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Efficient degradation of 4-chloro-2-nitrophenol using photocatalytic ozonation with nano-zinc oxide impregnated granular activated carbon (ZnO–GAC)

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ABSTRACT

In this paper, the catalytic capability of nano-zinc oxide impregnated granular activated carbon (ZnO–GAC) in photocatalysis and ozonation hybrid system was studied. ZnO–GAC hybrid was prepared by co-precipitation method. FeSEM, XRD, FTIR, EDAX were applied to characterize the structure and morphological feature. 4-chloro-2-nitrophenol (4C2N) was employed as model pollutant to evaluate the catalytic ability of ZnO-GAC. The effect of GAC content and stability of ZnO-GAC in photocatalytic ozonation was also evaluated. The findings indicated that photocatalytic ozonation of 4C2N with ZnO-GAC hybrid was a very efficient technique for 4C2N degradation. The TOC removal efficiency found 100% by ZnO-GAC/O_3/UV in 55 min, which is 1.20 times as great as that of ZnO/O_3/UV process. Moreover, the catalytic capability of ZnO–GAC hybrid remained very stable after recycling for five sequential tests. This enhancement is due to the enhanced separation efficiency of photo-generated charges, which simplified the electrons trapping by ozone and improved the yield of hydroxyl radical.

Keywords: 4-chloro-2-nitrophenol; Photocatalytic ozonation; ZnO–GAC

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1. Introduction

Today, the prevention of the introduction of pollutants into the environment is very important. In addition, searching for ways to remove contaminants is another important topic [1–3].

Chloronitrophenols (CNPs) are a group of chemicals that are widely used in the chemical industry, mainly in the pharmaceuticals, dyes, pigments, agricultural chemicals and pesticides [4–6]. 4-Chloro-2-nitrophenol (4C2NP) is one of the main isomers of CNP that is present in some industrial effluents due to its wide range application [7,8]. This compound is toxic, recalcitrant and persistent towards biodegradation which is known to cause severe contamination issues in water bodies due to electron withdrawing features of chloro-nitro groups [9]. Thus, it is highly recommended to utilize an effective method to removal of 4C2NP from wastewater before its discharge in order to reduce their adverse effects on the ecosystems and human health. In previous studies, a number of physicochemical techniques such as ultrasonic degradation [10], solvent extraction [11], photocatalytic degradation [12], ozonation [13] and decomposition by Fenton reagents [14] have utilized for abatement of effluents containing phenolic substances.

As stated above, ozonation is an appropriate method which is widely used in oxidation of pollutants [15,16]. However, it is very hard to reach high degradation degree

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for plain ozonation because of its selective reaction with organics [17]. One approach to promote ozone oxidizing capability is application of photocatalysis and ozonation simultaneously that considered as photocatalytic ozonation [18,19]. In this situation, the dissolved ozone can get photo-released electrons from photocatalyst and induce generation of hydroxyl radicals (°OH), and also ozone decomposition into °OH is facilitated [20,21]. Among photocatalysts, ZnO appears to be one of the most advisable and suitable options for photocatalytic ozonation [22]. However, the photocatalytic efficiency of ZnO is restricted by fast recombination ecombination of electrons and holes and the limited photoresponding range [23,24]. In order to enhance its photocatlytic performance, coupling ZnO with conjugative structure carbon materials has been proposed [25–27]. It is shown that when ZnO is coupled with carbon materials, carbon can effectively work as electron-acceptor/transport material to facilitate the transfer of photo-induced electrons. This phenomena can promote the efficiency of photocatalytic process [23,26]. According to these features of carbon materials, we considered immobilized ZnO on granular activated carbon (ZnO/GAC) hybrid material be a suitable option in photocatalytic ozonation process.

As mentioned above, ZnO/GAC nano-composite was prepared by co-precipitation method. Its capability as catalyst was investigated in photocatalytic ozonation hybrid system to remove 4C2NP from aqueous solution in this research. Moreover, in comparison with conventional ZnO/UV/O_3 process, the enhanced removal performance of photo-induced electrons can improve the reaction with ozone and promote the synergistic effects, so to obtain effective degradation of organic pollutant. Finally, stability of ZnO-GAC in photocatalytic ozonation was investigated.

