Preparation and characteristics of carbon-supported platinum catalyst and its application in the removal of phenolic pollutants in aqueous solution by microwave-assisted catalytic oxidation

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Abstract

Granular activated carbon-supported platinum (Pt/GAC) catalysts were prepared by microwave irradiation and characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). Pt particles dispersing onto the surface of GAC could be penetrated by microwave and acted as "reaction centre" in the degradations of p-nitrophenol (PNP) and pentachlorophenol (PCP) in aqueous solution by microwave-assisted catalytic oxidation. The reaction was carried out through a packed bed reactor under ambient pressure and continuous flow mode. Under the conditions of microwave power 400 W, influent flow 6.4 mL min^{-1} and air flow 120 mL min^{-1}, phenolic solutions with high concentration (initial concentrations of PNP and PCP solutions were 1469 and 1454 mg L^{-1}, respectively) were treated effectively by Pt/GAC, 86% PNP and 90% PCP were degraded and total organic carbon (TOC) removal reached 85% and 71%, respectively. Compared with GAC, loaded Pt apparently accelerated oxidative reaction so that Pt/GAC had a better degrading and mineralizing efficiencies for PNP. Hydraulic retention time was only 16 min in experiment, which was shortened greatly compared with catalytic wet air oxidation. Pyrolysis and oxidation of phenolic pollutants occurred simultaneously on the surface of Pt/GAC by microwave irradiation.
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1. Introduction

Phenolic pollutants are mainly distributed in the terrestrial and aquatic environments due to wide usage of pesticides, pharmaceutical products and chemical raw materials [1–3], which were synthesized and manufactured in great part by phenolic compounds. Because of the toxicity, phenolic pollutants can be treated by microorganism in a low concentration and a long hydraulic retention time (HRT) [4]. The treatment of phenolic wastewater with high concentration was reported mainly by advanced oxidation technologies, such as catalytic wet air oxidation (CWAO) [5], chemical oxidation [6], sonolysis technology [7] and photocatalysis techniques [8], etc. However, the severe reaction conditions (high temperature and high pressure), high capital costs, high noise and low quantum efficiency are their

defects, respectively, which need to be solved and improved with their further development. In recent years, microwave (MW) technology has attracted the attention of chemists due to its property of molecular-level heating which leads to homogeneous and quick thermal reactions [9]. MW heating can decrease activation energy, reduce reaction time, increase the selectivity of reaction and improve the speed of reaction, etc., while comparing with conventional heating mode. Therefore, MW has been applied widely in the fields of organic synthesis [10], polymerization and dehydration processes [11,12], preparation of catalyst [13], remediation of contaminated soil [14], treatment of wastes [15] and reduction of nitrogen oxides and sulfur dioxide [16], etc. Combining with microwave-absorbing materials, such as granular activated carbon (GAC), MW has also been utilized in the treatment of wastewater. In our previous works [17–19], phenolic pollutants in aqueous solution were degraded efficiently on the surface of GAC under microwave irradiation. However, it is well known that oxidation–reduction reaction can be catalyzed obviously by transition-metal due to its free electron, especially

for noble metal with the advantages of high activity, long lifespan and strong adaptability. Noble metals, including but not limited to platinum (Pt), could be loaded onto the surface of activated carbon (AC), and applied in the process of CWAO. Cao et al. [20] compared AC-supported Pt (Pt/AC) catalyst with AC-supported base metal catalysts, such as copper and manganese, etc., and found highest activity and stability for Pt/AC in the treatment of wastewater containing ammonia and phenol, and no leaching of Pt in the effluent. Gomes et al. [21,22] applied carbon-supported Pt and iridium catalysts to treat low molecular weight carboxylic acids, and also found that Pt/AC have a good degradation on short-chain acids. To the best of our knowledge, few reports were found in catalytic oxidation of pollutants in aqueous solution combining with microwave energy and carbon-supported metal catalyst, and also few reports on the behavior of carbon-supported metal catalyst in the field of microwave due to metallic shield and reflection on microwave [23].

In this study, GAC-supported Pt (Pt/GAC) catalyst was prepared by microwave irradiation and the characteristics and microwave-absorbing capacity of the catalyst were checked. Two typical phenolic pollutants, *p*-nitrophenol (PNP) and pentachlorophenol (PCP), considered as priority pollutants by the USEPA [24], were selected as the objectives and degraded by microwave-assisted catalytic oxidation using Pt/GAC catalyst. The results of PNP degradation between Pt/GAC and GAC were given. Adsorption capacity of Pt/GAC for target compounds and intermediates were also determined.

