

Efficiency Optimization of Pharmaceutical Wastewater Treatment by a Microwave-Assisted Fenton-Like Process Using Special Supported Catalysts

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Abstract

The efficiency of a microwave-assisted Fenton-like process using special supported catalysts was evaluated using total organic carbon (TOC) removal from pharmaceutical wastewater. No acidification was required. The highest level of TOC removal efficiency from wastewater achieved was 65.88%. Moreover, the maximum number of consecutive uses with high activity was four. Under optimal conditions, the influent value of BOD₅/COD was 0.25, and the effluent value of BOD₅/COD was elevated to 0.40. In addition, colour was completely removed. This efficiency was compared with the same MW-Fenton-like process using common supported catalysts, where the highest achieved TOC removal efficiency from wastewater was 39.25%, the colour of the wastewater decreased from 50 to 20, and the value of BOD₅/COD was elevated from 0.25 to 0.34. The maximum number of consecutive high activity uses was two. This advanced performance was attributed to no presence of copper carbonate or cerium carbonate on the surface of special supported catalysts. The preparation method for these catalysts combined the merits of the isometric impregnation method with some new improvements. Its advantages include high-efficiency performance, short preparation time, low reagent usage (cupric nitrate 3.6 g, cerium nitrate 1.2 g, ammonia 1 mL), and reusability. The properties of the catalyst with the most efficient performance were characterized by determining surface particle size, the relative amount of active components and promoters, and the stable crystal form of the active components.

Keywords: catalyst, Fenton-like, microwave, pharmaceutical wastewater, supported

Introduction

Microwave-assisted Fenton-like processes using special supported catalysts are one of the emerging types of advanced oxidation processes (Abbr. AOPs) that can

generate hydroxyl radicals (i.e. OH) through the catalysis of hydrogen peroxide (H₂O₂) by solid catalysts [1].

Moreover, MW-Fenton-like processes using special supported catalysts can result in high efficiency with simple catalyst separation. When performed under normal atmospheric pressure and temperature they are also known as microwave-assisted catalytic oxidation processes [2-4].

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Table 1. Characteristics of pharmaceutical wastewater filtered by quantitative filter.

Index	COD (mg/L)	BOD ₅ /COD	TOC (mg/L)	SS (mg/L)	pH	NH ₄ ⁺ -N (mg/L)	colour (multiple)
Value	1595	0.25	155.9	218	6.54	84	50

The supported catalysts are mainly composed of activity components, along with catalyst promoters and supports [5]. Catalysts are prepared by impregnation [6-9] or, in the field of environmental catalysis, by precipitation methods [10-12].

In impregnation methods [13] the support is immersed in a solution containing activity components. The remaining liquid is removed when equilibrium is achieved, and the finished catalyst is finally obtained by calcination. Impregnation uses the shape of the support, and does not require catalyst moulding. In impregnation methods, the physical structures of the catalyst are determined by the catalyst support.

In precipitation methods, a crystal structure (or gel) of oxide, hydrous oxide or carbonate is obtained by dosing the precipitant in the metal salt solution with active components. Then the deposits are separated, cleaned, and calcinated to obtain the finished catalyst.

In this study, copper oxide and hydrous oxide (without copper carbonate), cerium oxide and hydrous oxide (without cerium carbonate), and granular activated carbon (GAC) from coal were used as activity components, catalyst promoters, and catalyst supports, respectively. Given the merits and drawbacks of impregnation methods, a preparation method for special supported catalysts was developed. This preparation method retained the merits of isometric impregnation [14-16] with some improvements.

In this study, the finished catalyst was prepared with high efficiency, uniform particle size, short preparation time, low reagent use, and good reusability. A significant improvement was observed in wastewater treatment. The efficiency of the MW-Fenton-like process using special supported catalysts was evaluated by total organic carbon (TOC) removal efficiency from pharmaceutical wastewater. The properties of the catalyst with the highest efficiency performance were characterised and evaluated.

Materials and Methods

Wastewater and Materials

Chemical synthetic pharmaceutical wastewater was collected from a pharmaceutical factory in Tianjin, China. The main products of the factory were GCLE (7-Phenylacetamido-3-chloromethyl-3-chloromethyl-3-cephem-4-carboxylic acid p-methoxybenzyl ester, a cephalosporin intermediate) and riboflavin sodium phosphate, etc. Table 1 shows the characteristics of the pharmaceutical wastewater filtered using a quantitative filter. All reagents used in this study were analytically pure: cupric nitrate (Cu(NO₃)₂·3H₂O), cerium nitrate

(Ce(NO₃)₃·6H₂O), hydrogen peroxide (30%), aqueous ammonia (22-25%), etc.

Experimental Methods

Catalyst Preparation and Characterisation Methods

The special supported catalyst was prepared as follows. A total of 10 g of GAC (the minimum amount) was placed in a 250 mL beaker, 6.0 copper nitrate and 2.4 g cerium nitrate were added to the beaker, and 3.6 mL of distilled water was added dropwise until the water could not be completely absorbed. When the isometric impregnation method was performed, the amount of distilled water was fixed at 4 mL/10 g GAC.

