Enhancing Advanced Oxidation Process by Microbubbles Technology and the Analysis of Its Degradation Process

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**Abstract.** The simulated dyes tuff containing Indigo Carmine (IC), a highly toxic indigoid dye used as a textile coloring agent, was studied using hydrogen peroxide as oxidant enhanced by microbubbles. The decolorization rate, chemical oxygen demand (COD) and total organic carbon (TOC) removal extent were dramatically increased by the presence of microbubbles. The discoloration was observed in this system up to 94.27%, compared with about 49.6% without hydrogen peroxide in 60 minutes, and COD and TOC removal rate can achieve to 72% and 53.07%, respectively. In addition, the main degradation pathway was analyzed by Fluorescence (FLS), Ultraviolet Visible (UV-Vis) and Ultra High Liquid Chromatography and Time of Flight Mass Spectrometry (UPLC-Q-TOF-MS). The results showed that hydroxyl radicals (\(\cdot\)OH) induced strong oxidizing effects in the target solution and destroyed the chromophoric groups of the molecular structure. The application of microbubbles technology in the advanced oxidization process may provide an effective and low-cost approach for treating dye wastewater.

1. Introduction

Printing and dyeing wastewater effluent discharges of textile industrial wastewater often contains a large amount of non-biodegradable dye[1]. There will be harmful to the environment if these dyes were discharged into the environment without any treatment. Various organic colorant used dyes in the dye industries, indigo carmine is one of them. Besides it is also used as an additive in pharmaceutical tablets and capsules for medical diagnostic purposes[2]. Physical and chemical methods have been studied to remove indigo carmine in the waste water. Physical treatments such as adsorption, membrane filtration and coagulation flocculation[3]. However, further treatment still required with physical treatments due to these treatments only convert the pollutants from the liquid phase to a solid phase, beyond that it is also producing massive sludge, causing membrane fouling and phase change of the pollutants. Chemical treatment for instance bacterial and fungal cultures relied biological processes, but the limitation of those is the poor biodegradability characteristic of the dyeing wastewater[4]. For these reasons, it is necessary to find economical and efficient method to degrade indigo carmine[5].

Advanced oxidation processes (AOPs) were reported as one of a promising way to treat wastewater[6]. AOPs such as ozonation, hydrogen peroxide, ultrasonic, ultraviolet (UV) radiation and photocatalytic treatments has been utilised to decolorize textile wastewater[7]. However, finding a cost-effective treatment that insures complete elimination of dye wastewater is still in demand.
Table 1. Application examples of advanced oxidation process

| AOPs          | processing object | treatment efficiency             |
|---------------|-------------------|----------------------------------|
| UV/O₂         | ethenol           | TOC 18.0 → 1.5 mg/l              |
|               | chlorobenzene     | 40 → 20.6 ug/l                   |
| UV/O₂         | dioxin            | 40 → 5000 pg/l                   |
|               | PVA               | TOC removal 96.6%                |
| H₂O₂/O₂       | humic acid        | TOC removal 84.3%                |
|               | LAS               | TOC removal 72.6%                |
| UV/TiO₂       | dye wastewater    | TOC removal 40.6%                |
| UV/H₂O₂/O₂    | BOD=0mg/l         | BOD/COD 0→0.4                    |
| H₂O₂/O₂       | chlorobutane      | chlorobutane removal 93%         |

In recent years, microbubbles technologies have drawn increasing attention due to their widely applications in various fields in our society, such as biomedical engineering, water treatment and nanomaterials. The definition of microbubbles is the bubbles which diameters are less than 50 μm, the characteristic of microbubbles in water is small size, high adhesive efficiency and low floating tendency[8]. The microbubbles generator can produce a milky and high intensity microbubbles solution. The surface of bubbles immersed in a liquid phase would be charged due to the ions are adsorbed at the gas–liquid interface. The spatial distribution of ions would be influenced by these charged bubbles surface to form an electric double layer, the zeta (ζ) potential would be used to evaluate strength of this electric double layer. Meanwhile, free radicals can also be generated during the collapse of air microbubbles, even without dynamic stimulus[9]. It is previous reported that by changing the circumstance of the adsorbed ions around the gas–liquid interface of the microbubbles would occur some interesting phenomena[10]. However, it is a very limited amount of total •OH come from the collapse of air micro-bubbles[11]. Therefore, in our study, hydrogen peroxide was added as oxidation to enhance this technology in the practical applications.