2. Experimental

2.1. Materials

Analytical grade PNP and hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) were purchased from Shenyang Reagent Company, China. Chemical grade PCP was obtained from Beijing chemical factory, china, and coal-based GAC was acquired from Shanghai Zhenghai Co. Ltd., which was used after pretreatment described in the following paragraph. Other chemicals were analytical grade and purchased from domestic chemical companies.

2.2. Preparation and characterization of the Pt/GAC catalyst

Coal-based GAC was sieved firstly with 20 mesh screen to obtain 1–4 mm size granules, then immersed in 8–10% hydrochloric acid (HCl) for 18 h, and then seethed by steam for 2 h, then rinsed repeatedly with deionized water to remove oil and impurity until the pH of the washed water was 5–6. Finally, the washed GAC was dried in an oven at 105 °C for 8 h to constant weight.

Pretreated GAC were impregnated firstly with $H_2PtCl_6 \cdot 6H_2O$ aqueous solution (stoichiometric 1 wt.%), then the suspension was mixed in a shaker at 250 r min^{-1} for 2 h and evaporated to near-dryness in a microwave oven with 500 W power. The catalyst samples were then calcined by microwave

at 500 W for 5 min with nitrogen gas as the carrier at a flow rate of 600 mL min^{-1}. Finally, the Pt/GAC catalysts were taken out and cooled down under the protection of the nitrogen gas.

The surface morphology of the catalyst was observed by scanning electron microscopy (SEM) using Oxford JSM-5600LV microscope with an accelerating voltage of 20 kV, and the element analysis was carried out by energy-dispersive X-ray spectroscopy (EDX) equipped with the scanning electron microscope. The crystallinity of Pt/GAC catalyst was determined by X-ray diffraction (XRD) using a diffractometer with Cu Kα radiation (model, Shimadzu LabX-6000). The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. The average size of the Pt grain was calculated using Scherrer's equation, and the penetration depth of the Pt by microwave was evaluated by skin depth.

Pore structural properties of GAC were calculated by measuring nitrogen adsorption and desorption isotherms with an ASAP2010 (Micromeritics) at −196 °C. Before the experiment, the samples were heated at 120 °C and then outgassed at this temperature under a vacuum of 10^{-5} Torr to constant pressure. The micropore volume was calculated using the *t*-method, and the BJH model was used for pore size distribution in the range of 1.0–200 nm.

2.3. Microwave-absorbing capacity and adsorption experiments of Pt/GAC catalyst

In order to investigate the effect of loaded Pt on microwave-absorbing capacity of Pt/GAC catalyst, 3 g of prepared Pt/GAC catalyst and pretreated GAC were put into a quartz tube, respectively, and then radiated by microwave in 800 W and the temperature was measured by a sheltered type-K thermocouple [25].

The adsorption experiments were carried out at 60 °C, which was around the temperature of the influent after heat exchange, and the pH value kept at 5.3 and 10.35 constantly for PNP and PCP solution, respectively, in order to eliminate the effect of pH on adsorption, which were kept in accordance with the pH of the influent. Detailed experimental procedures could be seen in our previous work [18].

2.4. Microwave-assisted catalytic oxidation process

A schematic diagram of the experimental setup has been showed in our previous study [19], and also given in Fig. 1. A modified domestic microwave oven (2450 MHz), whose power could be adjusted continuously by a booster, was applied for supplying MW energy. A quartz column (inner diameter 28 mm, total length 440 mm) contained the catalyst and was inserted vertically in the MW oven and served as a packed bed reactor. A sheltered type-K thermocouple was used to measure the bed temperature.