For optimization of the catalyst preparation method, quantified amounts of copper nitrate (1.2, 2.4, 3.6, 4.8, 6.0 g) and cerium nitrate (0, 0.6, 1.2, 1.8, 2.4 g) were added into the beaker with 4 mL of distilled water (Table 2). The mixture was subsequently stirred to dissolve the reagents. Aqueous ammonia (1 mL) and quantified GAC (5, 10, 20, 30, 40 g) were also added to the mixture.

The entire mixture was transferred to a pressure pan, which was heated at 120°C for 20 min. High temperature water vapour was used as an inert gas. The hydrothermal reaction was a mutual reaction between ammonia and nitrate ions, which caused copper oxide and hydrous oxide (without copper carbonate) to play a more effective role as activity components in the inner or outer layers of the catalyst.

At the end of the reaction, the pressure pan was opened and the mixture was transferred to a crucible. Then the entire mixture in the crucible was transferred to a muffle furnace at a steady temperature (200, 300, 400, 500, 600°C) for 1.5 h. Finally, the finished catalyst was obtained. The properties of the special supported catalysts and GAC with the highest efficiency were characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) (Table 3), and X-ray diffraction (XRD).

Experiments for efficiency optimization of the MW-Fenton-like process using special supported catalysts were performed with no acidification in this study. Efficiency of the process was optimized by varying the amount of hydrogen peroxide; MW radiation power; irradiation time; the amounts of copper nitrate, cerium nitrate, and GAC; calcination temperature, etc. Amounts and intensity of factors are given in Table 4. Changes in efficiency were evaluated by TOC removal efficiency from pharmaceutical wastewater.

The wastewater treatment experiment was performed as follows. The finished catalyst and hydrogen peroxide

Table 2. Surface element component contents of GAC.

Element	Weight percentage (%)	Atomic percentage (%)
C	47.87	70.51
O	6.18	6.83
Mg	2.31	1.68
Al	3.35	2.19
Si	5.25	3.30
Ca	35.06	15.48
Total	100.00	100.00

Table 3. Surface element component contents of the special supported catalyst.

Element	Weight percentage (%)	Atomic percentage (%)
C	0.17	0.93
O	3.78	15.38
Ca	1.86	3.01
Ce	28.06	13.02
Cu	66.13	67.66
Total	100.00	100.00

were introduced into the wastewater and radiation was supplied using a MW oven without acidification at the beginning of the reaction. Hydroxyl radicals (OHs) were generated through catalysis of hydrogen peroxide by the finished catalysts.

Analytical Methods

In this study, chemical oxygen demand (COD) was measured using a COD rapid testing instrument (LianHua

Technology Company, Lanzhou, China). Biochemical oxygen demand (BOD₅) was determined using an IS6 BOD system (WTW Corporation, Germany), and TOC was analyzed using a TOC analyzer (SHIMADZU, Japan). Cu²⁺ ion concentration was measured using an atomic absorption spectrometer (HITACHI 180-80, Japan). Suspended solids (SS), NH₄⁺-N, and colour were determined according to standard methods [17]. pH was measured using a pH meter (pH-3C; LeiCi, Shanghai, China). A Midea household MW oven was used with different MW radiation power levels, namely high (700 W), medium-high (539 W), medium (385 W), and medium-low (281 W).

Results and Discussion

Effect of Hydrogen Peroxide Amount

To investigate the effect of hydrogen peroxide on the efficiency of the process, five 1L samples with the original concentration were prepared. Hydrogen peroxide was introduced at the proportion of 2.5, 5.0, 7.5, 10, and 25 mL/250 mL wastewater. The finished catalyst was added to these samples, and the MW radiation power was set at medium-high (539 W), with a radiation time of 6 min. Influent and effluent TOC were determined by the test methods shown in Figure 1a. When hydrogen peroxide was used at 2.5, 5.0, 7.5, 10, and 25 mL/250 mL, the TOC removal from pharmaceutical wastewater was 53.12%, 61.45%, 65.79%, 68.86%, and 70.94%, respectively. Thus, based on the efficiency of wastewater treatment and minimization of reagent usage, the optimal hydrogen peroxide ratio was 7.5 mL/250 mL.

Effect of MW Radiation Power

We used MW radiation power levels of high (700 W), medium-high (539 W), medium (385 W), medium-low (281 W), and none (0 W). Oxidation decomposition occurred in the Fenton-like process using the special

Table 4. Design of the activity optimization experiment on special supported catalysts.

