



Microwave-granular activated carbon (MW-GAC) system for carbofuran degradation: Analysis of characteristics and recyclability of the spent GAC

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ABSTRACT

Granular activated carbon (GAC) is frequently used to remove pollutants from wastewater. However, the mechanism of pollutant removal by GAC is by adsorption and hence spent GAC should be regenerated and used for several cycles for minimizing the cost of treatment. In the present study, the characteristics of GAC and carbofuran removal mechanism were explored in a microwave-GAC (MW-GAC) system. Carbofuran removal by adsorption was 52% at a GAC loading of 0.8 g/L. However, complete carbofuran degradation from aqueous solution as well as from GAC surface was obtained within 30 min in a MW-GAC system. In addition, A COD removal efficiency of 72% was observed in the MW-GAC system at pH 8 and 80°C after 30 min. The degradation occurred mainly through cleavage of carbamate group and oxidation of furan ring. Carbofuran removal by adsorption was enhanced with MW exposed GAC due to the improvement in the surface property on exposure to MW. On the other hand, recyclability of MW exposed GAC in the MW-GAC system indicated > 99% degradation of carbofuran in all the three cycles tested. As a whole, complete degradation of carbofuran and the effective recycling of the spent GAC could be achieved in the MW-GAC system.

Keywords: Carbofuran; Microwave; Granular activated carbon; Degradation; Recyclability

1. Introduction

Carbofuran (2, 3-dihydro-2, 2-dimethylbenzofuran-7-yl methylcarbamate) is a broad spectrum systemic acaricide, insecticide, and nematicide included in the general group of the carbamate derivative pesticides [1]. The maximum acceptable carbofuran concentration in drinking water is 0.09 mg/L as per the USEPA [2]. The organic carbon partition coefficient (K_{OC}) of carbofuran is in the range of 14–160, which indicates that it is more mobile through leaching [3]. Moreover,

carbofuran removal through volatilization from soil is insignificant; however, some evaporation from plant may occur [4]. Thus, investigation of carbofuran control/treatment methodologies should be focused on techniques that are effective in the aqueous phase.

Physicochemical processes are widely used for rapid removal of biorefractory pollutants. Several chemical methods either independent or in conjunction have been employed for carbofuran removal such as anodic Fenton process [5], ultrasonic process [6], UV [7], ozone [8], UV/TiO₂ [9], UV/H₂O₂/Fe(III) [10], UV/Fe(III) [11], UV/TiO₂ or ZnO [12], Fenton Process [13], the combination of ultrasound with Fenton

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process [14], adsorption [15,16], and photocatalysis in presence of photosensitizers [17]. The applicability of the above-mentioned methods is restricted sometimes by the economic considerations or by the stringent operating conditions. Granular activated carbon (GAC) serves as an excellent adsorbent for variety of pollutants. Due to its porous structure and special surface reactivity, activated carbon is used as an adsorbent in air and water purification and catalyst in the chemical and petrochemical industries [18]. However, the efficiency of pollutant removal using GAC is less compared to other methods like advanced oxidation process (AOPs). The high cost of commercial activated carbon and expensive regeneration process restrict its use in pollutant removal based on economic considerations. Moreover, the disposal of highly contaminated GAC after the adsorption process is a major problem. An effective recycling of the spent GAC (pollutant adsorbed GAC) will overcome this problem.

Microwave (MW) is an energy composed of electric and magnetic fields. It is a form of electromagnetic waves with wavelengths of 1 mm to 1 m (frequency 300 MHz–300 GHz) [19]. GAC is an excellent MW absorbing material, which could absorb and convert MW energy into thermal energy [20]. Combination of MW and GAC has exhibited a tremendous improvement in the degradation efficiency compared to GAC alone [21]. Moreover, the MW regeneration of spent GAC has also been proposed as a potentially viable alternative to the traditional regeneration methods [22]. Therefore, the present study was performed to investigate carbofuran removal from aqueous phase and to delineate carbofuran adsorption on GAC and its degradation in presence of MW. In addition, the change in the surface characteristics of GAC in a MW-GAC system was examined and the recyclability of GAC in the MW-GAC system was analyzed.

2. Materials and methods

2.1. Materials

Carbofuran ($C_{12}H_{15}NO_3$) (>98% purity) was obtained from Shida Chemical Industries Taoyuan, Taiwan. GAC used in the experiments was coal-based and supplied by Tangshan Chemical Corporation, China. Sodium hydroxide (98% purity) and hydrochloric acid (analytical purity) were used for pH adjustments. Methanol (99.8% purity) was used for carbofuran analysis.

