Preparation of Fe-Cu catalysts and treatment of a wastewater mixture by microwave-assisted UV catalytic oxidation processes

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Microwave-assisted UV catalytic oxidation (MW/UV) is a potential method to treat organic pollutants that have non-biological degradability and high toxicity. To achieve high treatment efficiency, it is crucial to prepare heterogeneous photocatalysts with a high activity. Iron–copper catalysts were prepared by four different methods. Synthetic wastewater containing aniline and nitrophenol (TOC = 1000 mg/L) was treated. The key parameters including the proportion of Fe$_2$O$_3$ and CuO and the total content of the active components are discussed. The optimum catalyst dosage and the whole catalytic oxidation process were investigated, and different catalytic oxidation systems were also compared. The catalyst prepared by impregnation was best: the highest TOC removal efficiency reached 78%. The optimum proportion of Fe$_2$O$_3$ and CuO and the content of the total active composition were 4:1 and 30%, respectively. The catalyst preparation method had a greater influence on the MW/UV system than on the microwave (MW) system, and the synergistic effect between MW and UV was verified. The MW/UV system was more susceptible to catalyst dosage than was the MW system, and the optimum catalyst dosage was 5 g/L. The catalyst and H$_2$O$_2$ had a synergistic effect. The presence of a possible non-thermal microwave effect could be expected.

Keywords: microwave; UV; catalytic oxidation; aniline; nitrophenol

Introduction

Aniline and nitrophenol are widely used in the chemical industries and are common pollutants in many natural water and wastewater systems. In recent years, these organic compounds have been listed as the priority pollutants by many countries because of non-biological degradability and high toxicity. The treatment methods for this kind of wastewater include adsorption [1], microbial degradation [2] and chemical oxidation [3]. However, each method has its own limitations and disadvantages. Adsorption cannot degrade pollutants but just transfers their phases. Microbial degradation requires a long residence time for microorganisms to degrade the pollutants. Chemical treatments require a post-treatment and are unable to mineralize all organic substances sometimes. Recently, advanced oxidation processes (AOPs) have emerged as a potential class of technologies that are capable of transforming organic pollutants in aqueous solutions into non-toxic material, and hydrogen peroxide is a safe, efficient and easy-to-use chemical oxidant suitable for wide usage in AOPs. However, the mechanism of hydrogen peroxide decomposition has long been controversial [4,5]. It has been reported that it relies on the generation of reactive free radicals, especially hydroxyl radicals (-OH) [6,7]. Usually, these radicals react rapidly and non-selectively with most organic compounds, resulting in a series of degradation oxidation reactions and ultimately achieving the complete mineralization of the organic compounds [8]. Recently, microwave (MW) irradiation has been widely applied to assist photocatalytic reactions [9–12]. As one of the most promising AOPs, heterogeneous photocatalysis has attracted much attention because this process can be operated at an ambient temperature and can mineralize refractory or toxic organic compounds to carbon dioxide, water and mineral acids [13]. Many investigators have been trying to improve the catalytic activity of heterogeneous catalysts to enhance the efficiency of the microwave-assisted catalytic oxidation process [14–17]. Nevertheless, few practical applications of photocatalytic degradation on the industrial scale have been reported because of low quantum efficiency. Therefore, it is crucial to prepare the heterogeneous photocatalysts with a high activity.

In the present study, our work is aimed at the preparation of new iron–copper catalytic materials with a high oxidation efficiency for microwave-assisted UV catalytic oxidation (MW/UV) of a wastewater
mixture containing aniline and nitrophenol. This study focuses mainly on (a) optimizing the catalyst preparation process in order to prepare the photocatalysts with a high activity, (b) examining the effect of catalyst preparation methods on the MW system and the MW/UV system, (c) studying the effect of the catalyst dosage on the catalytic oxidation efficiency in the MW/UV system, (d) the analysis of the whole catalytic oxidation process and (e) comparison of the treatment efficiency of different catalytic oxidation systems.

**Experimental**

**Materials and analysis**

All the chemical reagents used were analytical grade. Total organic carbon (TOC) in solution was measured by a TOC-V analyser (Shimadzu Co., Tokyo, Japan). The UV-Vis spectrum of the samples was recorded from 240 nm to 500 nm using an L600000B UV-Vis spectrophotometer (PerkinElmer Co., Massachusetts, USA). The concentration of hydrogen peroxide (H₂O₂) in the solution was determined by titration with potassium permanganate [17].