Pt/GAC catalysts pre-adsorbed phenolic pollutant firstly, before being packed into the quartz reactor, so as to abate the adsorption effect of GAC on degradation during reaction course, then the treated solution and air were mixed and pumped into the packed bed reactor, wherein phenolic pollutant was degraded on
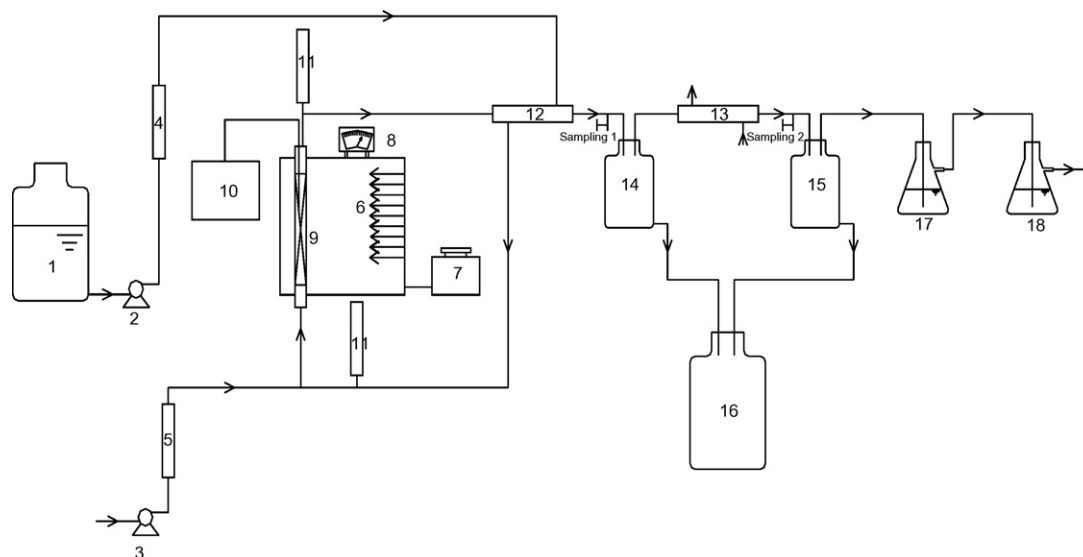
Fig. 1. Schematic diagram of experimental setup (1) phenolic solution container; (2) metrical pump; (3) air pump; (4) liquid flowmeter; (5) air flowmeter; (6) microwave generator; (7) booster; (8) amperemeter; (9) packed bed Quartz reactor; (10) thermocouple indicator; (11) thermometer; (12) heat exchanger; (13) condenser; (14) Effluent receiver; (15) secondary condensate receiver; (16) recycle vessel; (17) water-absorbing bottle; (18) alkaline solution-absorbing bottle.

the surface of the catalyst by microwave irradiation. The effluent exchanged heat with the influent through a heat exchanger and then flowed into a receiver. The off gas was condensed by tap water, and then absorbed by deionized water and dilute alkaline solution, respectively, before being discharged.

2.5. Analytical methods

PNP and PCP were analyzed by a high-performance liquid chromatograph (HPLC) (JASCO, PU-1580, Japan) equipped with UV detector (UV-1575) and C_{18} reverse-phase column (250 mm × 4.6 mm, 5 μm ODS, Kromasil, China). The detection wavelength was set at 280 nm, and the mobile phase was 0.6:0.4 methanol and water at a flow rate of 1 mL min^{-1} for PNP. As for the PCP, the detection wavelength was 220 nm, and the ratio of methanol and water in mobile phase was 0.8:0.2 at 1 mL min^{-1} flow rate. The difference of detection wavelengths and methanol:water ratios for PNP and PCP was due to their different molecular structures and polarities so that better analytical results could be obtained. Quantifica-

tion of PNP and PCP was performed by external standard method.

Total organic carbon (TOC) analyzer (TOC-V$_{CPH}$, Shimadzu, Japan) was employed to determine the residual amounts of organic substances in the effluent to investigate the mineralization of phenolic pollutant. Gas chromatography–mass spectrometry (GC–MS) was utilized to identify the intermediates in treated solutions. A GC (HP6890) with a capillary column (HP-5MS, 30 m × 0.25 mm × 0.25 μm) and a MS (HP5973N) were employed, and the intermediates were identified by comparing the mass spectra of the treated samples with spectra of the compounds stored in the NIST library.

