

Microwave assisted catalytic oxidation of *p*-nitrophenol in aqueous solution using carbon-supported copper catalyst

L.L. Bo, Y.B. Zhang, X. Quan*, B. Zhao

School of Environmental and Biological Science & Technology, Dalian University of Technology, Key Laboratory of Industrial Ecology and Environmental Engineering, Ministry of Education, Dalian 116024, China

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Abstract

Carbon-supported copper (Cu/GAC) catalyst was prepared by conventional impregnation method and characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). The sizes of Cu particles dispersing on the surface of GAC were 0.3–1.5 μm , which could be penetrated by microwave so that Cu/GAC catalyst could absorb microwave energy effectively. The catalysis of Cu/GAC in microwave assisted catalytic oxidation of *p*-nitrophenol (PNP) in aqueous solution was investigated through a fixed bed reactor under ambient pressure and continuous flow mode. PNP removal reached 91.8% under optimized conditions, corresponding to 88% of TOC removal. It showed a higher PNP degradation and total organic carbon (TOC) removal for Cu/GAC catalyst than GAC alone, and Cu/GAC catalyst kept on a high catalysis and a good stability for a long time run, which indicated that GAC structure and catalytic capacity were improved by the load of Cu.

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Keywords: Microwave; Catalytic oxidation; *p*-Nitrophenol; Fixed bed; Cu/GAC catalyst

1. Introduction

Microwave (MW) is a part of the electromagnetic spectrum occurring in the frequency range of 300 MHz to 300 GHz and can provide rapid heating of materials. In recent years, it has been applied in the researches on remediation of contaminated soil [1], purification of petroleum wastewater [2], reduction of nitrogen oxides and sulfur dioxide [3], etc. Combining with microwave-absorbing materials, including but not limited to, granular activated carbon (GAC) with a high surface area and a wide range of pore size distribution, microwave has also been employed in the degradation of organic pollutants in aqueous solution. Liu et al. [4] applied GAC to adsorb pentachlorophenol (PCP) in solution firstly and then the adsorbed GAC was radiated by microwave, which resulting in the decomposition of PCP on the surface of GAC and GAC regeneration simultaneously. In our previous works [5,6], GAC fixed bed was applied to treat *p*-nitrophenol (PNP) solution continuously under

MW irradiation and showed a high removal for PNP, and GAC acted as microwave-absorbing material and adsorptive catalyst together in the course of reaction. However, the catalysis of GAC-supported metal catalyst has not been investigated in our earlier works. It is well known that metal, while loaded on the surface of supporter, can have an apparent catalysis during reaction. Alumina-supported copper and carbon-supported copper (Cu/GAC) catalysts [7,8] have been reported to have the highest catalytic activity in catalytic wet air oxidation (CWAO) of dyeing and printing wastewater among $\text{Cu}(\text{NO}_3)_2$, CuO, FeSO_4 , $\text{Mn}(\text{NO}_3)_2$ and CuSO_4 , and CWAO, as one of the most promising processes for wastewater treatment, has been mainly applied to treat toxic or/and non-biodegradable pollutants under high temperature and high pressure. However, no report has been found with respect to CWAO of refractory compounds combining with microwave energy and GAC-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.

In this study, Cu/GAC catalyst was prepared and characterized to give an explanation for its microwave-absorbing capacity, and the catalytic activation and stability of the cat-

* Corresponding author. Tel.: +86 411 84706140; fax: +86 411 84706263.
E-mail address: quanxie@dlut.edu.cn (X. Quan).

alyst, compared with GAC, were also investigated in CWAO of *p*-nitrophenol, one of toxic and non-biodegradable pollutants existing extensively in the terrestrial and aquatic environments [9], assisted by microwave under atmosphere pressure.

