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Granular activated carbon adsorption and microwave regeneration for the treatment of 2,4,5-trichlorobiphenyl in simulated soil-washing solution

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Abstract

The treatment of 2,4,5-trichlorobiphenyl (PCB29) in simulated soil-washing solution by granular activated carbon (GAC) adsorption and microwave (MW) regeneration was investigated in this study. The PCB29 adsorption process was carried out in a continuous flow adsorption column. After adsorption, the PCB29-loaded GAC was dried at 103 °C, and regenerated in a quartz reactor by 2450 MHz MW irradiation at 700 W for 5 min. The efficacy of this procedure was analyzed by determining the rates and amounts of PCB29 adsorbed in successive adsorption/MW regeneration cycles. Effects of the regeneration on the textural properties and the PCB29 adsorption capacity of GAC were examined. It was found that after several adsorption/MW regeneration cycles, the adsorption rate of GAC increased, whereas, the adsorption capacity decreased, which could be explained according to the change of textural properties. Most of the PCB29 adsorbed on GAC was degraded within 3 min under MW irradiation, and the analysis of degradation products by GC-MS demonstrated that PCB29 experienced dechlorination during this treatment.

Keywords: PCB; Activated carbon; Microwave; Adsorption; Regeneration

1. Introduction

PCBs pose high toxicological risks to wildlife, to agricultural ecosystems, and consequently to the human food-chain, due to their stable properties and ubiquitous distribution [1]. Soil-washing has been widely used for the remediation of PCBs contaminated soil, where organic solvents or/and surfactant solutions are commonly employed to remove PCBs out of soil [2]. But, this operation has only transferred pollutants from one medium to another, leaving the soil-washing solution that needs further treatment for the elimination of hazard to the environment. Abdul and Gibson [3] adopted anaerobic biodegradation and activated carbon adsorption for the treatment of PCBs-containing soil-washing solution, and the concentration of PCBs decreased from 65 $mg\,L^{-1}$ to 10 $\mu g\,L^{-1}$.

Activated carbon adsorption is frequently used to remove apolar pollutants from waste water. Hence, this adsorbent can be used as an efficient remover of PCBs which are very apolar [4]. However, the large-scale use of granular activated carbon (GAC) is restricted due to its high cost. For economical and environmental reasons, the spent GAC should not be disposed of, but must undergo several cycles of regeneration [5]. In recent years, the microwave (MW) regeneration of spent GAC has been proposed as a potentially viable alternative to the traditional regeneration methods. Cha and Carlisle [6] found that MW regeneration of the fixed-bed-saturated carbon restored the original GAC adsorption capacity. After 20 adsorption/regeneration cycles, the adsorption capacity of GAC for methylethyl ketone only dropped from 135 $mg\,g^{-1}$ to 125 $mg\,g^{-1}$.

When adopting MW irradiation for the regeneration of PCBs-loaded GAC, much attention should be paid on the degradation of PCBs adsorbed on GAC. Processes applying the GAC adsorption and the MW decomposition to the treatment of VOCs have shown considerable advantages in energy consumption and process efficiency [7]. Abramovitch and Capracotta [8] recently applied soil adsorption and MW irradiation, an indirect process, to the treatment of pentachlorophenol in water. They found that irradiating the soil with MW energy either destroyed or bound pentachlorophenol to the soil irreversibly so that none could be extracted after long periods of time.

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The purpose of this study was to apply the GAC adsorption/MW regeneration coupled process to the treatment of a simulated PCB-containing soil-washing solution, and the effect of MW irradiation on GAC regeneration and PCB degradation was investigated, with PCB29 being selected as a model pollutant. A series of successive GAC adsorption/MW regeneration cycles were carried out, during which the changes of textural properties and adsorption capacity, as well as the degradation of PCB29 were determined. The results obtained by this investigation were expected to be helpful for the disposal of persistent organic pollutants (POPs) in soil or water.