2.2. Reactor system

A modified-MW system with a MW oven, Pyrex vessel, and Teflon tube connector (Fig. 1) was used for

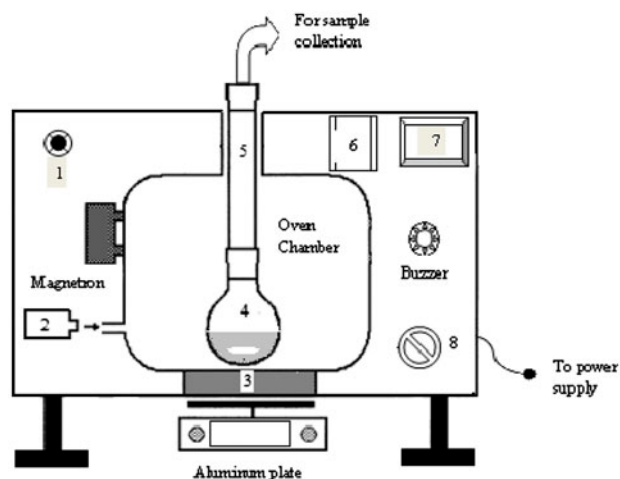


Fig. 1. Schematic diagram of the modified MW oven for MW-assisted carbofuran degradation study under pulsed MW heating: (1) power switch; (2) infrared pyrometer; (3) magnetic stirrer; (4) Pyrex vessel reactor with reaction mixture and a magnetic stir bar; (5) Teflon tube connector; (6) time controller; (7) temperature controller; and (8) switch to control speed of magnetic stirrer.

this study. The experiments were conducted at a fixed frequency of 2,450 MHz and MW output power of 750 W. The rotating plate of the MW oven was replaced with a magnetic stirrer for mixing the reactor contents. A non-contact infrared pyrometer was installed in the MW oven chamber for measuring the reaction temperature inside the reactor. In addition, an automated temperature control system, which will display the system temperature during the operation, was installed to cut off the MW power when the temperature reaches the desired value. A hole was pierced on the top portion of the MW-oven, and the Pyrex vessel reactor was connected with the Teflon tube connector to facilitate sampling. A timer was also fixed in the reactor and adjusted manually to set the MW operation time. Arrangements were made to collect the samples during the reaction time without stopping the reaction process. Samples for analysis were taken through a Teflon tube connecting the Pyrex vessel.

2.3. Experimental procedures

Batch adsorption experiment was carried out with 25 mL of carbofuran solution with a concentration of 250 mg/L, pH 8, and a GAC dosage of 0.8 mg/L. The mixture was kept in orbital shaker at 120 rpm for 2 h. After adsorption, the separation of GAC (i.e. carbofuran presaturated GAC) from the solution was done by filtration. Carbofuran presaturated GAC was used in the MW-GAC system in order to delineate carbofuran

degradation under MW-GAC system from carbofuran adsorption on GAC. MW-GAC experiment was performed with 250 mL of the solution containing 100 mg/L carbofuran. The carbofuran solution was added into the Pyrex vessel reactor and the pH was adjusted to 8 using HCl/NaOH solution. After pH adjustment, presaturated GAC was added into the reactor and kept in the MW oven. Subsequently, the modified MW-reactor was operated under 750 W MW power and the reaction contents were mixed uniformly at 120 rpm. The reaction temperature was maintained at optimum value (i.e. 80 °C) obtained from the preliminary study [21] by pulsed supply of MW. The samples were collected after 1, 5, 10, 20, and 30 min and the samples were collected for residual carbofuran analysis. After 30 min, the reaction was stopped and the MW exposed GAC was separated from solution by filtration. The MW exposed GAC was presaturated by adsorption process and recycled for subsequent MW-GAC experiments. The process was repeated for three cycles of MW-GAC experiments. Subsequently, carbofuran desorption experiments were conducted with (a) the presaturated GAC and (b) the presaturated GAC after MW-GAC experiments. For desorbing the remaining carbofuran from the GAC, 100 mL of 50% methanol/distilled water (v/v) was added to GAC and the solution was kept in the orbital shaker at 120 rpm for 1 h. Methanol is a good solvent for carbofuran; therefore, it is expected that 90–100% of the carbofuran from GAC could be brought to the solution phase. Finally, the carbofuran concentration in the liquid phase after desorption was analyzed in the HPLC. The amount of carbofuran desorbed from blank experiments and MW-GAC experiments were compared to identify the actual amount of carbofuran degraded under the MW-GAC experiment. In addition, the COD removal efficiency of the system was calculated by COD analysis of the sample at the beginning and end of the experiment. Moreover, the surface structure and elemental composition of the GAC obtained before and after adsorption study, after desorption study, after MW experiments, and after desorption of GAC used for MW experiments were determined and compared. Prior to the determination of surface structure and elemental composition, the GAC samples were air-dried and kept in vacuum desiccators. Subsequently, the samples were analyzed in the scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). Based on the results, the variation of the elemental composition in the GAC surface under different conditions was interpreted.

