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The surface characteristics of activated carbon as affected by ozone and alkaline treatment

Hung-Lung Chiang [a], C.P. Huang [b,*], P.C. Chiang [c]

[a] Department of Environmental Engineering, Fooyin Institute of Technology, Kaohsiung Hsien, 831, Taiwan, ROC
[b] Department of Civil and Environmental Engineering, University of Delaware, Newark, DE 19716, USA
[c] Graduate Institute of Environmental Engineering, National Taiwan University, Taipei, Taiwan, ROC

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Abstract

The surface chemical characteristics of activated carbon treated by ozone and alkaline are determined in terms of surface functional groups and surface acidity. Surface functional groups are analyzed by the IR spectroscopic method and Boehm's titration technique. The surface acidity of activated carbon is determined by electrophoretic mobility measurements. The oxygen concentration of activated carbon increases upon ozone and NaOH treatment. Surface functional groups increase mostly in the hydroxyl and carboxyl categories rather than the carbonyl category upon ozone and NaOH treatment. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Activated carbon; Ozone; Alkaline; Oxygen concentration; Surface functional groups

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1. Introduction

Activated carbon can be produced from a great variety of carbonaceous materials including coconut shells, sawdust, wood char, coal, petroleum coke, bone char, molasses, peat and paper-mill waste (lignin) (Mattson and Mark, 1971; Hassler, 1974; Bansal et al., 1990). Depending on the extent of oxidation reaction, two types of activated carbon can be produced (Mattson and Mark, 1971; Hassler, 1974; Corapcioglu and Huang, 1987; Bansal et al., 1990): H-type and L-type. H-type activated carbons exhibit positive charge in water, adsorb strong acid and are hydrophobic. L-type activated carbons display negative charge in water, neutralize strong bases and are hydrophilic. Much has been reported on the oxidation of activated carbon. Steebberg (1944) characterized the activation and oxidation of carbon at various temperatures and classified those carbons that were oxidized at low-temperature and adsorbed primarily hydroxide ion as L-carbons, and those activated at high temperatures and adsorbed strong acid as H-carbons. The L-carbon behavior is expected to intensify after long exposure to the atmosphere even at ambient temperatures. Cookson (1978) and Huang (1978) reported the adsorption of electrolytes and nonelectrolytes and its effect on the structure of the electrical double layer and the role of surface functional group on the nature of adsorption.

Bailey (1982) proposed two mechanistic extremes for the oxidation of carbon by ozone: a radical type, ozone-initiated autoxidation, and a concerted reaction, i.e., l, 3-dipolat insertion. Schubert and Pease (1956a) reported that in the high temperature range, molecular oxygen participates in the reaction as the temperature increases up to 270 °C. The reaction then becomes a slow combustion process that is indistinguishable from the reaction with oxygen alone. At low temperature, the mechanism of vapor-phase reaction is similar to that of liquid-phase ozonation, at least when only molecular

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* Corresponding author. Tel.: +1-302-831-8428; fax: +1-302-831-3640.

E-mail address: huang@mail.ce.udel.edu (C.P. Huang).

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ozone is involved. At ordinary temperature, reactions in general occur via an ozone insertion mechanism involving the hydrotrioxide ($RO_3^\bullet$) intermediate, its product, peroxides ($RO_2^\bullet$) and other radicals. If ozone is the principal reactant, no chain reaction will take place. In the presence of metal catalysts, radical chain mechanisms are involved and become an important part of the oxidation reaction.

Reaction between activated carbon and alkaline is another chemical means for the modification of surface property. Under alkaline environment, it is expected that OH^- will react with the surface functional groups of the activated carbon. However, little is available in the literature on the effect of alkaline and ozone treatment on the surface property changes of activated carbon. The objective of this study was to evaluate the surface property changes of an activated carbon upon treatment by ozone and alkaline. Infrared spectroscopy, electrophoretic measurements and alkalimetric titration were used to assess the changes of surface property of the activated carbon.