2. Materials and methods

2.1. Materials

The GAC used in current research was obtained from the Merck (Germany). To eliminate the impurities, GAC before being utilized as a support for ZnO was thoroughly rinsed with distilled water and then dried at 100°C for 24 h. Zinc chloride ($ZnCl_2$), sodium thiosulphate, potassium iodide sodium hydroxide (NaOH) and hydrochloric acid (HCl) were of laboratory reagent grade (Mecrk, Germany) and used without further purification. 4-chloro-2-nitrophenol as a model pollutant was purchased from Chem-service (USA).

2.1. Synthesis and characterization of ZnO/GAC

The obtained GAC was dried in an electric furnace at 1000°C for 4 h, and sieved (50 meshes). Co-precipitation method was applied to prepare ZnO-GAC nano composite [28]. A 0.1 mol/L solution of $ZnCl_2$ was prepared by dissolution of its powder into distilled water. GAC was added to the solution of zinc chloride in the ratio of 2:1 (w/w). NaOH solution was added gradually to the precursor solution with stirring for 7 h to obtain a white, gelatinous zinc oxide/GAC product. The obtained materials was centrifuged and then dried at 90°C in oven for 4 h. Prepared photocatalyst was washed with distilled water for the elimination of free ZnO particles. Fourier transforms infrared spectroscopy (FTIR, Tensor 27, Bruker, Germany), X-ray diffraction (XRD, BRUKER D8ADVANCE) with Cu-K (α–radiation), scanning electron microscopy (SEM, TESCA MIRA3, Czech Republic) and energy dispersive X-ray spectroscopy (EDX, TESCA MIRA3, Czech Republic) instruments were employed for characterization of the prepared ZnO/GAC. Eventually, specific surface area, and pore volume and pore size of the composites was quantified by nitrogen gas adsorption analyzer.

2.2. Photocatalytic ozonation procedure

A semi-batch stirred glass reactor (2L) was used for the ozonation photocatalytic activity measurements in the degradation of 4C2NP, where ozone gas was poured continuously into a reactor. A volume of 1 L of aqueous solution (containing 10 mg/L of 4C2NP and 0.5 g of catalyst) that was thoroughly mixed with a magnetic stirring bar. The ultraviolet light source consisted in a high pressure mercury lamp (Toshiba class, SHL-100UVQ-2, 100 W and 1.0–1.5 mW/cm^2) that placed in a quartz thimble. Ozone was produced by a laboratory ozone generator (X200, Baku) and the gas flow rate was kept constant at mL/min, and the dosage of ozone was 5.64 mg/L. In a photocatalytic mode of experiments, the ozone generator was turned off and pure oxygen was diffused into the reactor. To adjust the continuous reaction of ozonation in the samples $Na_2S_2O_3$ solution was utilized. In order to prevent the evaporation of liquid ozone the reactor was sealed during the reaction. All runs were done for three times at 25 ± 2 °C for verification of all results. In the catalyst recycle tests, the recovery of ZnO/GAC was measured as ≥96% in every cycle.

2.3. Analytical methods

High performance liquid chromatography (HPLC, CECIL, 4100) with a UV detector (UV/VIS model 4200) was utilized for quantified the concentration of 4-chloro-2-nitrophenol. Spherisorb ODS-3 (5 mL, 150 · 4.6 mm i.d.) column was used. The mobile phase was a mixture of cetonitrile and water (70:30% v/v) and 0.2% acetic acid at a flow of 1.0 mL/min. Before measurement in all of the experiments, sampling were done at intervals and filtered by 0.45 μm microfilters to collect the filtrate. 744 pH-meters (O Metrohm) were applied to measure the pH of solution. TOC-VCSH analyzer was applied to determine the Total Organic Carbon (TOC). All of the tests were done at ion temperature of 25°C.

3. Results

3.1. Characterization of ZnO and ZnO/GAC

The morphology of ZnO and ZnO/GAC is observed with Field emission scanning electronic microscopy (FE-SEM). As shown in the inset of Fig. 1a,b, both plane ZnO and ZnO/GAC are uniform in surface morphology. However, the SEM image of ZnO/GAC indicates densely packed particles with less uncoated spaces in comparison with ZnO.

The X-ray diffraction patterns (XRD) of ZnO and ZnO/GAC are presented in Fig. 2b. Peak placed at 2-theta of 32, 34 and 36 degrees are attributed to 100, 002 and 101 planes of hexagonal wurtzite ZnO. The average crystallite size of ZnO nanoparticles was calculated using the Debye–Sherrer's equation. Based on this equation the mean crystal size of the ZnO and GAC-modified ZnO was calculated as 56.4 and 54.1 nm, respectively. This shows the insignificant influence of imbobilization on the size of pure ZnO nanoparticles. This can be confirmed by reduction of total pore volume in the carbon upon coated with ZnO (Table 1).