In order to determine the recyclability of GAC used in the MW-GAC system, batch adsorption tests were

conducted at the previously mentioned conditions (i.e. 0.8 mg/L of GAC in 25 mL of 250 mg/L carbofuran solution at pH 8) with virgin GAC and GAC after the MW experiments (MW exposed GAC). Carbofuran removal/adsorption in the GAC was calculated from initial and equilibrium carbofuran concentrations in the solution. The GAC after MW experiment was separated by filtration and the similar procedure as reported above was adopted to estimate carbofuran removal by the GAC exposed to MW. In addition, GAC after MW was washed gently in distilled water, dried in air, and tested for the adsorption experiment. Subsequently, the recyclability of GAC in MW-GAC system was investigated by the carbofuran degradation efficiency of the system with recycling of MW exposed GAC.

2.4. Data analysis

The residual carbofuran concentration in the liquid phase was measured using the high-performance liquid chromatography (HPLC) (Hitachi Co., Japan) equipped with a RP-18 reverse-phase C18 column (4.6 m length, 250 mm diameter and 5 µm film thickness) and a Hitachi L-2420 UV detector. The mobile phase consists of a mixture of methanol and water (50:50, v/v) at a flow rate of 1 mL/min. For carbofuran determination, the UV detector was set at 280 nm. Under these analytical conditions, carbofuran peak was observed at a retention time of 12 min.

The COD removal efficiency in the MW-GAC system was determined by COD analysis as per standard method [23]. Moreover, the carbofuran metabolites were identified in the Gas Chromatography (5890 series II) interfaced with a Mass Spectrometer (Micro-mass TRIO-2000) (GC-MS). A mixture of sample and dichloromethane (5:1 v/v) was shaken vigorously in a rotary shaker at 150 rpm for 30 min, and subsequently, analyzed in the GC-MS equipped with DB5 capillary column (30 m length, 0.25 mm diameter, and 0.25 µm film thickness). Helium was used as the carrier gas at a flow rate of 1.5 mL/min. The GC oven temperature was programmed as follows: initially held at 80 °C for 2 min, increased to 210 °C at a rate of 10 °C/min, and held for 3 min, then raised from 210 to 300 °C at a rate of 30 °C/min and finally held at 300 °C for 2 min. The injector and detector temperatures were maintained at 220 and 250 °C, respectively. The mass spectrometer was operated in the full-scan electron-impact (EI) mode at 70 eV.

Surface properties of original and MW-exposed GAC were observed through a SEM (JSM-5800, JOEL Company, Japan). The distribution of elements on the surface or in the pores of carbon particles were

determined by the same SEM together with energy dispersive X-ray spectroscopy. The dried sample was mounted on gold sample holder and coated with carbon in a sputter coating unit and scanned for the analysis.

3. Results and discussion

3.1. Carbofuran degradation with MW-GAC system

A set of adsorption and desorption studies were conducted, and subsequently, carbofuran mass balance was worked out for delineating the mechanism of carbofuran degradation in the MW-GAC system from carbofuran adsorption on GAC. As a precursor to desorption experiments, two sets of carbofuran adsorption study with 25 mL of 250 mg/L carbofuran solution were conducted with a GAC loading of 0.02 g at pH 8. After 120 min, the adsorption experiment showed nearly 52% carbofuran removal by GAC adsorption (i.e. 3.22 mg of carbofuran adsorbed in 0.02 g of GAC which corresponds to 161 mg of carbofuran/g of GAC). Similar result was obtained in our previous study with a GAC dosage of 0.2 g/L [21]. At the end of the experiment, the carbofuran-saturated

GAC (from both the sets) was separated from liquid phase and used for the desorption studies (desorption study I and II). The schematic diagram of the experimental steps is shown in Fig. 2. Desorption study I was conducted with GAC saturated with carbofuran. Prior to the desorption study II, the carbofuran-saturated GAC was utilized for the MW-GAC experiments. MW-GAC experiment for carbofuran degradation was conducted for 30 min with 250 mL of 100 mg/L carbofuran solution at a reaction temperature of 80°C and pH 8. The MW-GAC system showed complete degradation of carbofuran in all the three cycles and the GAC was collected at the end of the experiment for desorption study II.

Desorption was done with 100 mL of methanol: DI water solution (50% v/v) for 60 min. In desorption study I, the methanol: DI water solution desorbed out 94% of the adsorbed carbofuran on GAC, i.e. 3.02 mg of carbofuran. The remaining 6% carbofuran was not desorbed from the GAC, which may be due to the irreversible adsorption of carbofuran on the adsorption sites. Interestingly, carbofuran concentration was below the detectable limit after 60 min of the desorption study II. This indicates that the presaturated carbofuran on GAC surface (i.e. 3.22 mg) as well as

