The Modification of Acidic Surface Functionality of Wood-Based Activated Carbon

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Abstract

The purpose of this work is to introduce and characterize the surface oxygen functional groups on the wood-based activated carbon. The activated carbons prepared from eucalyptus wood sawdust were oxidized with hydrogen peroxide [H_2O_2], ammonium persulfate [$(NH_4)_2S_2O_8$], nitric acid [HNO_3] and air in order to introduce and modify the surface oxygen functional groups. The existence of the oxygen functional groups was ascertained by several techniques including elemental analysis, determination of the point of zero charge (pH_{pzc}), Boehm titration and Fourier Transform Infrared Spectroscopy (FTIR). The porous structure of the original and oxidized activated carbons were also characterized by nitrogen adsorption isotherm data at −196°C. The total amounts of oxygen functional groups reported as meq/g of combined carboxylic, lactonic and phenolic groups obtained by Boehm titration technique were in the following order: HNO_3 > air > H_2O_2 > $(NH_4)_2S_2O_8$. The results from FTIR showed that the activated carbon oxidized with air gave the highest concentration of carboxylic acid and lactonic groups, which was in agreement with Boehm titration's results. The results of elemental analyses also showed an increase in the oxygen contents of all oxidized activated carbons, with HNO_3 > air > H_2O_2 > $(NH_4)_2S_2O_8$. Fixation of the oxygen functional groups on the surface of the activated carbons decreased the pH_{pzc}, surface area and porosity. The results indicated that oxidation with HNO_3 caused the drop in surface area and porosity of the activated carbons to a greater extent than with the other oxidizing agents.

Keywords: Activated carbon; Surface functional groups; Surface oxidation; Boehm titration; Adsorption isotherms

1. Introduction

Activated carbon has been widely used in adsorption processes because of its large surface area, high adsorption capacity and high degree of surface reactivity. The capacity of adsorption of activated carbon depends largely on its porous properties and to a lesser extent on the surface functionality. The contributing role of surface functional groups in adsorption is to interact with specific or polar adsorbates. The surface chemistry of activated carbon is determined by the acidic and basic character of the surface. The acidic behavior is associated with oxygen functional groups such as carboxyl, lactone and phenol. The purpose of this work is to modify the acid surface functional groups of wood-based activated carbon using different types of oxidizing agents both in liquid and gas phases.

2. Experimental

2.1. Materials

The eucalyptus wood was obtained from a furniture plant in a form of shredded wood chip and was milled and sieved to the size fraction of 20×30 mesh. The sieved wood sawdust was impregnated with 50 wt% H_3PO_4 solution for 1 h with the chemical weight ratio of H_3PO_4 and wood sawdust being 0.5. The impregnated wood sawdust was carbonized at 400°C for 1 h. For liquid phase oxidation, the original activated carbon (AC) was oxidized with 40% m/v H_2O_2 (AC-HO), saturated solution of $(NH_4)_2S_2O_8$ in 2 N H_2SO_4 (AC-NH) and 1 N HNO_3 (AC-HNO). For treatment with H_2O_2 and $(NH_4)_2S_2O_8$, the experiments were performed at room temperature for 24 h while for treatment with HNO_3, the experiment was performed by boiling with a reflux condenser for 24 h. For gas phase oxidation, the test activated carbon was oxidized with air (AC-air) in a tube furnace at 250°C for 24 h.

2.2. Characterization techniques

Different analytical techniques and instruments are used to detect and verify the existence of surface functional groups of the original and oxidized activated carbon. These include the Boehm titration method [1], Fourier Transform Infrared Spectrophotometer (FTS 175C, BIO-RAD), determination of point of zero charge (pH_{pzc}) by the pH drift method [2], C, H, O, N analyzer (LECO) and surface area and pore volume analyzer (ASAP 2010, Micromeritics).

3. Results and discussion

The values of the acidity, basicity and the amounts of surface oxygen functional groups determined from Boehm titration are shown in Table 1. The amounts of each acidic groups (carboxylic, lactonic and phenolic) increases with

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the oxidation treatment except the phenolic group of activated carbon oxidized with H_2O_2. Total acidity increases with the oxidation treatment, whereas the total basicity decreases except the activated carbon oxidized with HNO_3. The increase in basicity for HNO_3 oxidation may arise from the presence of nitrate or nitro surface groups introduced by oxidation [3]. The total acidity of the activated carbon oxidized with HNO_3 is maximum giving about eight times that of the original activated carbon. The order of total oxygen functional groups is HNO_3 > air > H_2O_2 > $(NH_4)_2S_2O_8$.