Influencing factor	Amount or intensity of each influencing factor						
	H ₂ O ₂ amount (mL)	MW radiation power (W)	Radiation time (min)	Copper nitrate (g)	Cerium nitrate (g)	GAC (g)	Calcination temperature (°C)
H ₂ O ₂	2.5~25	539	6	3.6	1.2	10	400
MW radiation power	7.5	0~700	6	3.6	1.2	10	400
Radiation time	7.5	539	2~10	3.6	1.2	10	400
Copper nitrate	7.5	539	6	1.2~6.0	1.2	10	400
Cerium nitrate	7.5	539	6	3.6	0~2.4	10	400
GAC	7.5	539	6	3.6	1.2	5~40	400
Calcination temperature	7.5	539	6	3.6	1.2	10	200~600

supported catalysts. The water samples containing 7.5 mL of H_2O_2 /250 mL wastewater and the finished catalyst were irradiated at five MW levels to optimize the MW-Fenton-like process. Influent and effluent TOC was determined using the test methods shown in Fig. 1b.

When the MW radiation power was high (700 W), medium-high (539 W), medium (385 W), medium-low (281 W), and none (0 W), values of TOC removal from pharmaceutical wastewater were 62.93%, 68.97%, 69.96%, 35.27%, and 23.43%, respectively. Thus, the optimal MW radiation power was medium-high (539 W). When the MW radiation power was increased to high (700 W), TOC removal efficiency from wastewater increased little, the reason being that high radiation power led to disabled decomposition of hydrogen peroxide.

Effect of Radiation Time

The MW-Fenton-like process with special supported catalysts was explored at radiation times of 2, 4, 6, 8, and 10 min, respectively. Influent and effluent TOC was determined after the reaction had ended by the test methods shown in Fig. 1c. When the radiation time was 2, 4, 6, 8, and 10 min, the TOC removal efficiency from pharmaceutical wastewater was 37.84%, 58.91%, 65.45%, 65.68%, and 65.73%. Thus, the optimal radiation time was 6 min. When the radiation time was increased from 6 to 10 min, the TOC removal of wastewater did not increase, the reason being that hydrogen peroxide was completely decomposed at a radiation time of 6 min.

Effect of Copper Nitrate Amount

Copper was the activity component of the catalysts for the Fenton-like process [18]. The amounts of copper nitrate were 1.2, 2.4, 3.6, 4.8, and 6.0 g (Table 2). The volume of wastewater, the amount of hydrogen peroxide, MW radiation power, and radiation time were 250 mL, 7.5 mL, 539 W, and 6 min, respectively. Influent and effluent TOC was determined using the test methods shown in Fig. 1d. In the catalyst preparation, copper oxide and hydrous oxide (without copper carbonate) was generated by the reaction of copper nitrate and a small amount of ammonia on the surface of the GAC, and was employed as a special supported catalyst. This method has not been previously reported [19-22].

Fig. 1d shows that TOC removal efficiency gradually increased from 59.15% to 66.11% when the copper nitrate amount increased from 1.2 g/10 g GAC to 3.6 g/10 g GAC. This relatively large increase resulted because more copper oxide and hydrous oxide was produced, and therefore more hydroxyl radical was generated. When the copper nitrate amount increased from 3.6 g/10 g GAC to 6.0 g/10 g GAC, the increase in TOC removal was small (from 66.11% to 66.68%). This result was attributed to an excess of copper oxide and hydrous oxide, resulting in the disabled decomposition of hydrogen peroxide. Thus, the optimal dosage of copper nitrate in catalyst preparation was 3.6 g/10 g GAC. This low reagent usage was a

characteristic of the process.

Leaching of copper was measured by atomic absorption spectrometry, and the value was calculated to be 0.089 g/3.6 g (for copper nitrate).

Effect of Cerium Nitrate Amount in the Catalyst Preparation

Ce played the role of catalyst promoter [23]. The cerium nitrate amounts were 0, 0.6, 1.2, 1.8, and 2.4 g. (Table 2). In the muffle furnace, cerium nitrate reacted with ammonia to generate cerium oxide and hydrous oxide (without cerium carbonate) on the surface of GAC. Five types of finished catalysts were obtained using different amounts of cerium nitrate. The volume of wastewater, the hydrogen peroxide amount, the MW power, and the MW radiation time were 250 mL, 7.5 mL, 539 W, and 6 min, respectively. Influent and effluent TOC was determined by the test methods shown in Fig. 1e.

As shown in Fig. 1e, TOC removal efficiency from wastewater increased from 60.89% to 69.75% when the cerium nitrate amount increased from 0 g/10 g GAC to 1.2 g/10 g GAC – a relatively large increase. Literature about AOPs has for a long time focused on catalyst promoters [24, 25]. Therefore, cerium oxide and hydrous oxide (without cerium carbonate) were used as promoters to cause copper oxide and hydrous oxide to play a role as activity components either at the inner or outer layers of the GAC, thereby improving the efficiency of the process by generating more hydroxyl radicals.