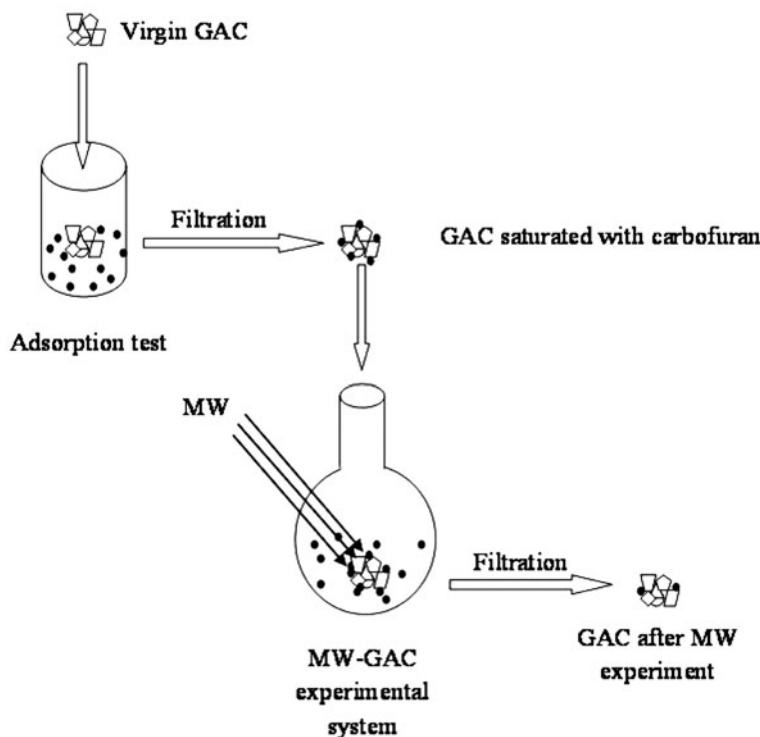


Fig. 2. Schematic diagram of MW-GAC experimental steps.

the carbofuran present in the aqueous solution in MW-GAC system (i.e. 25 mg of carbofuran from 250 mL of 100 mg/L carbofuran solution) was degraded in the MW-GAC system. The results of carbofuran removal by GAC alone and MW-GAC system is given in Table 1, which demonstrate that the carbofuran removal with GAC alone is by adsorption, whereas the carbofuran removal in MW-GAC system is by degradation. Therefore, the presence of MW has superior capability for degrading carbofuran present in the aqueous phase and GAC (presaturated carbofuran).

At the time of MW-GAC experiment, a vast number of collapsing bubbles were originated from the GAC surface especially when the temperature of the system was above 65 °C. Under such condition, the GAC was floating in the reaction mixture; however, this effect was suddenly stopped when the MW-power was turned off by the automatic temperature-power controller (while reaching the reaction temperature reached 80 °C). Thereafter, similar bubbling effect was observed when the MW power was turned on. It is hypothesized that this effect could be due to the polarization effect of MW, where the high frequency of MW result in the phase lag between polarization of carbon and applied MW; thus, leads to absorption of energy and heating of carbon particles to form hot spots.

3.2. COD removal efficiency and identification of degradation pathway

The success of a pollutant removal system depends not only on the degradation of the target compound, but also on the extent of mineralization caused by the system. A COD removal efficiency of 72% was observed in the MW-GAC system at pH 8 and 80°C after 30 min.

Subsequently, the samples collected at the end of 1 min from the MW-GAC systems (pH 8 and 80°C) were used to identify the degradation products by GC-MS analyses. The products identified from the molecular ion and fragment ions are listed in Table 2. In addition, the GC-MS spectra of the degradation course products are given in Table 2. The analysis of

the degradation products demonstrates that the carbofuran degradation in the MW-GAC systems was routed through two ways: (i) base hydrolysis reaction, i.e. the hydroxyl radical attacks the carbamate group resulting in the cleavage of C–O bond, which resulted in the formation of 2,3-dihydro-2,2-dimethylbenzofuran-7-ol [7]; and (ii) hydroxylation of carbofuran by substituting a hydroxyl group for one of the H atoms at C-3 position of the furan ring which resulted in the formation of 3-hydroxy-2,2-dimethyl-2,3-dihydro-1-benzofuran-7-yl methylcarbamate. Further oxidation of the product eliminates another H atom at C-3 position to form 2,2-dimethyl-3-oxo-2,3-dihydro-1-benzofuran-7-yl methylcarbamate. In addition, other degradation products may possibly exist in the system but were not detected because of their lower concentration, extraction efficiency, and limited sensitivity of the instruments.

