Comparison of Advanced Oxidation Processes (Sonication, Fenton Reaction and Ozone-Based Processes) for Water Decolorization

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Comparison of Advanced Oxidation Processes (Sonication, Fenton Reaction and Ozone-Based Processes) for Water Decolorization

Başak Savun-Hekimoğlu

Introduction

Advanced oxidation processes (AOPs) are known for their efficiency in removing refractory compounds such as azo dyes from water and wastewater. The efficiency of these processes depends on their capacity to generate hydroxyl radical (OH•) which is the strongest known oxidant (Frontistis et al., 2017). The most common AOPs include sonication, Fenton reaction, ozonation (O3), photocatalysis and their several combinations (Miklos et al., 2018; Krishnan et al., 2017; Tufail et al., 2020; Fast et al., 2017; Babu et al., 2017).

Sonication is the use of ultrasound waves to propagate the phenomenon called acoustic cavitation. Acoustic cavitation consists of three successive stages: i) nucleation, ii) bubble growth (expansion), iii) implosive collapse (Suslick, 1990). In the first stage, microbubbles are trapped in micro-crevices of small particles within the liquid form cavitational nuclei, where cavities are trapped in micro-crevices of small particles within the liquid form cavitational nuclei, where cavities are generated depending on the type and purity of the liquid. (Suslick, 1990; Peters, 1996). In the second stage, the microbubbles once formed grow and expand depending on the intensity of the applied sound, and when the intensity is too high, a small cavity may grow rapidly through inertial effects (Suslick et al. 1990). At this point, the extremes of temperatures and pressures create an unusual environment or high-energy micro-reactors that enable molecular fragmentation of the entrapped gases in the collapsing cavities (Ince et al., 2001). The reactions of sonication are shown in the following equations (Ince et al., 2001; Lorimer and Mason, 1991; Fischer et al., 1986):

\[
\begin{align*}
\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow & \text{OH}^+ + \text{OH}^- + \text{H}_2 \\
\text{OH}^+ + \text{H}_2\text{O} \rightarrow & \text{OH} + \text{H}_2\text{O} \\
\text{OH} + \text{H}_2\text{O} \rightarrow & \text{H}_2\text{O}_2
\end{align*}
\]

Another widely used AOP is Fenton reaction processes utilizing Fe^{2+} salts to activate H_2O_2 (Dewil et al., 2005). In the Fenton process, the reaction between dissolved Fe^{2+} and H_2O_2 in acidic aqueous solution leads to oxidation of Fe^{2+} to Fe^{3+} and formation of the highly reactive •OH.

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow & \text{Fe}^{3+} + \text{•OH} + \text{H}^{+} \quad \text{(chain initiation)} \\
\text{•OH} + \text{Fe}^{3+} \rightarrow & \text{•OH} + \text{Fe}^{3+} \quad \text{(chain termination)}
\end{align*}
\]

The third stage of cavitation occurs when the cavity is so overgrown that it can no longer absorb energy to sustain itself, and the surrounding liquid rushes in to lead to a violent implosion as a catastrophic collapse (Mason and Peters, 2002; Mason 1990; Suslick et al. 1990). At this point, the extremes of temperatures and pressures create an unusual environment or high-energy micro-reactors that enable molecular fragmentation of the entrapped gases in the collapsing cavities (Ince et al., 2001). The reactions of sonication are shown in the following equations (Ince et al., 2001; Lorimer and Mason, 1991; Fischer et al., 1986):
As seen in the reactions (6) and (8), H$_2$O$_2$ is both an initiator and an •OH scavenger, particularly when its concentration is high.

Another important class of AOPs is based on the use of ozone. These homogeneous AOPs include single ozonation, ozonation with UV-light and the UV-peroxide processes. Single ozonation is an AOP only if the process is operated at highly alkaline pH, at which O$_3$ decomposes to produce OH radicals. At low pH, however, ozone is in molecular form and reacts selectively through direct electrophilic reactions (Soares et al., 2006). The reaction of ozone with OH radical.

$$2\text{OH} + \text{H}_2\text{O} \rightarrow \text{HO}_2 + \text{H}_2\text{O}$$

Generation of •OH in O$_3$/H$_2$O$_2$ and O$_3$/UV processes proceed via the interaction of ozone with H$_2$O$_2$, and the photolysis of ozone, respectively, as presented in Eq (10) and (11). The rate of H$_2$O$_2$ photolysis in these systems is directly related to the incident power or intensity of light and the dose of H$_2$O$_2$, while that of organic matter degradation is a function of the quantity of O$_3$ and •OH available in solution (Muruganandham et al., 2014).

$$\text{O}_3 + \text{H}_2\text{O}_2 \rightarrow \text{•OH} + \text{O}_2 + \text{HO}_2$$

$$\text{O}_3 + \text{hv} + \text{H}_2\text{O} \rightarrow 2\text{•OH} + \text{O}_2$$