2. Experimental

2.1. Materials

PCB29 was purchased from AccuStandard without further purification. The stock solution of 100 mg L^{-1} PCB29 was prepared in methanol. And the simulated soil-washing solution consisted of 20% methanol, a nonionic surfactant Brij30 [$C_{12}H_{25}(OCH_2CH_2)_4OH$] 1.0 g L^{-1} and PCB29 2.0 mg L^{-1}.

The GAC used in this study was made from coal, and was purchased from Taipingyang Activated Carbon Corporation, Beijing, China. The GAC was immersed in 10% hydrochloric acid for 24 h and heated in boiling water for 30 min, washed with deionized water to remove fine particles and impurities, then dried at 103 °C for 24 h and stored in a desiccator for use.

2.2. Methods

The PCB29 adsorption was carried out in a continuous flow adsorption column (12 mm i.d. and 30 cm length), where 10 g of GAC sample was placed. Before the commencement of dynamic adsorption, the GAC bed was immersed with the PCB29 solution to ensure that the whole GAC bed be fully utilized. The solution passed through the GAC bed at a constant flow rate of 3.0 mL min^{-1}, and the effluent stream was collected for analysis every 26 min. When the effluent concentration was close to the restricted level, the flow was cut and adsorption stopped.

After adsorption, the GAC was dried at 103 °C for 6 h and regenerated by 2450 MHz MW irradiation at 700 W for 5 min. The regeneration parameters were chosen based on the temperature rising of GAC in MW field [9]. And the experimental setup was described in our previous paper [10]. Briefly, the equipment consisted of a modified 700 W domestic MW oven and a quartz reactor (34 mm i.d.) installed into the MW oven. At the bottom of the reactor, a perforated quartz plate was fixed to sustain GAC, and the top of the reactor was connected to a condensing system. A vessel was used to collect distillate, and the vapor generated passed through a series of two bottles both containing 20 mL of 0.1 mol L^{-1} NaOH solution.

2.3. Analysis

The determination of PCB29 concentrations in filtrate, distillate and absorption solution was performed by a HPLC using a Diamonsil ODS (5 μm, 4.6 mm × 150 mm) reverse phase column, a acetonitrile/water 0.9/0.1 mL min^{-1} of the mobile phase and UV detector (247 nm). The adsorption breakthrough curves were obtained by plotting the PCB29 concentration in the effluent solution against effluent volume. The amount of PCB29 adsorbed on the GAC was then calculated using the integrated area above the breakthrough curve (difference between inlet 2.0 mg L^{-1} and breakthrough concentration curves) and the mass of GAC. These GAC adsorption/MW regeneration cycles were repeated for six times. The regeneration yield was calculated according to the following expression:

$$\text{Regeneration yield} = (\text{amount adsorbed on MW treated GAC})/(\text{amount adsorbed on virgin GAC}).$$

In order to know the textural changes suffered by the GACs during the MW regeneration cycles, the determination of the physical properties of virgin and MW treated GAC samples was performed with an automated gas sorption system, using N_2 as the adsorbate at 77 K. Before the determination, the samples were heated at 120 °C and outgassed to a vacuum of around 10^{-5} Torr. The micropore surface area and external surface area were calculated using the *t*-plot method with non-porous carbon as standard reference solid, while the pore size distribution was determined by use of the BJH model [11].

The adsorption equilibrium isotherms of PCB29 on virgin GAC and on MW treated GAC after six adsorption/regeneration cycles were also measured in accordance with the method provided by Walker and Weatherley [12] for the evaluation of adsorption capacity.

The degradation of PCB29 on GAC during MW irradiation was also determined by HPLC. The pretreatment procedure for instrumental analysis was as follows: about 5 g of GAC was heated at 103 °C for 6 h to constant weight. After cooling to the room temperature, 1 g of GAC was weighed accurately. The PCB29 on GAC was extracted by a 20 mL mixture of acetone and dichloromethane (2:3, v/v) in ultrasonic water bath for 30 min. The extraction procedure was repeated for six times. Afterwards, the combined extract was evaporated in a 60 °C water bath to incipient dryness. The resultant sample was dissolved in 10 mL acetonitrile and analyzed by HPLC. A Finnigan Trace DSQ GC-MS was employed for the analysis of degradation products as presented by Liu and Yu [13].

