

Adsorption of Specific Organics in Water on GAC and Regeneration of GAC by Countercurrent Oxidative Reaction

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Granular activated carbon (GAC) is highly effective in removing organic compounds which are resistant to biological disintegration in wastewater treatment. However, when GAC has reached its full adsorptive capacity, GAC needs to be regenerated before it can be used for a further adsorption cycle. Countercurrent oxidative reaction (COR) technique has been developed and evaluated for the regeneration of spent GAC. Various parameters such as flame temperature, the loss of carbon, destruction and removal efficiency (DRE) of organic compounds, surface area, surface structure, adsorptive capacity, etc. were examined to determine the performance of COR. The results of these tests showed that adsorptive capacity of regenerated GAC was completely recovered, the loss of carbon was controllable, flame temperature was high enough to insure complete destruction and removal ($\geq 99.9999\%$) of specific organics of interest, polychlorinated biphenyls (PCBs), that are thermally stable, and no formation of toxic byproducts such as polychlorinated dibenzo-p-dioxins (PCDDs) or polychlorinated dibenzofurans (PCDFs) were detected during the regeneration process. The COR technique is environmentally benign, easy to use and less capital intensive than other available regeneration technologies.

Keywords : GAC, COR, PCBs, Waste water treatment.

Introduction

The legislation for decontamination of waste water containing organic substances has become more and more stringent under increased public concern. It is well known that biological treatments are not able to remove all organic compounds, especially if they are toxic, from the waste water.¹⁻³ Thus toxic organic compounds accumulate in the effluent water, causing an increase in pollution of our natural environment. So far, various methods to solve this problem have been attempted, *e.g.*, precipitation by special coagulants, solvent extraction and the adsorption on suitable adsorbents.⁴⁻⁶ At the present time, the adsorption on activated carbon is considered an attractive technology for removing a variety of organic contaminants from the waste water. The application of activated carbon in waste water treatment process is, however, limited due to the lack of effective and low-cost regeneration technology. Clearly, in order to recycle activated carbon in the waste water treatment plants, regeneration techniques capable of destroying the adsorbed organics while preserving the bulk of activated carbon are definitely required.

The regeneration of spent carbon has been generally accomplished using solvent, steam, and thermal routes.^{4,7} Solvent extraction is conducted with a solvent in which the adsorbate is highly soluble. Extraction with solvent is, however, disadvantageous if the organics being removed is toxic and therefore the spent solvent itself is disposed of as a hazardous waste. Regeneration by steam is applied only if

activated carbon contains substances that vaporize at temperatures below 150 °C. It has been reported that steam is not useful when very strongly adsorbing or environmentally persistent chlorinated aromatic compounds such as dioxins, PCBs, DDT, and PCP are present. For substances of higher boiling points, thermal regeneration is the most widely employed technology.^{8,9} The process of thermal regeneration is carried out in regular sequence as follows: (a) drying (≤ 200 °C); (b) vaporization of volatile adsorbates (200-500 °C); (c) pyrolysis of non-volatile adsorbates, with the formation of carbonaceous material (500-700 °C); and (d) gasification of this material, using suitable oxidizing agents such as steam, carbon dioxide, air, or any mixture of these gases (≥ 700 °C). When carbon reacts with H₂O or CO₂, the gasification occurs in accordance with endothermic reactions. Therefore, external heat has to be continuously supplied to maintain isothermal situation. On the other hand, the gasification reaction is extremely exothermic in the presence of air (oxygen). This reaction is difficult to control, and excessive loss of carbon easily occurs, resulting in a decrease in average particle size.

The present research is directed towards the decontamination of waste water using GAC and the development of low-cost and effective regeneration technology of spent GAC. The newly developed regeneration technique, a countercurrent oxidative reaction (COR) is similar to reverse burn methodology used for simulating *in-situ* gasification of coal.^{10,11} The COR process utilizes a self-sustained flame that moves in the reverse direction to the flow of oxidants

(air or O₂). The reaction is exothermic, and the overall process is completed in a single step, with minimum external energy to initiate a flame. To evaluate the performance of COR on regeneration of spent GAC, the loss of carbon and the temperature of a flame in affecting regeneration efficiency and destruction and removal efficiency (DRE) of adsorbed organics were examined, as well as surface area, surface structure, and adsorptive capacity of regenerated GAC, by comparing with virgin GAC.