2. Experimental

2.1. Preparation and characterization of Cu/GAC catalyst

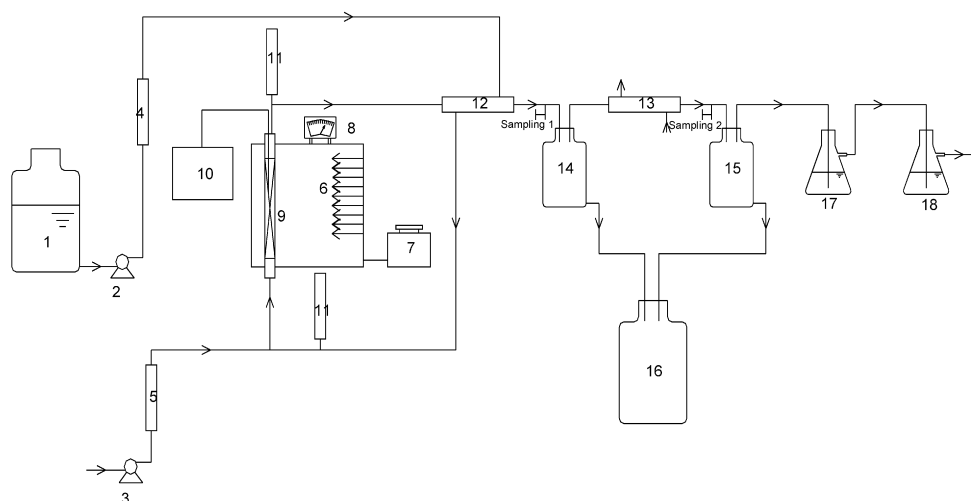
Coal-based GAC, obtained from Shanghai Zhenghai Activated Carbon Co. Ltd, China, was sieved firstly with 20 mesh screen to obtain 1–4 mm size granules, then immersed in 8%–10% hydrochloric acid (HCl) for 18 h, and then seethed by steam for 2 h, then rinsed repeatedly with deionized water until the pH 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. Pre-treated GAC were impregnated firstly with aqueous solution of analytical grade copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) (stoichiometric 10 wt.%), then the suspension was mixed at 250 rpm for 2 h and dried at 105 °C for 8 h. The dried catalyst samples were calcined in an oven at 400 °C for 4 h with nitrogen gas at a flow rate of 600 mL min^{-1} , and copper nitrate was decomposed to copper oxides that combined with GAC firmly during calcination. And then the catalyst was reduced by hydrogen gas at 70 mL min^{-1} at 350 °C for 4 h. Finally, the Cu/GAC catalyst was taken out after cooled down to room temperature 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 was determined by X-ray diffraction (XRD) using a diffractometer with Cu $K\alpha$ radiation (model, Shimadzu LabX-6000). The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. The average size of the Cu grain was calculated using Scherrer's equation, and the penetration depth of the Cu was evaluated by skin depth.

2.2. Microwave assisted catalytic oxidation of PNP

A schematic diagram of the experimental setup has been showed in previous study [6], 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 catalyst, was inserted vertically in the MW oven and served as a fixed bed reactor. A sheltered type-K thermocouple was used to measure the temperature of the bed.

The catalyst pre-adsorbed PNP firstly, and then was packed into the reactor so as to eliminate the adsorption effect of GAC on PNP degradation, then PNP solution and air were mixed and pumped into the fixed bed reactor, wherein PNP was degraded on the surface of the catalyst under microwave irradiation. The effluent exchanged heat with the influent through a heat



(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.

Fig. 1. Schematic diagram of experimental setup.

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 discharged.

2.3. Analytical methods

PNP was analyzed by a high-performance liquid chromatograph (HPLC) (JASCO, PU-1580, Japan) equipped with UV detector (UV-1575) and reverse-phase column (250 × 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. The peak of PNP could be observed at 5.9 min and separated clearly from the intermediates. PNP quantification was performed by external standard method, and the detection concentration of PNP was between 5 and 50 mg L⁻¹, based on the calibration curve (R^2 0.9998).

TOC analyzer (TOC-V_{CPH}, Shimadzu, Japan) was employed to determine the residual amounts of organic substances in the effluent to investigate the mineralization degree of PNP solution.

Textural properties of GAC samples were measured by nitrogen adsorption/desorption isotherms at 77 K with a Micromeritics ASAP 2010 sorptometer. The measurement of the surface area was carried out using Brunauer–Emmett–Teller (BET) method [10], and micropore analysis was performed using *t*-method [11], the pore size distributions were calculated by Barrett–Joyner–Halenda (BJH) equation [12].