When the cerium nitrate amount was increased from 1.2 g/10 g GAC to 2.4 g/10 g GAC, there was a small decrease in TOC removal efficiency from 69.75% to 67.95%. At higher amounts of cerium nitrate (>1.2 g/10 g GAC), cerium oxide (or hydrous oxide) and copper oxide (or hydrous oxide) competed with each other for loading on the catalyst support (GAC). Too much cerium nitrate led to lower loading of copper oxide (or hydrous oxide) on the catalyst support, reducing the efficiency of the process. Thus, the optimal ratio of cerium nitrate in catalyst preparation was 1.2 g/10 g GAC.

Effect of GAC Amount in the Catalyst Preparation

GAC played the role of catalyst support, providing a reaction surface for generating hydroxyl radicals by the reaction of hydrogen peroxide and the finished catalyst. The GAC amounts used were 5, 10, 20, 30, and 40 g. (Table 2). Five types of finished catalyst were obtained using different amounts of GAC. The volume of wastewater, the amount of hydrogen peroxide, MW power, and MW radiation time were 250 mL, 7.5 mL, 539 W, and 6 min, respectively. Influent and effluent TOC was determined by the test methods shown in Fig. 1f.

Use of 5g of GAC resulted in relatively low TOC removal efficiency from wastewater (62.30%; Fig. 1f). This result was attributed to the small reaction surface between the catalyst and hydrogen peroxide.

However, when the GAC amount was increased from 5 g to 10 g, there was a large increase in TOC removal efficiency from wastewater (from 62.30% to 68.16%). Further increases in the amount of GAC used (such as 20, 30, or 40 g) would result in further increased TOC

removal efficiency from wastewater because the reaction surface area of the finished catalysts would be increased accordingly. Compared amounts of all reagent usages with the surface of GAC, the optimal amount of GAC in the catalyst preparation was 10 g.