Materials and Methods

Adsorption Isotherm Study for PCBs. To evaluate the adsorptive capacity of GAC for a specific organic compound of interest in contaminated water, the isotherm experiments were conducted. Activated carbon used in these experiments was a granular type (Darco, 20-40 mesh) supplied by Aldrich Chemical Company, Inc., USA. Aroclor 1242 (a mixture of PCBs composed of mostly 3 and 4 chlorines on biphenyl ring) and Aroclor 1260 (a mixture of PCBs with mostly 5 and 6 chlorines), purchased from Accustandard Inc., USA, were used as model adsorbates because they are toxic and not readily decomposed by any biological means in the waste water treatment plants.¹² The contaminated water was made by spiking above-mentioned two PCB formulations (5 mg each) in 100 mL of distilled water, respectively. A series of known weights (1.0 g, 2.5 g, 5.0 g, and 10.0 g each) of GAC was packed into a quartz tube (2 cm i.d. × 50 cm long), and spiked water was pumped to the tube at the flow rate of 10 mL/min. Subsequently, the concentration of PCBs in the effluent water was measured with a GC/ECD (Trace GC 2000, Italy). Separation of PCBs was achieved with a capillary DB-5 column (0.25 mm i.d. × 30 m long) through a temperature program. Chromatographic peaks were identified by relative retention time, with pentachlorobenzene (PCBz) as the retention time marker. The total concentration of PCBs was calculated by summing up the concentration of individual PCB.

Countercurrent Oxidative Reaction Process. Spent GAC was simulated by adsorption of PCBs from PCB-contaminated water. Oxygen, used as an oxidant in COR process, was forced to flow from the top of tube to the bottom. The flow rate of oxygen in the process was adjusted at 300 mL/min, by controlling with a flow controller. The heat was applied at the bottom of carbon in the tube until a flame was generated. The flame was then moved slowly and evenly upward in the direction counter to the oxygen flow, consuming a portion of the carbon and, at the same time, destructing adsorbed PCBs. The oxygen flow was halted when the flame arrived at the top of carbon. The velocity or residence time of the flame was determined by dividing the height of carbon bed in tube by total burn time. The effluent gases released from the tube during the COR process were collected in a gas-collecting tube. The gas composition and relative ratio of CO and CO₂ were analyzed with a GC/TCD (Trace GC 2000, Italy), by measuring the response relative to standard gas mixtures (Scott Specialty Gases, Inc., USA). The sepa-

ration of gases was carried out, using a carbosieve (60-80 mesh) packed column at 80 °C oven temperature. The loss of carbon burnt away in the process was examined by difference in weight before and after COR. Flame temperature was calculated from both the loss of carbon and the relative ratio of CO/CO₂ in the effluent gases.

Evaluation of Countercurrent Oxidative Reaction. In order to evaluate the performance of COR on the destruction and removal efficiency (DRE) of adsorbed PCBs, regenerated GAC was withdrawn from the tube and soxhlet-extracted with *n*-hexane/acetone (1 : 1 V/V) for 24 hours, and then silica gel (grade 923, 60-200 mesh, Aldrich) column clean-up was introduced to remove the interferences from the extract. The final extract was reduced in volume to 1 mL using a rotary evaporator and a gentle stream of N₂, and the analysis of PCBs was followed. The DRE was determined by difference in initial and final PCB concentration. Identification of PCDDs/PCDFs, obtained from Accustandard Inc., USA, was accomplished by GC interfaced with a quadrupole mass spectrometer (Shimadzu QP-5000, Japan), operating in selected ion monitoring (SIM) mode. The analysis of HCl was done with an IC (DX-100, USA). The surface area measurement of regenerated GAC was carried out with a Surface Area Analyzer (ASAP 2010, Micrometrics, USA), using N₂ BET adsorption at 77 K. Scanning electron micrographs (Jeol, JSM-6300, Japan) were also taken to assess the impact of COR on the appearance of the carbon surface. To estimate the adsorptive capacity of regenerated GAC, a batch adsorption experiment was carried out. A 5 g sample of regenerated GAC was contacted with 50 g of mineral oil containing Aroclor 1260 in a flask. The carbon/oil system was brought to equilibrium by rotating end-over-end in a rotary shaker for 24 hours. After a given equilibration time, the aliquot of oil above the regenerated GAC in the flask was removed and filtered through 0.45 μm nitrocellulose filter paper. After the filtered oil was exchanged with hexane, the concentration of PCBs was measured.