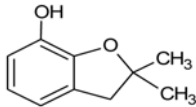
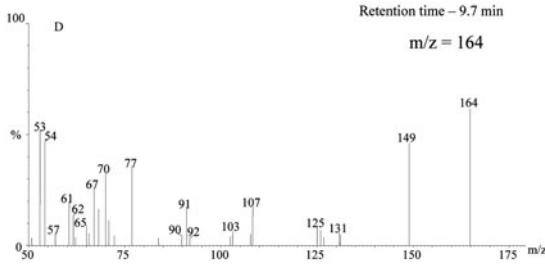
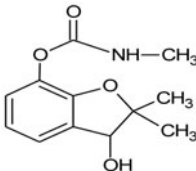
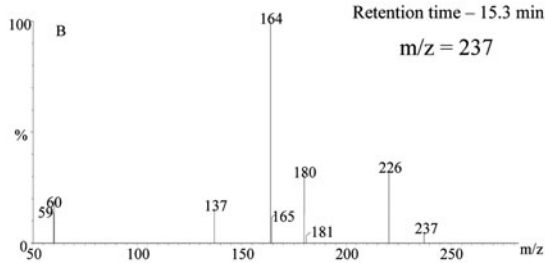
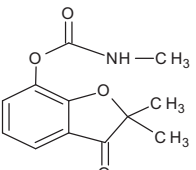
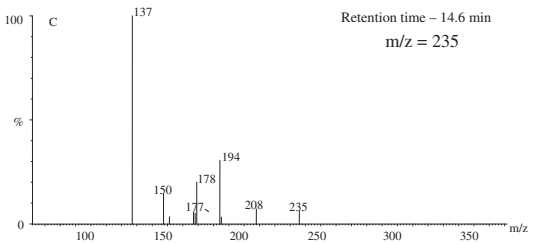
3.3. GAC characteristics on MW exposure

The SEM/EDX analysis provided information on the distribution of elements in the original and MW exposed GAC, which was necessary to understand the chemical reaction occurring in the process of carbofuran adsorption and/or degradation. The SEM pictures of the GAC (a) before and after adsorption study, (b) after desorption study, (c) after MW experiments, and (d) after MW experiments and desorption are shown in Fig. 3. From the figure, it is clear that there was significant difference in the appearance of the GAC surfaces. Fig. 3(a) shows that the virgin GAC particle is mostly irregular in shape with identical porous surface. In Fig. 3(b), the blurred image shows the surface of the GAC particles is less porous and is covered mostly by adsorbed material. On the other hand, many pores appeared on the surface of the exposed GAC which indicates the degradation of adsorbed material on GAC surface. Moreover, GAC exposed to MW showed more micro-pores compared to the others (Fig. 3(d) and (f)). This may be due to the special heating effect of MW. The micro-porosity of the MW exposed GAC remains almost the same even after the desorption study (Fig. 3(e)).

Table 1
Carbofuran removal by GAC and MW-GAC system

Type of system	Carbofuran loading (mg)	Carbofuran removal (mg)	Carbofuran removal (%)	Desorption (%)	Mechanism of removal
GAC alone	6.25	3.22	52	4	Adsorption
MW-GAC	28.22	28.22	100	0	Degradation

Table 2
Carbofuran degradation products identified in the present study

Products identified	Chemical structure	MS spectra of carbofuran degradation products	Previous studies reporting the product
2,3-Dihydro- 2,2-dimethyl-benzofuran-7-ol ($C_{10}H_{12}O_2$)			Photocatalysis, Fenton process [11, 13]
3-Hydroxy-2,2-dimethyl-2,3-dihydro-1-benzofuran-7-yl methylcarbamate ($C_{12}H_{15}NO_4$)			Photocatalysis in presence of photosensitizers [17]
2,2-Dimethyl-3-oxo-2,3-dihydro-1-benzofuran-7-yl methylcarbamate ($C_{12}H_{13}NO_4$)			—

The EDX analysis of the selected spots on the GAC surface provided information on the distribution of elements in the virgin GAC, GAC after adsorption study, GAC after desorption study, MW exposed GAC (GAC after MW experiments), and MW exposed GAC after desorption (Fig. 4). Table 3 lists the weight percentages of each element in various composites as calculated from the EDX diagrams. The virgin GAC mostly consisted of carbon and the detected Mg, Si, and K come from impurities in GAC. After adsorption experiment, the concentration of K was reduced significantly whereas the relative concentrations of Mg and Si showed a slight increase compared to the virgin GAC. However, the concentrations of all three elements decreased significantly after the desorption process. On the other hand, when the GAC (after adsorption study) was exposed to MW, the concentrations of all three elements were decreased slightly compared to the GAC after adsorption study. Moreover, desorption of the MW exposed GAC showed higher concentration of carbon compared to virgin GAC. Besides, the

concentration of Si was very less compared to the virgin GAC and the elements Mg and K were removed completely after desorption test of the MW exposed GAC.