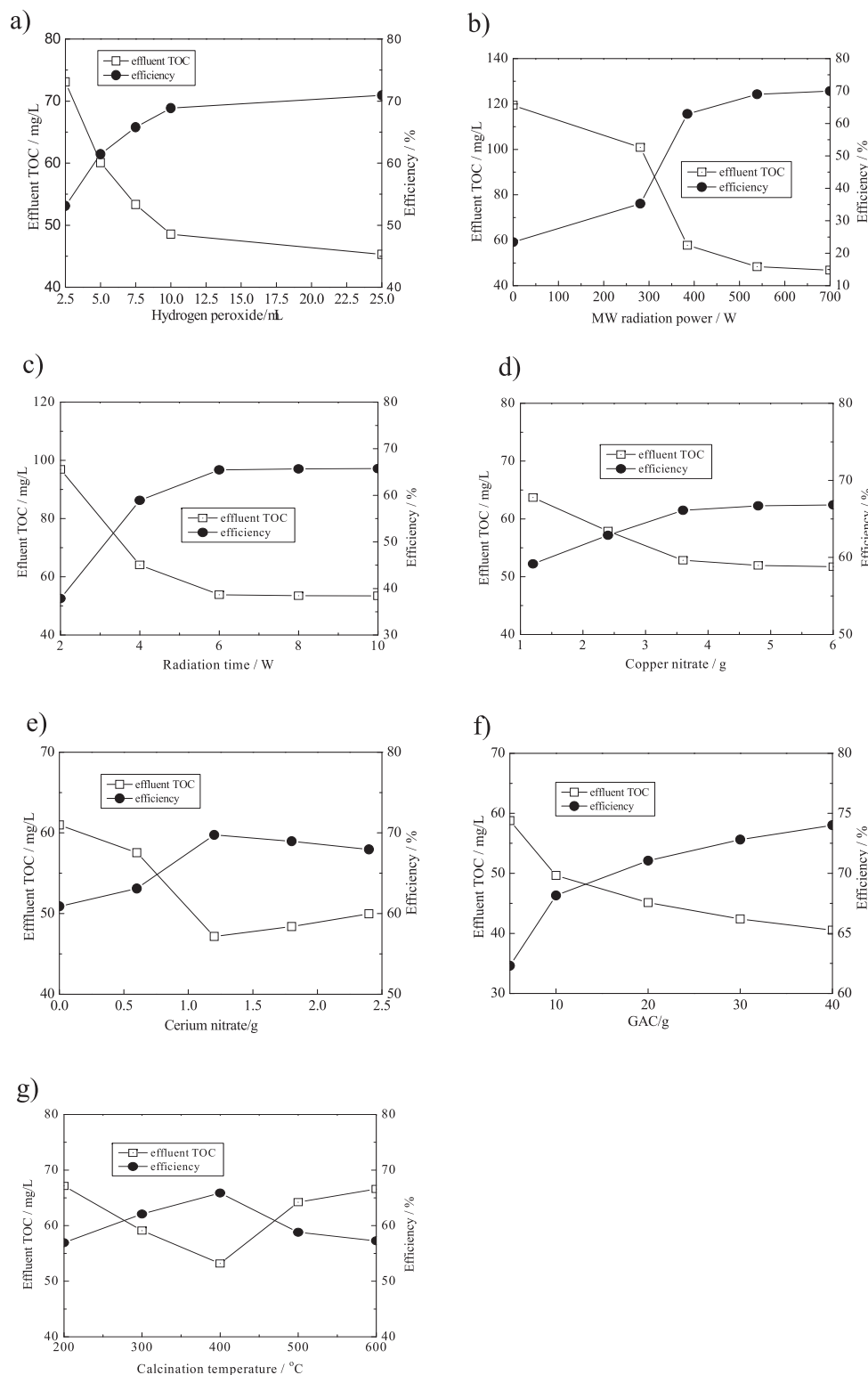


Fig. 1. Effects of factors a) hydrogen peroxide amount, b) MW radiation power, c) radiation time, d) copper nitrate amount, e) cerium nitrate amount, f) activated carbon amount, and g) calcination temperature on the efficiency of the MW-Fenton-like process using special supported catalysts (TOC₀ = 155.9 mg/L, no acidification).

Effect of Calcination Temperatures in Catalyst Preparation

The calcination temperatures were 200°C, 300°C, 400°C, 500°C, and 600°C. The other preparation conditions are shown in Table 2. Five types of finished catalysts were obtained using different calcination temperatures. Influent and effluent TOC was determined by the test methods shown in Fig. 1g. The highest TOC removal efficiency of wastewater was obtained (65.88%) with the catalyst prepared at a calcination temperature of 400°C (Fig. 1g). TOC removal efficiency of the wastewater with catalysts prepared at other calcination temperatures was lower. The temperature of calcination influenced the bonding force among copper oxide, cerium oxide (or hydrous oxide) and GAC. There are several reasons for these results. First, a very low temperature (200°C) led to the low yield and poor adhesion ability of copper oxide and cerium oxide (or hydrous oxide) on the surface of the support. Second, very high temperatures (500°C, 600°C) led to strong oxidation of GAC and was antagonistic to the generation and loading of copper oxide and cerium oxide (or hydrous oxide). Thus, the optimal calcination temperature in catalyst preparation was 400°C.

Change in BOD₅/COD and Colour of the Wastewater under Optimal Conditions

The MW-Fenton-like process using special supported catalysts was explored under predetermined optimal conditions. The volume of wastewater, hydrogen peroxide amount, MW radiation power, and MW radiation time were 250 mL, 7.5 mL, 539 W, and 6 min, respectively. The COD and BOD₅ of influent and effluent under optimal conditions were determined by the test methods outlined in Materials and Methods.

The BOD₅/COD value of the influent was 0.25, and the BOD₅/COD value of effluent was increased to 0.40. Thus, the biodegradation of the wastewater was obviously

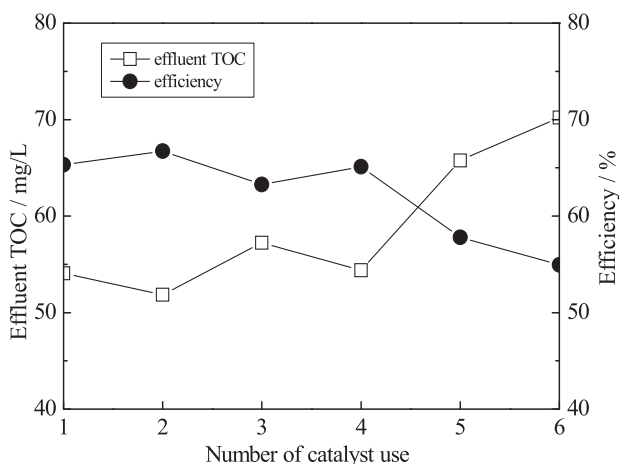


Fig. 2. Effects of the number of uses of the special supported catalyst on TOC removal efficiency (TOC₀ = 155.9 mg/L, no acidification).

improved by the MW-Fenton-like process using special supported catalysts.

Moreover, the initial colour of the pharmaceutical wastewater was 50; after the treatment, the colour of the effluent was 0.

Catalyst Efficiency after Regeneration and Possibility for Multiple Use

In the process of catalyst regeneration, catalysts were washed with distilled water after wastewater treatment [26-28], transferred to a drying box at a constant temperature of 110°C, and the drying time was 1.5 h. The efficiency of the process was evaluated by TOC removal efficiency from wastewater, the experimental conditions were the same as above, and the possibility for multiple use of the catalyst with high-efficiency performance was checked. As shown in Fig. 2, the regenerated catalyst could be used with highly efficient performance four times. After being used four times, the catalyst starts to deactivate and should be discarded.