Results and Discussion

Adsorption Isotherms of Aroclor 1242 and 1260 on GAC. Adsorption isotherm studies were performed with contaminated water containing a mixture of PCBs (Aroclor 1242 and Aroclor 1260). Isotherm is extremely valuable in getting an evaluation of the effectiveness of GAC for treating contaminated water. Data for isotherms were obtained by treating fixed volumes of the contaminated water with known weights of GAC. To assess the adsorptive capacity of GAC for Aroclor 1242 and Aroclor 1260, the Freundlich adsorption isotherm equation was introduced. The Freundlich isotherm equation empirically relates isotherm data, and has been found to fit many types of adsorption in dilute solutions. The equation is of the form:

$$X = kC^{1/n} \quad (1)$$

where, X represents the amount of PCBs adsorbed per unit

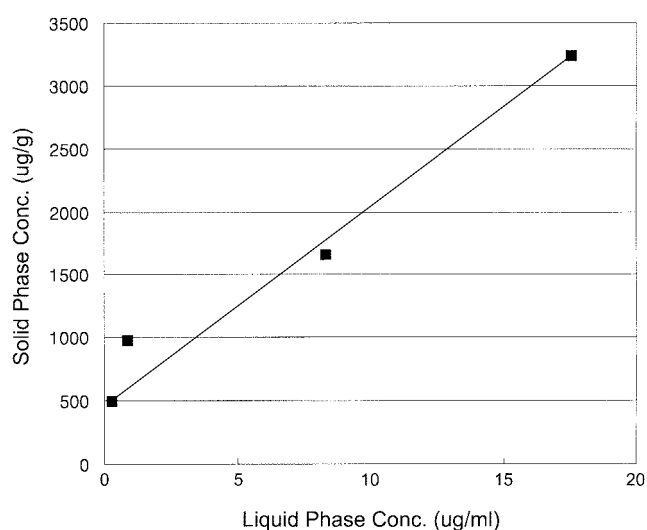


Figure 1. Aroclor 1242 Isotherms at 298.15 K in Darco GAC (20-40 mesh)/Water System.

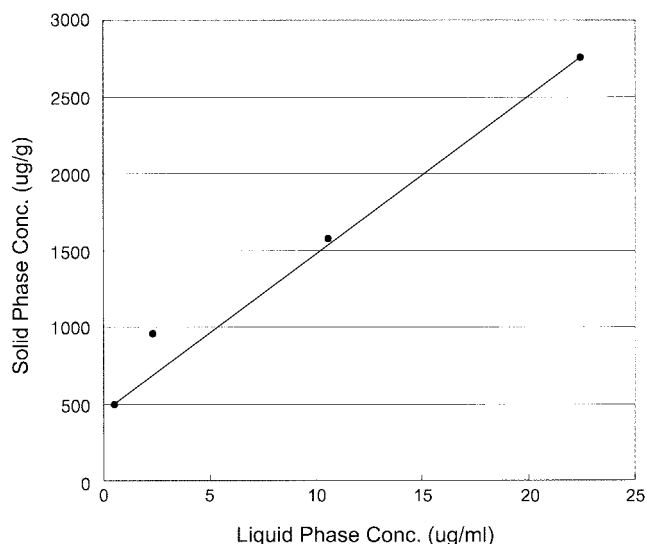


Figure 2. Aroclor 1260 Isotherms at 298.15 K in Darco GAC (20-40 mesh)/Water System.

mass of GAC, C is the concentration of residual PCBs in contaminated water after the GAC and the contaminated water reach adsorptive equilibrium, and k and n are the Freundlich constants for each sample tested.

Adsorption isotherms, shown in Figures 1 and 2, were obtained over the experimental concentration range. The values of k and n for Aroclor 1242 and Aroclor 1260 are listed in Table 1. The higher value of k for Aroclor 1242 given in Table 1 represents that the sorption capacity for Aroclor 1242 is greater than that for Aroclor 1260 on GAC. The observed difference in the adsorption efficiency of Aroclor 1242 and Aroclor 1260 in GAC/contaminated water system can be explained by the geometry (chlorine numbers and their substituted positions on biphenyl ring) of PCB constituents that make up Aroclor 1242 and Aroclor 1260. It is generally known that Aroclor 1242 is consisted almost

Table 1. Freundlich Adsorption Isotherm Parameters for Aroclor 1242 and Aroclor 1260 in GAC/Water System

Carbon Type	Aroclor 1242		Aroclor 1260	
	k^*	n	k^*	n
Darco GAC (20-40 Mesh)	904.26	2.24	657.5	2.17

*In unit of μg PCBs/g of GAC.