**Preparation of catalysts**

For preparation of the simple mechanical mixing catalysts (SMC), 5 wt% CuO, 5 wt% Fe₂O₃, 30 wt% Al₂O₃, 50 wt% TiO₂, 5 wt% SiO₂, 3 wt% CeO₂ and 2 wt% ZrO₂ were weighed and calcined at 600 °C for two hours. Then the components were mixed mechanically in a dry-mix machine.

For preparation of the impregnation catalysts (IC), 30 wt% Al₂O₃, 50 wt% TiO₂, 5 wt% SiO₂ were mixed in a dry ball mill as the carrier. After immersing 50 g of the above carrier into a mixed aqueous solution containing 3.79 g Ce(NO₃)₃·6H₂O, 2.62 g ZrCl₃, and 15 mL distilled water by an equivalent-volume incipient wetness impregnation method [18], the compound was dried at 110 °C and calcined at 600 °C for 12 hours. Then the compound was sifted through a 40-mesh sieve and was used as the catalyst.

For preparation of the dry milling catalysts [19] (DMC): 5 wt% CuO, 5 wt% Fe₂O₃, 30 wt% Al₂O₃, 50 wt% TiO₂, 5 wt% SiO₂, 3 wt% CeO₂ and 2 wt% ZrO₂ were weighed and mixed in the dry ball mill. Then the compound was dried at 110 °C for six hours and calcined at 600 °C for 12 hours. After cooling to room temperature, the compound was sifted through a 40-mesh sieve and was used as the catalyst.

For preparation of the wet milling catalysts [19] (WMC): 5 wt% CuO, 5 wt% Fe₂O₃, 30 wt% Al₂O₃, 50 wt% TiO₂, 5 wt% SiO₂, 3 wt% CeO₂ and 2 wt% ZrO₂ were weighed. After adding 15 mL of distilled water and 10% anhydrous ethyl alcohol, the compound was mixed by wet ball milling. Then, the compound was dried at 110 °C for six hours and calcined at 600 °C for 12 hours. After cooling to room temperature, the compound was sifted through a 40-mesh sieve and was used as the catalyst.

**Catalyst characterization**

The powder X-ray diffraction (XRD) measurement was carried out using an X’TRA diffractometer (Switzerland, Cu Ka radiation, 1.54056 nm). Scans were taken over a 2θ range of 10°–80° with a step size of 0.02° and a scan rate of 10° min⁻¹. The catalyst image was observed with a Hitachi S3400 scanning electron microscope (SEM) with 30 kV of accelerating voltage under high vacuum.

**Method**

The microwave instrument was produced by Nanjing Yongan Architecture Company (Nanjing, China) (power, 1000 W; frequency, 2.45 GHZ). A cylindrical quartz glass reactor (9 cm in diameter and 30 cm in height) was fixed all through the instrument. Air (0.036 m³ h⁻¹) was bubbled through a sintered glass filter fixed at the bottom of the reactor in order to mix the solution and sustain the catalysts. The power was controlled at 800 W during the reaction. The reactor was placed inside the erect microwave reactor. Four microwave electrodeless lamps (MWL), which were made of quartz and filled with mercury and argon, were placed symmetrically around the cylindrical quartz glass reactor. Before running each test, 1.5 L of the synthetic wastewater (mixed aniline and nitrophenol) containing 1000 mg L⁻¹ TOC (total organic carbon) was added to the reactor. The solid catalyst (10 g L⁻¹) was put into the synthetic wastewater, and 20 g L⁻¹ hydrogen peroxide (30%, w/w, in H₂O) solution (according to the number of electron transfer of the two substrates and H₂O₂) was added to the reactor after the pH of the solution was adjusted to 3.0. After 30 min reaction, the residual TOC value in the solution, the concentration of H₂O₂, and the theoretical quality proportion between H₂O₂ and 1000 mg L⁻¹ TOC was added to the reactor after the pH of the solution was adjusted to 3.0. After 30 min reaction, the residual TOC value in the solution, the concentration of H₂O₂, and the pH of the solution were determined after the samples were filtrated. The UV-Vis spectrum was determined after the pH of the filtrated samples was adjusted to 5.0. The value of oxidant exhausted (X) was calculated as shown below [20]:

\[ X = (a_0 - a_1)(b_0 - b_1) \]

where \(a_0\) and \(a_1\) are the initial and final concentrations of H₂O₂; \(b_0\) and \(b_1\) are the initial and final TOCs.
Results and discussion

Comparison of the different technologies for the preparation of catalysts

Comparison of the different technologies for the preparation of catalysts was investigated in the MW and MW/UV system. The results showed that a similar treatment efficiency was obtained for the four different kinds of catalysts in the microwave-induced H$_2$O$_2$ catalytic oxidation; the efficiency of the catalyst produced by the impregnation method was slightly better than the three other catalysts produced by different methods of mixing. Moreover, in the experiments, the best intensity was observed for the catalyst produced by impregnation.