In this paper, some critical parameters were studied, such as pH, hydrogen peroxide dosage and gas-flow rate. An investigation of these parameters during the treatment is vital for understanding the mechanism of degradation. Besides, the FLS, UV-Vis and MS were used to analysis degradation process and products of the degradation pathway.

2. Experimental methods and materials

2.1 Experimental apparatus
The microbubbles generator was made by Xiazhichun Environmental Tech (China). Figure 1 shows an experimental set-up which contains a recycling pump, an efficient gas-water mixer and a microbubble nozzle. The simulated dyestuff wastewater prepared in a 5-L beaker and then circulated by the microbubbles generator. In this experiment: the gas and water were sucked in the pump and then mixed by the turbulent flow, next the gas was dissolved in the water at a pressure of 0.4 MPa in the gas-water mixer, the pressurized water was then delivered to a tank at atmospheric pressure via a specially-designed nozzle which comprised of a bottom valve.
2.2 Materials
A commercial dye, indigo carmine (figure 2.) with the chemical formula of C_{16}H_{8}N_{2}Na_{2}O_{8}S_{2} (molecular weight of 466.37) was used in this study. The simulate dye wastewater was prepared by dissolving the indigo carmine in deionized water. Indigo carmine, hydrogen peroxide (30%), sodium hydroxide, sulphuric acid purchased from Sinopharm Chemical Reagent.

![Figure 2. Chemical structure of indigo carmine dye (IC)](image)

2.3 Analysis methods
Free-radicals produced by the collapsed microbubbles were detected by the fluoro-spectro-photometer (QM/TM, Unite States PTI), a method for detecting the hydroxyl radical (•OH), Ce^{3+} can produce its characteristic fluorescence with is excitation and emission wavelength at 280nm and 360nm in diluted acid, respectively. But the fluorescence will be quenched if Ce^{3+} is oxidized to Ce^{4+} by oxidizing agent such as hydroxyl radical (•OH). Therefore, we can indirectly determine the concentration of hydroxyl radicals (•OH) by testing the changes of fluorescence intensity [12].

For testing the effective of removing dye in the wastewater, indigo carmine was chosen as the target dye to determine the generation of •OH from microbubbles collapsing in three different systems. Indigo carmine dye wastewater was prepared in a 10 L reactor, microbubbles was continuously produced in the solution, the total organic carbon (TOC) content of the water samples was measured by a TOC analyser (Shimadzu, Japan) to quantize the level of indigo carmine removal efficiency. Chemical oxygen demand (COD) removal rate was also measured by the potassium dichromate standard method, the decolorization extent measurement was carried out with a UV-2300 UV-Vis (Avantes, Netherlands) spectrophotometer. COD, TOC and color removal rate (R) were calculated as follows:

\[ R = \frac{C_0 - C_i}{C_0} \times 100\% \quad \text{.........(1)} \]

Where Co and Ci are the initial and final concentration value of dye , TOC, or COD respectively[13].

The pathway analysis was analyzed by UV-Vis and mass spectroscopy techniques. Quantitative analysis of IC was done by UV visible spectrophotometer in a spectronic UV/Vis spectrophotometer set at 608 nm, the intermediates generated during the degradation were analysed by a UPLC & Q-TOF MS (Waters, USA) equipped with Mass Spectra which has a duo spray ion source, the data were
recorded in positive ion mode, the ion source parameters: capillary voltage=5.5kV; temperature=550°C and scan range (m/z) =100-400 amu.

3. Results and discussion

3.1 Oxidation Enhancement

In order to investigate the enhancement of the oxidation by microbubbles, the performance of the microbubble with hydrogen peroxide system, a conventional mechanical agitation machine with hydrogen peroxide system, and microbubble-only system were compared in the indigo carmine degradation process, the initial dye concentration used in the experiments was about 100mg/l, the oxidation efficiency was represented by the colour, COD and TOC removal rate.

