Ozonation of activated carbon and its effects on the adsorption of VOCs exemplified by methylethylketone and benzene

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Abstract

Ozonation can modify the surface property of an activated carbon such as specific surface area, pore volume, and functional group. Results indicate that ozonation can increase the specific surface area of an activated carbon from 783 ± 51 to 851 ± 25 m^2/g due in part to increasing micropores (those below 15 Å). However, there is no change in macropore and mesopore upon ozonation. The amount of oxygen functional group (OFG) increases from 197 ± 4 to 240 ± 4 µeq/g, mostly in hydroxyl and carboxyl groups upon ozone treatment. These oxygen-containing functional groups are stable in the temperature range 30–250 °C, but begin to decompose when temperature increases beyond 300 and 350 °C. When the temperature reaches 1200 °C, all OFGs virtually disappear. The effect of ozone treatment on the adsorption of volatile organic carbon (VOC) was exemplified by methylethylketone (MEK) and benzene. The adsorption density of MEK and benzene by ozone treated activated carbon (AC(O$_3$)) are greater than that by the untreated (AC), with MEK being more adsorbable than benzene. Results of factorial analysis indicate that physical characteristics, namely, micropore, BET surface area, pore diameter (PD), micropore volume (MV) play an important role on benzene and MEK adsorption. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

When activated carbon is exposed to the atmosphere and allowed to react with oxygen, its surface property changes (Mattson and Mark, 1971). Ozone oxidation of activated carbon can modify the surface oxygen functional group (OFG), thereby enhancing its polarity and subsequently affect the adsorption capacity for organic contaminants.

Many factors can affect the adsorption capacity of an activated carbon. These include specific surface area, pore-size distribution, pore volume, and surface functional group. Generally, the adsorption capacity increases with specific surface area, due to the availability of adsorption site (Ruthven, 1984). Pore size and pore-size distribution are closely related to the composition of the activated carbon, the degree of activation and the frequency of regeneration. Urano et al. (1982) indicated that the adsorption capacity is proportional to the cumulative micropore volume (MV) (micropore size less than 3.2 nm). Stern (1977) found that the average molecular size of air pollutant is between 40 and 85 nm and suggested that micropores can play an important role in the adsorption of air pollutants.

The non-polar nature of virgin activated carbon displays a high affinity toward non-polar organic compounds. Kinoshita (1988) reported that the surface functional group of activated carbon consists of oxygen, hydrogen, nitrogen, sulfur, halogen, and other elements.

These surface elements are responsible for the adsorption of air contaminants. At room temperature, activated carbon reacts readily with oxygen to form functional groups of oxygen complexes on the surface Walker and Janov, 1968. The surface functional groups can affect the physico-chemical characteristics (such as dampness, catalytic effect, and electrical properties) of the activated carbon.

Boehm (1966) and Puri (1970) classified the functional group into acid, base, and neutral type. The acidic group includes –COOH, –OH, –C=O, and –COO–. In order to attain a high concentration of OFG, oxidants are used as activation agents during the manufacturing of activated carbon (Mattson and Mark, 1971). The following chemicals, mostly gases, are commonly used as activation agents: O_2, NO, CO_2, and H_2O (Laine et al., 1963; Hart et al., 1967; Lussow et al., 1967; Walker and Janov, 1968; Turkdogan and Vinter, 1969, 1970; Bansal et al., 1970a,b; Phillips et al., 1970; Kinoshita, 1988). Other strong oxidants such as $KMnO_4$, HNO_3, and $KClO_4$ can also be used in liquid-phase activation processes (Puri and Bansal, 1964; Norwitr and Galan, 1967; Matsumura et al., 1976; Hagiwan et al., 1978; Hahn et al., 1981).

Zarifyanz et al. (1967) have shown that oxygen reacts with graphite at temperatures below −40 °C to form surface oxides, which can be readily removed as CO or CO_2 at temperatures above 200 °C. In general, carboxylic and lactone groups begin to decompose at about 250 °C, and the phenol and quinone groups decompose almost completely between 500 and 900 °C. At 900 °C, the hydroxyl group decreases drastically and the other oxygen-containing surface functional groups are completely eliminated (Kinoshita, 1988).