3. Results and discussion

3.1. Characterization of GAC and Cu/GAC catalyst

It is well known that metal can reflect MW so as to be used widely as shielding material for MW device, however, quartz glass and polytetrafluorethylene are almost no absorption and block to MW so that can be taken as materials for reactor. In order to investigate the effect of loaded Cu on microwave-absorbing capacity of Cu/GAC catalyst, 3 g of Cu/GAC catalyst and dried GAC were put into a quartz tube, respectively, and then radiated by microwave in 800 W. The variation of temperature was measured by a sheltered type-K thermocouple [13], and the results were shown in Fig. 2. It was seen that GAC and Cu/GAC could both absorb microwave energy strongly, and the temperature rose rapidly and exceeded 1000 °C within 20 s. There are no apparent difference in microwave-absorbing capacity between GAC and Cu/GAC catalyst. Why loaded Cu has no effect on microwave-absorbing ability of the Cu/GAC catalyst? In order to explore the reason, Cu/GAC catalyst was characterized by SEM, EDX and XRD, and the photographs were shown in Figs. 3–5.

It could be seen in Fig. 3 that Cu particles dispersed asymmetrically on the surface of GAC, and had irregular shapes and different sizes. The sizes of Cu grains varied from 0.3 to 1.5 μm and the average size was 0.6 μm. Because the temperature of calcination and reduction were both much lower than the melting point of Cu (1083 °C), decomposition and reduction of Cu salts and Cu oxides had been conducted slowly during the preparation of Cu/GAC catalyst in order to obtain the smaller Cu grains and not destroy the structure of GAC simultaneously. Reaction

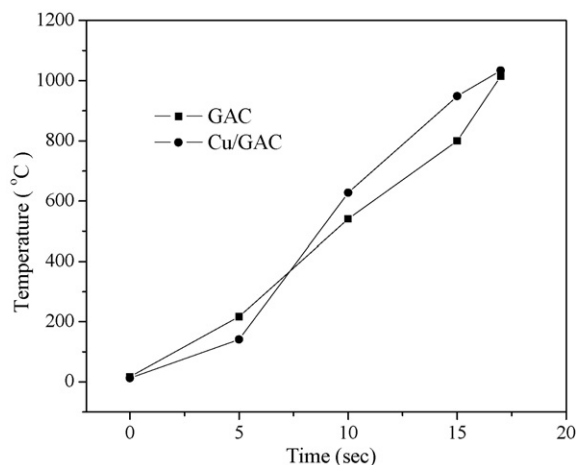


Fig. 2. The rising temperature curves of GAC and Cu/GAC catalyst in the microwave field.

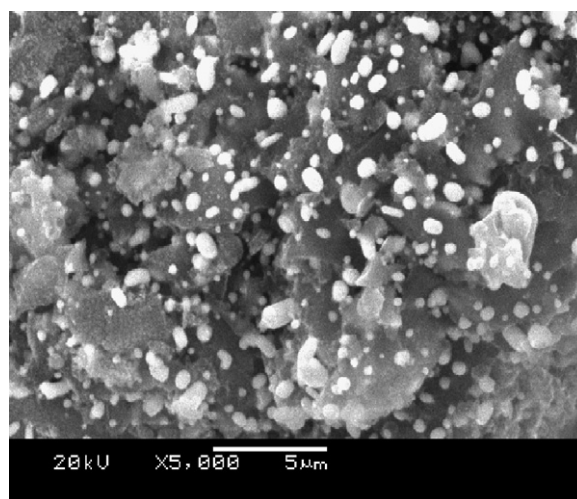


Fig. 3. SEM of Cu/GAC catalyst prepared by conventional impregnation method.