3. Results and discussion

3.1. Characterization and microwave-absorbing capacity of Pt/GAC catalyst

Microwave can be reflected and shielded by metal. Thus, prepared Pt/GAC catalyst was characterized by SEM (Fig. 2),
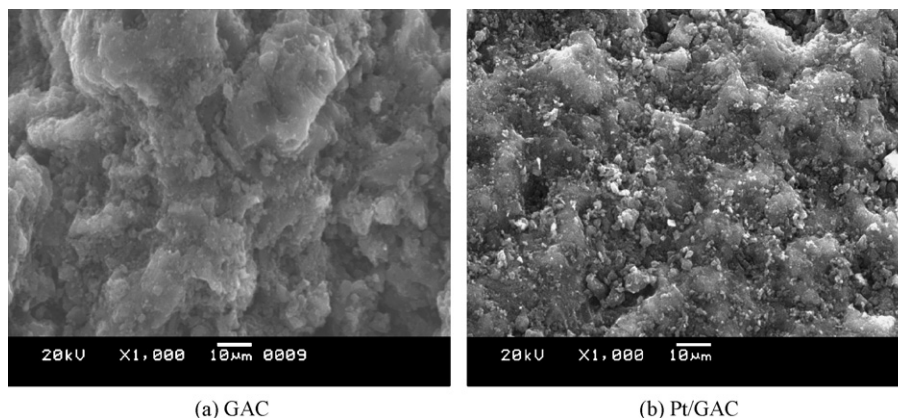

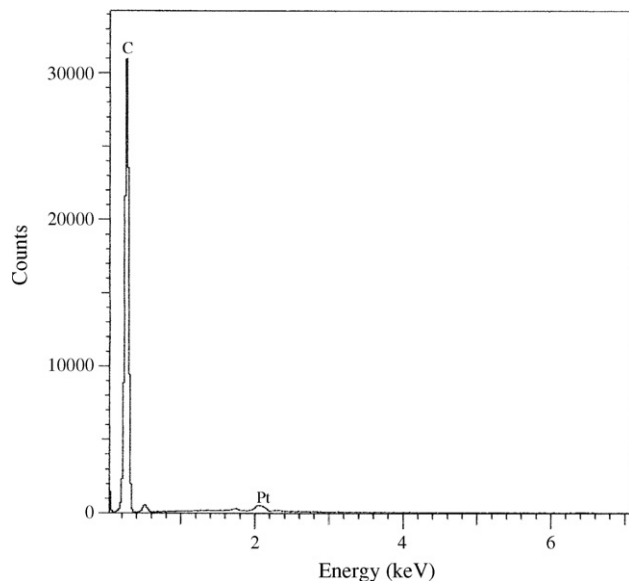Fig. 2. SEM of GAC and Pt/GAC prepared by microwave irradiation.

Fig. 3. Element analysis of Pt/GAC catalyst by EDX.

EDX (Fig. 3) and XRD (Fig. 4), which can examine the size and formation of Pt particle, in order to analyze its microwave-absorbing capacity according to the MW penetration depth for Pt grain that is calculated by skin depth.

GAC was reported to have abundant pore structure, high specific surface area and strong adsorption capacity so as to be widely used in purifying air, drinking water and wastewater [26]. It could be seen from Fig. 2a that plentiful pores and defective sites with different sizes and irregular shapes existed on the surface and the inner side of GAC. Pore structural analysis of GAC was given in latter paragraph. Pt particles, seen in Fig. 2b, dispersed asymmetrically on the surface of GAC and had irregular shapes and small sizes, which were about 0.1–0.8 μm. Chen et al. [27] reported that Pt nanoparticles synthesized by microwave had a sharp size and highly dispersed on the surface of carbon nanotubes. Many smaller Pt grains could be found inside the pores of GAC.
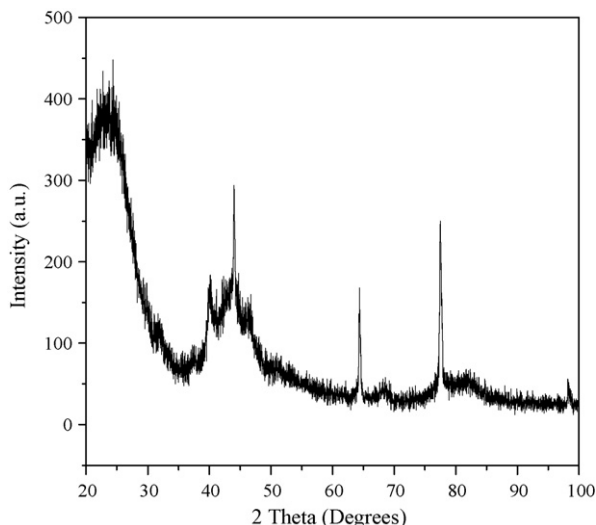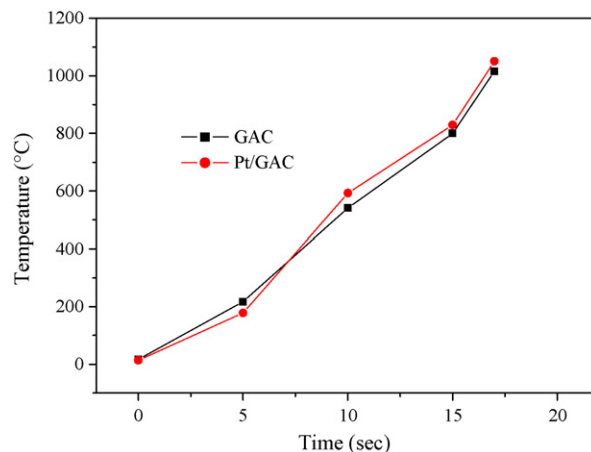