Pretreatment of activated carbon increases the surface area and the concentration of surface functional group, which in turn can enhance the adsorption capacity. Two mechanisms are involved in the oxidation of carbon black by ozone: (i) direct oxidation of elemental carbon to CO_2 and (ii) oxidation of elemental carbon to intermediates that are soluble in alkaline solutions and are subsequently oxidized to CO_2. Deitz and Bitner (1972, 1973) showed that a large amount of ozone was adsorbed on the graphite surface, C, with the formation of ozonated surface complexes such as $\underline{C}O_3$ and CO:

$$\underline{C} + O_3 = \underline{C}O_3$$

$$C + O_3 = \underline{C}O + O_2$$
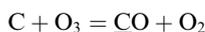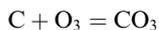
It has been reported that gas-phase oxidation by ozone takes place at the edge and terrace of the graphite structure and the basal plane, and subsequently pits the surface. Donnet et al. (1970a,b, 1982) conducted experiments on the ozonation of activated carbon and reported that at a dosage of 13 mg O_3/l, 65% of the activated carbon surface were oxidized to CO_2. The degree of oxidation, however, was independent of temperature and O_3 concentration. While literature reports appear to suggest that O_3 treatment can alter the surface functional group of an activated carbon, very little quantitative information is available on the possible modification of the physical property of the treated activated carbon. The objective of this research was to examine the change of physical–chemical properties of an activated carbon by ozonation and its effects on the adsorption of volatile organic compounds (VOCs) exemplified by methylethylketone (MEK) and benzene. Factorial analysis technique was used to determine the important parameters controlling the VOC adsorption.

2. Experimental methods

An activated carbon, KOWA-COSMOS (8×30 mesh), was selected for this study. The activated carbon was treated continuously by ozone for 30 min at a concentration of 40 mg/l and a flow rate of 2.5 l/min (or a mass rate of 100 mg/min). The activated carbon was then stored in an oven at 105 °C and dried for 48 h. The physical characteristics of activated carbon, including specific surface area, total pore volume, MV, pore-size distribution, and pore diameter were measured. Most of the above properties can be measured by N_2 (g) adsorption at 77 K using an ASAP 2000 micropore analyzer. Micropore characteristics diameter was measured with Ar (g) adsorption also using an ASAP 2000 micropore analyzer at 77 K in liquid N_2.

The specific surface area was calculated by the BET method (Brunauer et al., 1938). The micropore surface area was determined by subtracting the external surface area from the BET surface area.

The total pore volume was determined by the BJH method (Barrett et al., 1951). The MV was calculated by the t-plot and the Harkins–Jura method (Harkins and Jura, 1944; Lippens and de Boer, 1965).

Surface elemental composition, namely, carbon, nitrogen, hydrogen and oxygen was analyzed with a Heraeus CHNO rapid element analyzer. A total of five samples were analyzed in duplicate. Acetanilide was used as the standard. Sulfur and chlorine were analyzed with Tacussel Coulomax 78 using sulfanilic acid and 1-chloro-2,4-dintrobenzene standards. Other elements such as Ca, S, Fe, K, Al, Mg, Na, Cr were analyzed with ICP-AES against a standard reference, NBS SRM-1648.

OFG was analyzed by alkalimetric titration according to procedures of Boehm (1966) and Fabish and Schleifer (1984). Activated carbon sample (ca. 5 g) was first dried in a vacuum oven at 10^{-2} to 10^{-3} mm Hg, and 105 °C for 24 h before titration. The titration began by adding 25 ml of NaOH (0.1 N) solution to a series of test tubes containing a given amount of the activated carbon. The sample was mixed over a vibrator at

100 rpm and 25 °C for 24 h. A given amount of the supernatant (5 ml) was then drawn from the test tubes and back-titrated with HCl (0.1 N) solution. The concentrations of various functional groups were calculated by the net amount of alkali consumed.

The surface OFGs are generally stable under vacuum below their formation temperatures (Puri and Bansal, 1964; Bansal et al., 1977) and definitely stable at temperatures below 200 °C. The thermal desorption processes, carried out in vacuum at a linearly programmed heating rate, typically 2.5 °C/min, followed those of Puri and Bansal (1964), and Bansal et al. (1977). The surface OFGs of activated carbon after pyrolysis in vacuum were analyzed by Boehm's method.

Procedures for kinetic adsorption experiments and related adsorption conditions were as the following. Placed 50 mg of activated carbon in an electrical-balance that was already connected to a data acquisition system. The influent relative vapor pressure of benzene was set at the range from 0.005 to 0.016 atm and that of MEK was from 0.003 to 0.010 atm. The inflow rate of benzene and MEK vapor was set at 2.0 l/min and the adsorption temperature was maintained at 30 ± 0.1 °C. The kinetic adsorption runs were repeated four times for all experimental concentrations.

Factor analysis was conducted. Factor analysis involves several steps. First, the correlation or covariance matrix is computed from the usual case-by-variables data file. Second, the factor loadings are estimated. Third, the factors are rotated to make the loadings more interpretable, that is, rotation methods make the loadings for each factor either large or small, not in-between.