The value of elemental analysis is not the absolute mass but the relative weight percentage of the surface composition. Therefore, the increase or decrease in the relative amount of impurities is mainly due to the increase or decrease in the amount of carbon and oxygen on GAC surface. The concentration of oxygen on GAC increased significantly after adsorption process (i.e. from 1.3 to 9.41%) (Fig. 5). The higher weight percentage of oxygen in the GAC after adsorption process indicates that the functional group containing oxygen is higher on its surface. Remarkable variation in the relative amount of carbon and oxygen was observed in the adsorption desorption process prior to MW exposure. However, the carbofuran adsorbed on GAC surface could be degraded in the presence of MW and thus decreases the possibility of oxygen containing species on its surface. Therefore, the variation in the percentage of carbon and oxygen on GAC surface was not signifi-

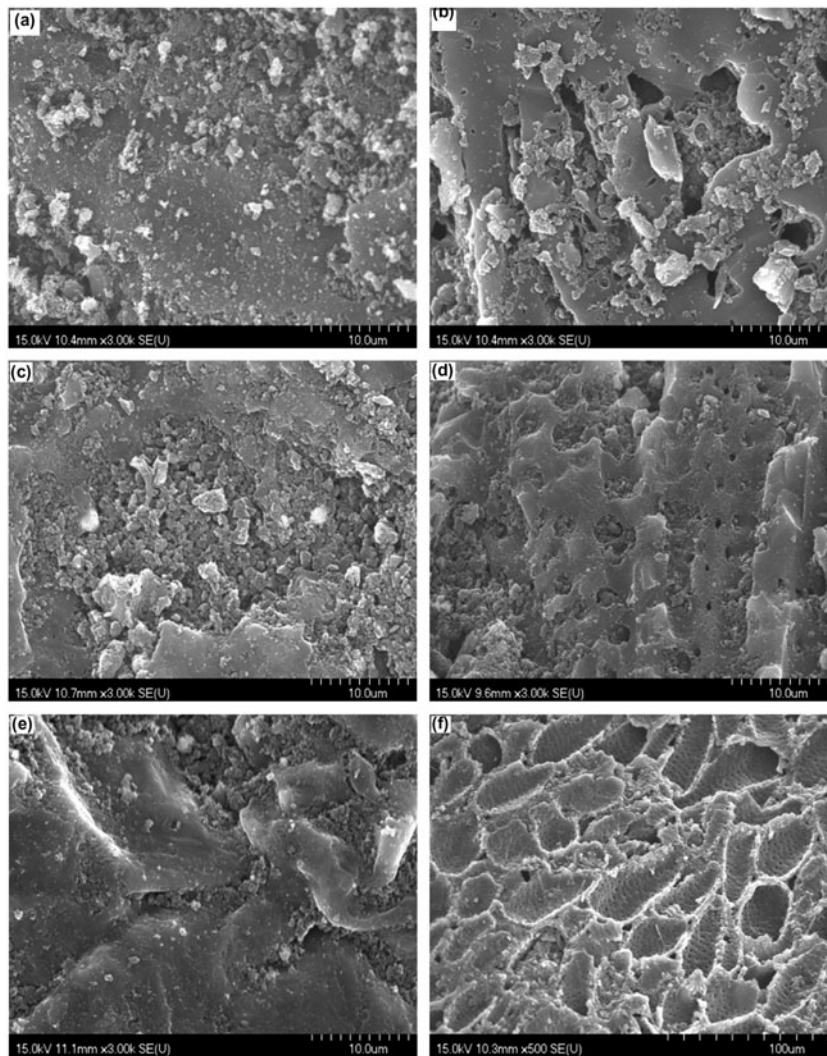


Fig. 3. SEM picture of GAC (a) before adsorption; (b) after adsorption; (c) after desorption; (d) after exposure to MW; (e) after desorption of MW exposed GAC; and after recycling (f).

cant after MW exposure. Although carbofuran contains nitrogen in its structure, the peak corresponding to nitrogen was not detected in the spectra. This indicates that the nitrogen in mineralized or converted to different forms in the process. Our previous study revealed that around 59% of nitrogen from carbofuran was converted to either ammonium or nitrate and the rest of nitrogen was mineralized [24].

3.4. Recyclability of GAC

Carbofuran adsorption study conducted at pH 8 with virgin GAC loading of 0.08 g/L showed nearly

52% carbofuran removal by GAC adsorption after 120 min. The detailed experimental conditions of the adsorption study are shown in Table 4. The carbofuran-saturated GAC was separated and used for the MW-GAC experiments. The MW-GAC experiment was carried out for 30 min with 250 mL of 100 mg/L carbofuran solution with pH 8. At the end of the MW-GAC experiment, the pH of the system increased from 8 to 8.77. Following to the completion of the MW-GAC experiment, the MW exposed GAC was separated from the solution and the adsorption study (cycle 1) was repeated as per the conditions reported in Table 2. In cycle 1, the carbofuran