entirely of tri and tetra substituted chlorines on biphenyl ring, whereas, the PCBs comprising Aroclor 1260 have mostly hexa and hepta chlorine atoms. It means that adsorption efficiency of PCBs decreases with increasing number of chlorine atoms attached on biphenyl ring. Besides, the planar congeners in Aroclor 1242 constitute approximately 38%, while the concentration of such planar congeners is only 14.5% in Aroclor 1260. The conformation of PCB planar/non-planar congeners depends on the degree of chlorine substitution on the four ortho positions relative to the biphenyl ring. For instance, those PCBs which have non- and mono-ortho substitution and are heavily substituted at meta and para positions are capable of assuming a planar conformation. But, if chlorine atoms are on at least two ortho positions, rotation of the phenyl rings occurs due to the steric crowding caused by chlorine atoms. Therefore, it is called as a non-planar structure. It is apparent that adsorption efficiency of PCBs on GAC is also very dependent on planar or non-planar structure of PCBs. This certainty was more clearly illustrated by the adsorption study of selected non- and mono-ortho PCBs, and the result is shown in Figure 3.

Countercurrent Oxidative Reaction (COR). The regeneration of spent GAC is generally affected not only by the gradual loss of carbon, but also by the efficient destruction and removal of adsorbed materials to make fresh carbon surface available for the further adsorption. In order to lengthen the life-time of activated carbon, the bulk of activated carbon is needed to be preserved as much as possible during the regeneration process. In the case of COR, the loss of carbon inevitably occurs by the combustion reaction of carbon and oxygen in flame front zone (analogous to combustion zone by conventional thermal regeneration) during the process. From the preliminary COR test (devoid of any organics on GAC), the amount of carbon loss was found to be dependent on the flow rates of oxygen. The test showed that the loss of carbon increased with increasing oxygen flow rates. Therefore, during the COR process, the flow rate was kept to a minimum so that not too much of carbon matrix is burnt away. The result showed that the amount of carbon loss was about 8% at the oxygen flow rate of 300 mL/min. Generally, the oxygen flow rate is difficult to control in the conventional thermal regeneration process where violent reaction results from excess oxygen, and excessive loss of carbon can easily occur. On the other hand, in the COR, the oxygen supply is limited and this permits a better control of the loss of carbon.

The destruction and removal of organics adsorbed on activated carbon could be generally achieved by maintaining high flame temperature, thus allowing more thorough regene-

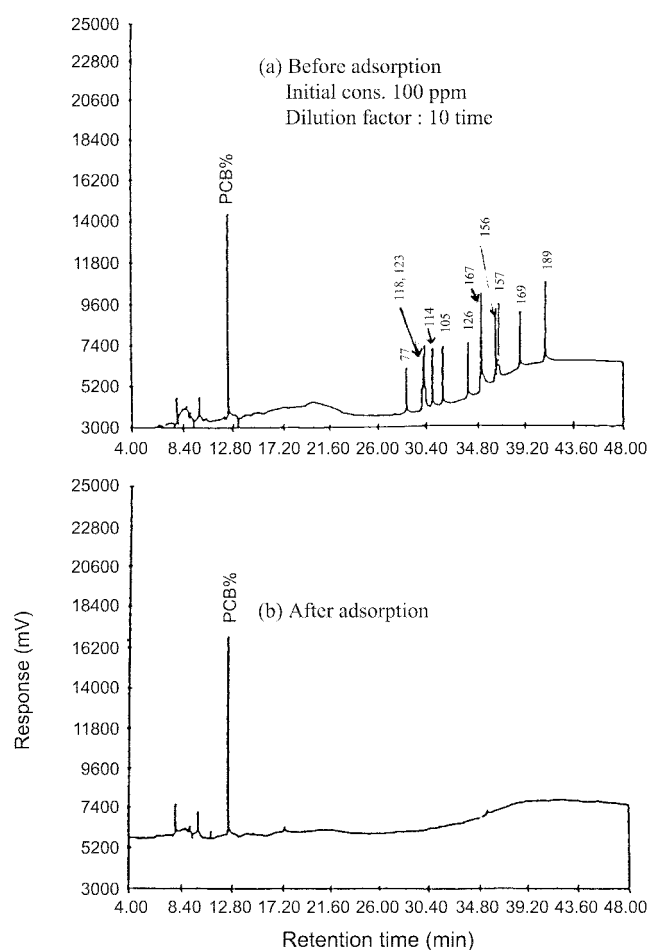


Figure 3. Chromatograms of Coplanar PCBs in water (a) before and (b) after Adsorption on GAC.

ration of the spent GAC. Therefore, during the COR process, direct measurement of flame temperature was repeatedly attempted, using temperature transducers such as Pt sensors connected to a pyrometer and an infrared sensor. However, due to the transient nature of the flame, these measurements proved futile. Hence, the flame temperature was determined indirectly by the relative ratio of the CO and CO₂ gas exiting from the tube and the loss of carbon. At previous-mentioned oxygen flow rate, relative molar ratio of CO and CO₂ was approximately 1 : 0.8.