2. Experimental

2.1. Material

An activated carbon (8 × 30 mesh), made from coconut shells and provided by Kowa Cosmos Company, Japan was used in this study. Prior to chemical treatment, the surface property of this activated carbon was characterized. Detailed experimental procedures for the characterization of surface property were reported elsewhere (Chiang et al., 1999).This activated carbon has a BET surface area, average pore diameter, macropore volume (>500 Å), mesopore volume (between 20 and 500 Å), and macropore volume (<20 Å) of 795 ± 50 m^2/g, 14.7 ± 0.05 Å, 0.011 ± 0.009 cm^3/g, 0.041 ± 0.012 cm^3/g, 0.325 ± 0.023 cm^3/g, respectively. All solutions were prepared from chemicals provided by Merck Chemicals Company, Germany. A pH meter (model 420 A) was used for pH measurements. Strong acid (0.1 N HCl) and base (0.1 N $NaHCO_3$, Na_2CO_3, and NaOH) were used for the analysis of surface functional group. Unless otherwise mentioned, strong acid (0.1 M $HClO_4$) and strong base (0.2 M NaOH) were used for all pH adjustments.

2.2. Chemical treatment of activated carbon

500 g of activated carbon was weighed and placed into each of the five 2-l polyethylene bottles. 1 l of NaOH solution at various concentrations was added to each of the five bottles containing the activated carbon. The bottles were then placed on a rotating vibrator and mixed constantly for 24 h. The activated carbon was then separated from the solution and placed in an oven at 105 °C and dried for 48 h. The NaOH-treated activated carbon samples were divided into two parts. One part received further ozone treatment at an inflow concentration of 40 mg/l and flow rate of 2.5 l/min (or mass rate of 100 mg/min) for 30 min. The reaction temperature was controlled at level below the combustion point of the activated carbon using a water tank.

Both activated carbon samples were washed with distilled water until the sodium ion concentration of the rinsed water reached that of the distilled water. The activated carbon was dried in an oven at 105 °C for 48 h then transferred to a desiccator until use.

2.3. IR spectrum analysis

The activated carbon samples were ground in an agate motar to fine powder. The activated carbon powder was mixed with KBr by a weight ratio of 700:1. A given amount of the mixture (200 mg) was used for the preparation of KBr pellets. The KBr pellets were stored in a desiccator until IR analysis. The IR instrument was a Bomem, model DA 3.002 FTIR. The IR spectrum was obtained over a frequency between 500 and 4000 cm^{-1}.

2.4. Boehm titration

Procedures for the analysis of oxygen functional group follow those established by Boehm (Puri and Bansal, 1964; Boehm, 1966; Barton et al., 1973; Fabish and Schleifer, 1984; Magane and Dupong-Parlovskky, 1988; Arico et al., 1989). The activated carbon samples were first dried in a vacuum oven (10^{-2} – 10^{-3} mm Hg, 105 °C) for 24 h. 25 ml of an alkali solution (0.1 N $NaHCO_3$, Na_2CO_3, or NaOH) were added to test tubes containing a given amount of the activated carbon sample (5 g). The samples were constantly mixed over a vibrator (100 rpm) at 25 °C for 24 h. A given amount of the supernatant (5 ml) was then drawn from the test tubes and back titrated with HC1 (0.1 N) solution. The concentrations of various functional groups were determined by the residual bases after back titration as described by Boehm (1966).

2.5. Electrophoretic mobility measurements

Zeta potential measurements of activated carbons were made with Zeta Meter System 3.0. The activated carbon (5 g) was placed in a porcelain mortar and ground to fine powder. A given amount of the activated carbon powder (100 mg) was added to 1 l distilled water. After mixing for several minutes, the coarse particles were allowed to settle, and the colloidal size particles were collected for electrophoretic mobility measurements. After electrolyte addition (10^{-2} M NaCl) and pH adjustment, the activated carbon suspension was placed in the electrophoresis cell for zeta potential measurements.