3. Results and discussion

Besides focused on analyzing the effect of MW regeneration on adsorption kinetics, textural properties and adsorption capacity of GAC, as concerned by other researchers [14–17], this work also put much attention on the degradation of PCB29 adsorbed on GAC during MW irradiation.

In the regeneration experiment, once irradiated by 700 W MW, the GAC bed turned red soon and its temperature rose to higher than 1000 °C in 2 min, as indicated by a sheltered type-K thermocouple. Although the final temperature of GAC bed was not clearly known due to the limitation of thermocouple,

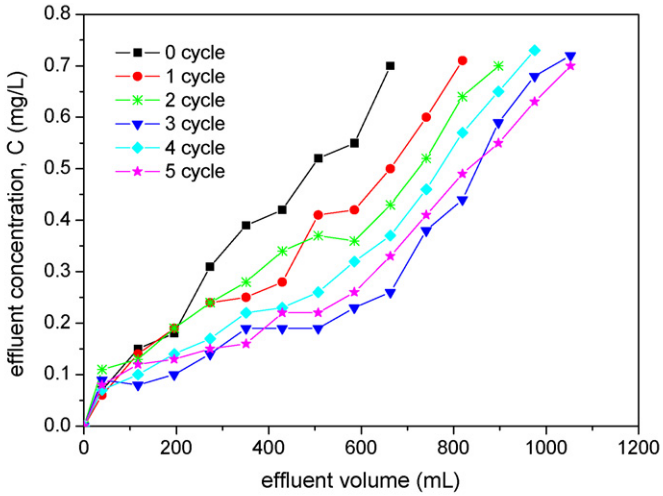

Fig. 1. Breakthrough curves of 2.0 mg L^{-1} PCB29 (3.0 mL min^{-1}) on GAC bed after different MW regeneration cycles.

the temperature rising courses of GAC bed before 1000 °C displayed little difference with different cycles.

3.1. Adsorption kinetics

Since breakthrough curves can reveal very useful information, a GAC bed was used in this study to obtain breakthrough curves for each successive adsorption/regeneration cycles, so as to find the effectiveness of microwave regeneration process on the rate of PCB29 adsorption. The breakthrough curves for GAC in the five adsorption/MW regeneration cycles are collected in Fig. 1.

It is easily understood that the lower the effluent concentrations the higher the adsorption rates [18]. For certain effluent volume or adsorption time, lower effluent concentration means larger adsorption capacity, so in this period, the corresponding adsorption rate is averagely higher. It may be observed from Fig. 1 that the MW irradiation was effective for regenerating the spent adsorbent. The amount of PCB29 adsorbed was estimated by integrating the area between the respective influent and effluent profiles. The calculated amounts of PCB29 adsorbed on GAC and regeneration yields, as well as average adsorption rates in different cycles are summarized in Table 1. The results indicated that the efficacy of the regeneration was very high in most cycles, and MW irradiation can effectively regenerate the adsorption rate of GAC for PCB29 in the simulated soil-washing solution. After five cycles' reuse, the adsorption rate of GAC was even higher than that of the virgin one.

3.2. Textural properties

As the adsorption rate depends strongly on the porous structure of the GAC and the molecular size of the pollutant, in most cases there is control by diffusion [19], it was assumed that MW irradiation might have modified the pore structure to be more accessible to the PCB29 molecules. It should be bear in mind that the GAC used for textural properties characterization had undergone once more MW treatment after the last time adsorption.

The N_2 adsorption isotherms at 77 K are shown in Fig. 2. Compared with that of the virgin GAC, the shape of the nitrogen isotherm of the six-cycle MW treated GAC moved downwards, indicating the amount of nitrogen adsorbed decreased. Ania et al. [14] has also reported that successive cycles of MW regeneration on activated carbons caused a sharp decrease in the amount of adsorbed nitrogen.