The flame temperature was calculated according to the following procedures. A known amount of carbon was placed in a quartz tube of cross-sectional area A cm² and length L cm. The number of carbon moles per cm³ is $C_c = \text{weight}/(12AL)$. In a section of this length of tube, the carbon and oxygen at T are converted to carbon(C), CO(g), and CO₂(g) at temperature T' , with loss of some of the carbon (Δn_C). All of the oxygen delivered at a volumetric flow rate (F , cm³/sec) and pressure P (atm) is assumed to be consumed. The amount of oxygen consumed depends on the total burn time. This calculation neglects oxygen which is present in the interparticle and intraparticle pore space at the beginning of the burn. The flame advances through this section at a linear burning rate (B , cm/sec). The time required is $t = L/B$.

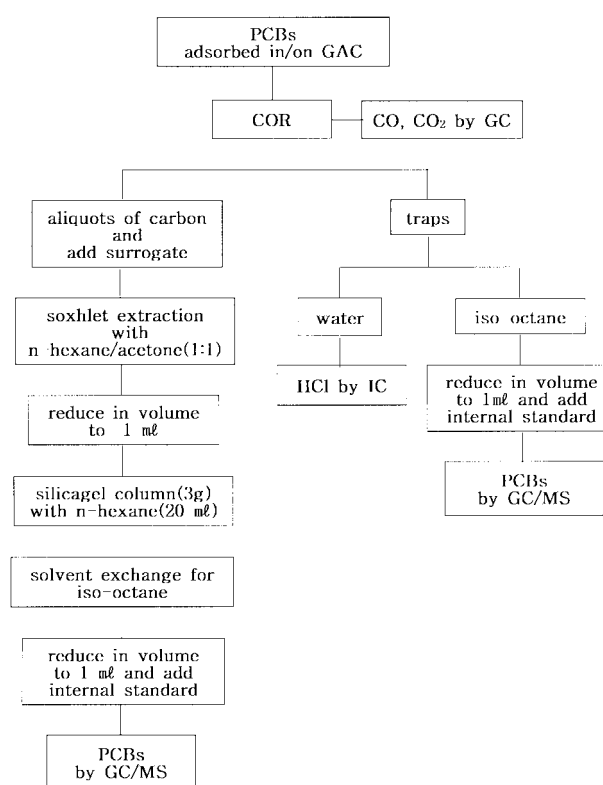
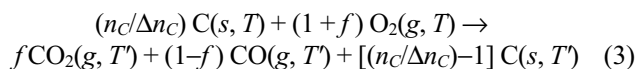


Figure 4. Flow schematic of countercurrent oxidative reaction (COR).

B . The volume of O₂ burned is: $V_{O_2} = Ft = FL/B$. Moles of O₂ burned are: $\Delta n_{O_2} = FPL/RBT$, where R is the gas constant. The ratio of carbon to oxygen burned is: $\Delta n_C/\Delta n_{O_2} = 2/(1+f)$, and $\Delta n_C = 2FPL/RBT(1+f)$. Where f is the mole fraction of CO₂ in product stream. The total moles of carbon involved is $n_C = AC_cL$, so

$$\Delta n_C/n_C = 2FP/AC_cRBT(1+f). \quad (2)$$

The process is



and is assumed to occur adiabatically, so that

$$0 = f[\Delta_f H_{CO_2} + \int_T^{T'} C_{PCO_2} dT] + (1-f)[\Delta_f H_{CO} + \int_T^{T'} C_{PCO} dT] + [(n_C/\Delta n_C)-1] \int_T^{T'} C_{PC} dT \quad (4)$$

with enthalpy of formation at T , which is taken as 298.15 K. The flame temperatures, T' , were estimated from both enthalpy of formation and heat capacity of CO and CO₂ gas and the loss of carbon at the desired oxygen flow rate. The flame temperature calculated was about 1,100 °C.

Destruction and Removal Efficiency (DRE) of PCBs by COR. The COR process was carried out for destruction and removal of PCBs that had adsorbed on GAC after adsorption tests of GAC/PCB-contaminated water. In case of combustive degradation of PCBs, the possible products or by-products formed from decomposition of PCBs are as follows.