For the MW/UV system, the treatment efficiency of the catalyst produced by the impregnation method was greatly better than the others. The results indicated that this kind of catalyst could enhance the surface area, improve the dispersion of active components and result in good catalytic properties. This could arise for two possible reasons. Firstly, microwave could generate additional defect sites on the catalyst, which probably decreased the recombination of photo-generated holes and electrons [21,22]. In addition, perhaps some active free radical on the surface of the catalyst under UV irradiation could improve the treatment efficiency. As a result, the impregnation method was used in the preparation of catalyst in the following tests.

Comparing the MW and MW/UV systems, the influence of catalyst preparation method on the MW system was less than on the MW/UV system, and the order of the TOC removal efficiency was IC > WMC > SMC > DMC. It was observed that the treatment efficiency of the catalyst produced by impregnation was best (TOC removal = 61%), and the dry milling catalyst was worst (TOC removal = 54%). So the difference in TOC removal between these two kinds of catalysts was only 7%; moreover, the value of oxidant exhausted (X) among the four catalysts was the same on the whole. In contrast to the MW system, the influence of catalyst preparation method on the MW/UV system was greater, and the order of the TOC removal efficiency was IC > SMC > WMC > DMC. The difference between the percentage TOC removals of the IC and DMC catalysts could reach 30%. Moreover, when the TOC removal reached the highest in the MW/UV system, the corresponding X-value was the lowest (only 1.5), 0.3 less than for the MW system. The reason for this was attributed to the mineralization mechanism being different between the MW system and the MW/UV system. The catalytic activity of the components of the catalyst depended on the microwave radiation in the MW system, and the microwave-absorbing properties were not changed by catalyst preparation method, resulting in no significant influence. Furthermore, the recombination and generation of photo-generated holes and electrons were presented in the MW/UV system. If the different components of the catalyst were effectively mixed at the atomic level, the recombination of holes and electrons could be decreased, the transition probability of photon-generated electrons was increased and more powerful oxidizing holes could be generated. However, this beneficial effect was not achieved by the four catalyst preparation methods, except for impregnation, leading to their low efficiency of utilization of light energy generated by the microwave radiation. Also, both the utilization rate of H$_2$O$_2$ and the TOC removal could reach higher levels in the MW/UV system than in the MW system, indicating that MW and UV had a synergistic effect, by which the treatment efficiency could be further increased.

Optimization of different proportions of Fe$_2$O$_3$ and CuO

Fixing the total content of the two kinds of active metal components (iron and copper) to 50% of the total content, the catalysts containing different proportions of Fe$_2$O$_3$ and CuO were prepared by impregnation. The effect of different proportions of Fe$_2$O$_3$ and CuO on the treatment efficiency was studied in the MW/UV system, in order to optimize the technological conditions for the catalyst preparation.

The results are shown in Figure 1. It can be seen from the results that the treatment efficiency was best when the relative proportions of Fe$_2$O$_3$ and CuO reached 8:2 (4:1), when the TOC removal of the mixture wastewater could exceed 57%, and the corresponding X-value was the lowest. From the curve of the TOC removal efficiency, it can be seen that the content of iron played an important role in the MW/UV catalytic oxidation process. With the increasing content of iron, an increase in the TOC removal was observed, but the treatment efficiency decreased in the presence of the iron only, showing that the treatment efficiency of the two-component system was more effective than the single component. Compared with the treatment efficiency of the 0:0 and 0:10 Fe$_2$O$_3$:CuO combinations, the decomposition rate of H$_2$O$_2$ for the CuO alone was much faster than that of the Fe$_2$O$_3$ alone; moreover, the utilization rate of H$_2$O$_2$ could reach a higher level in the coexistence of iron and copper. Therefore, the two compounds had a synergistic effect to increase the catalytic activity, resulting in improved treatment efficiency.