2.6. Surface acidity determination

The surface acidity of the activated carbon was determined according to concept and procedures proposed by Huang and associates (Corapcioglu and Huang, 1987). Upon hydration, the surface acidity develops on the activated carbon

$$\underline{C}OH_2 = \underline{C}OH + H^+; \quad K_{a1}^{int} \tag{1}$$

$$\underline{C}OH = \underline{C}O^- + H^+; \quad K_{a2}^{int} \tag{2}$$

where $\underline{C}OH_2^+$, COH, and $\underline{C}O^-$ represent protonated, neutral and ionized surface hydroxyl groups, respectively. The intrinsic acidity constant, K_{a1}^{int} and K_{a2}^{int} are defined as follows:

$$K_{a1}^{int} = \{\underline{C}OH\}\{H^+\}/\{\underline{C}OH_2^+\} \tag{3a}$$

$$K_{a2}^{int} = \{\underline{C}O^-\}\{H^+\}/\{\underline{C}OH\} \tag{3b}$$

where i stands for the surface concentration of the ith species. The total number of surface Bronsted acidity site, N_B, is therefore the sum of all the three surface hydroxo groups, i.e.,

$$N_B = \{\underline{C}OH_2^+\} + \{\underline{C}OH\} + \{\underline{C}O^-\} \tag{4}$$

The surface proton concentration is not directly measurable; rather it is calculated from the pH measurements in the bulk phase, i.e., $\{H^+\}_b$, and by the Boltzmann equation

$$\{H^+\} = \{H^+\}_b \exp(-F\psi_o/RT) \tag{5}$$

where ψ_o, F, R, T denote the surface potential, Faraday constant, gas law constant and absolute temperature, respectively. The surface potential is not a directly measurable quantity. In a dilute inert electrolyte solution, the surface potential, ψ_o, is close to the potential at the outer Helmholtz plane, or the diffuse layer potential, ψ_d. H^+ and OH^- are considered the sole potential determining ions, as indicated by the change of electrophoretic mobility at different pH values. In the absence of specific adsorption such as in dilute inert electrolyte solution, the surface charge obtained from alkalimetric titration can be set equal to the diffuse layer charge, σ_d. The surface potential can therefore be calculated by the Gouy–Chapman electrical double layer theory (Corapcioglu and Huang, 1987; Hunter, 1987)

$$\Psi_o \cong \Psi_d = (2RT/zF)\sinh^{-1}\left[\sqrt{\pi/2RT\varepsilon I}\right]\sigma_d, \tag{6}$$

where z, ϵ, and I are absolute valence of (1:1) electrolyte, dielectric constants of water and ionic strength, respectively. In aqueous solution at 20 °C, Eq. (6) can be further simplified (Corapcioglu and Huang, 1987)

$$\Psi_o = 0.05\sinh^{-1}\left[\frac{\sigma_d}{11.7\sqrt{I}}\right]. \tag{7}$$

The unit for ψ_o, σ_d and I in Eq. (7) are volt, $\mu C/cm^2$, and M, respectively. As shown above, at $pH < pH_{zpc}$ the surface is predominately positively charged, therefore

$$N_B \cong \{\underline{C}OH_2^+\} + \{\underline{C}OH\} \tag{8}$$

Similarly, at $pH > pH_{Zpc}$, the surface is negatively charged

$$N_B \cong \{\underline{C}OH\} + \{\underline{C}O^-\} \tag{9}$$

The quantity for the term $\{\underline{C}OH\}$ and $\{\underline{C}O^-\}$ are determined from alkalimetric titration, i.e.,

$$\{\underline{C}OH_2^+\} = \sigma_+/S \tag{10a}$$

and

$$\{CO^-\} = \sigma_-/S \tag{10b}$$

where σ_+, σ_- are positive surface charge and negative surface charge, respectively. S is a charge conversion factor from C/cm^2 to surface concentration (mol/g or mol/cm^3). By substituting the above relationships into Eqs. (3a) and (3b) and with further mathematical arrangement, one has

$$1/\{H^+\} = N_B/K_{a1}^{int}(1/\sigma_+) - (1/K_{a1}^{int}) \quad \text{at } pH < pH_{zpc} \tag{11a}$$

and

$$\{H^+\} = N_B/K_{a2}^{int}(1/\sigma_-) - (1/K_{a2}^{int}) \quad \text{at } pH < pH_{zpc}. \tag{11b}$$

A plot of $1/\{H^+\}$ versus $1/\sigma_+$ for the positive surface and of $\{H^+\}$ versus $1/\sigma_-$ for the negative surface will yield intercepts and slopes from which the intrinsic acidity constants, K_{a1}^{int} and K_{a2}^{int}, and total surface acidity capacity, N_B, can be calculated. This method has been used previously by Huang and Stumm for their studies of hydrous oxide systems (Huang and Stumm, 1973; Huang, 1981; Corapcioglu and Huang, 1987).