3. Results and discussion

3.1. Surface physical characteristics

For each adsorbent, five separate samples were taken for the analysis of physical characteristics. For quality assurance, three of the five samples were analyzed in duplicate. Surface physical characteristics analyzed were BET specific surface area, micropore area (MA), MV and pore diameter (PD). Table 1 shows the results of physical characteristics of activated carbons studied.

The BET specific surface area of the activated carbon (AC) and the oxidized activated carbon ($AC(O_3)$) are 783 ± 51 and 851 ± 25 m²/g, respectively. The specific surface area of $AC(O_3)$ increases by 8.7% over that of the AC. Apparently ozonation alters the pore size and its distribution which in turn increases the specific surface area.

The MA is 677 ± 41 and 727 ± 16 m²/g for AC and $AC(O_3)$, respectively. Results indicate that oxidation increases mainly the micropore surface area as MA contributes 74% of the specific surface area increase.

Upon oxidation, the MV also increases from 0.320 ± 0.002 to 0.344 ± 0.009 cm³/g (an increase of 7.5%) and the PD slightly rises from 14.60 ± 0.03 to 14.67 ± 0.03 Å (an insignificant increase of 0.5%). There is almost no difference in PD between AC and $AC(O_3)$.

There is no significant difference in macropore and mesopore volume distribution between AC and $AC(O_3)$ (Figs. 1 and 2). As seen in Figs. 1 and 2, the variation of pore volume distribution curves obtained from desorption runs is greater than that from adsorption runs. This can be attributed in part to the presence of a hysteresis during nitrogen desorption caused by the micropore structure. The pore volume for pore size in the range between 6 and 7 Å of AC is greater than that of $AC(O_3)$. The pore volume for pore size under 6 Å of $AC(O_3)$ is greater than that of AC (Fig. 3).

3.2. Chemical characteristics

Table 2 gives the concentration of major surface elements of AC and $AC(O_3)$. The concentration of nitrogen, carbon, hydrogen, and oxygen of AC are 0.22%, 87.13%, 1.70%, and 10.95%, respectively. The concentration of N, C, H, and O of $AC(O_3)$ are 0.20%, 86.84%, 1.61%, and 11.35%, respectively. Results indicate that the concentration of oxygen slightly increases by 0.29%, whereas hydrogen decreases by 0.09% upon ozone treatment.

Tables 3 and 4 show the changes in surface functional groups of the activated carbon due to ozonation. As expected, there is a substantial increase in oxygen surface functional groups by ozone oxidation. The functional group –OH of AC is 117 ± 7 μeq/g and upon ozonation it increases by 23% to 144 ± 5 μeq/g. The

Table 1
Physico-chemical characteristics of activated carbon as affected by ozone oxidation[a]

Items	BET (m²/g)	MA (m²/g)	PD (Å)	Total pore volume (cm³/g)	MV (cm³/g)
AC	783 ± 51	677 ± 41	14.60 ± 0.03	0.367 ± 0.006	0.320 ± 0.002
$AC(O_3)$	851 ± 25	727 ± 16	14.67 ± 0.03	0.400 ± 0.005	0.344 ± 0.009
Percent variation[b]	8.7%	7.4%	0.5%	9.0%	7.5%