The characteristics of the pore structure of the virgin and six-cycle MW treated GACs are presented in Table 2. The results showed that after MW treatment, the GAC samples exhibited larger external surface area (defined as those not associated with micropores) and average pore diameter. However, the BET surface area decreased because the micropore areas of the GAC decreased in a large scale. The measurement of the pore size

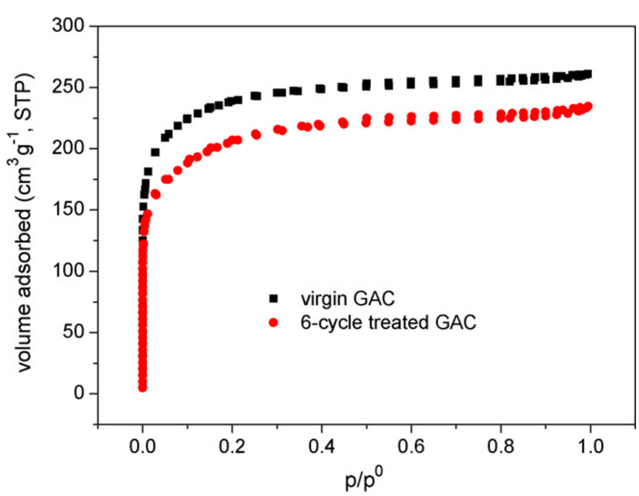

Fig. 2. N_2 adsorption isotherms at 77 K of virgin GAC and six-cycle MW treated GAC.

Table 1
PCB29 adsorbed on GAC in different adsorption/MW regeneration cycles

Regeneration cycle	Amount adsorbed (mg)	Total adsorption time (min)	Average adsorption rate (μg PCB29/g GAC/min)	Regeneration yield (%)
0	1.10	663	0.166	
1	1.37	819	0.167	125
2	1.49	897	0.166	135
3	1.81	1053	0.172	164
4	1.65	975	0.169	150
5	1.79	1053	0.170	163

Table 2
Characteristics of the pore structure of the virgin and six-cycle MW treated GACs

Sample	Surface area (BET, $m^2 g^{-1}$)	Micropore area ($m^2 g^{-1}$)	External surface area ($m^2 g^{-1}$)	Average pore diameter (Å)
Virgin GAC	814	505	309	19.7
Six-cycle MW treated GAC	712	347	366	20.1

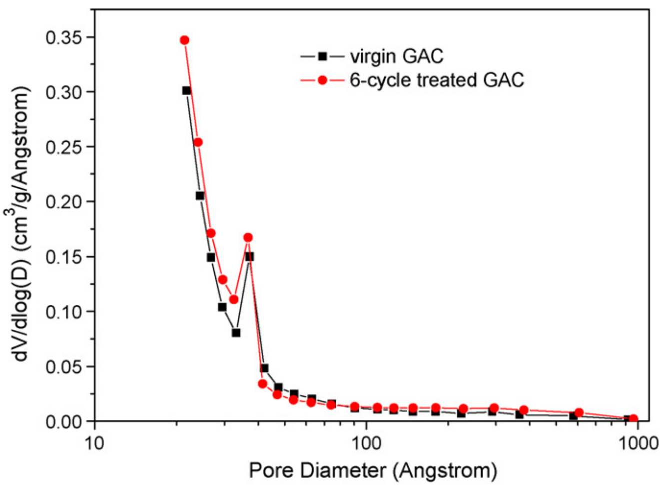

Fig. 3. Pore size distribution of virgin GAC and six-cycle MW treated GAC by BJH method.

distribution using the BJH method provided the distribution of pores in the range 2–100 nm (Fig. 3). It seemed that the GAC had more pores in the mesopore range with MW treatment. Mesopores are defined as pores of width between 2 and 50 nm. Their contribution to the total surface area of GAC is usually small compared to micropores. However, they play an important role in the adsorption of compounds, which, owing to their very large molecular size, do not have access to pores of smaller dimensions [20].