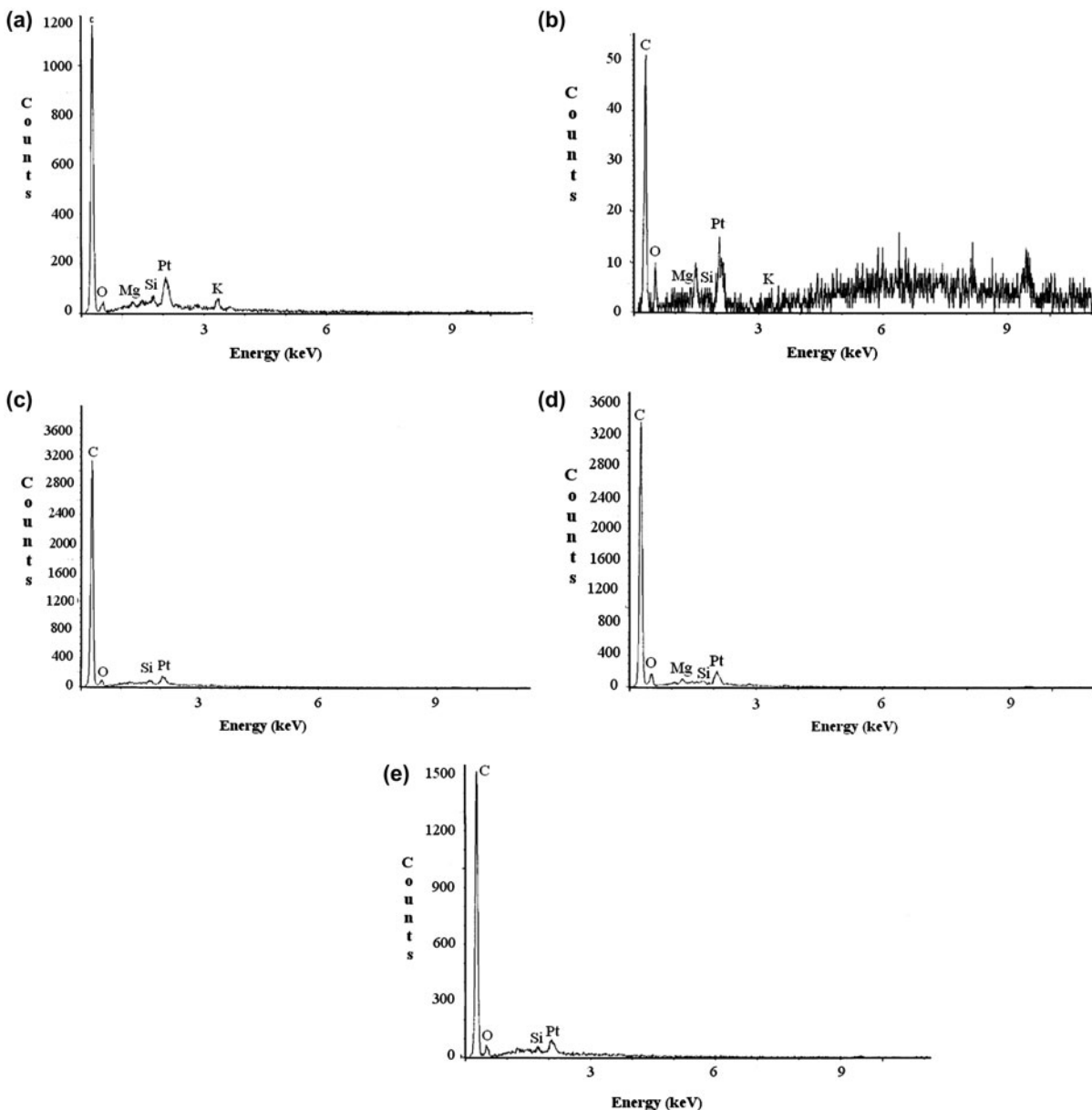


Fig. 4. EDX analysis of (a) virgin GAC; (b) GAC after adsorption; (c) GAC after desorption; (d) MW exposed GAC; and (e) MW exposed GAC after desorption.

removal by GAC adsorption was around 41%. Simultaneously, the MW exposed GAC was pretreated (i.e. washed with distilled water and air dried) and the cycle 1 was repeated under the identical conditions. Interestingly, the adsorption test with pretreated GAC showed slightly higher or almost similar carbofuran removal compared to the virgin GAC. When the MW exposed GAC was directly used for adsorption, the higher pH (8.77) might have decreased the adsorption

capacity of GAC. On the other hand, the pretreatment could decrease the pH of GAC, which favors the increase in adsorption on GAC surface. Moreover, effective degradation of carbofuran was achieved even after three cycles of MW exposed GAC (after presaturation) in the MW-GAC system (Fig. 6). More than 99% degradation was obtained within 10 min in all three cycles of MW-GAC experiments conducted with recycled GAC.