[a] Sample number is 5 and the measurement of PD is less than 2000 Å.
[b] Percent of variation = $(AC(O_3) - AC)/AC \times 100\%$.
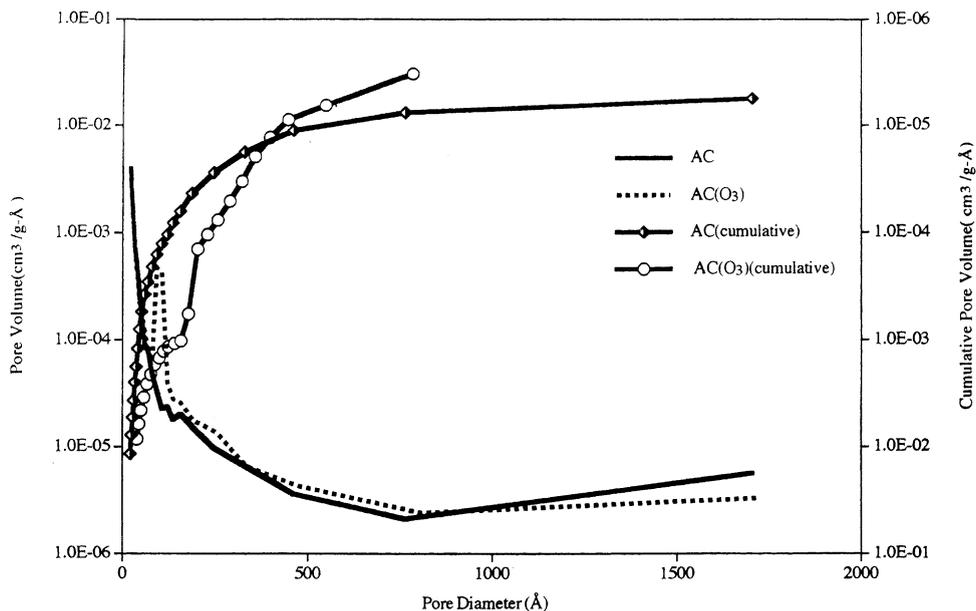
Fig. 1. Macropore and mesopore volume distribution of AC and AC(O$_3$) under adsorption process.
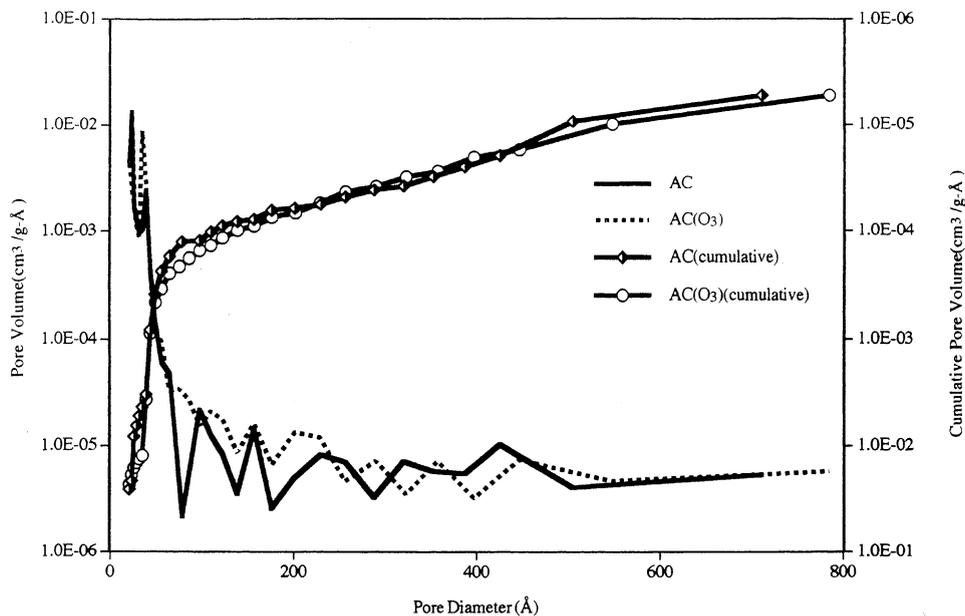
Fig. 2. Macropore and mesopore volume distribution of AC and AC(O$_3$) under desorption process.

–C=O functional group increases from 46 ± 6 to 52 ± 14 µeq/g and the –COOH functional group increases from 34 ± 4 to 44 ± 10 µeq/g upon ozone treatment. In terms of surface area, the OFGs increase by 12% due to ozone treatment.

The sum of the OFGs increases from 197 ± 4 to 240 ± 4 µeq/g by ozonation. This is an overall increase of 22%. The increase in –OH, –C=O, and –COOH functional group is 23%, 13%, and 29%, respectively.

Fig. 4 shows the desorption of OFGs as a function of temperature between 30 and 1200 °C. Results indicate that the OFGs are stable in the less than 250–300 °C range. The amount of OFG decreases drastically in the 250–300 °C range. The amount of OFG desorption be-
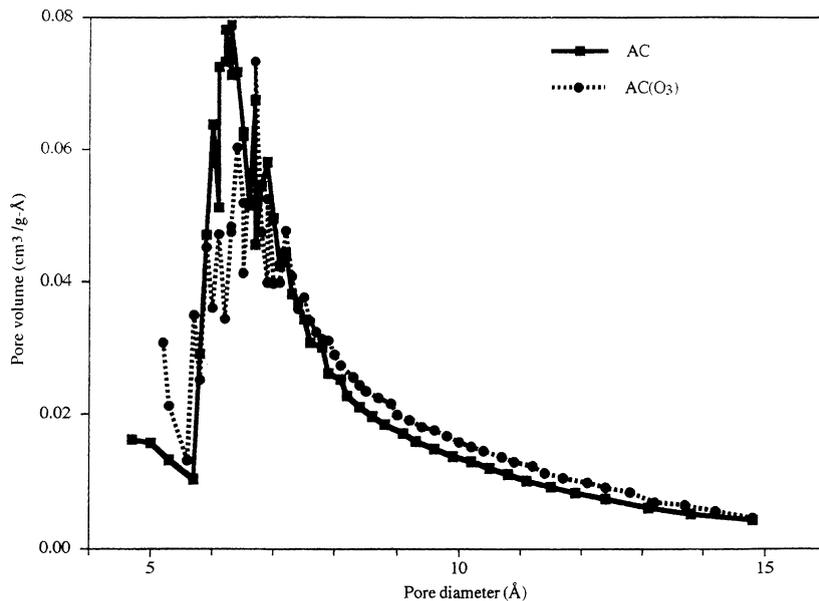
Fig. 3. MV distribution of AC and AC(O_3).