Fig. 4. XRD of Pt/GAC catalyst.

Fig. 5. Temperature variations of GAC and Pt/GAC catalyst by microwave irradiation.

Fig. 3 showed that there were only two elements of carbon and platinum in the catalyst, and chlorine element was not found. Hydrogen reduction reaction was not performed during the preparation of the Pt/GAC catalyst; therefore, it is speculated that GAC took part in the reduction of H_2PtCl_6 and chlorine was removed completely in the course of calcination. XRD result in Fig. 4 showed that Pt crystal grains existed in the catalyst and the characteristic peaks were observed at $2\theta = 40.2°$, 44°, and 64.36°. It indicated that the particles dispersing on the surface of GAC were metallic Pt grains. The average size of Pt crystal was calculated to be 30.18 nm based on Scherrer's equation ($D = 0.89\lambda/\beta \cos\theta$), which was much lower than the size (0.1–0.8 μm) observed in SEM photograph. Thus, we could draw a conclusion that those big Pt particles, distributing asymmetrically on the surface of the catalyst, were formed most probably by the agglomeration of Pt crystallites, and their different sizes were due to different agglomerating amounts of Pt crystals.

It could be seen in Fig. 5 that GAC and Pt/GAC could both absorb microwave energy strongly, and their temperature rose rapidly and exceeded 1000 °C within 20 s under microwave irradiation. There were no apparent differences in microwave-absorbing capacity between GAC and Pt/GAC. The depth of penetration for metallic particle by microwave can be calculated by skin depth ($\delta = \sqrt{2/\omega\mu_0\sigma}$) [28], and the skin depth of Pt is calculated to be 3.3 μm according to the related data. As mentioned above, the maximum size of Pt grain on the surface of the catalyst was 0.8 μm, so microwave could penetrate Pt particles easily. The reason for the rising temperature of Pt/GAC catalyst was probably due to the loss of penetration and strong microwave-absorbing capacity of GAC carrier.

3.2. Adsorption isotherms of phenolic pollutants onto Pt/GAC catalyst

In this study, we are interested in the degradation of phenolic pollutant by microwave-assisted catalytic oxidation, and not in the adsorption by GAC. Therefore, the adsorption capacities of Pt/GAC catalyst for PNP and PCP were evaluated in
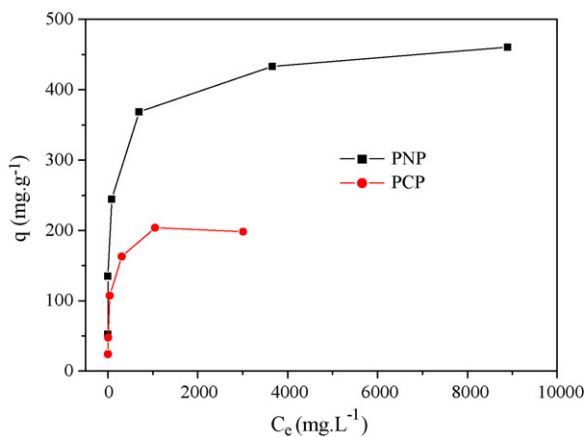
Fig. 6. Adsorption isotherms of PNP and PCP by Pt/GAC catalyst at 60 °C.

terms of their adsorption isotherms and the results were shown in Fig. 6.