Comparison with the MW-Fenton-like Process Using Common Supported Catalysts

Common supported catalyst means a catalyst prepared using the ordinary impregnation method. 3.6 g of copper nitrate and 1.2 g of cerium nitrate were added into the beaker with 4 mL of distilled water. The mixture was subsequently stirred to dissolve the reagents. 10 g of GAC was also added to the mixture, which was transferred to a crucible and moved to a muffle furnace at a steady temperature of 400°C for 1.5 h. Finally, the finished catalyst was obtained by ordinary impregnation method.

The MW-Fenton-like process using common supported catalysts was explored using radiation times of 2, 4, 6, 8, and 10 min. The wastewater started to boil at 8 min. Influent and effluent TOC was determined by the test methods shown in Fig. 3.

At radiation times of 2, 4, 6, 8, and 10 min, TOC removal efficiencies from wastewater were 21.47%,

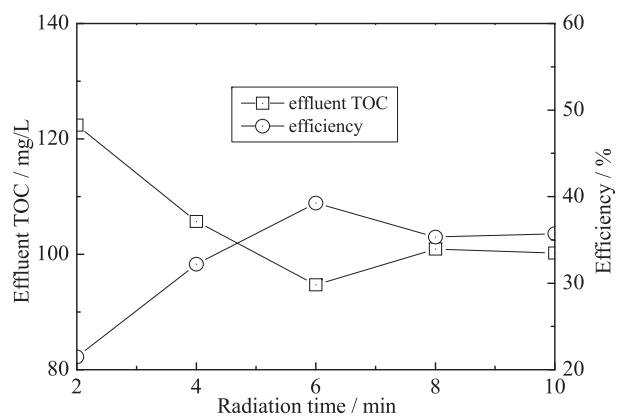


Fig. 3. Effects of radiation time on TOC removal efficiency in the experiment using common supported catalysts.

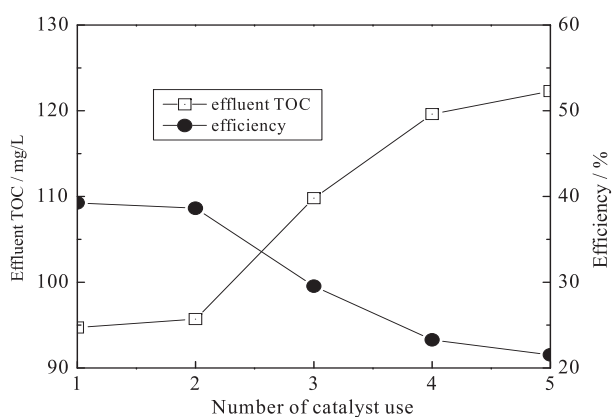


Fig. 4. Effect of the number of uses of common supported catalysts on TOC removal efficiency.

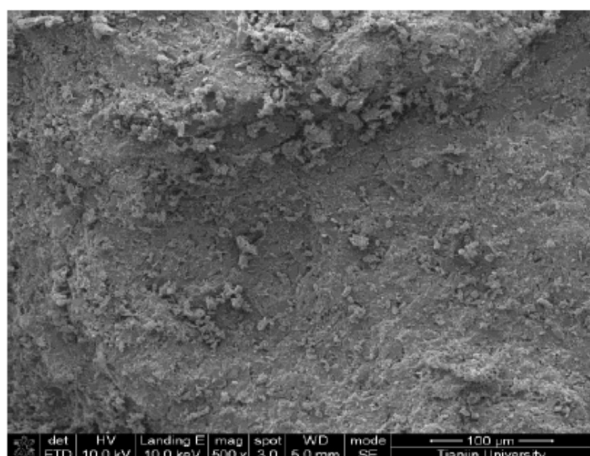
32.18%, 39.25%, 35.31%, and 35.72%, respectively. Thus, the optimal radiation time was 6 min (39.25%). Under these conditions, the coloration of the wastewater decreased from 50 to 20, and the BOD₅/COD value was

elevated from 0.25 to 0.34. The efficiency of the MW-Fenton-like process using common supported catalysts was lower than the process using special supported catalysts. The special supported catalysts performed better because copper carbonate or cerium carbonate were not present on the catalyst surface.

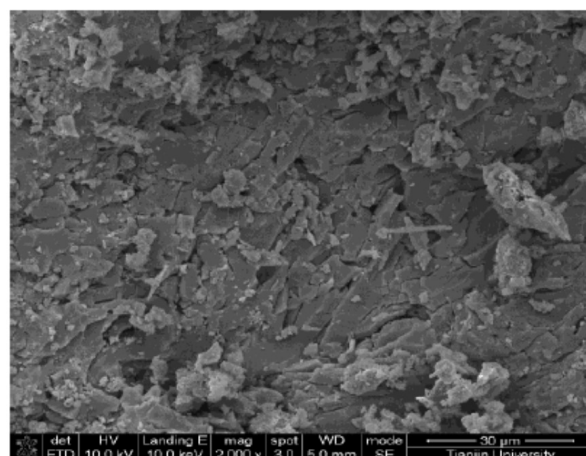
The catalysts were washed with distilled water after wastewater treatment, and transferred to a drying box with a constant temperature of 110°C. The drying time was 1.5 h. The experimental conditions were invariant. As shown in Figure 4, the maximum number of uses of the catalysts with high performance was two. After being used two times, the catalyst started to deactivate.