With the introduction of microbubbles, the oxidation activity in the wastewater increased rapidly. The rate of the oxidation was obviously faster in the microbubble with hydrogen peroxide system. Discoloration was observed in this system up to 94.27% compared with about 49.6% for the mechanical agitation with hydrogen peroxide system in 60 minutes, and COD and TOC removal rate can achieve to 72% and 53.07%, respectively. As shown from the figure 3. The molecule of the dye stuff in the waste water starts to be oxidized to mineral ions results in the decreasing of the concentration of COD[14]. In the indigo carmine degradation process, some aromatic compounds will be transferred into aliphatic compounds by ring-opening reaction. The total organic carbon concentration is one the index could indicate this reaction[15].

Oxidation efficiency initially increased sharply and then increased slightly, COD and TOC have the same tendency, it can be explained by the reason of the large driving forces for the mass transfer of the microbubbles and then reached saturated. The total mass transfer coefficient in the hydrogen peroxide-microbubble system was much larger than that in the mechanical agitation system by maximizing the surface area-to-volume ratio[2, 8]. Furthermore, the formation of the •OH could be accelerated by the microbubbles during the oxidation process[16].

![Image](image_url)  
**Figure 3.** Different system of removal extents of colour (a), COD(b) and TOC (c) of IC

3.2 Influence of the reaction variables

3.2.1 Effect of the hydrogen peroxide dosage. The impacts of the dosage of hydrogen peroxide was investigated varying the initial hydrogen peroxide concentration introduced into the reactor and the rest of the operational variable parameters kept constant. Figure 4. shows the difference in the experiment carried out from 0 ml hydrogen peroxide to 30 ml hydrogen peroxide. The degradation of the indigo carmine with the microbubbles and hydrogen peroxide in 60 minutes: the color removal extent of the indigo carmine was almost 100%, TOC decrease 72.7%, the result showed the higher the hydrogen peroxide dosage, the higher the degradation extent. The interaction between microbubbles and hydrogen peroxide could be explained as follows: from previous studies, the concentration of free-radicals involved reaction mechanism keeps increasing as the introduction of hydrogen peroxide, so this would eventually enhance the organic compounds degradation[11].
3.2.2 Effect of solution pH. Another important factor is the influence of pH in the wastewater, pH plays a vital role to remove colour and COD in the degradation process of the dye. For purpose of finding the optimum operational conditions, the experiments of the solution varied in pH was carried out with the range from strongly alkaline to strongly acidic by adjusting by sodium hydroxide and sulphuric acid. The changes in indigo carmine concentration and TOC removal are shown in figure 5 (a) and (b), respectively. The dye decomposition efficiency is greatly dependent on the pH of the solution and the pH would affect the amount of hydroxyl radicals produced by hydrogen peroxide-microbubbles system. The optimal pH value found in this study was 2 and a higher mineralization rate and colour removal efficiencies could be yielded under this pH. Dissolved oxygen and hydrogen peroxide react with OH$^{-}$ was reported to produce HO$_2$• and O$_2$•$^-$ free radicals[1]. OH$^{-}$ ions can accelerate the production of O$_2$•$^-$ free radicals while H$^+$ ions can promote the formation of HO$_2$• free radicals, both ions could enhance •OH free hydroxyl radical generation. But in our study, we found under the strongly acidic condition, it would be more efficient to remove the colour and TOC[17]. Therefore, in the hydrogen peroxide-microbubbles system, more hydroxyl radicals are formed at lower pH.

3.2.3 Effect of reaction pressure. Experiments of indigo carmine were also performed at different reaction pressure in this study to reveal the potential index that reaction pressure played in the degradation process. As shown in figure 6. The solution with reaction pressure of 0.4 MP indicates the highest oxidation rate a higher reaction pressure would increase the efficiency. It has been reported that the formation of free radicals is dependent on the concentration of dissolved oxygen[18]. It presents...
that oxygen microbubbles would increase the dissolved oxygen which could enhance the decolorization ability of indigo carmine.

![Graph showing color removal ratio vs time for different pressures](image)

**Figure 6.** Effect of the reaction pressure on the decolorization and TOC removal rate of IC Dye concentration=100mg/L, hydrogen peroxide dosage=30ml, pH7.0

### 3.3. Mechanism of oxidation degradation

#### 3.3.1 Exploration of degradation

Fluorimetry method is used to determine the mechanism of the indigo carmine in figure 7.[12], suggesting that •OH radicals were generated by the collapse of oxygen microbubbles.