EDX analyze is used in conjunction with FE-SEM to characterize the elemental composition of the ZnO and ZnO/GAC (Fig. 3a,b). According to Fig. 3, share of Zn and O in the ZnO sheets was 58 and 43, and share of C, Zn and O in the ZnO/GAC was series 45, 34 and 11%, respectively.

Table 1
Some features of GAC and the synthesized GAC/ZnO composite

Characteristics	Unit	Value	
		GAC	ZnO/GAC
Structure	–	Micropore	Micropore
Average pore diameter	Nm	1.69	1.71
BET	m^2/g	1209	1042
BET Constant	–	909.45	721.87
Monolayer volume	cm^3/g	281.67	241.43
Pore volume (P/P0 = 0.990)	cm^3/g	0.5212	0.4471

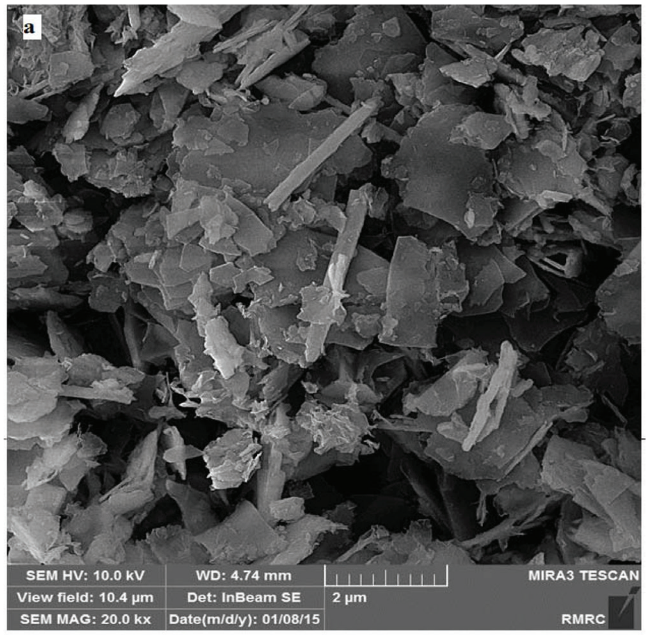

Fig. 1a. FESEM images of samples; pure ZnO.

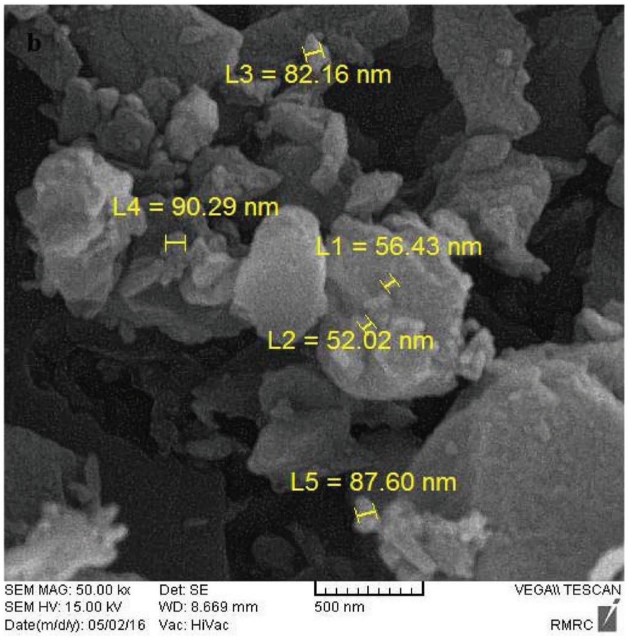

Fig. 1b. FESEM images of samples; Immobilized ZnO on granular activated carbon.

The result of BET analysis about GAC and the ZnO/GAC catalysts are given in Table 1. As shown in Table 1, the BET specific surface areas of GAC and the ZnO/GAC catalysts were 1209 and 102 m^2/g, respectively, and pore volumes of GAC and the ZnO/GAC catalysts were 0.5212 and 0.4471 cm^3/g, respectively.