Optimization of different total content of Fe$_2$O$_3$ and CuO

The content of active components in the catalyst played a critical role in the MW/UV system. The proportion of
Fe₂O₃ and CuO was fixed at 4:1, and catalysts containing different proportions of total active components were prepared by impregnation. The effect of varying the content of the total active components on the treatment efficiency was studied to further optimize the technological conditions for the catalyst preparation. The results are presented in Figure 2. It can be seen from the figure that the catalytic activity was influenced by the content of the total active components. At the beginning, with the increasing content of the total active components, an increase in the TOC removal was observed. When the content reached 30%, the TOC% removal could exceed 62%. Nevertheless, the final percentage TOC removal decreased when the proportion of active components reached 100%, showing that an excess of these components could not improve the treatment efficiency. The reason for this was attributed to the ineffective decomposition of TOC when the decomposition of H₂O₂ became too fast. Also, the excess H₂O₂ would react with •OH, competing with organic pollutants and consequently reducing the treatment efficiency [23]. Moreover, when the proportion of the total active components was less, the decomposition rate of H₂O₂ became slow; correspondingly, a small portion of the active intermediate oxidant was generated at the surface of the catalyst, causing the unsatisfactory treatment efficiency. Therefore, the best content of the total active components was 30%.

**Characterization of catalysts**

The catalyst prepared by impregnation, with the relative proportions of Fe₂O₃ and CuO being 4:1 and the total active components being 30%, was analysed by SEM and XRD. The SEM image and XRD pattern of the catalyst are shown in Figures 3 and 4, respectively. The crystallite size was around the µm level in diameter and basically uniform on the surface of the catalyst, as shown in the SEM image. The XRD was employed to identify the mineral phases and to estimate crystallinity. A TiO₂ phase could easily be seen in the pattern, because it was added by the simple mechanical mixing method. By comparing with the criterion card, the peaks characterizing the main active components, including Fe₂O₃ and CuO crystals, could also be seen in the pattern of the catalyst. The main diffraction peaks were marked differently in the pattern.
Figure 2. Optimization of different total content of Fe$_2$O$_3$ and CuO. TOC: total organic carbon; X: the value of oxidant exhausted.

Figure 3. SEM image of the catalyst.
The effect of the catalyst dosage on the treatment efficiency

Based on the above results, the optimum proportion of Fe$_2$O$_3$ and CuO and the content of the total active components were fixed at 4:1 and 30%, respectively. The effect of the different catalyst dosages on the treatment efficiency was investigated, and the results are shown in Figure 5. The TOC% decrease at first and then increased with the increase in the catalyst dosage. When the addition of catalyst reached 5 g/L, the highest TOC% of 70% was reached. The reason for this was that the MW/UV catalytic oxidation system was susceptible to the catalyst dosage, and the transmission of the UV light through the system was inhibited if the dose of catalyst was not suitable, correspondingly the catalytic oxidation efficiency decreased. Therefore, the optimum catalyst dosage was fixed at 5 g/L.

The analysis of the whole catalytic oxidation process

According to the above experimental results, the catalyst was prepared under the optimum conditions. The whole oxidation process was studied by the change in the UV-Vis spectra, TOC, and pH. Figure 6 shows the change in the UV-Vis spectra from 240 nm to 500 nm during the MW/UV catalytic oxidation of the mixture wastewater. Two absorption peaks at 330 nm and 380 nm were displayed from the absorption spectral analysis prior to the catalytic oxidation. At the beginning of the reaction, new absorption bands appeared in the ultraviolet spectral region, indicating that new intermediate substances, which had a significant absorption in the region of 380–400 nm, were generated in the MW/UV system. However, the content of these substances gradually diminished with the prolonging of reaction time and finally disappeared at 50 min. Moreover, the colour of the solution became deeper at 5 min compared with the initial solution, which also indicated the formation of new intermediate material. Actually, another study [24] showed that some hydroxylated aromatic intermediate material, such as phenol, hydroquinone and nitrobenzene, could be detected during the photodegradation of aniline. Nevertheless, in contrast to the 380 nm peak, catalytic oxidation directly caused the substances with an intense absorption peak at 330 nm to decrease with time and finally to disappear.
at 50 min. This indicated that the wastewater mixture containing benzene rings was possibly oxidized by breaking the C–C bond or the C–N bond.