Table 1
Results from Boehm titration (meq/g)

Sample	Carboxylic	Lactonic	Phenolic	Acidic	Basic
AC	0.03	0.31	0.14	0.48	0.72
AC-HO	0.34	1.29	0.04	1.67	0.67
AC-NH	0.14	0.82	0.55	1.52	0.60
AC-HNO	1.01	1.33	1.43	3.78	1.98
AC-air	1.53	1.07	0.19	2.79	0.25

The FTIR results are shown in Fig. 1. After oxidation, the peaks that are characteristic of oxygen functional groups are present. The band around 1700 cm^{-1} is ascribed to the stretching vibration of carboxyl groups on the edges of layer planes or to conjugated carbonyl groups (C=O in carboxylic acid and lactone groups) [4]. In this region, the oxidized activated carbons present more pronounced bands than the original activated carbon. The activated carbon oxidized with air gives the highest concentration of carboxylic acid and lactone groups. The order of carboxylic acid and lactone groups concentration is air > HNO_3 > H_2O_2 > $(NH_4)_2S_2O_8$, and this result is also in agreement with that obtained from the Boehm titration.

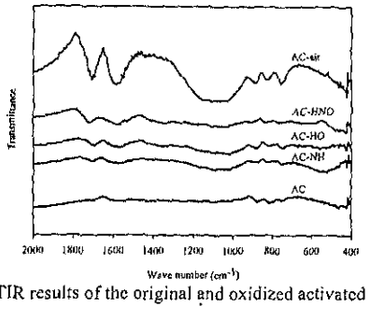

Fig. 1. FTIR results of the original and oxidized activated carbons.

Table 2 gives the pH_{pzc} and porous properties obtained from the N_2 adsorption isotherms. The decrease of pH_{pzc} values of oxidized activated carbons shows that they are more acidic than the original activated carbon. The results show that the oxidation treatment decreases S_{BET}, V_{DR} and V_T. This could attribute to the destruction of some thin pore walls by the oxidizing agents, resulting in the widening of the micropore hence giving the decrease in S_{BET} and V_{DR}. Moreover, the presence of oxygen functional groups may obstruct the pore entrance of N_2 adsorbate. The results also show that oxidation with HNO_3 decreases the surface area and the porosity of the activated carbons to a greater extent than the other oxidizing agents.

Table 2
The pH_{pzc} and porous characteristics obtained from N_2 isotherm

Sample	pH_{pzc}	S_{BET}[a] (m^2/g)	V_{DR}[b] (cm^3/g)	V_T[c] (cm^3/g)
AC	7.5	1200	0.55	0.58
AC-HO	6.6	689	0.31	0.35
AC-NH	6.9	738	0.34	0.36
AC-HNO	3.7	223	0.11	0.12
AC-air	5.1	626	0.29	0.31

[a] S_{BET} = BET surface area
[b] V_{DR} = Dubinin-Radushkevich (DR) micropore volume
[c] V_T = total pore volume

The results of elemental analyses are shown in Table 3 and indicate that all oxidized activated carbons give a significant increase in the oxygen contents. The order of O content is HNO_3 > air > H_2O_2 > $(NH_4)_2S_2O_8$. The N content for the oxidation with HNO_3 also shows a higher content than that of the original activated carbon, also in support of the result from Boehm titration.

Table 3
Results of elemental analyses (wt%)

Sample	C	H	O	N
AC	79.68	2.74	17.15	0.43
AC-HO	74.10	3.18	22.37	0.35
AC-NH	75.29	2.86	21.42	0.43
AC-HNO	61.43	2.82	33.98	1.77
AC-air	72.81	2.96	23.57	0.66

4. Conclusions

The oxidation of the activated carbons with different oxidizing agents including H_2O_2, $(NH_4)_2S_2O_8$, HNO_3 and air resulted in the forming of more oxygen surface functional groups. The results from several analytical techniques showed that HNO_3 was the most effective among the various oxidizing agents tested. Adsorption tests of oxidized activated carbons with polar adsorbates such as water vapor and methanol vapor will be performed to check the role and effectiveness of the introduced surface functional groups in adsorption.

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References

[1] Salame II, Bandosz TJ. Role of surface chemistry in adsorption of phenol on activated carbons. Journal of Colloid and Interface Science 2003; 264(2):307-12
[2] Lopez-Ramon MV, Stoeckli F, Moreno-Castilla C, Carrasco-Marin F. On the characterization of acidic and basic surface sites on carbons by various techniques. Carbon 1999; 37(8): 1215-21
[3] Haydar S, Ferro-Garcia MA, Rivera-Utrilla J, Joly JP. Adsorption of p-nitrophenol on an activated carbon with different oxidations. Carbon 2003; 41(3):387-95
[4] El-Hendawy ANA. Influence of HNO_3 oxidation on the structure and adsorptive properties of corncob-based activated carbon. Carbon 2003; 41(4):713-22