Regeneration of Exhausted Activated Carbon by a Countercurrent Oxygen Reaction

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Countercurrent oxygen reaction (COR) was developed and evaluated for regeneration of exhausted activated carbon. Whether the regeneration technique is feasible or not is affected strongly by gradual loss and physical changes of activated carbon, energy consumption, and effective removal of adsorbed materials during the process. Various parameters such as reaction temperature, the loss of activated carbon, surface area, pore volume, surface structure, adsorptive property, etc. were examined to determine the effectiveness of COR. The results of these tests showed that the parameters were strongly dependent on oxidant flow rate, and suggest that the newly developed COR is comparable and, in some ways, possibly superior to conventional regeneration techniques because the overall process runs in a single step and is less energy intensive, and also because the adsorptive capacity of exhausted activated carbon was completely recovered.

Introduction

Granular activated carbon is widely used for the removal of hazardous and/or pollutant chemicals from wastewater and for purification of water, air, and other materials.[1-4] The widespread use of activated carbon, however, is economically viable only if exhausted activated carbon can be regenerated and therefore recycled in the process.[5,6] Regeneration refers to removal of the adsorbate and restoration of previous adsorptive capacity of the original activated carbon. The currently available regeneration methodologies which include thermal desorption, wet air oxidation, steam, infrared radiation, and solvent extraction have been extensively reviewed.[7,8] Among those methodologies, the most frequently used regeneration method is wet air oxidation (WAO).[9-12] WAO is subjected to partial oxidation of organic materials to be treated at high pressures (0.7-21 MPa) and temperatures (175-320 °C). Randall *et al.* demonstrated that a wide range of organic compounds such as aldehydes, nitriles, aromatic hydrocarbons and phenols could be destroyed by WAO.[13] However, it has been reported that WAO is not useful when very strongly adsorbing or environmentally persistent chlorinated compounds, e.g., PCBs, DDT, and pentachlorophenol, are present.

The purpose of the research reported in this paper is to assess the ability of countercurrent oxidation reaction (COR), developed in our laboratory, to regenerate exhausted activated carbon. The COR process is based on controlled oxidation in an oxygen depleting environment. The process utilizes a flame front which propagates in the direction counter to the flow of oxygen. The flame front consumes the surface of activated carbon and adsorbed organic compounds in a localized zone, utilizing most of the available oxygen. The reaction is exothermic, and the overall process is carried out in a single step with minimum external energy. To evaluate the effect of COR on regeneration of exhausted activated carbon, the following contents were investigated; (1) optimization of regeneration process for minimum loss of activated carbon and maximum removal of refractory organic compounds, (2) reaction conditions such as flame temperature, off-gas compositions, and heat energy, and (3) characterization of regenerated activated carbon with respect to surface area, surface structure, and adsorptive capacity.

Experimental Section

Apparatus and Procedure.   The schematic diagram of instrumental setup for COR process is shown in Figure 1. The reactor was constructed with a 2.2 cm i.d. × 30 cm long quartz tube. The top and bottom of the reactor were fitted with stainless steel O-rings. Both fittings were connected to oxygen gas supply and exhaust lines. A stream of oxygen gas, saturated with water vapor by bubbling it through water heated to 80 °C, was permitted to flow into the reactor. Activated carbon (Darco, granular, 20-40 mesh) was packed from the top of the reactor, and oxygen flow was then started. The flow rates of oxygen were 60 mL, 120 mL, 350 mL, and 600 mL per minute respectively, and the rates were controlled with a calibrated rotameter. After flow equilibration for several minutes, content in the reactor was ignited by applying heat at the bottom of the reactor until flame was generated.
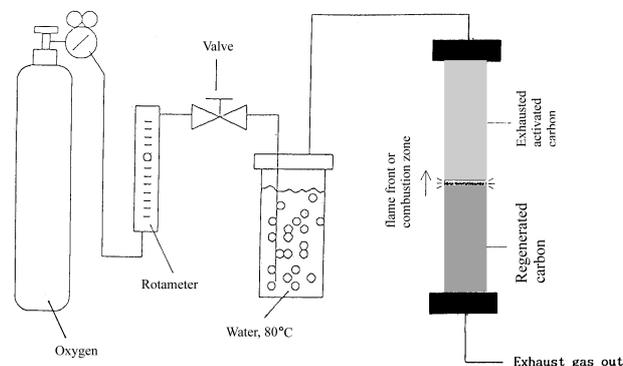
Figure 1. Schematic of instrumental setup for COR process.