3. Results and discussion

3.1. Surface functional groups – IR analysis

IR results in Table 1 show clearly that the C–C band (normal paraffin alkanes), out of plane C–C band, and the aromatic CH band position are at 497–521, 661–680 and 777–802 cm^{-1}, respectively. There are two absorption bands at 917–934 and 1382–1392 cm^{-1}, which can be attributed to the COOH band. The absorption positions of the C-bands are 1187–1205 and 1272 cm^{-1}, individually. The absorption bands of C=C double bonds are 1560–1572 and 1633–1639 cm^{-1}. There is a weak band at 1723 cm^{-1} in the sodium salt treated activated carbon, which may be a normal carbonyl group. Magane and Dupong-Parlovskky (1988) have proposed that NaOH reaction with unsaturated *n*-lactones will form both carboxylate anions and a normal carbonyl group in the form of an aldehyde. The spectra of activated carbon observed show a chemical shift which is due to the reaction of NaOH and O_3 with activated carbon.

3.2. Surface functional groups – Boehm's titration carboxylic, lactone, and phenolic groups

The Boehm titration method allows the determination of the surface functional groups such as phenolic group (–OH), lactone group (C=O) and carboxylic group (–COOH). Fig. 1 shows the results of surface functional groups of various activated carbon samples by the Boehm method.

For virgin activated carbon (AC), the total oxygen containing function group is 0.196 meq/g with a breakdown of 0.117 meq/g (60%), 0.046 meq/g (23%), and 0.034 meq/g (17%), individually, for phenolic, lactone and carboxylic groups. When treated with O_3, the total oxygen containing functional group increases to 0.240 meq/g, which is an increase of 22% compared to the untreated AC. Increase in oxygen containing functional groups, takes mostly in the phenolic and lactone categories. The phenolic group increases from 0.117 to 0.144 meq/g and the lactone group increases from 0.034 to 0.052 meq/g. The concentration of the carboxylic group slightly increases from 0.034 to 0.044 meq/g upon O_3 treatment. It is interesting to note that the composition among these three oxygen containing functional groups remains relatively unchanged compared to AC, that is, 60% versus 60%, 22% versus 23% and 18% versus 17% for the phonemic, lactone and carboxylic groups respectively, between $AC(O_3)$ and AC.

Treatment of AC with NaOH (1–5 N) increases the total concentration of the oxygen containing functional groups from 0.196 meq/g to between 0.275 and 0.309 meq/g dependent on the NaOH concentration. This is an increase of almost 40–88%. As far as the individual oxygen containing functional groups are concerned, the phenolic group increases from 0.117 to between 0.143 and 0.204 meq/g, the lactone group increases from 0.046 to between 0.073 and 0.096 meq/g and the carboxylic group increases from 0.034 to between 0.053 and 0.094 meq/g. Like the ozone-treated activated carbon, the major increase takes place in the phenolic group.

Tryk et al. (1984) proposed the following reaction between NaOH and activated carbon:

Table 1
IR spectra of activated carbon treated with ozone and NaOH (N=2)

Vibration group	Adsorption peaks (cm^{-1})											
	A	B	C	D	E	F	G	H	I	J	K	L
C–C band (Normal paraffins alkanes)	509	520	520	508	515	515	521	508	505	497	507	515
Out of plane ring C–C band	680	673	661	667	661	680	667	675	667	663	–	–
Out of plane aromatic C–H band	790	790	777	802	784	796	777	–	802	–	–	–
COOH	924	918	–	924	931	924	–	936	–	917	–	–
	1389	1389	1389	1395	1382	1395	–	1394	1389	1388	1389	1896
C–O–C	1199	1205	1187	1205	1205	1193	1193	1196	1199	1208	1193	1193
	–	–	1272	–	–	–	–	–	–	–	–	–
C=C	1572	1567	1572	1572	1572	1572	1560	1587	1572	1562	1566	1572
	1633	–	–	–	–	–	–	–	1639	–	–	–
C=O[a]	–	–	–	–	–	–	–	1723	–	1723	–	–
CH_3	–	–	–	–	–	2630	2373	2951	2366	–	2360	–
–OH	3461	3472	3436	3436	3461	3448	3485	3435	3436	3453	3454	3442