Fig. 4a,b show the FT-IR spectra of ZnO and ZnO/GAC. For ZnO, there are four characteristic peaks in the in the range of 400–4000 L/cm. The peaks at 460, 730, 915 and 3500 L/cm are belonging to ZnO. This peak is seen in the FTIR patterns of immobilized ZnO on GAC, too.

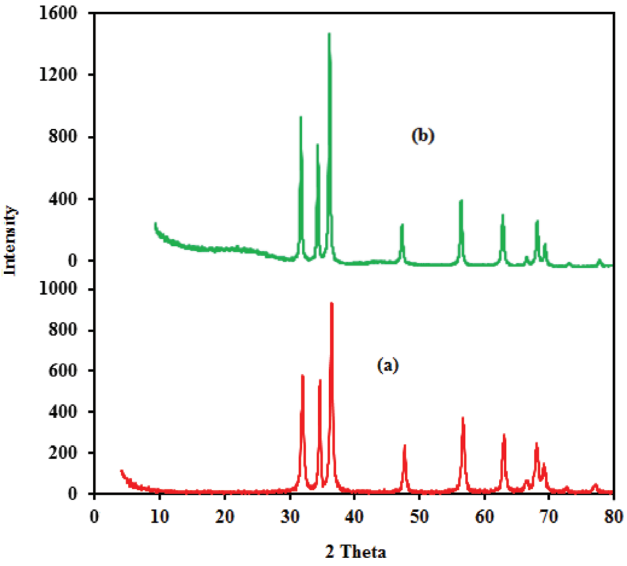

Fig. 2. Typical XRD patterns of samples; (a) pure ZnO (b) immobilized ZnO on granular activated carbon.

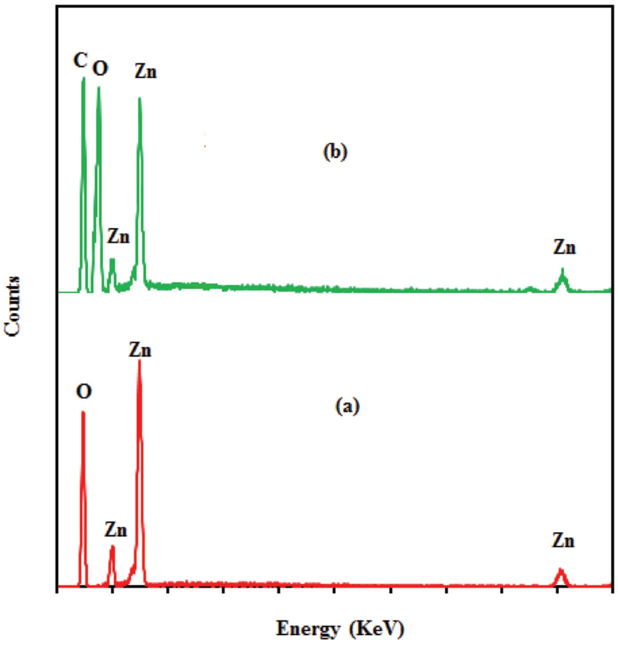

Fig. 3. Typical EDX patterns of samples; (a) pure ZnO (b) immobilized ZnO on granular activated carbon.

3.2. Photocatalytic degradation of C2NP with ZnO –GAC

The photocatalytic degradation of 4C2NP with ZnO–GAC under UV light irradiation is studied. Direct photolysis of 4C2NP employed as control. The findings are depicted in Fig. 5. As shown in Fig. 5 (a) 41% of 4C2NP is eliminated for direct photolysis during 16 min. In the presence of ZnO, 81% of 4C2NP is eliminated. In compare to pure ZnO, the removal efficiency of 4C2NP is increased by as-prepared ZnO/GAC. 94.0% of 4C2NP is degraded during 16 min.

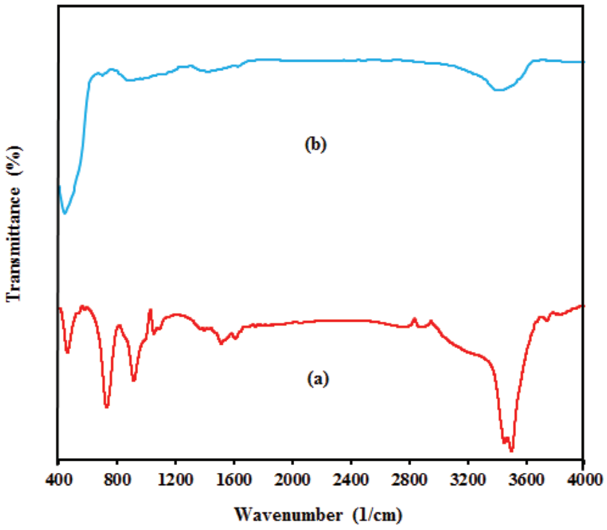

Fig. 4. FT-IR image of samples; (a) pure ZnO (b) immobilized ZnO on granular activated carbon.