Three systems in terms of decolorizations were compared during the study. TOC and COD removal efficiency (Dye concentration=100mg/L, hydrogen peroxide dosage=30ml, pH=2, Reaction pressure=0.4 MP). The results are showed in the figure 7. Results found that all the samples in the three systems increased with the continuous micro-bubbles produced into the solution and then reached steady state. The fluorescence intensity of the samples from the hydrogen peroxide-microbubble system was much higher than that from the other two systems. But it is clearly implied that the amount of hydroxyl radicals was higher in the hydrogen peroxide-microbubble system which would contribute to the degradation of the dye molecules.

![Graph showing fluorescence intensity vs wavelength for different conditions](image)

**Figure 7.** Fluorescence detection of hydroxyl radical formed in microbubble water under different conditions

To understand the degradation mechanism of the indigo carmine in degradation process and determine the chemical reaction during the process of the change of colour. COD and TOC. UV-Vis and UPLC-Q-TOF MS were used to analysis in the oxidation process.UV-Vis absorption spectra of the degradation in whole degradation and at some typical time were investigated. Figure 8. showed the variation of absorbance intensity at two specific wavelengths: 608 nm and 275 nm. The peak of
appeared at 275 nm in the visible region indicates the benzene rings in the indigo molecule. This is due to the maximum absorption peak of aromatic compounds is mainly at 210-320nm[19]. The peak in the visible region at 608 nm which corresponding to the blue colour of the solution and it is because of the $n \rightarrow \pi$ group orbital of the double bond (C=C) system[20]. The decreasing of absorbance at 608nm close to zero indicated the degradation of indigo. During the process, the phanic trending was: the residual absorbency at visible light region decreased fast that suggesting the initial accumulation and the intermediates might be further degraded to mineral compounds[4, 5, 21].

**Figure 8. UV-Vis spectra of indigo carmine during degradation**

Moreover, Ultra Performance Liquid Chromatography – Quadrupole – Time of Flight Mass Spectrometer (UPLC-Q-TOF MS) gives an accurate and specific detection with reliable identification of the analysis in a precise instrument. It provides a qualitative analytical data for the characterization of the oxidation products in the process of degradation of the dye ingredients. Four intermediate compounds were found by LC-MS technique, as shown in figure 9. We detected that $C_{16}H_{10}O_8N_2S_2$ (A), $C_8H_5O_5NS$ (B), $C_8H_6O_6NS$ (C) and $C_8H_7O_5NS$ (D) are appeared, it can be shown in the figure 10. The reaction process could be considered that the free radical first attack the double bond (C=C), in the compound A which oxidized to the B occurred with the decolorization of indigo carmine, but the product B peaked at about 5 min and then gradually decreased, due to the transformation to C. $C=O$ groups of carboxyl acids in the C were oxidized to the hydroxyl groups. Based on the results of UV-Vis and UPLC & Q-TOF MS analysis, the possible degradation process of indigo carmine is concluded here. In the first step, lower molecular weight compounds were formatted by the olefinic bond cleavage. Then the second step is the further oxidation of lower molecular weight organic matter.

**Figure 9. Mass spectrometry spectra of indigo solution after 1 min(a) and 2 min(b) of oxidation**
4. Conclusions
Microbubble technology applied to increase the mass transfer rate reaction as well as to enhance the oxidation of indigo carmine gained increasing attention in the recently work. It is clearly exhibited by the color disappearance, COD and TOC decreased in indigo carmine solutions in this study. The removal rate of color, COD and TOC were 94.27%, 72% and 53.07%, respectively in 1 hour. Fluorimetry method was used to determine the mechanism of the indigo carmine, showing that hydroxyl radical (•OH) radicals were generated by the collapse of oxygen microbubbles. The analysis of UV-Vis, MS spectra showed that the double bond and the groups of carboxylic acids were destroyed at the first stage of the degradation.

Although, research on microbubble is still required to indicate the mechanism for the microbubbles induced oxidation, the high decolorization achievements of this technology presents a promising way to treat dye wastewater with indigo carmine.

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