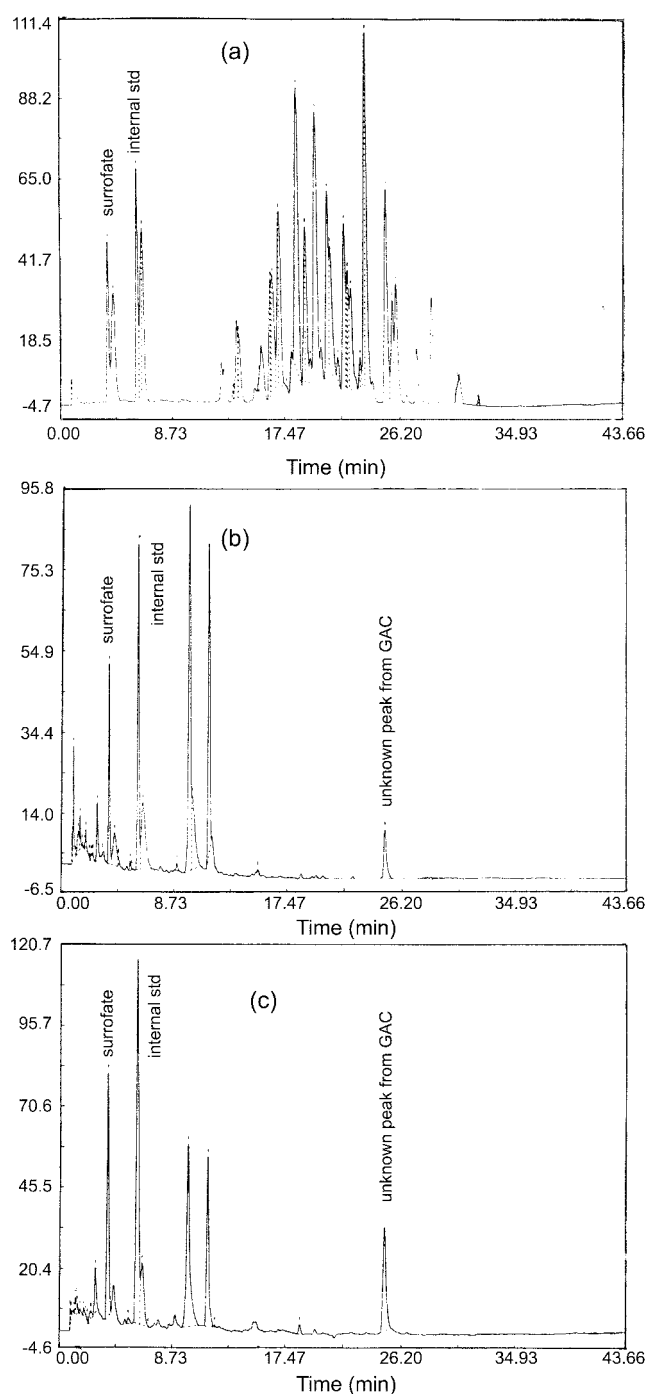
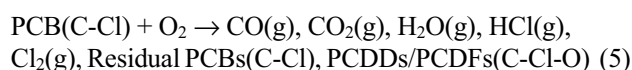


Figure 5. Chromatograms of Aroclor 1260 (a) adsorbed on GAC, (b) in GAC after COR, (c) in impinger trap after COR.



A comprehensive experimental procedure is presented in Figure 4 as a flow schematic. The schematic is subject to destruction and removal efficiency of PCBs and characterization of PCDDs/PCDFs. Destruction and removal of PCBs by COR requires very high temperature because PCBs are very difficult to burn, due to their thermal stability. A few experimental and theoretical works have shown that, at

temperatures higher than 800 °C, PCBs are thermodynamically unstable.¹³ Therefore, it is obvious that destruction and removal of PCBs could be achieved by maintaining temperature higher than at least 800 °C.

The destruction and removal efficiency was calculated by measuring the relative concentration of PCBs before and after COR process. It was observed that, as shown in Figure 5, destruction and removal efficiency of a PCB formulation (Aroclor 1260) was very high ($\geq 99.9999\%$) with the reproducible values. It is quite certain that a COR technique is particularly effective for destroying refractory chlorinated organic compounds, and therefore essentially all organics can be destroyed. The possible formation of PCDDs/PCDFs were also monitored during the COR process, because many studies indicated that they were emitted from the pyrolysis combustion of PCBs at 300 °C in the presence of air.¹³⁻¹⁶ The results showed that toxic by-products such as PCDDs/PCDFs were not found on the carbon residues and neither in the exhaust gases over a 5 ppb detection limit. This result is attributed to the extremely high flame temperature and presence of appreciable hydrogen which combines with the released chlorine.