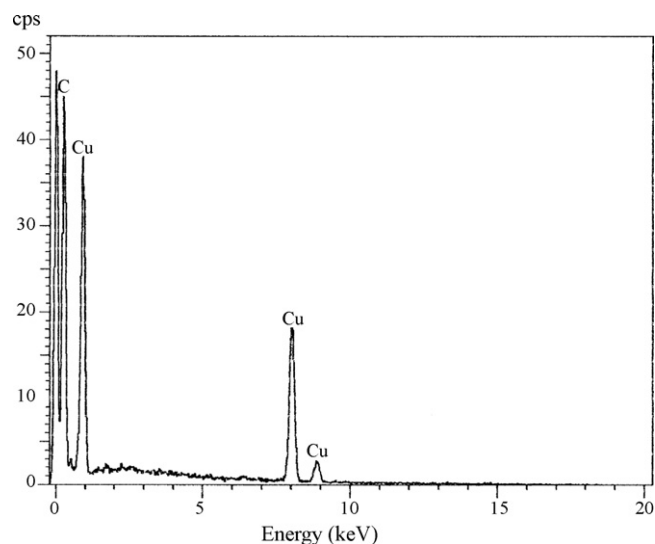


Fig. 4. Element analysis of Cu/GAC catalyst by EDX.

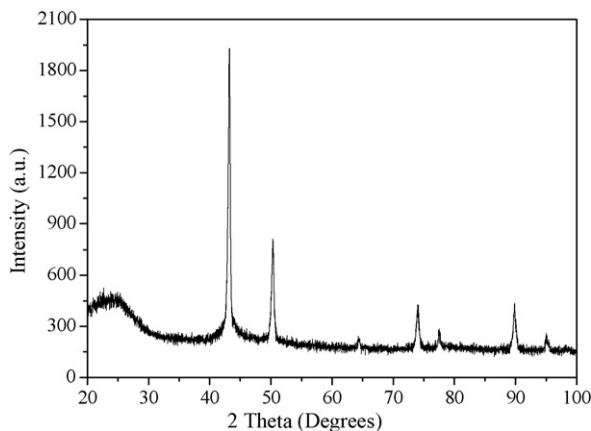


Fig. 5. XRD of Cu/GAC catalyst.

was happened in the sites where copper nitrate was adsorbed. The reason for asymmetric distribution and different sizes of Cu particles was speculated to be connected with the asymmetrical dispersal of Cu salts and Cu oxides on the surface of GAC, which was caused probably by the thermal diffusion in the process of dryness.

Generally, microwave can penetrate metallic particle when its size is lower than a given value, although metal, such as copper, can reflect and transmit microwave as shielding material. The depth of penetration can be calculated by skin depth [14] as follows:

$$\delta = \sqrt{\frac{2}{\omega\mu_0\sigma}} \quad (1)$$

Where δ is the skin depth, ω is the angular frequency, μ_0 is the permeability of free space ($\mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1}$) and σ is the electric conductivity. For Cu, σ is $5.81 \times 10^7 \text{ } \Omega^{-1} \text{ m}^{-1}$, and microwave frequency 2450 MHz, so the skin depth of Cu is calculated to be $1.3 \text{ } \mu\text{m}$ based on equation (1). It is bigger than $0.6 \text{ } \mu\text{m}$, the average size of Cu particle on the surface of GAC, so microwave can penetrate Cu particles. The reason for the rising temperature of Cu/GAC catalyst in the field of microwave was attributed to the loss of penetration and strong microwave-absorbing capacity of GAC.

Fig. 4 showed an element composition of Cu/GAC catalyst. It could be seen that there were only two elements of carbon and copper existing in the catalyst, and nitrogen or oxygen element was not found. It indicated that Cu nitrate and Cu oxides were decomposed and reduced completely in the process of preparation. Fig. 5 displayed XRD pattern of Cu/GAC catalyst. Sharp intensive peaks were observed at $2\theta = 43.2^\circ$, 50.34° and 70.01° , which were the positions of the characteristic peaks of metal Cu and showed good crystallinity. It indicated that elemental Cu in the catalyst was zero-valent Cu, which was consistent with the EDX analysis. The average size of Cu crystal could be calculated based on Scherrer's equation as follows:

$$D = \frac{0.89\lambda}{\beta \cos \theta} \quad (2)$$

Where D is the size of crystal, λ is the wavelength of X-ray radiation (0.15406 nm for Cu $K\alpha$ radiation), β is the full width at half maximum (FWHM), and θ is the diffraction angle. According to the data of XRD and formula (2), the size of Cu crystal was calculated to be 23.7 nm , which was much lower than the size of Cu particles ($0.3\text{--}1.5 \text{ } \mu\text{m}$) observed in SEM photograph. Therefore, it was speculated that those big Cu particles, distributing asymmetrically on the surface of the catalyst, were formed by the agglomeration of lots of Cu crystallites. Different sizes of Cu particles were due to different agglomerating amounts of Cu crystals.