Heating was discontinued at the point when the flame front started to move upward. The oxygen flow was shut off when the flame front arrived at the top of the activated carbon. The velocity or residence time of the flame front was determined by dividing the height of activated carbon bed in reactor by total burn time.

Adsorption study was run in two ways; batch (equilibrium) and column (non-equilibrium) adsorption. Virgin and regenerated carbon sample, prior to their use, were prewashed several times with deionized water to remove all fine particles, subsequently dried in an oven at 110 ℃ for one day, and cooled in a desiccator. Batch adsorption experiment was performed, using Aroclor 1260 (the mixture of PCBs composed of mostly 5 and 6 chlorine atoms on biphenyl frame). Each virgin and regenerated carbon (10 g) was placed in contact with 50 g of mineral oil containing Aroclor 1260 in a flask. The flask was placed in a shaker and allowed to equilibrate. The time taken to reach complete equilibrium was on order of 1 day. A system consisting of liquid pump, column, flow-through UV cell, and UV detector was prepared for column adsorption experiment. The contaminated water was prepared by dissolving phenol in 1 L water at the concentration of 200 ppm. Ten grams of virgin and regenerated carbons were packed in the column, respectively. Deionized water was then pumped through the column until the detector achieves a stable baseline absorbance. Afterwards, the solution was changed to the contaminated water and elution of phenol was monitored as breakthrough curve at 254 nm UV absorbance. The breakthrough volume treated was taken when breakthrough point reaches 10%.

Analysis of Samples. The loss of activated carbon during the COR process was determined gravimetrically. The off-gas compositions were determined with an on-line GC-TCD, by measuring the response relative to standard gas mixtures (CO, CO_2, H_2, CH_4, and O_2, Scott Specialty Gases, Inc., Durham, NC). The gases were separated with a carbosieve (60-80 mesh) packed column at 80 ℃ oven temperature. The flame temperature of the COR was obtained from both the loss of activated carbon and the relative ratio of CO/CO_2 in the off-gases. The N_2 BET (Brunauer-Emmett-Teller) surface area measurement was carried out with a Quantasorb Surface Area Analyzer (Quantachrome Corp., Syosset, NY). Surface characterization of the virgin and regenerated carbons was performed using a scanning electron microscope (SEM). PCBs were analyzed with a GC-ECD. A 30 m × 0.25 mm (i.d.) fused silica tubing with 95% methyl + 5% phenylpolysiloxane stationary phase column was used for separation of PCBs. The concentrations of PCBs were determined by comparing the relative peak area to that of a certified standard.

Results and Discussion

Loss of Activated Carbon. In order to lengthen the life of activated carbon, the bulk of exhausted activated carbon is needed to be preserved as much as possible during the regeneration process. In COR case based on thermal regeneration, activated carbon is gradually lost by combustion

reaction of carbon and oxygen in combustion zone during the process. Therefore, it is necessary for the flow rate or the volume of oxygen injected into the reactor to be controlled so that too much of the activated carbon matrix is not burnt away. The loss of activated carbon, as expected, was dependent on the flow rates of oxygen, and showed that the amount lost was in the range of 5-15%, varying with the oxygen flow rate operated within the limits of experiment. 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 activated carbon can easily occur. On the other hand, in the COR, the oxygen is limited in supply and permits a better control of the loss of activated carbon.

Physical Property of Activated Carbon. Adsorptive property of the activated carbon is utterly dependent on the surface area. Therefore, it is essential to preserve the original surface area during the regeneration process. A plot of percent changes in surface area was represented in Figure 2. A measurable change in surface area occurred in the first regenerated carbon, which experienced 4% increase compared to that of the virgin carbon. The surface areas for the second and third regenerated carbons remained relatively constant. The results demonstrate that adsorptive capability of regenerated carbons remains largely intact over three successive COR cycles.