It can be seen that Pt/GAC catalyst can adsorb both PNP and PCP strongly, and the equilibrium adsorption amount (q) reached 400 mg g^{-1} for PNP and 200 mg g^{-1} for PCP while the equilibrium concentration (C_e) was higher than 2000 mg L^{-1}. The difference in adsorbed amounts was related to the polarity and water-solubility of target compounds. In this work, the initial concentration (C_0) of phenolic solutions was around 1450 mg L^{-1}, so q values were determined to be 360 and 190 mg g^{-1} for PNP and PCP, respectively.
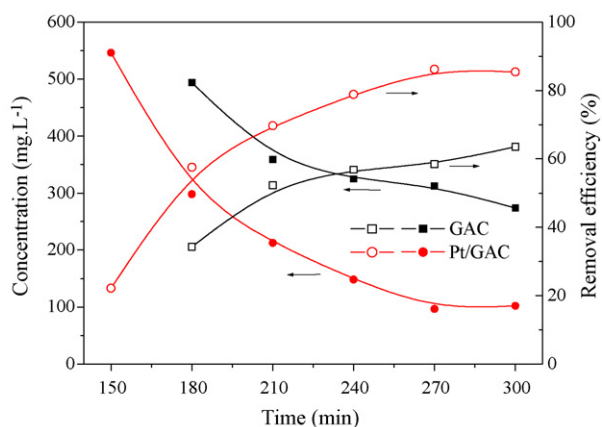
3.3. Microwave-assisted catalytic oxidation of PNP and PCP

Based on results in Section 3.2, 19 g PNP and 10 g PCP were pre-adsorbed onto 52.5 g Pt/GAC catalyst separately in order to eliminate the adsorption effect of the catalyst on degradation of phenolic pollutants. In this way, we could confirm that the decay of PNP or PCP concentration resulted from degradation, not from adsorption. During the treatment of PNP solution (C_0 1469 mg L^{-1} for Pt/GAC and 1734 mg L^{-1} for GAC), GAC was also used as a comparison with Pt/GAC, the reaction conditions were microwave power (P_{MW}) 400 W, solution flow (Q_S) 6.4 mL min^{-1} corresponding to HRT 16 min, and air flow (Q_A) 120 mL min^{-1}, and the results were shown in Fig. 7. Because of a continuous flow mode, HRT was constant under given conditions, thus the abscissa in Fig. 7 indicated the operational time. At the beginning of experiment, the concentrations of PNP and TOC were unsteady, due to a balance between desorption and degradation for PNP, and detailed description could be seen in our previous work [19]. Therefore, the experimental data before 150 min was not given here.

It can be seen in Fig. 7 that PNP could be degraded and mineralized apparently by GAC and Pt/GAC, respectively. However, Pt/GAC had a better removal and mineralization efficiencies for PNP than GAC. In Fig. 7a, residual concentrations of PNP in the effluent were 534 mg L^{-1} for GAC and 204 mg L^{-1} for Pt/GAC at 5 h, corresponding to 69% and 86% removal efficiencies, respectively. It could be seen from Fig. 7b that 63.5%
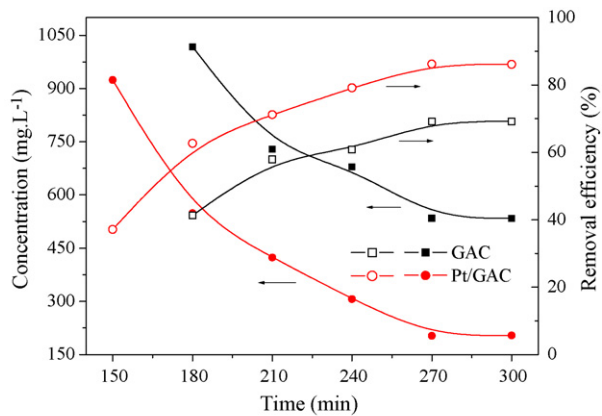
Fig. 7. Comparison of GAC and Pt/GAC for the degradation and mineralization of PNP by microwave-assisted catalytic oxidation.

removal of TOC was for GAC and 85% for Pt/GAC at 5 h. GAC can absorb microwave energy stronger than water so as to have a higher temperature on its surface under microwave irradiation; simultaneously, the oxidation time of target compound can be prolonged due to the adsorption of GAC. Thus, PNP could be decomposed and oxidized on the surface of GAC in the absence of Pt. Based on the advantages of GAC, the existence of Pt particles could decrease activation energy of reaction and act as "reaction centre" in the oxidation of PNP. The synergy effect between Pt and GAC may coexist in reaction course so that higher removal efficiencies for PNP and TOC were observed. Most of degraded PNP were mineralized in the course of oxidation. Gomes et al. [21,22] reported that low molecular weight acids could be degraded effectively by Pt/AC in CWAO so that Pt/GAC could probably be considered a good catalyst for the mineralization of organic substance.