3.2. Adsorption isotherms of PNP on GAC and Cu/GAC

GAC has a strong adsorption capacity for organic compounds and is used widely as adsorbent in purifying air, drinking water and wastewater [15]. However, we are interested in the degradation of PNP by microwave and not in the adsorption by GAC in this study, so the adsorption capabilities of Cu/GAC and GAC for PNP should be evaluated in terms of their adsorption isotherms. The adsorption experiments were carried out at 60°C , which is close to the temperature of the influent after heat exchange with the effluent (seen in Fig. 8), and the results were shown in Fig. 6.

It can be seen from Fig. 6 that Cu/GAC and GAC reached equilibrium simultaneously while the equilibrium adsorption amount (q) reached 370 mg g^{-1} , the corresponding equilibrium concentration (C_e) was higher than 4000 mg L^{-1} . Metal Cu particles occupy a part of adsorption sites of GAC, but calcination and reduction can remove impurity, such as sulfur, phosphor and organic matters etc, to clean the inner pores of GAC, which improve the adsorbing capacity of GAC. As a result of the two effects, the adsorption capability of Cu/GAC remained the same level as GAC has. The adsorption data is higher than that in our previous report [5], which is due to different sizes of GAC. In this work, the initial concentration (C_0) of PNP solution was around $1700\text{--}1800 \text{ mg L}^{-1}$, q value was determined to be 330 mg g^{-1} .

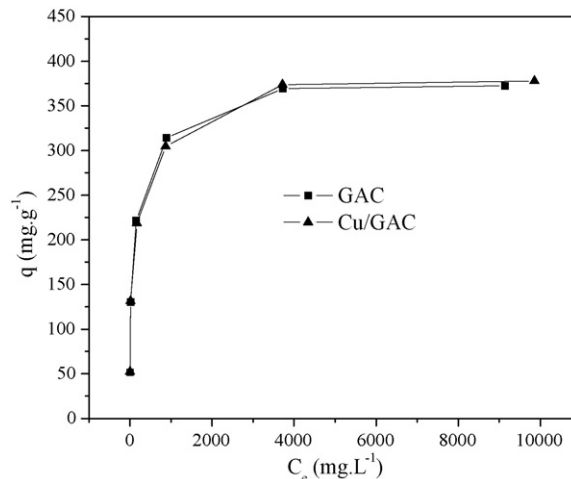


Fig. 6. Adsorption isotherms of PNP onto GAC and Cu/GAC catalyst at 60°C .

3.3. Microwave assisted catalytic oxidation of PNP

Based on the q value (330 mg g^{-1}) and the catalyst amount, 17.5 g PNP were pre-adsorbed onto 52.5 g Cu/GAC catalyst and GAC, respectively, in advance. In this way, we could confirm that the decay of PNP concentration resulted from degradation, not from adsorption. The effect of parameters and PNP concentration variation at the beginning of experiment were discussed in former work [5], therefore, microwave power (P_{MW}) decreased to 400 W and other parameters kept constant, such as PNP solution flow (Q_{S}) 6.4 mL min^{-1} (corresponding to hydraulic retention time (HRT) 16 min) and air flow (Q_{A}) 120 mL min^{-1} , were applied to treat PNP solution with C_0 1734 mg L^{-1} using Cu/GAC catalyst in this study. Experiment using GAC was also carried out under the same conditions as a comparison, and the results were illustrated in Fig. 7.