Note. A: VAC, B: $AC(O_3)$, C: AC(1N NaOH), D: AC(2N NaOH), E: AC(3N NaOH), F: AC(4N NaOH), G: AC(5N NaOH), H: AC(1N NaOH + O_3), I: AC(2N NaOH + O_3), J:AC(3N NaOH + O_3), K: AC(4N NaOH + O_3), L: AC(5N NaOH + O_3).

[a] Unsaturated β-lactones.

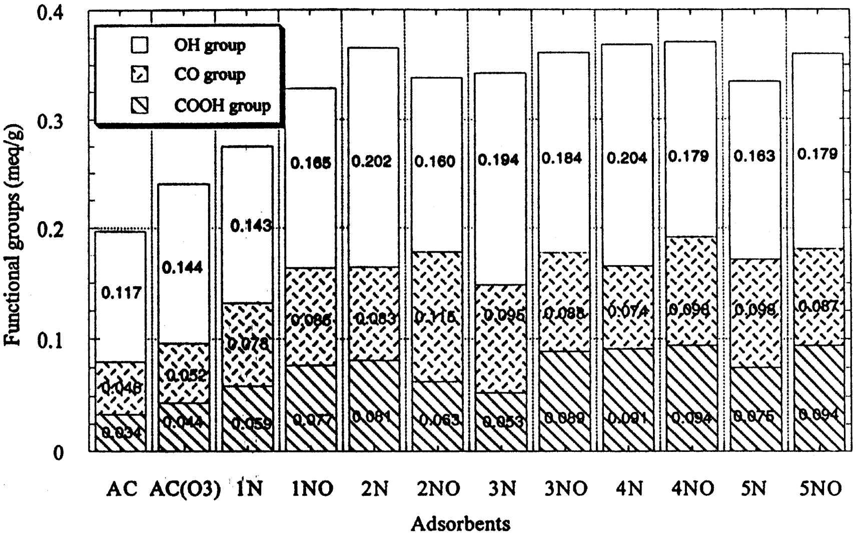


Fig. 1. Intensity of surface oxygen containing functional group as affected by O_3 and NaOH. Adsorbents: A = AC, B = AC(O_3), 1N: AC(1N NaOH), 2N: AC(2N NaOH), 3N: AC(3N NaOH), 4N: AC(4N NaOH), 5N: AC(5N NaOH), 1NO: AC(1N NaOH + O_3), 2NO: AC(2N NaOH + O_3), 3NO: AC(3N NaOH + O_3), 4NO: AC(4N NaOH + O_3), 5NO: AC(5N NaOH + O_3).

$$\mathrm{C + 6OH^- = CO_3^{2-} + 3H_2O + 4e^-;}$$
$$\Delta G^\circ = -70.72\ \mathrm{kcal/mole.} \tag{12}$$

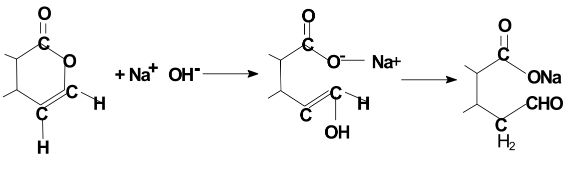
It is further known that

$$\mathrm{4H^+ + O_2 + 4e^- = 2H_2O;}$$
$$\Delta G^\circ = -113.38\ \mathrm{kcal/mole.} \tag{13}$$

Combining Eqs. (12) and (13), one has

$$\mathrm{C + 2OH^- + O_2 = CO_3^{2-} + H_2O;}$$
$$\Delta G^\circ = -184.10\ \mathrm{kcal/mole.} \tag{14}$$

The following shows the conceptual scheme of NaOH reaction with activated carbon:



Treatment of AC with combined NaOH and O_3 increases the oxygen containing functional group even further. Results indicate that the total oxygen containing functional group increases from 0.197 (AC) to 0.275–0.369 meq/g (NaOH–AC) to 0.328–0.371 meq/g (AC(O_3)–NaOH). This is an increase by 67–85% compared to the untreated AC. The concentration of phenolic group increases from 0.117 to 0.143–0.202 meq/g (NaOH–AC) to 0.165–0.184 meq/g (AC(O_3)–NaOH). The concentration of lactone group increases from 0.046 (AC) to 0.052–0.098 meq/g (NaOH–AC) to 0.086–0.115 meq/g (AC(O_3)–NaOH). The concentration of the carboxylic group increases from 0.034 (VAC) to 0.053–0.091 meq/g (NaOH–AC) to 0.063–0.094 meq/g (AC(O_3)–NaOH).

3.3. Reaction pathways

Results show that major functional groups of the treated activated carbon include phenolic, lactone, carboxylic, carbon–hydrogen bond and carbon–carbon double bonds. Results of the Boehm titration and FTIR analysis clearly indicate that hydroxyl carbonyl, carboxylic, C–H and C═C bonds are the major surface functional groups. Based on the literature (Schubert and Pease, 1956b,c; Schubert and Pease, 1956c), a conceptual reaction pathway can be proposed (Fig. 2).

The surface of activated carbon is thought to be assemblies of hexagon structure (a) and the reaction site is at the carbon–hydrogen bond. The reaction of carbon–hydrogen bond and ozone follows two pathways, one is the formation of hydroxide compounds (b) and the other is the generation of hydrotrioxide intermindates (c). The hydroxide site may be further transformed to carbon–carbon double bond (d). The hydrotrioxide intermindates will undergo three reaction pathways. First, hydrotrioxide losses a hydrogen peroxide (H_2O_2) to form the carbon–oxygen double bond (e). Second, the

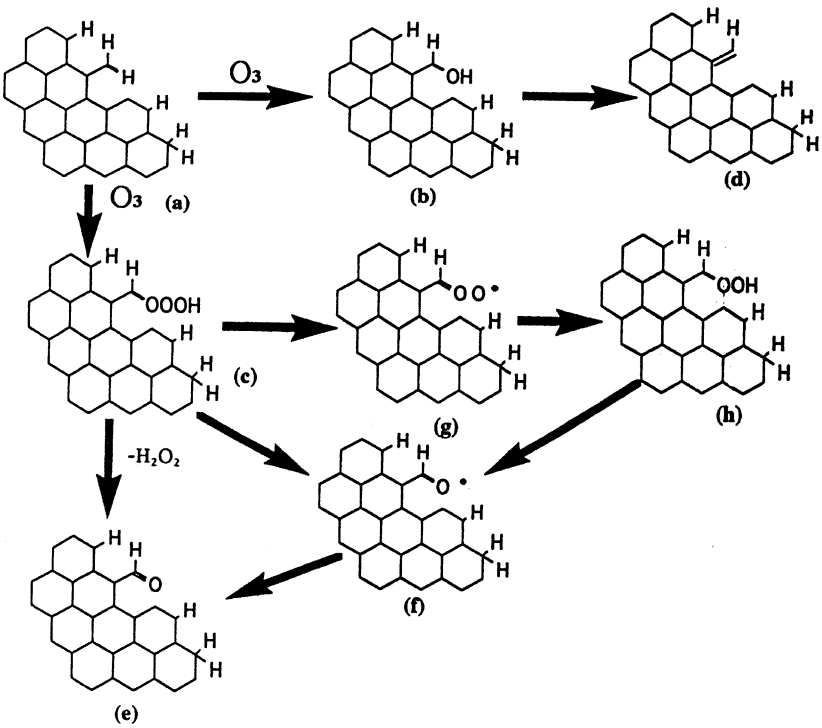


Fig. 2. Proposed reaction pathways for O_3 reaction with activated carbon.

hydrotrioxide loses an O_2 H to produce radical ($O^•$) (f). Third, the deprotonation of hydrotrioxide yields the peroxide radical ($OO^•$) (g). The peroxide and oxygen radical compounds may be further transformed to carboxyl compounds and subsequently carbonyl compounds (h).