Scanning electron micrographs, shown in Figure 3, were taken to observe the surface of the virgin and regenerated carbons before and after COR process. The carbons were examined at 1500X magnification. At this magnification, the micrographs showed larger pores of the carbon surface, but did not allow observation of micropores. Virgin carbon exhibited a relatively smooth surface. Regenerated carbons gradually developed a sponge-like appearance with the large pores due to the fracture of the carbon particles caused by thermal stress. The generation of large pores in regenerated carbons could make faster the adsorption kinetic in dynamic (non-equilibrium) carbon adsorption which transports solutes
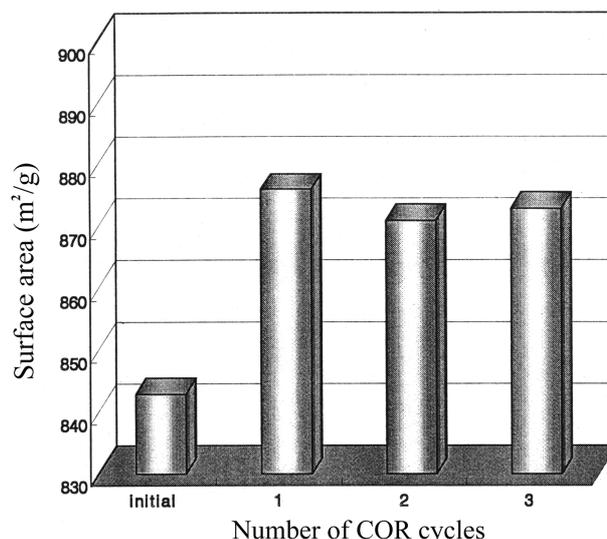
Figure 2. Surface area of regenerated carbons during successive COR cycles.

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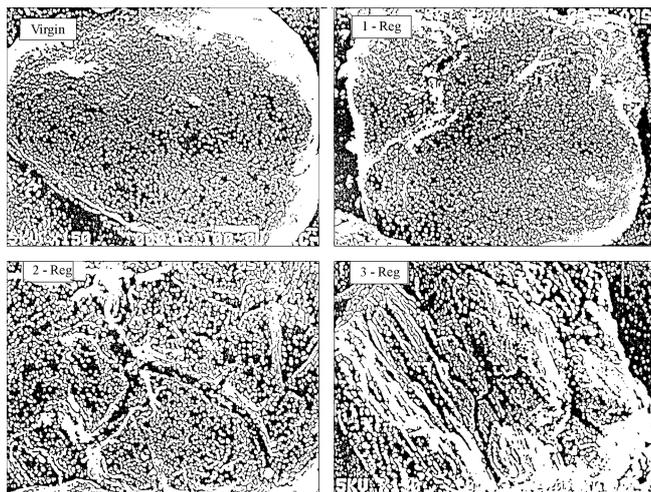
Figure 3. SEM photographs of virgin and 1,2,3-regenerated carbons.

from the solution into the interior micropores. But, thermal cracking and development of sponge texture, on a negative side, lead to weakening of the physical strength of the regenerated carbons.