The change in TOC mirrored the degree of mineralization as a function of irradiation time. The results of TOC measurements obtained during the MW/UV catalytic oxidation of the mixture wastewater are presented in Figure 7. It was observed that the catalytic oxidation system exhibited good performance for the mineralization of these organic compounds, and the TOC removal could reach over 78% after 50 min treatment. Obviously, the mineralization process in the MW/UV system was divided into two stages. During the first stage (the initial 30 min), the TOC removal rate was very fast and TOC removal could reach about 70%; correspondingly, the absorption value decreased quickly both at about 300 nm and 400 nm (Figure 6). However, during the second stage (30–50 min), the TOC removal rate was slow and a similar trend could also be observed in the absorption spectra.

The temporal change in pH during the MW/UV catalytic oxidation of the mixture wastewater is displayed in Figure 8. The reaction caused a significant decrease in pH from pH 5.0 at 0 min to pH 3.2 at 30 min. As had been shown in a previous study [25], the drop in pH with time was associated with the formation of acid products through the destruction of organic compounds. However, the pH of the solution only decreased to 3.1 at the end of the experiment. This indicated that further degradation of the acid products formed was difficult in the MW/UV catalytic oxidation system.

**Comparison of the efficiencies of different catalytic oxidation systems**

Four different catalytic oxidation systems consisting of conventional heating in the water-bath (A), microwave catalytic oxidation (B), microwave-assisted UV catalytic oxidation (C), microwave-assisted UV oxidation without catalyst (D) and microwave assisted UV catalytic oxidation without H₂O₂ (E) were investigated to compare the treatment efficiency of different catalytic oxidation systems. The results are presented in Figure 9.
Firstly, comparing systems A and B, the TOC removal increased by 19% in the presence of MW (from 42% to 61%) and the corresponding X-value decreased from 1.9 to 1.6 under the same temperate condition. This indicated that conventional heating and microwave dielectric heating were dramatically different. Conventional heating energized the aqueous medium first and then transferred the energy to the substrates, whereas dielectric heating energized the substrates directly [26]. Therefore, the presence of a possible non-thermal microwave effect could be expected in our study. In addition, it can be seen from systems D and E that the treatment efficiency was very poor for the individual H₂O₂ (TOC removal = 18%) or the individual catalyst (TOC removal = 8%) in the MW/UV system, but when combining H₂O₂ and the catalyst, TOC was clearly oxidized to a considerable degree, and the TOC removal could increase to 78% (C). This indicated that the catalyst played a critical role in the MW/UV system because of its sorption and catalysis functions, and the TOC removal and the utilization rate of H₂O₂ could be obviously improved in the presence of the catalyst. Moreover, the catalyst and H₂O₂ have a synergistic effect, which might improve the TOC removal percentage.

Conclusions
The catalytic properties of the catalyst prepared by impregnation were better than those of the three other catalysts prepared by different methods of mixing, both in the MW system and MW/UV system, and the highest TOC removal reached over 78%. The optimum proportion of Fe₂O₃ and CuO and the proportion of the total active components were 4:1 and 30%, respectively. The influence of catalyst preparation method on the MW/UV system was greater than on the MW system, and the synergistic effect between MW and UV was verified, to further improve the treatment efficiency. The MW/UV catalytic oxidation system was more susceptible to the catalyst dosage than the MW system. The optimum catalyst dosage was fixed at 5 g/L. The presence of a possible non-thermal microwave effect could be expected in our study. The catalyst and H₂O₂ had a synergistic effect in the MW/UV system. Microwave-assisted
UV catalytic oxidation has potential for use in treating wastewater with non-biological degradability and high toxicity. However, in our next study, further questions need to be addressed regarding the analysis of the intermediate substances, the mechanism of the MW/UV catalytic oxidation and reduction of the treatment cost.

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Figure 8. Change in pH of the wastewater mixture during MW/UV catalytic oxidation as a function of treatment time.

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Figure 10. Experimental instrument for the MW/UV catalytic oxidation of the wastewater mixture. Four microwave electrode-less lamps, which are fixed in the middle of the microwave chamber, produce UV light under microwave radiation. In the upper right corner of the instrument, there is an auto digital display power-controlling unit, which is used to automatically control power, time and temperature of the reaction.

Figure 11. The four microwave electrode-less lamps used in the experiments. The lamps were made of quartz and filled with different content of mercury and argon.