It can be seen from Fig. 7 that Cu/GAC catalyst showed higher PNP degradation and TOC removal than GAC under microwave irradiation. After 5 h of operation, PNP concentration decreased from initial 1734 mg L^{-1} to 142 mg L^{-1} , corresponding to 91.8% PNP removal, but only 69.2% PNP were degraded

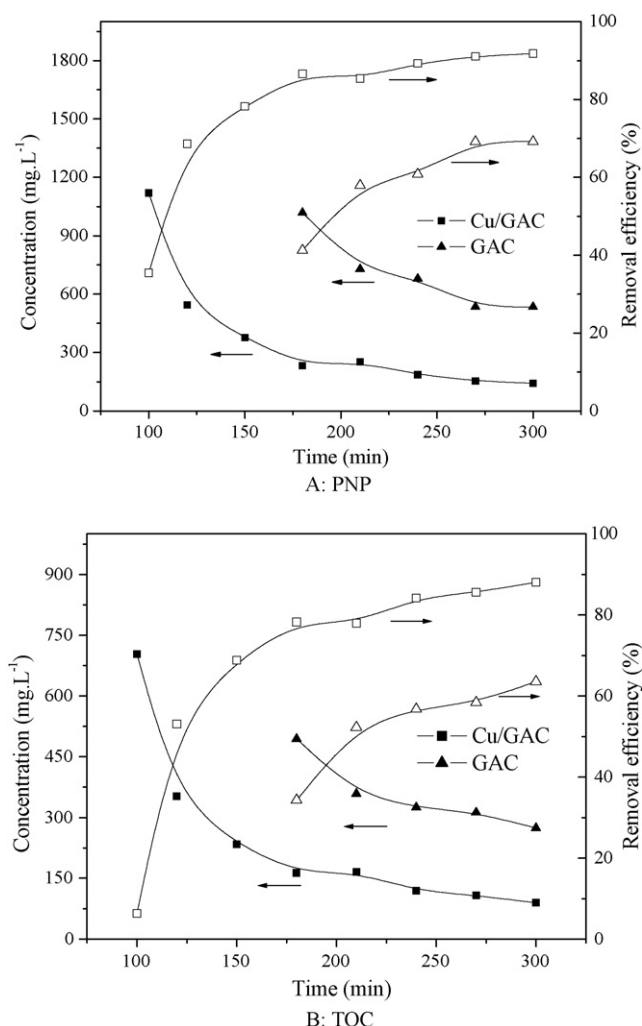


Fig. 7. Comparison of Cu/GAC and GAC for the degradation and mineralization of PNP.

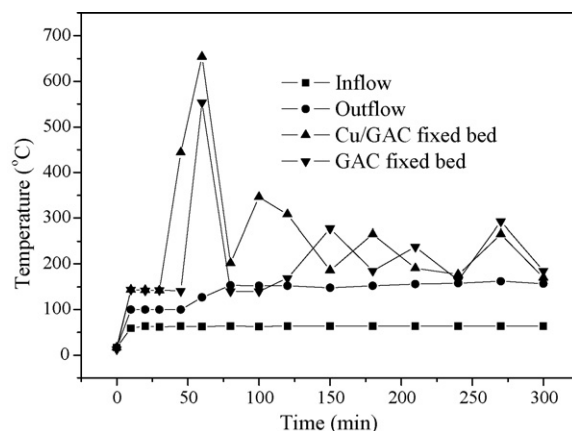


Fig. 8. Temperature curves of the influent, the effluent, Cu/GAC fixed bed and GAC fixed bed.

by GAC. A similar pattern appeared to TOC removal, TOC concentration reduced from 752 to 89.5 mg L^{-1} at 5 h , corresponding to 88% TOC removal for Cu/GAC catalyst, but 56.8% TOC removal for GAC at the same time. PNP degraded were mostly mineralized by Cu/GAC. It inferred that Cu and its oxides apparently accelerated the degradation and mineralization of PNP, and played a role of “reaction centre” in the process of degradation. Gomes et al. [16] reported that the activity of catalyst was correlated with the exposed metal area, and hydrogen abstraction occurred at the metal surface and a long elementary chain reaction proceeded subsequently. Cao et al. [17] suggested that the high activity of Pt/AC (activated carbon), used in CWAO of wastewater containing ammonia and phenol, could be due to the interaction between Pt and AC surface, although this interaction has not yet been elucidated. In this work, the synergic effect between Cu and GAC must exist in reaction, which showed a higher catalytic activity and a better PNP removal for Cu/GAC catalyst than GAC.

During reaction, the temperatures of fixed beds, the influent and the effluent were recorded and shown in Fig. 8.