In UV/H$_2$O$_2$ process hydrogen peroxide is activated by UV light and hydroxyl radicals (•OH) are generated by the photolysis of hydrogen peroxide (12). H$_2$O$_2$ photolysis rate directly depends on the incident power or intensity. In addition, the dosage of H$_2$O$_2$ needs to be optimized, since excess H$_2$O$_2$ may scavenge hydroxyl radical.

$$\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\text{•OH}$$

This study aims to evaluate the efficiency of several AOPs for the degradation of an azo dye. Remazol Brilliant Blue R (RBBR) was selected as the model dye. RBBR is known for its resistance to chemical oxidation due to its unique chemical structure (Chang et al., 2009). Sonication, Fenton reaction, and ozone-based AOPs (O$_3$, O$_3$/UV, O$_3$/UV/H$_2$O$_2$) were compared for their efficiency in decolorization and mineralization.

Materials and Methods

Materials

RBBR was obtained from Sigma Aldrich. A stock solution was prepared according to the method described by Garcia-Montano et al (2008). Reagent grade hydrogen peroxide (35%, w/v), and FeSO$_4$.7H$_2$O were obtained from Merck and used as Fenton’s reagents. Reagent grade NaOH and H$_2$SO$_4$ (1N) were used for pH adjustment. The structure and chemical/ physical properties of the compound are as given (Rahmat et al., 2016; Bagchi and Ray, 2015; Rodriguez-Couto, 2011):

Experimental Set-Up

Sonication

An ultrasound probe (Bandelin Sonoplus HD2200) emitting ultrasonic waves at 20 kHz was immersed into a 100 mL glass cell surrounded by a water-cooling jacket to keep the reactor at constant temperature (25 ± 0.5 °C). The power was adjusted to 30%. The samples were pre-aerated for 20 min before sonication.

Fenton Reaction

250 mL of azo dye solutions were acidified to pH 3 by 1 N H$_2$SO$_4$. In order to initiate Fenton oxidation reaction, after 20 min pre-aeration 0.1mM Fe$^{2+}$, and H$_2$O$_2$ was added to provide 1:20 Fe:H$_2$O$_2$ ratio and the samples were mixed (mixing rate 125 rpm) for 1 h.

Ozonation

Using an Ozonelab-100 Model generator ozone was generated onsite and 21 mg/min O$_3$ was applied to 250 mL solution. The pH of the solution was adjusted to 11 by 1N NaOH.

O$_3$/UV and O$_3$/UV/H$_2$O$_2$

In photolytic experiments, a low-pressure Hg-UV lamp emitting at 254 nm was used. The pH of the 2L sample solution was adjusted to 11. The ozone dose was 21 mg/min. In the O$_3$/UV/H$_2$O$_2$ process, 0.1 mM H$_2$O$_2$ was added to the solution.

Analytical

In every experimental set-up, samples were collected at time t= 0, 5, 10, 20, 30 and 40 min. The pH of the solution was monitored using a Metler Toledo pH meter. Mineralization was measured in terms of Total Organic Carbon (TOC) using a Shimadzu TOC-V CSH Analyzer. Color removal was measured spectrophotometrically. The absorbance of the test solutions at 588nm was analyzed using a Unicam Helios Alpha/Beta double beam spectrophotometer. Hydrogen peroxide was measured by measuring absorbance at 351 nm wavelength. Then the measured absorbance values were converted to concentration values by preparing a standard curve of known hydrogen peroxide concentrations (10, 20, 30, 40 ppm).
Results and Discussion

Experiments were conducted in one of the following setups: the sonication setup, the Fenton reaction setup, ozonation \((O_3)\) setup, ozonation and UV irradiation \((O_3/UV)\) setup, and \(O_3/UV/H_2O_2\) setup. The initial concentration of RBBR was 10 ppm in all set-ups. Test samples were prepared by dilution of a stock solution with deionized water. The results of each AOP was given and discussed in this section.

Sonication

In this set of experiments 20 kHz ultrasound was applied to the dye solution for 40 min. No pH adjustment was done and the initial (natural) pH of the solution was 6.67. The collected samples were analyzed for hydrogen peroxide, pH, TOC, and decolorization. The results of sonication experiments are shown in Figure 1. It is obvious that sonication alone was ineffective in removing RBBR. As shown in Figure 1 (a) the reaction rate of RBBR degradation by single sonolysis was slow \((k=0.0095 \text{ min}^{-1})\). Figure 1 (b) shows that the process was not very efficient for mineralization. After 40-min sonication only 21% mineralization was achieved.