Physicochemical Properties of Regenerated GAC

Surface Structure. Scanning electron micrographs (SEMs), shown in Figure 6, were taken of virgin and regenerated GAC to assess the impact of COR on the appearance of the carbon surface. Virgin and regenerated GAC were examined at 200X magnification. At this magnification, the micrographs clearly showed larger pores of the carbon surface, but did not allow observation of micropores. Virgin GAC exhibited a relatively smooth surface. Regenerated GAC developed a sponge-like appearance with the large pores appearing on the surface. The formation of large pores are due to the fracture of the carbon caused by thermal stress. The large pores in regenerated GAC could make faster the



Figure 6. Scanning Electron Micrographs (SEMs) of (a) Virgin and (b) Regenerated GAC (200 X Magnification).

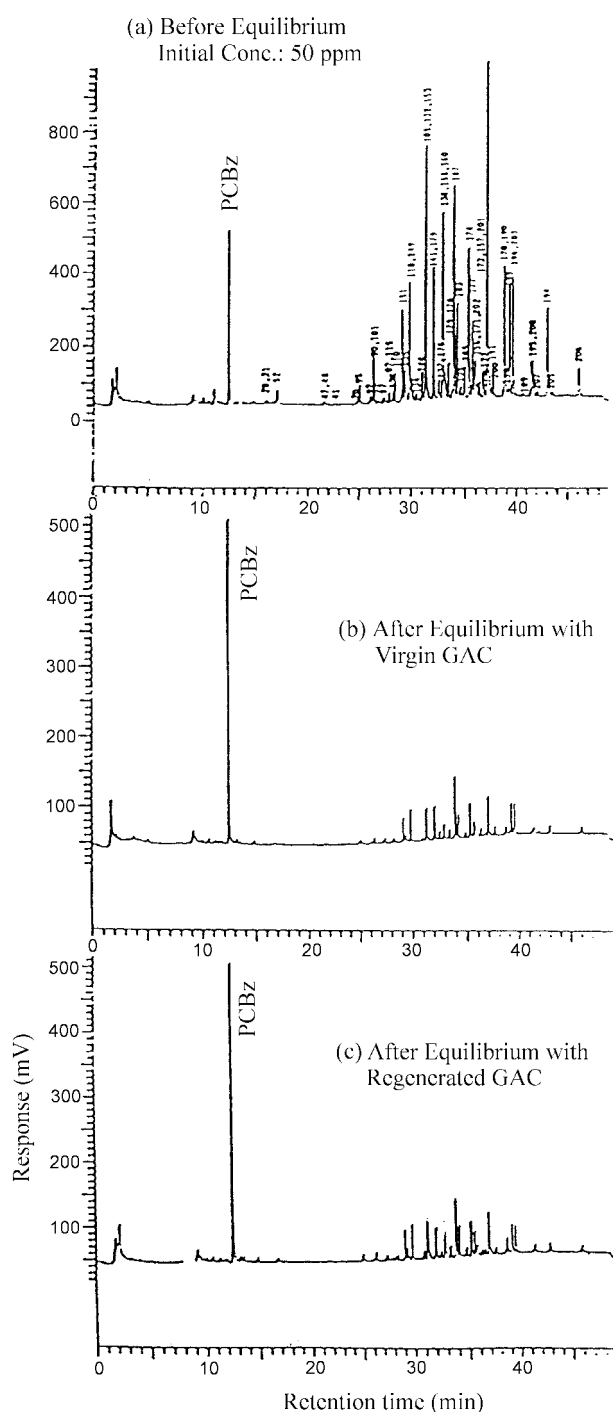


Figure 7. Chromatograms of Aroclor 1260 in Mineral Oil (a) Before and (b, c) After 1-Day Equilibrium with Virgin and Regenerated GAC.

adsorption kinetic in dynamic (non-equilibrium) carbon adsorption which transports solutes from the solution into the interior micropores. But, thermal cracking and development of sponge-like texture, on the negative side, may lead to a weakening of the physical strength of the regenerated GAC.

Specific Surface Area. Adsorptive power of the activated carbon is dependent mainly on the surface area. Therefore, it is essential to preserve the original surface area during the

regeneration process. Surface areas of virgin and regenerated GAC were determined by nitrogen adsorption at 77K using the BET theory. The nitrogen BET values express the surface area in square meters per gram of adsorbent that can be covered by nitrogen in a monomolecular layer. The results showed that no measurable change occurred in the surface area of regenerated GAC (827 m²/g), compared to that of virgin GAC (843 m²/g). It bears out that the adsorptive capacity of regenerated GAC was largely recovered.