Characterization of the Special Supported Catalysts with the Highest Performance Efficiency

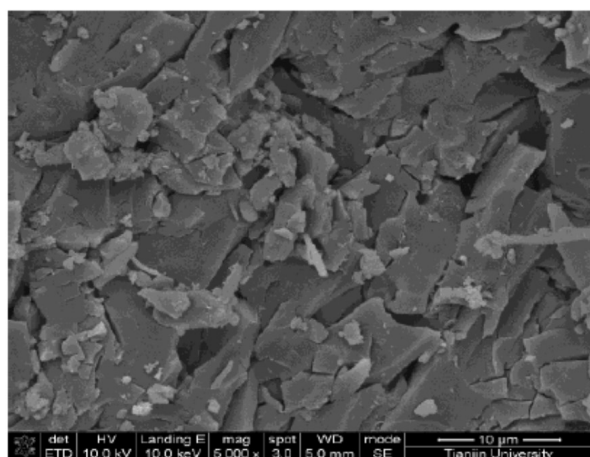
The catalyst preparations combined the merits of the isometric impregnation method with some improvements, such as the hydrothermal reaction. The special supported catalysts also achieved better effects when used in wastewater treatment. The special supported catalysts



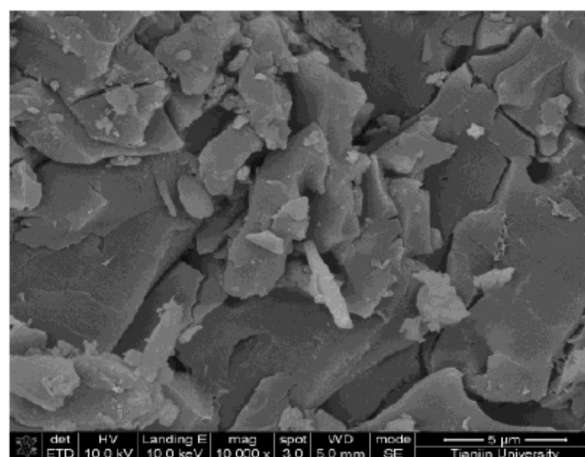
(a) GAC×500



(b) GAC×2000



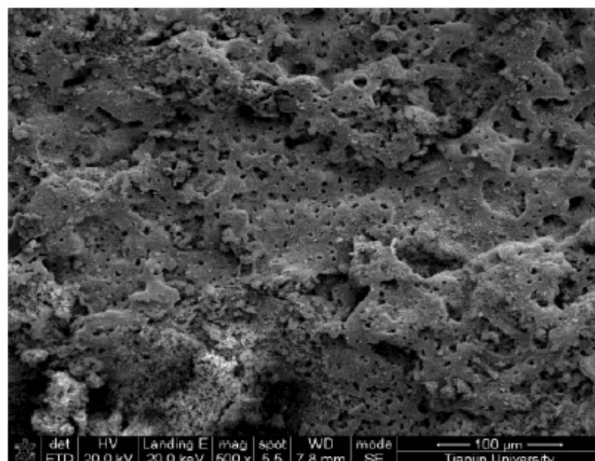
(c) GAC×5000



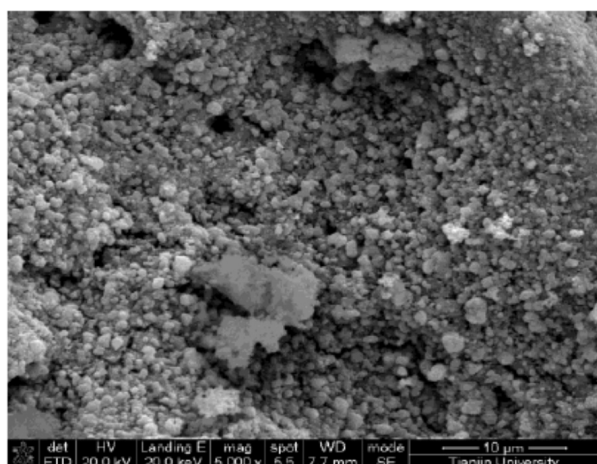
(d) GAC×10000

Fig. 5. SEM images of granular activated carbon (GAC).