In homogenous sonochemistry, there are three main reaction sites: the cavitation bubble, the interface between gas bubbles and the surrounding liquid, and the bulk solution (Adewuyi, 2001; Ince et al., 2001). Oxidation reactions in the bulk solution are limited by the number of available, uncombined, free radicals migrated from the collapsing cavities and the interface into the bulk (Ince et al., 2001).

RBBR is a hydrophilic compound with low volatility. Therefore the compound is not expected to migrate towards the bubble or the interfacial region, but rather remain in the bulk solution, where the concentration of \(•\text{OH}\) is very low. Moreover, Figure 1 (d) shows an increase in H\(2\)O\(_2\) confirming the recombination of the produced \(•\text{OH}\) to form H\(2\)O\(_2\). A slight decrease in the solution pH might be due to the formation of acidic by-products.

Fenton Reaction

The results of the Fenton process are shown in Figure 2. As shown in Figure 2 (a) the degradation of dye was very fast. The process was found to be effective not only for degradation but also for mineralization. At the end of the reaction time (40 min) approximately 60% mineralization was achieved. We can say from figure 2(d) that OH radicals were formed by reaction (6). The constant pH of the solution indicates that the RBBR was not converted to by-products but more than half of it was efficiently mineralized. However, Fenton’s reaction...
alone was not able to completely mineralize the azo dyes as the process is limited by the redox cycle between Fe²⁺ and Fe³⁺ (Ameta et al., 2013). According to a review study on dye degradation by Fenton process, Nidheesh et al. (2013), our results are in complete agreement with the literature.

Ozonation-Based AOPs (O₃, O₃/UV, O₃/UV/H₂O₂)

For O₃, O₃/UV and O₃/UV/H₂O₂ processes the pseudo-first-order degradation curves of RBBR and the percentage of mineralization are shown in Fig. 3. The data show that the single ozonation process was inadequate for dye degradation and mineralization. This finding can be explained by the low reactivity of the parent compound, RBBR, as well as its oxidation byproducts with O₃.

The combination of ozone with UV irradiation resulted in an enhancement in the reaction rate. Figure 3 (a) shows that by the addition of UV light to the ozone reactor, the reaction rate constant increased from 0.002 min⁻¹ to 0.02 min⁻¹. In addition, mineralization increased from 14% to 33% with the integration of UV irradiation. This synergistic effect between UV light and ozone is in complete agreement with the literature and explained by the production of more hydroxyl radicals than in the case of single ozonation (Cuiping et al. 2011; Cortez et al., 2011).

O₃/UV/H₂O₂ process was found to be the most effective AOP between the tested processes. By using this process complete decolorization was achieved in less than 10-min reaction time and 83% mineralization was achieved at the end of 40-min reaction time. The efficiency of this hybrid process is due to the production of •OH by several individual and combined processes. The efficiency of the process can be attributed to: i) photolysis of the RBBR, ii) generation of •OH by single ozonation, iii) photolysis of ozone by UV, iv) photolysis of the added H₂O₂ by UV, v) the combined effect of H₂O₂ and O₃.

Relative mineralization of RBBR upon 40-min reaction by all tested AOPs is summarized in Figure 4. It is obvious that RBBR was not completely mineralized in any of these five processes. RBBR mineralization efficiencies were in the decreasing order of Ozonation/UV/H₂O₂ > Fenton > Ozonation/UV > Ultrasound > Ozone.

Conclusion

Five AOPs, sonication, Fenton reaction, O₃, O₃/UV, O₃/UV/H₂O₂ were tested for the elimination of a recalcitrant azo dye, RBBR, from water. The least effective AOP was found to be the single ozonation process. However, by combining with UV irradiation and H₂O₂, the efficiency of the process was significantly increased. The addition of UV irradiation to single ozonation process provided a 27% additional mineralization (42% mineralization). The most effective process was O₃/UV/H₂O₂ due to individual as well as combined effects of O₃, UV irradiation and H₂O₂.
It is also demonstrated that the application of ultrasound provided limited mineralization of the azo dye solution. The inefficiency of sonication is attributed to the low volatility of the dye which inhibited its transfer into the cavity bubble. Hence, the reaction took place in the bulk solution where the •OH concentration is the lowest. Fenton reaction was also found to be the second most effective process. This process provided complete decolorization after the 20-min reaction. However, at the end of the 40 min reaction time, only 62% mineralization was achieved, indicating the formation of small-weight oxidation byproducts, which were resistant to further decomposition.

Further research is needed to investigate the toxicity of the reaction by-products of the compared processes. Also, an economic analysis on the initial investment costs and operating costs of the AOPs should be conducted to determine the most economical processes.

Acknowledgements

Başak Savun-Hekimoğlu is a post-doctoral researcher at Istanbul University, Institute of Marine Sciences and Management. The author is thankful to the Istanbul University Research Fund (BAP) for post-doctoral scholarship granted with an identity number MAB-2019-34967.

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