Adsorptive Property. The efficiency of COR is strongly affected by restoration of regenerated carbon's adsorptive capacity for further adsorption. Virgin and regenerated GAC were therefore examined directly to compare the difference in the behavior of their adsorptive capacity. Batch adsorption experiment was carried out with the mineral oil containing Aroclor 1260. Figure 7 represents the chromatograms of Aroclor 1260 before and after one-day equilibration of virgin and regenerated GAC. By inspection of the chromatograms in this Figure, it is seen that the adsorption efficiency of regenerated GAC was almost equivalent to that of the virgin GAC. It proves that the adsorptive capacity of regenerated GAC is not significantly affected by the COR process. The confidence was also supported by the surface area measurements which showed little change in surface area of regenerated GAC compared to that of virgin GAC.

Conclusions

The adsorption isotherm studies were carried out to evaluate the feasibility of removing PCBs (Aroclor 1242 and Aroclor 1260) from PCB-contaminated water with GAC. Adsorption efficiency for Aroclor 1242 which is composed of lower chlorinated PCBs was about 94% for 10 g of GAC, whereas, that for Aroclor 1260 consisting of higher chlorinated PCBs was relatively lower with the adsorption efficiency falling to 83%. Spent GAC was simulated by adsorption of PCBs from PCB-contaminated water. A regeneration process, named countercurrent oxidative reaction (COR), developed in our laboratory, was employed and evaluated for the regeneration of spent GAC. Various tests such as carbon loss, flame temperature, surface structure, adsorptive property, and destruction and removal of adsorbed materials affecting the regeneration efficiency were examined. The results showed that the loss of carbon was controllable, and adsorptive capacity of the regenerated GAC was retained although deep cracks form on the carbon surface. Furthermore, COR showed also considerable potential for the removal and destruction of refractory chlorinated organic compounds, PCBs, that are thermally stable without any toxic formations of PCDDs/PCDFs on the carbon residues and in the effluent gases. Clearly, it proves that the COR technique is a highly effective method for the regeneration of spent GAC in the waste water treatment or for the treatment of hazardous wastes.

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References

1. Abu Zeid, N.; Nakhla, G.; Farooq, S.; Osei-Twum, E. *Water Research* **1985**, *29*, 653.
 2. Urano, K.; Yamamoto, E.; Tonegawa, M.; Fujie, K. *Water Research* **1991**, *25*, 1459.
 3. Streat, M.; Patrick, J. W.; Camporro Perez, M. J. *Water Research* **1995**, *29*, 467.
 4. McDougall, G. J. *J. S. Afr. Inst. Min. Metall.* **1991**, *91*, 110.
 5. Tambo, N. In *Chemical Water and Water Treatment*; Springer, Berlin Heidelberg: U.S.A., 1990; p 17.
 6. Glaze, W. H.; Lay, Y. S.; Kang, J. W. *Ind. Eng. Chem. Res.* **1995**, *34*(7), 2314.
 7. Wigmans, T. *Carbon* **1989**, *27*, 13.
 8. Cannon, F. S.; Snoeyink, V. L.; Lee, R. G.; Dagois, G. *J. Am. Water Works Assoc.* **1997**, *89*, 111.
 9. Moreno-Castilla, C.; Rivera-utrilla, J.; Jolly, J. P.; Lopez-Ramon, M. V.; Ferrero-Garcia, M. A. Carrascosa-Martin, F. *Carbon* **1995**, *33*, 1417.
 10. Larsen, D. W.; Manahan, S. E. *Process for Treatment of Hazardous Wastes by Reverse Burn Gasification*; U. S. A.: Patent 4,978,477, 1990.
 11. Ryoo, K. S.; Kim, T. D.; Kim, Y. H. *Bull. Korean Chem. Soc.* **1999**, *20*, 1447.
 12. Erickson, M. D. *Analytical Chemistry of PCBs*, 2nd ed.; Lewis/CRC: Boca Raton, Fla., U.S.A., 1997.
 13. Buser, H.; Bosshardt, H. P. *Chemosphere* **1978**, *1*, 109.
 14. Buser, H.; Rappe, C. *Chemosphere* **1979**, *3*, 157.
 15. Buser, H. *Chemosphere* **1979**, *6*, 415.
 16. Tsuji, M.; Nakano, T.; Okuno, T. *Chemosphere* **1987**, *16*, 1889.
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