It showed that the temperature of Cu/GAC fixed bed or GAC fixed bed had big fluctuation at the beginning of experiment, and even attained $650 \text{ }^{\circ}\text{C}$ at 60 min . It was caused by desorption and oxidation of pre-adsorbed PNP. After running 80 min , the reaction was in steady state and the surface temperature of Cu/GAC or GAC fixed bed varied from 200 to $300 \text{ }^{\circ}\text{C}$. Usually, at about 250 – $320 \text{ }^{\circ}\text{C}$, practically all compounds can be completely transformed [18]. Therefore, PNP could be easily degraded and mineralized on the surface of Cu/GAC catalyst. Initial PNP solution was preheated and its temperature kept constantly at $64 \text{ }^{\circ}\text{C}$, and the temperature of the effluent was about 150 – $160 \text{ }^{\circ}\text{C}$ in steady state.

3.4. Stability of experiment for Cu/GAC catalyst and GAC

In order to investigate the activation and stability of Cu/GAC catalyst, the experiment was carried out for 800 min under conditions of C_0 1778 mg L^{-1} , P_{MW} 500 W , Q_{S} 6.4 mL min^{-1} (HRT 16 min) and Q_{A} 120 mL min^{-1} . For GAC, C_0 was 1700 mg L^{-1}

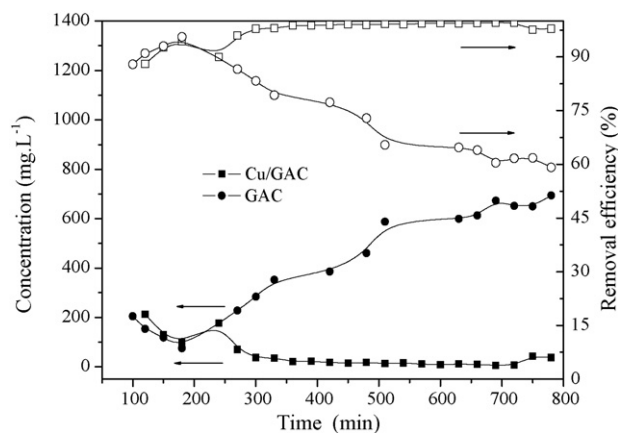


Fig. 9. Stability of Cu/GAC catalyst in the treatment of PNP solution under microwave irradiation.

and other parameters were the same as those of Cu/GAC catalyst. The results were given in Fig. 9.

As seen in Fig. 9, PNP concentration in the effluent was kept at 6–20 mg L⁻¹ and PNP removal higher than 98% for Cu/GAC catalyst in the whole of runs. A high catalytic activation and good stability were observed. Compared with Cu/GAC catalyst, PNP removal decreased from 90% to 60% for GAC during the whole course. Therefore, it was obvious that loaded Cu not only provided more chance for pollutants to be oxidized, but also was benefit to maintain high PNP removal. It was speculated that the load of Cu enhanced effectively the porous structure of GAC and the structure of Cu/GAC catalyst had no obvious change under microwave irradiation so that the Cu/GAC catalyst could keep a high catalytic level and good stability during the course of reaction.

According to the BET method and the analysis of pore size distribution, it was found that the specific surface area of GAC decreased from 1086 to 843 m² g⁻¹ and micropore volume decreased from 0.2616 to 0.1872 cm³ g⁻¹, respectively, after reaction, and the amount of micropore was also lessened. However, the molecule diameter of PNP belongs to the range of micropore (<2 nm). It was speculated that the change of GAC structure, mainly the decrease of micropore volume, resulted in the decrease of PNP removal. In the case of Cu/GAC catalyst, the catalytic activity from the synergy effect between Cu and GAC would cover the effect of micropore volume decrease during the course of reaction so that the operation could keep a high and stable level.

4. Conclusions

Cu/GAC catalyst prepared by conventional impregnation method showed a strong microwave-absorbing ability and a high adsorption capability for PNP as GAC. The loss of penetration and strong microwave-absorbing capacity of GAC resulted in a rapid temperature increase for Cu/GAC catalyst under microwave irradiation. Compared with GAC, Cu/GAC catalyst showed higher catalytic degradation and mineralization efficiencies in microwave assisted catalytic oxidation of PNP. A higher catalytic activity and better stability of Cu/GAC catalyst than

GAC were also observed in the course of reaction. The load of Cu enhanced obviously the structure of GAC. In this study, the reaction of microwave assisted catalytic oxidation is carried out under a milder condition (ambient pressure) than CWAO, which could show a better application prospect than CWAO in future.