Pore structural properties of virgin and spent GACs were analyzed and shown in Table 1. Due to only 1 wt.% Pt amounts in the Pt/GAC catalyst, which was considered to have a similar pore structure as GAC and not analyzed in this work. It showed that virgin GAC had a specific surface area of 1086 m^2 g^{-1} and micropore volume 0.2616 cm^3 g^{-1}, which was nearly 43% of total pore volume. Compared with virgin GAC, specific surface area and micropore volume of spent GAC decreased 22% and

Table 1
Pore structural properties of virgin and spent GAC samples

Sample	A_{BET} (m² g⁻¹)	A_M (m² g⁻¹)	A_{EX} (m² g⁻¹)	V (cm³ g⁻¹)	V_M (cm³ g⁻¹)	d (nm)
GAC-virgin	1086	631.5	455	0.6056	0.2616	2.229
GAC-spent	842.8	457.8	385	0.4877	0.1872	2.315

Note: A_{BET}, specific surface area; A_M, micropore surface area; A_{EX}, external surface area; V, total pore volume; V_M, micropore volume; d, average pore diameter.

28%, respectively. Deposition of target compound or intermediates on the surface and inner pores of GAC was probably the main reason for it. Some micropores could also combine and form mesopore during experiment due to an increase of average pore diameter from 2.229 to 2.315 nm. Therefore, the variation of GAC pore structure could affect the removal of target compound after using several times; it could be examined in the further work.

PCP solution (C_0 1454 mg L⁻¹) was also treated by Pt/GAC under the same conditions as PNP solution, and the results were seen in Fig. 8. A rapid decrease of PCP and TOC concentrations occurred in the beginning and kept stable after 60 min. The removal of PCP reached 90% at 4 h, and TOC removal was 71%, simultaneously, which was obviously lower than that of PNP solution. The difference of mineralization between PNP and PCP may be connected with their different molecular structures.
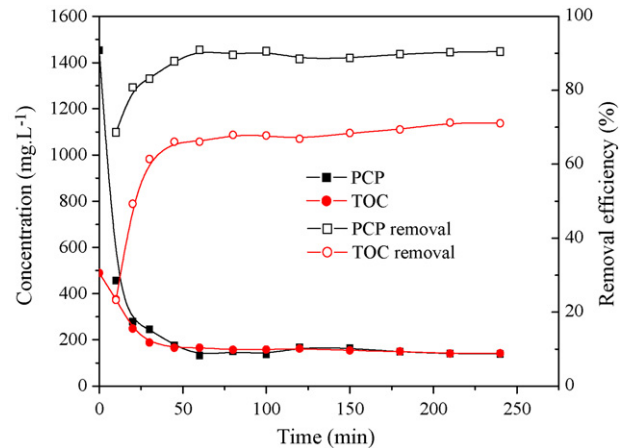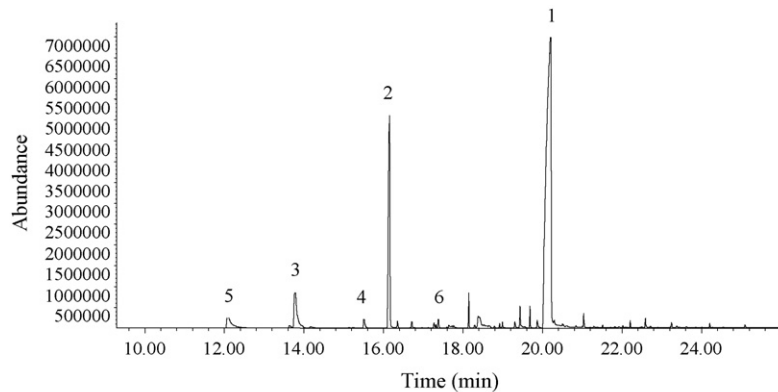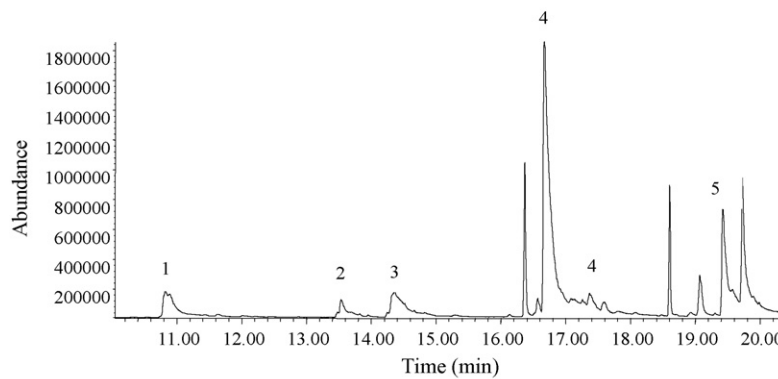

Fig. 8. Degradation and mineralization of PCP by Pt/GAC catalyst.