Table 2
Major surface elements of activated carbon as affected by ozone oxidation[a]

Activated carbon (%)	N	C	H	O	S	Cl
AC	0.22 (0.22)[b]	86.52 (87.13)	1.69 (1.70)	10.87 (10.95)	ND[c]	ND
AC(O_3)	0.20 (0.20)	87.21 (86.84)	1.62 (1.61)	11.40 (11.35)	ND	ND

[a] Triplicate samples.
[b] Figures in parentheses designated correction data that based on the sum of the concentration of N, C, H, O, S and Cl which is equal to 100%.
[c] ND: detection value $< 0.01\%$.

Table 3
OFGs concentration of AC and AC(O_3)[a]

Activated carbon		OH	CO	COOH	OFG
AC	μeq/g	117 ± 7	46 ± 6	34 ± 4	197 ± 4
	μeq/100 m²	15 ± 9	6 ± 0.8	4 ± 0.5	25 ± 0.5
AC(O_3)	μeq/g	114 ± 5	52 ± 14	44 ± 10	240 ± 4
	μeq/100 m²	17 ± 0.6	6 ± 1.6	5 ± 1.2	28 ± 0.5
Percent variation[b] (%)	μeq/g	23	13	29	22
	μeq/100 m²	13	0	12	12

[a] Sample number is 5.
[b] Percent of variation $= (AC(O_3) - AC)/AC \times 100\%$.

comes insignificant in the 700–1000 °C range. Generally, the decomposition of carboxylic and lactone groups begins at about 250 °C. Phenolic and quinone groups are removed between 450 and 900 °C. When the temperature exceeds 900 °C, all OFGs are almost completely destroyed.

Fig. 5 shows the rate of MEK and benzene adsorption onto ozone-treated and untreated activated carbons as a function of relative pressure, p/p_0. The adsorption rate (AR) of benzene increases from 32 to 102 mg/g h for AC and from 20 to 114 mg/g h for AC(O_3) when the influent relative vapor pressure increases from 0.005 to

Table 4
The results of factorial analysis (rotated factor pattern)

Items	Group I	Group II	Group III
(a) *Benzene adsorption*			
MA	0.97[a]	0.26	
BET	0.95	0.31	
PD	0.86	0.45	
MV	0.72	0.62	
OFG	0.58	0.80	
AR	0.66	0.71	
Q	0.19	−0.98	
Variance	3.89	2.85	
Percent of total variance	55.52	40.73	
(b) *MEK adsorption*			
MA	0.93	0.03	0.27
BET	0.91	0.06	0.61
PD	0.80	0.16	0.61
MV	0.66	0.34	0.67
OFG	0.30	0.60	0.54
AR	0.55	−0.05	0.83
Q	−0.01	−0.96	−0.01
Variance	3.40	1.41	2.85
Percent of total variance	55.52	40.73	40.73

[a] Factor loading.

0.015. In the case of MEK, when the influent relative vapor pressure increases from 0.003 to 0.010, the AR increases from 18 to 102 mg/g h for AC and from 30 to 106 mg/g h for AC(O₃). Moreover, the AR by AC(O₃) is generally greater than that by AC. This can be attributed to the change of the physical characteristics. It is noted that the BET surface area and the MV of AC(O₃) are greater than those of AC. The pore diameter of AC(O₃) is narrower than that of AC. Moreover, the average micropore size of AC(O₃) is smaller than that of AC. As predicted by the Kelvin equation (Adamson, 1982), the smaller the PD, the lower the relative vapor pressure during capillary condensation. As a result, the AR of AC(O₃) will be greater than that of AC under otherwise identical experimental conditions. Results also indicated that the AR of MEK is greater than that of benzene over the relative vapor pressure range studied. This is attributed in part to the adsorption energy of benzene (34.4 kJ/mol) higher than MEK (23.5 kJ/mol) (Chiang et al., 2002).