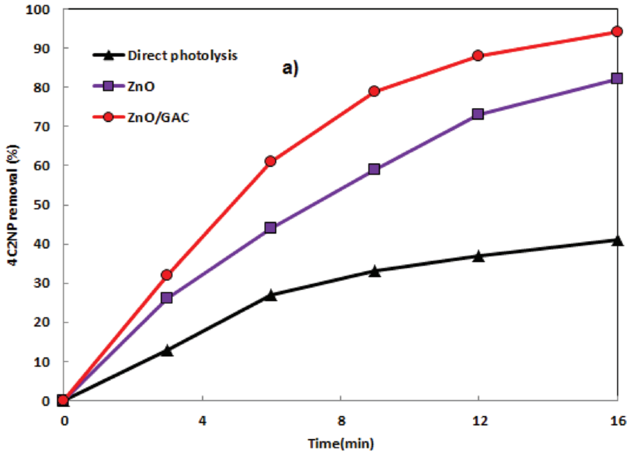

Fig. 5. Photocatalytic removal of 4C2NP (a) 4C2NP removal, (b) TOC removal (catalyst dose: 0.5 mg/l; initial concentration of 4C2NP solution: 10 mg/l; temperature: 25°C).

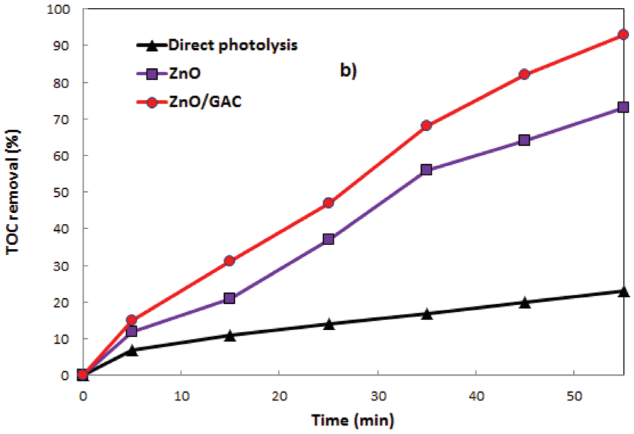

Fig. 5. Photocatalytic removal of 4C2NP (a) 4C2NP removal, (b) TOC removal (catalyst dose: 0.5 mg/l; initial concentration of 4C2NP solution: 10 mg/l; temperature: 25°C).

The TOC elimination efficiency for 4C2NP degradation is depicted in Fig. 5b. During 55 min, The TOC elimination efficiency of 4C2NP with ZnO and ZnO/GAC was 73% and 93%, respectively.

3.3. Photocatalytic ozonation of 4C2NP with ZnO/GAC

Fig. 6 indicates the removal of 4C2NP by various processes in the presence of ozone. As shown in Fig. 6a, ZnO/GAC-UV-O_3 process has the highest capability for 4C2NP degradation. In addition to, this enhancement was shown more clearly in TOC elimination. In the absence of UV and catalysts, only 21% of TOC removal was resulted with ozonation alone after 55 min. In the presence of ZnO-O_3 and ZnO-GAC-O_3, the TOC removal slightly increases for 4C2NP removal. 23% and 25% of TOC is removed during 55 min in the presence of ZnO-O_3 and ZnO/GAC-O_3, respectively. With UV irradiation, 51% of TOC is