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References

- [1] D.A. Jones, T.P. Lelyveld, S.D. Mavrofidis, S.W. Kingman, N.J. Miles, Microwave heating applications in environmental engineering—a review, *Resour. Conserv. Recy.* 34 (2002) 75–90.
- [2] L.X. Xia, S.W. Lu, G.Y. Cao, Demulsification of emulsions exploited by enhanced oil recovery system, *Separ. Sci. Technol.* 38 (2003) 4079–4094.
- [3] C.Y. Cha, D.S. Kim, Microwave induced reactions of sulfur dioxide and nitrogen oxides in char and anthracite bed, *Carbon* 39 (2001) 1159–1166.
- [4] X.T. Liu, X. Quan, L.L. Bo, S. Chen, Y.Z. Zhao, Simultaneous pentachlorophenol decomposition and granular activated carbon regeneration assisted by microwave irradiation, *Carbon* 42 (2004) 415–422.
- [5] L.L. Bo, X. Quan, S. Chen, H.M. Zhao, Y.Z. Zhao, Degradation of *p*-nitrophenol in aqueous solution by microwave assisted oxidation process through a granular activated carbon fixed bed, *Water Res.* 40 (2006) 3061–3068.
- [6] L. Bo, S. Chen, X. Quan, X. Liu, H. Zhao, Microwave assisted wet oxidation of *p*-nitrophenol, *Sci. China Ser. E* 48 (2005) 220–232.
- [7] L. Lei, X. Hu, H.P. Chu, G. Chen, P.L. Yue, Catalytic wet air oxidation of dyeing and printing wastewater, *Water Sci. Technol.* 35 (1997) 311–319.
- [8] X. Hu, L. Lei, H.P. Chu, P.L. Yue, Copper/activated carbon as catalyst for organic wastewater treatment, *Carbon* 37 (1999) 631–637.
- [9] B. Bhushan, A. Chauhan, S.K. Samanta, R.K. Jain, Kinetics of biodegradation of *p*-nitrophenol by different bacteria, *Biochem. Biophys. Res. Commun.* 274 (2000) 626–630.
- [10] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, *J. ACS* 60 (1938) 309–319.
- [11] B.C. Lippens, J.H. de Boer, Studies on pore system in catalysts V. The method, *J. Catal.* 4 (1965) 319–323.
- [12] E.P. Barrett, L.G. Joyner, P.P. alenda, The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms, *J. ACS* 73 (1951) 373–380.
- [13] J.A. Menéndez, E.M. Menéndez, A. García, J.B. Parra, J.J. Pis, Thermal treatment of active carbons: a comparison between microwave and electrical heating, *J. Microwave Power E. E.* 34 (1999) 137–143.
- [14] Q.H. Jin, S.S. Dai, K.M. Huang, *Microwave Chemistry (Chinese)*, Science Press, Beijing, 1999, pp. 1–2.
- [15] C. Moreno-Castilla, J. Rivera-Utrilla, M.V. López-Ramón, F. Carrasco-Marín, Adsorption of some substituted phenols on activated carbons from a bituminous coal, *Carbon* 33 (1995) 845–851.
- [16] H.T. Gomes, J.L. Figueiredo, J.L. Faria, Ph. Serp, Ph. Kalck, Carbon-supported iridium catalysts in the catalytic wet air oxidation of carboxylic acids: kinetics and mechanistic interpretation, *J. Mol. Catal. A-Chem.* 182–183 (2002) 47–60.
- [17] S. Cao, G. Chen, X. Hu, P.L. Yue, Catalytic wet air oxidation of wastewater containing ammonia and phenol over activated carbon supported Pt catalysts, *Catal. Today* 88 (2003) 37–47.
- [18] G. Deiber, J.N. Foussard, H. Debellefontaine, Removal of nitrogenous compounds by catalytic wet air oxidation: Kinetic study, *Environ. Pollut.* 96 (1997) 311–319.