3.4. Surface acidity

The presence of surface functional groups such as hydroxyl, carboxyl, and carbonyl on activated carbon can bring about surface charge upon hydration. This is evident of the fact that a positive charge evolves when introducing an H-type activated carbon into water. Likewise, a negative charge is observed on the L-type activated carbon when it is placed in water (Huang, 1981).

Fig. 3 shows the zeta potential of various activated carbon samples as a function of pH. Generally, a flesh H-carbon has a pH_{zpc} of ~7. The pH_{zpc} value shifts to 5.3 upon exposure to atmosphere over an extended period of time which is indicative of an L-type conversion. Exposing an H-carbon to the atmosphere tends to gradually oxidize the carbon and converting it to an L-carbon. Upon treatment with ozone and sodium hydroxide, the pH_{zpc} shifts to $pH < 2$, which clearly indicates an oxidizing surface on the activated carbon.

Table 2 summarizes the total surface acidity density obtained by alkalimetric titration and the Boehm method. Results indicate that alkalimetric titration yields a total surface acidity larger than the Boehm titration. This can be attributed to the extra surface charge contributed by other functional groups such as sulfur and nitrogen which cannot be detected by the Boehm method.

4. Conclusions

Ozone and NaOH treatment of activated carbon results in an increase of surface oxygen functional groups, especially in the phenolic and carboxylic categories. Because the increase in the formation energy of lactone is greater than that of other functional groups, the increase of lactone group intensity on activated carbon is not significant by either ozone or NaOH treatment. Based on the results obtained from this study and reported literature information, a preliminary pathway for O_3 reaction with activated carbon can be proposed. The reaction of carbon–hydrogen bond and ozone follows