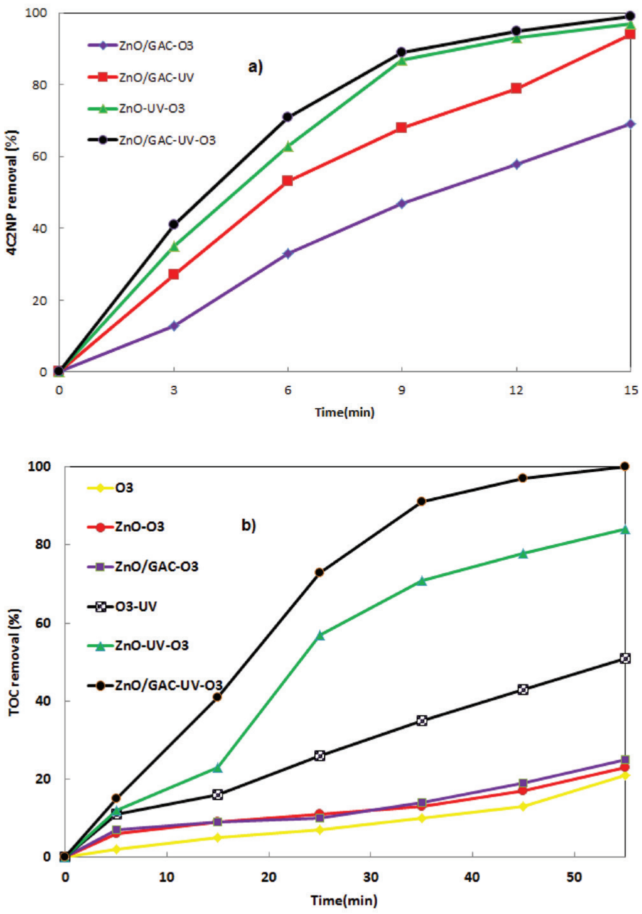

Fig. 6. 4C2NP removal (a) and TOC removal (b) efficiency by different processes in the presence of ozone.

degraded by O_3/UV. TOC and 4C2NP removal efficiency are 97% and 84% by ZnO/O_3/UV, respectively. After GAC is introduced into the catalyst, the TOC elimination reached 100% by ZnO/GAC-UV-O_3 in 55 min.

3.4. Effect of GAC content on ZnO/GAC catalytic activity

Fig. 7 indicates the TOC removal of 4C2NP for ZnO/GAC hybrid with various mass ratios. When the share of GAC which added into the ZnO precursor solution got to 0.02 g, catalyst had a highest catalytic efficiency that TOC removal by 100% in 55 min. However, the removal rate reduced gradually when the ratio of GAC increases more, but it remained more than that of alone ZnO.

3.5. Stability of ZnO/GAC in catalytic ozonation

The stability of the ZnO/GAC nanocomposite in photocatalytic ozonation is further studied by recycling for five sequential runs. The findings are shown in Fig. 8. After five sequential tests, the catalytic activity of ZnO/GAC declines slightly and still remains a high level. The TOC removal of 4C2NP decreased from 99.2% to 94.7%.

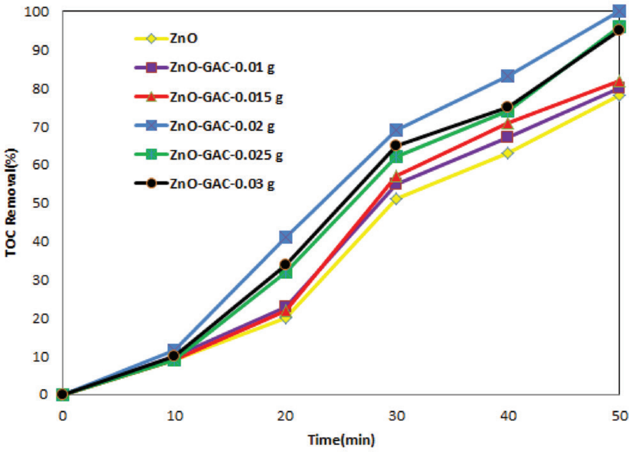

Fig. 7. TOC removal efficiency in ZnO/GAC/UV/O_3 process with GAC content.

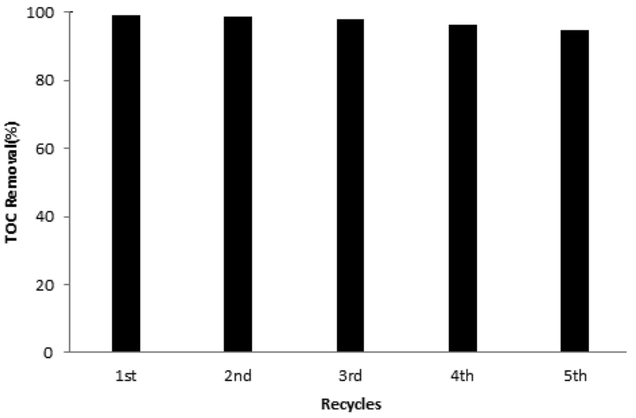

Fig. 8. TOC removal efficiency in 55 min by ZnO/GAC/UV/O_3 process for five cycles.