Adsorptive Property of Activated Carbon.   The efficiency of COR is strongly affected by restoration of regenerated carbon's adsorptive capacity for further adsorption. Virgin and regenerated carbons were therefore examined directly to compare the difference in the behavior of their adsoptive capacities. This was done in two ways: batch (equilibrium) and column (non-equilibrium) adsorptions. Batch adsorption
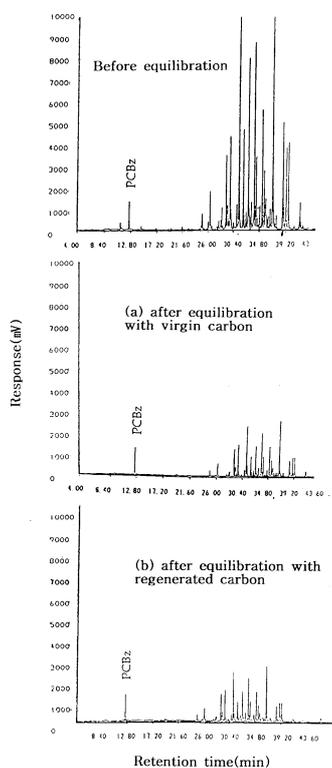
Figure 4. Chromatograms for Aroclor 1260 contaminated mineral oil before and after 1-day equilibration with virgin(a) and regenerated carbon(b).
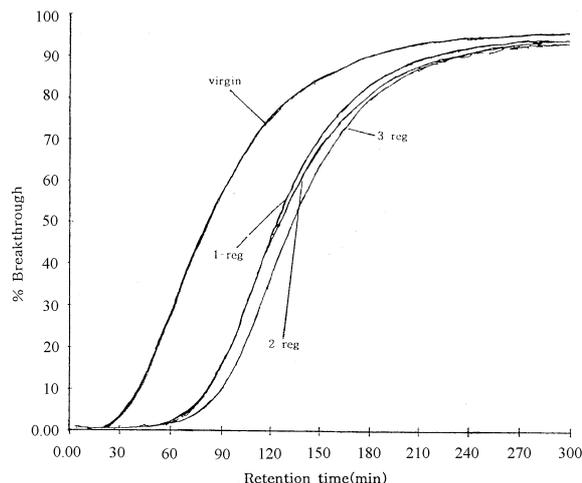
Figure 5. Breakthrough curve for phenol contaminated water on virgin and 1,2,3-regenerated carbons.

experiment was carried out with the mineral oil containing Aroclor 1260. Figure 4(a, b) represents the chromatograms of Aroclor 1260 before and after 1-day equilibration of virgin and the first regenerated carbon. The results showed that the adsorption efficiency of the regenerated carbon was almost equivalent to that of the virgin carbon. Therefore, it proves that the adsorptive capability of exhausted activated carbon regenerated by the COR process was completely recovered.

Column adsorption experiment was done using phenol dissolved in water. The evaluation on adsorptive capacity of virgin and 1,2,3-regenerated carbons was monitored by breakthrough curve, as shown in Figure 5. The results showed that adsorptive capacities of the regenerated carbons were not significantly affected during the COR process, as indicated in the analysis of surface area and batch adsorption. The phenol volumes treated by virgin and 1,2,3-regenerated carbons at 10% breakthrough were given in Table 1. The results showed that a significant increase in volume was obtained after the first regeneration cycle, but the volume remained constant thereafter. The apparent increase in volume is attributed to the opening of large pores resulting from the thermal stress related cracking, although it may have little effect on the total surface area. These characteristics of regenerated carbons absolutely allows for better transport of solutes into the carbon particles by opening channels to the interior.

Heat Energy.   The reaction of carbon with oxygen in the COR process produces gaseous products such as CO, CO_2, CH_4, and H_2. The ratio of CO to CO_2 concentration was varied from 1 : 0.7 to 1 : 1 with increase in the oxygen flow rate. Heat output (ΔH) of COR was determined from the CO/CO_2

Table 1. The phenol volume treated by virgin and 1, 2, 3-regenerated carbons at 10% breakthrough

Type of carbon	Volume (mL)
virgin	924
1-reg	1838
2-reg	1853
3-reg	1871

ratio, and the result showed that it varied from 55 to 60 per mole of carbon. The standard heat output (ΔH) per mole of carbon for COR was calculated from the following expression.

$$C(s) + (1 + f)\, O_2(g) \rightarrow a\, CO(g) + b\, CO_2(g)$$
$$\Delta H = (1\text{-}f) \cdot \Delta_f H_{CO} + f \cdot \Delta_f H_{CO2}$$
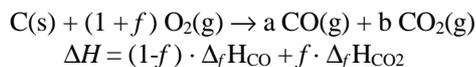
where, $a + b = 1$, $a + 2b = 2(1 + f)$, f = mole fraction of CO_2 in the off-gas.