One special point to be noted here is the GAC loss during MW irradiation and the adsorption/MW regeneration operations. The GAC loss after six cycles of MW irradiation was approximately 7.0%.

3.3. Adsorption capacity

Sabio et al. [21] suggested that a simple comparison between adsorption isotherms allows us to get average information about the changes introduced in surface accessibility to the adsorbate and affinity. Fig. 4 shows the adsorption isotherms of PCB29 on virgin GAC and on six-cycle adsorption/MW regeneration treated GAC. The regeneration process did not affect the nature of adsorption: the shape of the PCB29 adsorption isotherm on MW regenerated GAC, when plotted as q versus C, did not differ after six regeneration cycles from that of the virgin GAC.

These two isotherms exhibited very good fits with the Freundlich isotherm. The Freundlich isotherm describes adsorption where the adsorbent has a heterogeneous surface with adsorption sites that have different energies of adsorption and which are not always available [12]. According to the Freundlich equation, the amount adsorbed increases infinitely with increasing concentration. This equation is, therefore, satisfactory for low concentration. In the Freundlich equation $q_e = K_F C_e^n$, q_e is the solid phase equilibrium concentration (mass adsorbate/mass adsorbent), C_e is the liquid phase equilibrium concentration, K_F ($L g^{-1}$) and n (dimensionless) are coefficients representing the capacity and affinity of adsorption, respectively [22]. The two coefficients are empirical constants, which depend on the nature of adsorbent and adsorbate, and on the temperature. Data obtained from Freundlich plots for these two GAC samples are listed in Table 3.

Table 3
Data obtained from Freundlich plots for two GAC samples

Sample	K_F ($L g^{-1}$)	n	R^2
Virgin GAC	9.88	2.31	0.9999
Six-cycle MW treated GAC	8.39	1.93	0.9950

It was found that after microwave regeneration, the adsorption capacity of GAC to PCB29 reflected by the isotherm decreased, which is in accordance with the decrease of BET surface area and micropore area. Combining this information with the increase of the dynamic adsorption amount to PCB29, as well as the external surface area and the average pore diameter, it was suggested that in the dynamic adsorption of PCB29 molecules that have relatively larger size, the mesopores and macropores played more important role, while in the shaking adsorption for a long time to obtain isotherm, the PCB29 molecules could more easily enter into the micropores.

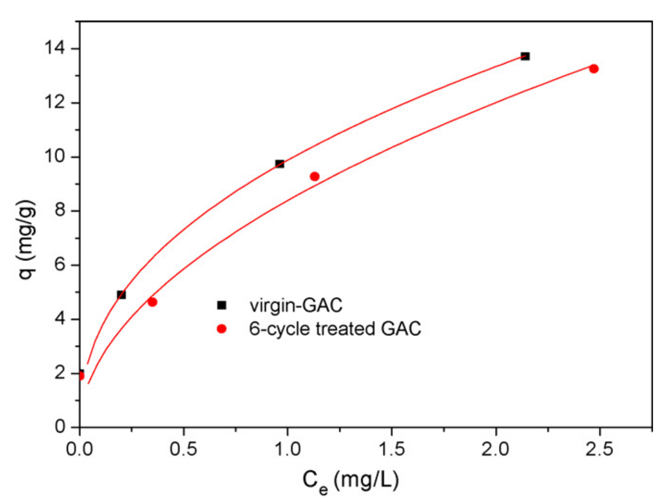

Fig. 4. Adsorption isotherms of PCB29 on virgin GAC and on six-cycle MW treated GAC.

3.4. Degradation of PCB29 on GAC during microwave irradiation

From the above-described investigation, it was confirmed that PCB29-loaded GAC could be effectively regenerated by MW irradiation. Another matter that we concern is the degradation of PCB29 on GAC during MW irradiation, including the degradation kinetics and mechanisms.