Fig. 6 shows the adsorption of MEK and benzene as a function of partial pressure. The increase in influent relative vapor pressure of benzene from 0.005 to 0.016 resulted an increase in adsorption density from 208 to 226 mg/g on AC and from 188 to 210 mg/g on AC(O₃). The benzene adsorption capacity of AC is greater than that of AC(O₃) at various benzene concentrations. This is expected as the surface of AC(O₃) is more polar than that of AC and benzene is a nonpolar adsorbate, the benzene-specific adsorption sites will be less on AC(O₃) than AC.

The adsorption capacity of MEK increases from 166 to 214 mg/g by AC and from 192 to 214 mg/g by AC(O₃)
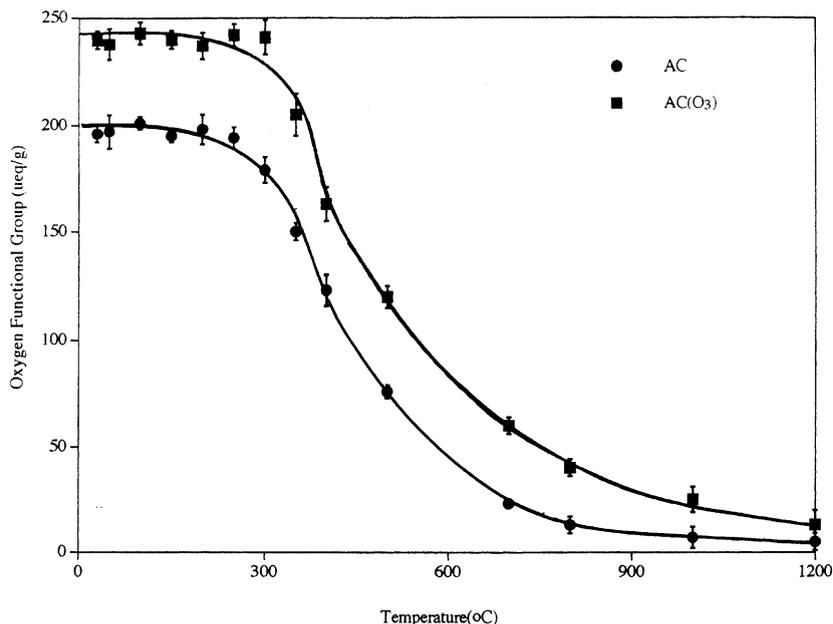

Fig. 4. Concentration of OFGs at various temperatures.
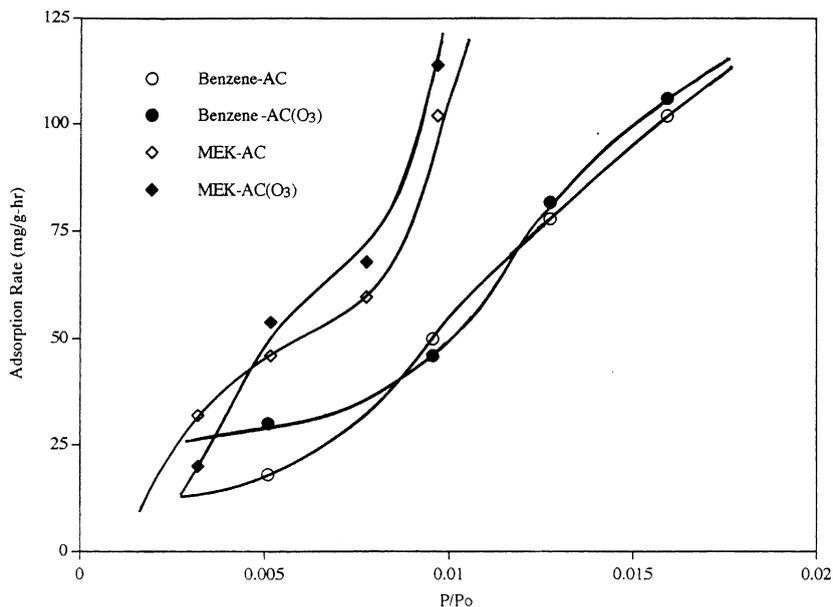
Fig. 5. AR of benzene and MEK on AC and AC(O$_3$).
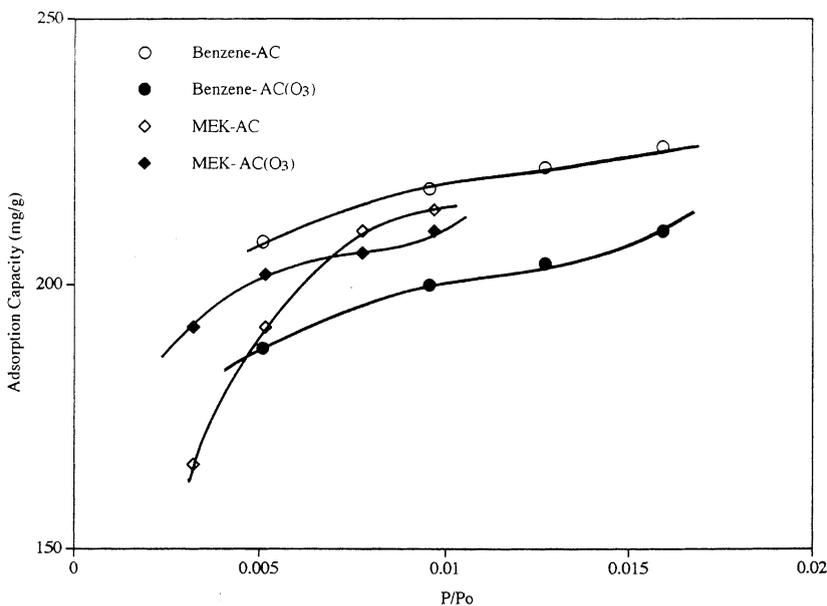
Fig. 6. Adsorption capacity of benzene and MEK on AC and AC(O$_3$).