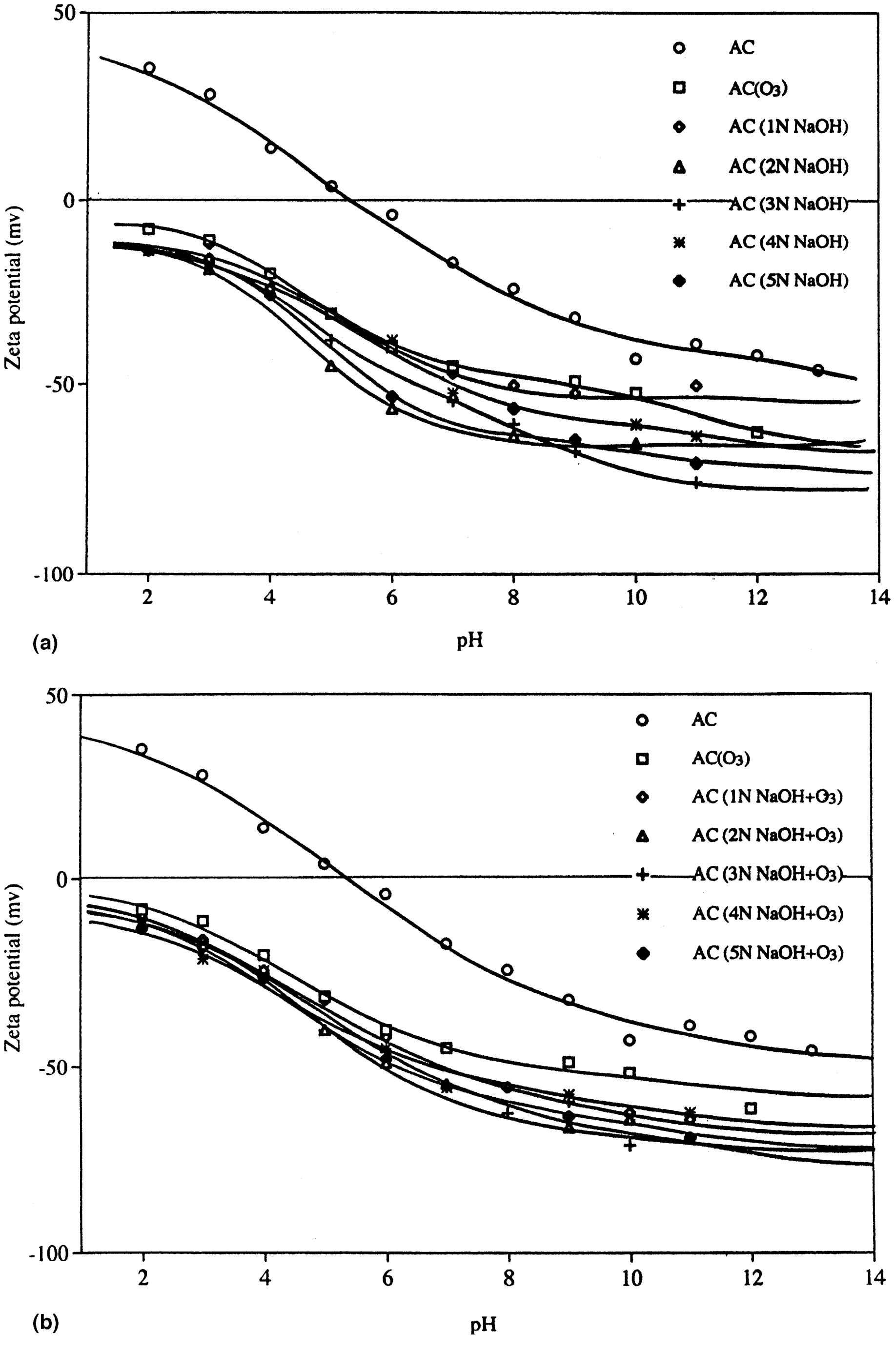


Fig. 3. (a) Effect of NaOH treatment on the zeta potential of activated carbon. (b) Effect of O_3 treatment on the zeta potential of activated carbon.

two pathways, one is the formation of hydroxide compounds and the other is the generation of hydrotrioxide intermindates. The hydroxide site may be further transformed to carbon–carbon double bond. The hydrotrioxide intermindates will undergo three reaction pathways: First, the hydrotrioxide losses a hydrogen

Table 2
Effect of O_3 and NaOH treatment on the surface acidity of activated carbon[a]

Adsorbents[b]	Ionic strength 5×10^{-2} M[c]		pH_{zpc}^{d}	Zeta potential-N_B ($\mu C/cm^2$)	Boehm's method-N_B ($\mu C/cm^2$)
	pK_{a1}^{int}	pK_{a2}^{int}			
A	4.09	6.25	5.30	3.01	2.42
B	(−0.67)	4.67	2.00	10.54	2.72
C	(−0.79)	4.79	2.00	6.85	3.21
D	(−0.16)	4.16	2.00	6.60	4.23
E	(−0.84)	4.84	2.00	9.54	3.92
F	(−0.83)	4.83	2.00	8.84	4.40
G	(−0.40)	4.40	2.00	7.29	3.88
H	(−0.79)	4.79	2.00	13.00	3.88
I	(−0.79)	4.79	2.00	8.78	3.97
J	(−0.74)	4.74	2.00	8.97	4.26
K	(−1.19)	5.19	2.00	7.92	4.28
L	(−0.27)	4.27	2.00	9.28	4.24

[a] The concentration of activated carbon is 100 mg-PAC/l-$NaClO_4$ (aq) and experiment is performed in closed system at 25 °C.

[b] A: VAC, B: AC(O_3), C: AC(1N NaOH), D: AC(2N NaOH), E: AC(3N NaOH), F: AC(4N NaOH), G: AC(5N NaOH), H: AC(1N NaOH + O_3), I: AC(2N NaOH + O_3), J: AC(3N NaOH + O_3), K: AC(4N NaOH + O_3), L: AC(5N NaOH + O_3).

[c] $NaClO_4$ as inert electrolyte.

[d] $pH_{zpc} = (pK_{a1}^{int} + pK_{a2}^{int})/2$.

peroxide (H_2O_2) to form carbon–oxygen double bond. Second, the hydrotrioxide losses an O_2H to form radical ($O^{\bullet}$). Third, the hydrotrioxide deprotonates to form peroxide radical ($OO^{\bullet}$). The peroxide and oxygen radical compounds may be further transformed to carboxylic compounds and subsequently lactone compounds. Alkalimetric titration gives a surface acidity larger than the Boehm titration due in part to the extent of neutralization reaction.

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