PCB29-loaded GAC was obtained by mixing 100 mL of PCB29 solution (20 mg L^{-1}, 50% methanol) with 10 g pretreated GAC in 250 mL flasks. The flasks were sealed and placed in a thermostatic shaker (150 rpm, 20 °C) for 24 h to obtain equilibrium. The separation of GAC from the solution was completed by filtration. By analyzing the filtrate, it was known that the amount of PCB29 adsorbed on GAC was approximately 195 μg g^{-1}. The wet GAC was dried at 103 °C for 6 h and irradiated by MW irradiation at 700 W for 1 min, 3 min and 5 min. The degradation kinetics of PCB29 on GAC under MW irradiation was plotted in Fig. 5.

The results in Fig. 5 revealed that most of the PCB29 adsorbed on GAC was degraded within 3 min under MW irradiation. The degradation in 3 min could be more suitably fitted by the apparent pseudo-first-order kinetics ($k = 1.367$ min^{-1}, $R^2 = 0.994$) than that in 5 min ($k = 1.018$ min^{-1}, $R^2 = 0.945$). According to our previous work [10,13], it was deduced that the degradation of PCB29 might occur through pyrolysis, fixation and volatilization. But, the detection for the distillate and the absorption solution did not find any PCB29 or its degradation products.

In order to capture the degradation products for GC-MS analysis, the wet PCB29-loaded GAC was directly treated by MW irradiation after filtration. The distillate collected was extracted by hexane, condensed in rotary evaporator, cleaned by column containing anhydrous sulphate sodium, aluminium oxide and florisil soil, and finally analyzed by GC-MS. The di- and tri-chlorinated biphenyl peaks were observed on the total ion chromatogram, which suggested that PCB29 adsorbed on GAC underwent dechlorination under MW irradiation.

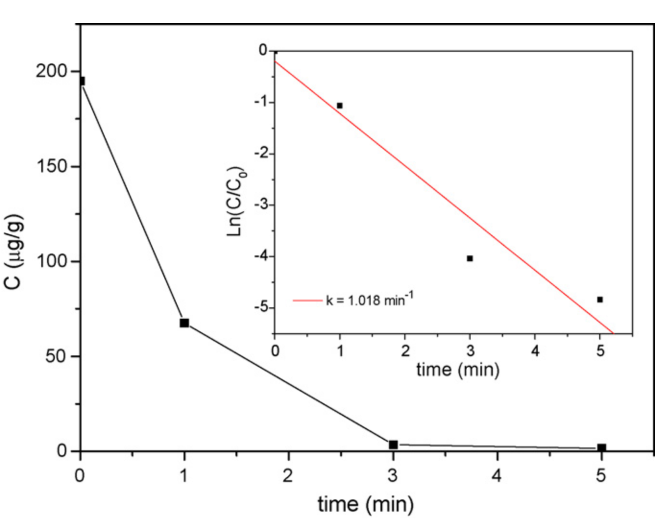

Fig. 5. PCB29 residues on GAC after different periods of MW irradiation.

4. Conclusion

A GAC adsorption/MW regeneration process was adopted for the treatment of PCB29-containing simulated soil-washing solution. The results of breakthrough curves indicated that MW regeneration could effectively recover the adsorption amount of GAC to PCB29 in dynamic adsorption, and the adsorption amount maintained high level after five adsorption/regeneration cycles. But, the information provided by isotherms implied that the adsorption capacity of GAC decreased after six adsorption/regeneration cycles. These could be well explained according to the change of textural properties of GAC by MW irradiation. That is, although the decreased total surface area and micropore area led to a lower adsorption capacity, the increased external surface area was in favor of the dynamic adsorption of PCB29 molecules with relatively large size, thereby the adsorption amount was enhanced. The degradation of PCB29 adsorbed on GAC was very fast under MW irradiation, and dechlorination occurred in this treatment.

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