when the influent relative vapor pressure increases from 0.003 to 0.010. The adsorption density of MEK by AC is greater than that on AC(O$_3$) when the influent relative vapor pressure is greater than 0.008. Results indicate that capillary condensation (physical adsorption) is the predominant mechanism for VOC adsorption at high concentrations. At low VOC concentrations, however, chemisorption plays an important role in the adsorption process. MEK is a slightly polar adsorbate, therefore the MEK adsorption density on AC(O$_3$) (a more polar surface) is greater than of AC. The benzene adsorption density of AC is greater than that of MEK due to greater affinity exhibited by evident of the greater adsorption energy of benzene (34.4 kJ/mol) than as in

MEK (23.5 kJ/mol), as reported above (Chiang et al., 2002).

3.3. Factorial analysis

In order to evaluate the relationship among adsorption density, AR and various physical–chemical properties of the activated carbon, a statistical analysis of these parameters was conducted using the software, Statistical Analysis System (SAS). The data were inputs into the software program, which generate "factor loading". Table 4 shows results of the SAS analysis.

Results clearly indicated that all physical properties (variables), i.e., MA, BET surface area (BET), PD, and MV are closely related to each other as indicative of their corresponding high "factor loadings". For benzene adsorption, OFG is the sole important factor affecting both adsorption density (Q) and AR.

OFG again becomes the sole important factor affecting the adsorption capacity of MEK (Group II). The AR of MEK is only affected by the MV.

4. Conclusions

Ozonation of activated carbon can increase the specific surface area and surface OFGs. Ozone reacts with the physical structure of the activated carbon enlarging the pore size and creates new pores. Increase in pore structure is seen at the micropore level. Increase in surface functional groups is seen mostly in hydroxyl and carboxyl groups. OFGs are stable between 30 and 250 °C and begin to decompose at 350 °C. Results of factorial analysis indicate that physical characteristics of the adsorbent, e.g., BET specific surface areas, MAs and pore diameter are the major parameters for benzene and MEK adsorption.

References

Adamson, W.A., 1982. Physical and Chemistry of Surface. Wiley, New York.

Bansal, R.C., Dhami, T.L., Parkash, S., 1977. Surface characteristics and surface behaviour of polymer carbons. I. Associated oxygen and hydrogen. Carbon 15, 157–160.

Bansal, R.C., Vastola, F.J., Walker, P.L., 1970a. Studies on ultra-clean carbon surface. IV. Decomposition of carbon–oxygen surface complex. Carbon 8, 443–448.

Bansal, R.C., Vastola, F.J., Walker, P.L., 1970b. Studies on ultra-clean carbon surface. II. Kinetics of chemisorption of oxygen on graphon. J. Colloid Sci. 32, 187–194.

Barrett, E.P., Joyner, L.S., Halenda, P.P., 1951. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherm. J. Am. Chem. Soc. 73, 373–380.

Boehm, H.P., 1966. Chemical identification of surface groups. In: Eley, D.D., Pines, H., Weisz, P.B. (Eds.), Advances in Catalysis, vol. 16. Academic Press, New York, p. 179.

Brunauer, S., Emmett, H.P., Teller, E., 1938. Adsorption of gas in multimolecular layers. J. Am. Chem. Soc. 60, 309–319.