4. Discussion

According to the FE-SEM results, the surface of GAC was covered with ZnO nanosheets after immobilization. EDX analyses also clearly prove the presence of ZnO on the GAC. The band located at 710–890 L/cm indicates the existence of aromatic C–H stretching and a band located at 3500 L/cm is belong to the hydroxyl groups (–OH) [29]. XRD pattern of the ZnO and ZnO/GAC indicate a good crystal structure of ZnO nanoparticles even after immobilization on GAC. Based on Debye–Sherrer's equation the mean crystal size of the ZnO and GAC-modified ZnO shows the insignificant influence of imbobilization on the size of pure ZnO nanoparticles.The photocatalytic efficiency of both 4C2NP and TOC with ZnO/GAC was more than alone ZnO. This is attributed to the enhanced photo-induced electrons separation efficiency result from hetero-junction built between ZnO and GAC [30].

The dispersion of ZnO into the pore on GAC let to blocking those and consequently reduction in specific surface areas and pore volumes [31]. Arfaeinia et al. [32] also reported that metal oxides can reduce the BET area and the pore volume of the granular activated carbon.

This study also shows that ZnO/GAC-UV-O_3 process has the highest efficiency for both of 4C2NP and TOC removal. In the absence of UV and catalysts, only a small percentage of TOC removal was resulted with ozonation alone after 55 min. This suggests that the addition of GAC have no effect to the catalytic degradation of ozone in the absence of UV. In the presence UV irradiation, the degradation efficiency increases dramatically. This is due to the UV can intensify the decomposition of ozone. Ozone molecules absorbs UV wave below 320 nm and then reacts with water generating H_2O_2 [33]. Consequently, hydroxyl radical (·OH) are produced from hydrogen peroxides and improve the removal of 4C2NP [34].

When ozonation and photocatalysis are simultaneously conducted, 4C2NP removal rate is enhanced significantly. For ZnO/GAC/O_3/UV, various parallel reactions path are mostly contributing to the degradation of 4C2NP including: 1) homogeneous oxidation by ozone in the presence of UV, 2) heterogeneous photocatalytic ozonation reaction. In the presence of UV, ZnO was excited and the photo-induced electrons first transferred from the valence band to the conduction band. Because of the heterojunction built between ZnO and GAC, the photo-induced electrons then transferred to the GAC surface, which declined the electron–hole recombination and improved the removal efficiency [35]. On the other hand, the availability of electron on the ZnO is enhanced, which facilitated the electron capturing with ozone [36]. More °OH would be produced by the electron transfer and further reactions. Moreover, many holes are left on the valence band of ZnO because of the rapid consumption of photo-induced electrons. Both the two key issues as noted above improve the synergistic effects among photocatalysis and ozonation effectively. Finally, the degradation of 4C2NP is promoted [37]. It is obviously seen that the catalytic activity is improved gradually with raising the content of GAC. Nevertheless, the removal rate declined gradually when the ratio of GAC increases further, but it maintain larger than that of alone ZnO. It can be found that when the content of GAC increased initially, the transferring of photo-generated carriers and degradation of O_3 are improved. So, the catalytic activity for ZnO/GAC was improved [38]. After five sequentially runs, the catalytic activity of ZnO/GAC declined slightly and still remains a high level. This indicates that the ZnO/GAC catalyst has a good catalytic activity and stability. Finally, the results of this research show that ZnO-GAC/O_3/UV degrades the 4C2NP more quickly and more effectively in compare to biological methods [39,40].

5. Conclusions

In summary, ZnO/GAC nonocomposite was prepared by co-percipitation method. This nonocomposite showed efficient catalytic activity and degradation capability for photocatalytic ozonation of 4C2NP with UV light irradiation. Compared with alone ZnO, the improved catalytic capability majorly is due to enhanced separation efficiency of photogenerated charge, facilitate the transfer of photo-induced electrons trapping by ozone, which promote the photocatalytic ozonation efficiency. This study shows that ZnO/GAC nonocomposite is good option for water treatment and provides new insights for prepare of effective catalyst for photocatalytic ozonation.

Disclosure statement

No potential conflict of interest was reported by the authors.

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