Table 3
Elemental analysis of GAC surface

Element	Atom (wt.%)				
	GAC before adsorption	GAC after adsorption	GAC after desorption	MW exposed GAC	MW exposed GAC after desorption
C	97.95	89.95	99.39	96.90	97.84
O	1.30	9.41	0.46	2.86	2.03
Mg	0.12	0.18	0.00	0.11	0.00
Si	0.30	0.39	0.15	0.14	0.13
K	0.33	0.07	0.00	0.00	0.00

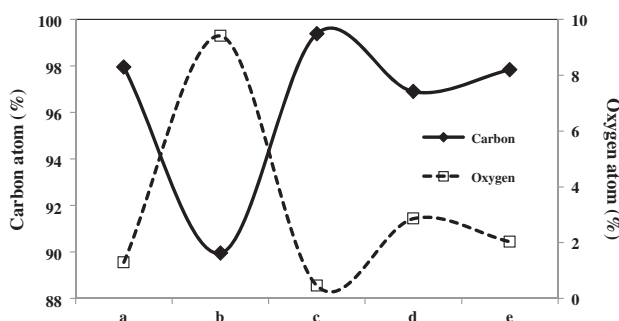


Fig. 5. Variations in the relative amount of carbon and oxygen on the surface of (a) virgin GAC; (b) GAC after adsorption; (c) GAC after desorption; (d) MW exposed GAC; and (e) MW exposed GAC after desorption.

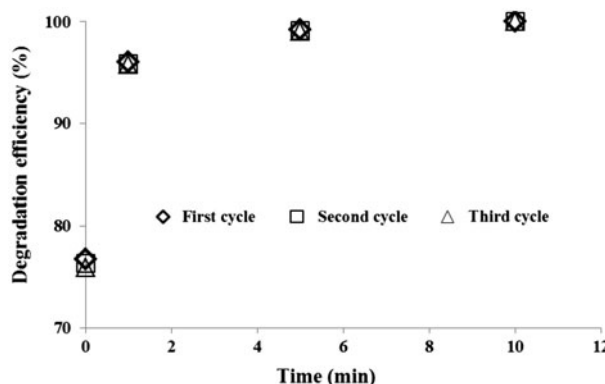


Fig. 6. Carbofuran degradation in the MW-GAC system with recycled GAC.

3.5. Economic analysis of MW-GAC systems

The outcomes of the carbofuran degradation in MW-GAC system indicate that a combination of MW with GAC has a great potential in rapid degradation of bio-refractory pollutants. On the other hand, the economic analysis of the process should be compared with other treatment techniques for its cost effective application. Fig. 7 shows the power consumption in kWh per removal of carbofuran (kg) for carbofuran

degradation using various AOPs. The results indicate a drastic decrease in power consumption for carbofuran degradation in UV-TO₂ system [12] compared to that of sonolysis [14]. Moreover, the power consumption was further reduced in UV-TiO₂ system in presence of photosensitizers [17]. However, MW-GAC system resulted in minimum power consumption compared to the other methods for carbofuran degradation.

Table 4
Carbofuran removal by GAC before and after MW exposure

Parameters	Type of GAC		
	Virgin GAC	MW exposed GAC	MW exposed GAC after pretreatment
Dosage (g)	0.02	0.02	0.02
pH	8	8	8
Initial volume (mL)	25	25	25
Initial concentration (mg/L)	250	250	250
Equilibrium concentration (mg/L)	121.2	147.4	117.4
Carbofuran removal by adsorption (%)	52	41	53

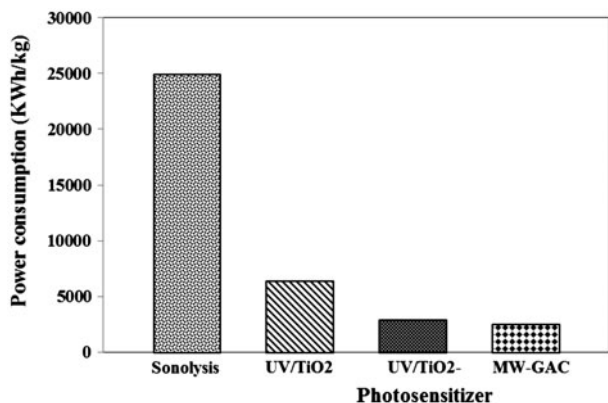


Fig. 7. Power consumption in different AOPs for carbofuran degradation.

4. Conclusions

Analysis of the GAC characteristics and recyclability of the spent GAC in a microwave-granular activated carbon (MW-GAC) system was performed in this study. Complete degradation of carbofuran from the aqueous phase as well as the adsorbed carbofuran on GAC surface could be achieved in a MW-GAC system. Moreover, exposure to MW showed improvement in the surface structure and characteristics of GAC. Adsorption test with MW exposed GAC after pretreatment showed slightly higher or almost similar carbofuran removal compared to the virgin GAC. Therefore, the GAC used in the system could be effectively regenerated. Moreover, the MW exposed GAC could be effectively recycled for several cycles in the MW-GAC system without any reduction in the degradation efficiency. As a whole, the MW-GAC system is a powerful and cost effective technology for pollutant removal from aqueous phase as well as the effective recycling of the spent GAC.

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