Flame Temperature. In the process of countercurrent oxygen reaction, accurate measurement of flame temperature by thermocouple, thermometer, and IR was futile, due to the transient nature of the flame front. Hence, the flame temperature was determined by the relative ratios of the CO and CO_2 gas and the loss of carbon at such ratios. 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 and length L. The number of carbon moles per cm^3 is C_c = weight/($12AL$). In a section of this tube of length(L), the carbon and oxygen at T are converted to carbon(C), CO(g), and $CO_2(g)$ at temperature T', with loss of some of the carbon (Δn_C). All of the oxygen delivered at a volumetric flow rate (F, cm^3/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 $t = L/B$. The volume of O_2 burned is: $V_{O_2} = Ft = FL/B$. Moles of O_2 burned are: $\Delta n_{O_2} = kFPL/BT$, where k (reciprocal number of gas constant) = $1/R = 0.001/0.08205 = 0.01219$ (mol · K/cm^3 · atm). The ratio of carbon to oxygen burned is: $\Delta n_C/\Delta n_{O_2} = 2/(1 + f)$, and $\Delta n_C = 2kFPL/BT$ $(1 + f)$. f = mole fraction of CO_2 in product stream. The total moles of carbon involved is

$$n_C = AC_cL, \text{ so } \Delta n_C/n_C = 2kFP/AC_cBT(1 + f).$$

The process is

$$(n_C/\Delta n_C)\, C(s, T) + (1 + f)\, O_2(g, T) \rightarrow f\, CO_2(g, T')$$
$$+ (1\text{-}f)\, CO(g, T') + [(n_C/\Delta n_C)\text{-}1]\, C(s, T')$$
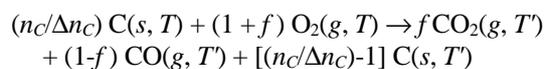
and is assumed to occur adiabatically, so that

$$0 = f\, [\Delta_f H_{CO_2} + \int_{T}^{T'} C_{P_{CO_2}} dT] + (1 - f)$$
$$[\Delta_f H_{CO} + \int_{T}^{T'} C_{P_{CO}} dT] + [(n_C/\Delta n_C)\text{-}1]\int_{T}^{T'} C_{P_c} dT$$

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 CO_2 gas and the loss of carbon at different oxygen flow rates. The flame temperatures calculated varied from 800 °C to 1500 °C. The temperature of flame affects degradation of adsorbed species and characteristics of the carbon surface. Generally, high temperature is desirable for destruction of adsorbates, thus allowing more thorough regeneration for exhausted activated carbon. However, it brings about increased burn-off and deteriorates physical property of the carbon particles.

Removal and Destruction of Refractory Organics. For the comparison of COR and WAO which is characteristically ineffective for removal and destruction of adsorbed refractory organic compounds, PCBs were chosen as a model compound because it has been known that PCBs are persistent in environment and thermodynamically stable at temperatures lower than 800 °C.[14] PCBs are loaded to activated carbon at 1% by weight. The COR process was conducted at oxygen flow rate of 350 mL/min. The removal and destruction efficiency was calculated by measuring the relative concentration of PCBs before and after COR process. It was observed that removal and destruction efficiency of COR with the reproducible values of $\geq$ 99.99% was considerably higher than that of WAO. This result is attributed to the extremely high flame temperature. It convinces us that COR is a very efficacious method against refractory organics, and therefore essentially all organics can be destroyed.

Conclusion

The entire process of countercurrent oxygen reaction utilizes a self-sustained flame which propagates itself in a direction counter to the flow of oxygen. Various tests such as carbon loss, flame temperature, and changes in physical and adsorptive properties of activated carbon were examined. The carbon loss was controllable. The analysis of surface area over 3 successive COR cycles showed that adsorptive capability of the regenerated carbons was largely recovered. The confidence was supported by batch and column adsorption experiments. Furthermore, COR has also considerable potential for the removal and destruction of refractory organic compounds. The overall results obtained during this study demonstrate that the COR is a single process, and proves to be highly effective for the regeneration of exhausted activated carbon.

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