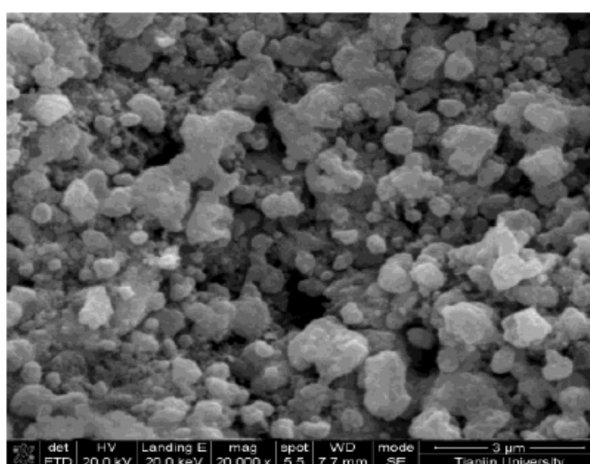
with the highest performance efficiency were produced at a calcination temperature of 400°C. The catalyst preparations were characterized by SEM, EDX, and XRD [29-30].



(a) special×500



(b) special×5000



(c) special×20000

Fig. 6. SEM images of the special supported catalysts with the highest efficiency performance.

SEM Analysis of Special Supported Catalysts

As shown in Figs 5 and 6, the surface structure of GAC (support) was stable and exhibited a uniform pore distribution. The particle size on the catalyst surface was also uniform. SEM analysis of the special supported catalysts indicated satisfactory catalyst distribution.

EDX Tests on Special Supported Catalysts

Surface element tests were performed using EDX (Table 3 and Table 4). GAC from coal was used as the catalyst support. Table 3 shows the relative amounts of Ca, Si, Al, Mg, C, and O, and Table 4 shows that the relative amounts of the activity components and promoters were Cu at 66.13% and Ce at 28.06%. No copper carbonate or cerium carbonate was detected.

XRD Tests on Special Supported Catalysts

As shown in Fig. 7, copper oxide was the only crystal component in the special supported catalysts, cerium oxide was undersized and amorphous, and other crystal components detected were part of the GAC.

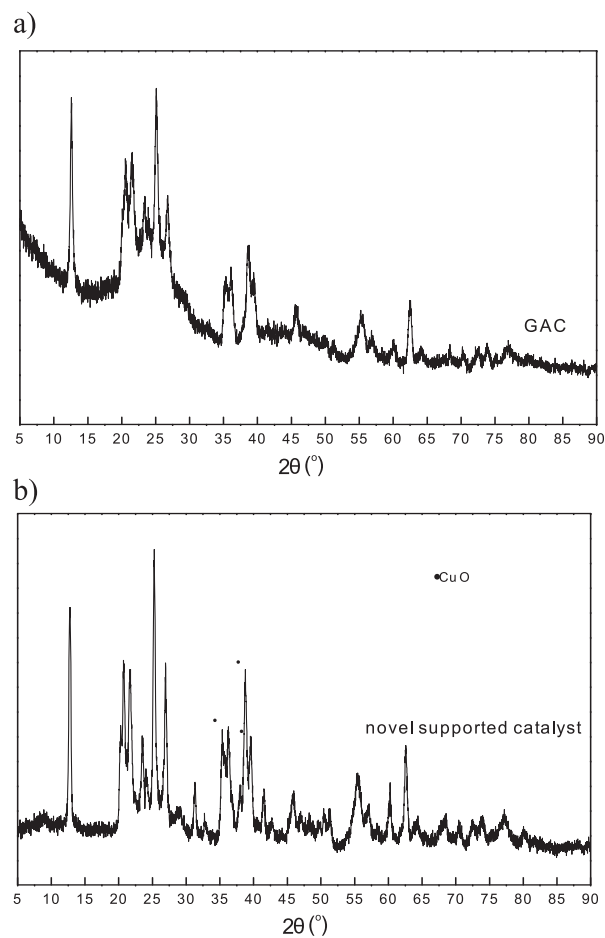


Fig. 7. XRD pattern of a) GAC and b) special supported catalysts with the highest efficiency performance.

Conclusions

The efficiency of an MW-Fenton-like process using special supported catalysts was evaluated by TOC removal efficiency from wastewater. The highest TOC removal efficiency was 65.88% under optimal conditions without acidification. Moreover, the BOD₅/COD value was elevated from 0.25 to 0.40, colour was removed completely, and the maximum number of consecutive uses was four. By comparison, the MW-Fenton-like process using common supported catalysts (efficiency = 39.25%) achieved a BOD₅/COD increase from 0.25 to 0.34, and a decrease in colour of the wastewater from 50 to 20, and could be used for two times at most.

The properties of the catalysts with the highest efficiency performance were characterized. Particles sizes were uniform and the relative amounts of activity components and promoters were excellent (the copper and cerium percentages were 66.13% and 28.06%, respectively). Copper oxide was the only crystal form, and no copper carbonate or cerium carbonate was detected.

In the catalyst preparation, copper oxide and hydrous oxide (without copper carbonate) was generated by copper nitrate and a small amount of ammonia, which was employed as the special supported catalyst. The high efficiency performance of the process was attributed to the lack of copper carbonate. Cerium oxide and hydrous oxide (without cerium carbonate) were used as promoters, causing the copper oxide and hydrous oxide to play the role of activity components either at the inner or outer layers of the GAC.

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