving a synergy index of 1.1 ± 0.2 . Considering that this value is only slightly greater than 1, and within experimental error of the measurements, it suggests that there is an additive effect in combining sonolysis and photocatalysis, rather than a synergistic effect.

Within experimental error, the sonophotocatalytic degradation rate at pH 12 is almost equal to the photocatalytic degradation rate (Fig. 4), giving a synergy index of 0.7 ± 0.2 . Hence, we propose that



Fig. 5. Change in TOC as a function of time for different degradation processes at pH 5.8 and 12. (\blacklozenge) Sonolysis at pH 5.8; (\blacklozenge) photocatalysis at pH 5.8; (\blacktriangle) sonophotocatalysis at pH 5.8; (\Box) sonolysis at pH 12; (\bigcirc) photocatalysis at pH 12 and (\triangle) sonophotocatalysis at pH 12.



Fig. 6. HPLC chromatogram obtained as a function of sonication time for orange-G (0.09 mM) at pH 5.8.

sonophotocatalytic degradation at pH 5.8 is more efficient than at pH 12, due to the sonolytic effect rather than photocatalysis.

3.4. Mineralization studies

A rather straightforward way of measuring oxidation progress of an organic compound is the determination of carbon content of the oxidation product mixture. This can be obtained by monitoring the total organic carbon (TOC) content of the treated solutions. The TOC content directly relates to the extent of water pollution. Based on our TOC studies of the OG degradation using sonolysis, photocatalysis and sonophotocatalysis (Fig. 5) the following conclusions were made: (1) the TOC removal rate was much less than that of the decolourization process under the same experimental conditions. (2) Mineralization becomes important after the initial degradation of OG. (3) Sonophotocatalysis achieves higher TOC removal than the individual processes such as sonolysis and photocatalysis. (4) Similar to degradation, an additive effect was observed with TOC removal rate. (5) The TOC decrease at pH 5.8 is more favourable than pH 12 which is evident from 82% TOC reduction after 4 h of sonophotocatalytic reaction at pH 5.8 whereas at pH 12 about 60% TOC reduction was observed under the same experimental conditions.

The above trend may be due to the formation of more stable intermediates in the process of decolourization and also the difference between the photocatalytic mechanisms of decolourization and TOC decrease. The decolouring mechanism of OG might proceed predominantly through the destruction of the azo group by oxidation via reaction with positive holes and by reduction from conduction band electrons in a manner similar to that of decolourization of other azo dyes in photocatalytic processes, while TOC was decreased only by the oxidation of the organic material [26].

3.5. Possible degradation pathway

Since the sonolysis, photocatalysis and sonophotocatalytic degradation showed almost the same degradation products, the degradation products formed during sonolysis were analyzed in the present investigation.

The mechanism of the degradation of the dye by sonolysis can be expected to be very complex due to the non-selective nature of attack of OH radicals on OG. Bokare et al. [33] reported the degradation of OG using Fe–Ni bimetallic nanoparticles and proposed the reaction mechanism involving the formation of aniline and naphthol amine. Kanazawa and Onami [34] proposed a mechanism for the degradation of OG by sodium hypochlorite. Based on their studies, it was evident that certain reaction products are



8-[(E)-(2,4-dihydroxyphenyl)diazenyl]-5,7-dihydroxynaphthalene-1,3-disulfonic acid

Scheme 1. A schematic representation showing the initial degradation pathway of orange-G during sonolysis.

subsequently converted to other products, step by step. Similarly, different reaction intermediates due to the different reaction possibilities, like hydrogen abstraction, hydroxyl radical addition etc., would occur in the present study.

In order to identify reaction by-products accompanying OG degradation, samples collected at various time intervals were analyzed by means of HPLC and ESMS. The results indicate that sonolysis degrades the azo group of OG and results in its irreversible transformation into a number of products including aromatic amines.

HPLC chromatogram obtained for the sonication of OG at different time intervals is given in Fig. 6. As seen in Fig. 6, the peak due to OG (R_t = 300–380 s) decreased with increased sonication time while the peaks for the products correspondingly increased. The major product of sonication is 7-hydroxy-8-(hydroxyamino)naphthalene-1,3-disulfonic acid (I) (R_t = 100–130 s) was found as a protonated form in the mass spectrum. Formation of aniline and phenol were confirmed by comparing the retention time of pure aniline and phenol standards with the retention time of the reaction sample at 170–200 s and 140–170 s, respectively (Scheme 1).

By comparing the product formation yields, it was observed that the quantity of aniline (II) formation was very low and this leads to the conclusion that it undergoes further degradation into other products. Since sonolysis mainly involves the attack of OH radicals on the aromatic ring, it can be expected that the first intermediates formed would be OH-added products of OG. Apart from aniline, other products detected were also OH-added products such as 5,7dihydroxy-8-[(*E*)-phenyldiazenyl]naphthalene-1,3-disulfonic acid (IV, m/z 424) and 8-[(*E*)-(2,4-dihydroxyphenyl)diazenyl]-5,7-dihydroxynaphthalene-1,3-disulfonic acid (V, m/z 456). The above ESMS findings together with the results of HPLC support the notion that during the sonolytic oxidation of dye molecule two processes occur (a) hydroxylation of the aromatic ring and, (b) reductive cleavage of the azo bond that lead to the formation of aromatic primary amines.

From all our observations, it can be concluded that partially water soluble materials such as OG do not degrade synergistically using a combined AOP process. Also, enhanced degradation by operating ultrasound in the presence of particles, for these types of pollutants is not observed under our operating conditions.

4. Conclusions

The conclusions drawn from this study can be summarized as follows:

(1) Degradation of OG depends on the initial dye concentration and pH of the reaction mixture. Sonolytic degradation is favoured at acidic pH and the reverse is true for the photocatalyic degradation. The surface active nature of OG at acidic pH can account for the higher degradation efficiency in acidic pH during sonication. In the case of photocatalysis, the higher concentration of OH⁻ ions at pH 12 produces more hydroxyl radicals than at pH 5.8 and hence a higher degradation rate at elevated pH.

- (2) Even though the sonophotocatalysis process is shown to be more efficient than the individual processes for the degradation of OG, only an additive effect of combining sonolysis and photocatalysis was observed rather than a synergy effect. TOC studies also support the above conclusion.
- (3) Aniline, phenol and aromatic hydroxyl amine are formed as the intermediates during the sonolysis process.

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