(a) PNP

1-PNP, 2-o-Nitrophenol, 3-Phenol, 4-Nitrobenzene, 5-Benzoquinone, 6-Hydroquinone.

(b) PCP

1-Phenol, 2-Trichlorobenzene, 3-Dichlorophenol, 4-Trichlorophenol, 5-Tetrachlorophenol

Fig. 9. Total ion chromatograms of the condensates by Pt/GAC catalyst.

The effluents were determined by atomic absorption spectrum in order to investigate the leaching of Pt; however, Pt was not found in the effluents, which was identical with the report by Cao et al. [20]. Few loaded amount (1 wt.% in this work), high catalytic capacity, and nonoxidation of Pt were also the advantages for Pt/GAC catalyst. In our study, HRT in the packed bed is 16 min under the flow rate of 6.4 mL min^{-1}, which is too short than that in the CWAO process. Garcia et al. [29] investigated the CWAO of nitrogen containing compounds using Pt/MWNT catalyst, and the HRT was 2 h. The 3 h HRT was reported in the CWAO of stearic acid by cerium oxide supported noble metal catalysts [30], and 50 h operational period was carried out in the CWAO of phenol through a trickle bed [31]. Therefore, the HRT in our study was shortened greatly. Due to operation under atmosphere pressure, the reaction setup is low cost and easy to maintain, which is also superior to a high capital cost and maintenance fee in CWAO.

3.4. Identification of course products

In order to investigate the degradation pathway of phenolic pollutants in the process of microwave-assisted catalytic oxidation by Pt/GAC catalyst, GC–MS was applied to identify the organic course products, and the results were shown in Fig. 9.

It can be seen in Fig. 9a that pyrolyzed products such as phenol and nitrobenzene, and oxidized intermediates benzoquinone and hydroquinone were identified in the course of PNP degradation. An isomer of PNP, *o*-nitrophenol, was also found in the condensate. Pyrolysis and oxidation coexisted in the course of reaction. Ultimately, these intermediates were further oxidized to carbon dioxide and water. Due to the same intermediates for PNP degradation while using GAC, the degradation pathway was given elsewhere [19]. Loaded Pt metal only accelerated the degrading reaction and not changed the degrading pathway.

In the process of PCP degradation, phenol, trichlorobenzene, dichlorophenol, trichlorophenol and tetrachlorophenol were identified as the intermediates (seen in Fig. 9b), and their confidence measures were all higher than 90% comparing with spectra of the compounds stored in the NIST library. The courses of dechlorination and/or dehydroxylation occurred in PCP degradation, and most of these intermediates were mineralized finally. Same as PNP degradation, pyrolysis and oxidation also occurred simultaneously in PCP degradation. The degrading pathway was same as that reported by Liu et al. [17].

4. Conclusions

Pt/GAC catalyst prepared by microwave method can absorb microwave energy strongly due to the penetration loss of Pt particles and microwave-absorbing capacity of GAC carrier. Pt particles, dispersing on the surface of GAC with the sizes of 0.1–0.8 μm, were formed probably by the agglomeration of Pt crystallites. Compared with GAC, Pt/GAC had a better degradation and mineralization in the treatment of PNP solution, and the synergy effect between Pt and GAC coexisted in the course of reaction. PCP solution was also treated by Pt/GAC under microwave irradiation, and 90% removal for PCP and 71% TOC

removal were achieved at 4 h. No leaching of Pt was found in this study. Pyrolysis and oxidation coexisted in the degradation of phenolic pollutants by microwave-assisted catalytic oxidation using Pt/GAC catalyst, and Pt only accelerated the degrading reaction. Compared with CWAO, microwave-assisted catalytic oxidation had a milder reaction condition and a very short HRT, which showed a better application prospect in future.

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