Chiang, H.L., Huang, C.P., Chiang, P.C., 2002. The adsorption of benzene and methylethylketone onto activated carbon: thermodynamic aspects. Chemosphere 46 (1), 143–152.

Deitz, V.R, Bitner, J.L., 1972. The reaction of ozone with adsorbent charcoals. Carbon 10, 145–154.

Deitz, V.R., Bitner, J.L., 1973. Interaction of ozone with adsorbent charcoals. Carbon 11, 339–401.

Donnet, J.B., Ehrburger, D., Voet, A., 1970a. Etude cinetique de l'oxydation d'un noir au four par l'ozone en milieu aqueux. Carbon 8, 697–705.

Donnet, J.B., Ehrburger, D., Voet, A., 1970b. Etude du mecanisme d'oxydation des noirs de carbone par l'ozone en milieu aqueux. Carbon 10, 737–746.

Donnet, J.B., 1982. Structure and reactivity of carbons: from carbon black to carbon composites. Carbon 20, 266–282.

Fabish, T.J., Schleifer, D.E., 1984. Surface chemistry and carbon black work function. Carbon 22, 19–38.

Hagiwan, S., Tsutsumi, K., Takahashi, H., 1978. Surface polarity of carbon blacks. Carbon 16, 89–93.

Hahn, C.S., Cho, H.S., Yang, H.S., 1981. Conversion of graphite into mellitic acid. Carbon 19, 225–229.

Harkins, W.D., Jura, G., 1944. Surfaces of solids XIII: a vapor adsorption method for the determination of the area of a solid without the assumption of a molecular area and the areas occupied by nitrogen and other molecules on the surface of a solid. J. Chem. Phys. 66, 1366–1373.

Hart, P.J., Vastola, F.J., Walker, P.L., 1967. Oxygen chemisorption on well leaned carbon surface. Carbon 5, 363–371.

Kinoshita, K., 1988. Carbon: Electrochemical and Physicochemical Properties. Wiley, New York.

Laine, N.R., Vastola, F.J., Walker, P.L., 1963. The importance of active surface area in the carbon–oxygen reaction. J. Phys. Chem. 67, 2030–2032.

Lussow, R.O., Vastola, F.J., Walker, P.L., 1967. Kinetics of oxygen interaction with graphon between 450 and 675 °C. Carbon 5, 591–602.

Matsumura, Y., Hagiwara, S., Takahashi, H., 1976. Automatic potentiometric titration of surface acidity of carbon black. Carbon 14, 163–167.

Mattson, J.S., Mark Jr., H.B., 1971. Activated Carbon: Surface Chemistry and Adsorption from Solution. Marcel Dekker, New York.

Norwitr, G., Galan, M., 1967. Dissolution of carbon blacks by nitric acid. Carbon 5, 287–289.

Lippens, B.C., de Boer, J.H., 1965. Studies on pore system in catalysts V the t method. J. Catal. 4, 319–323.

Phillips, R., Vastola, J.F., Walker, P.L., 1970. Factors affecting the product ratio of the carbon–oxygen reaction. II. Reaction temperature. Carbon 8, 205–210.

Puri, B.R., 1970. In: Walker, P.L. (Ed.), Chemistry and Physics of Carbon. Marcel Dekker, New York, p. 191.

Puri, B.R., Bansal, R.C., 1964. Studies in surface chemistry of carbon blacks. II. Surface acidity in relation to chemisorbed oxygen. Carbon 1, 457–464.

Ruthven, D.M., 1984. Principles of Adsorption and Adsorption Process. Wiley, New York.

Stern, A.C., 1977. Engineering Control of Air Pollution: Air Pollution-IV. Academic Press, New York.

Turkdogan, E.T., Vinter, J.V., 1969. Kinetics of oxidation of graphite and charcoal in carbon dioxide. Carbon 7, 101–117.

Turkdogan, E.T., Vinter, J.V., 1970. Effect of carbon monoxide on the rate of oxidation of charcoal, graphite and coke in carbon dioxide. Carbon 8, 39–53.

Urano, K.S., Omori, S., Yamamoto, E., 1982. Prediction method for adsorption capacities of commercial activated carbon in removal of organic vapors. Environ. Sci. Technol. 12, 10–14.

Walker, P.L., Janov, J., 1968. Hydrophilic oxygen complexes on activated carbon. J. Colloid Sci. 28, 449–458.

Zarifyanz, Y.A., Kisekv, V.F., Lezhnev, N.N., Nikitina, O.V., 1967. Interaction of graphite fresh surface with different gases and vapor. Carbon 5, 127–135.