

Silver elimination effect by sulfuric acid for Ag pre-treated activated carbon

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Abstract : In this study, silver pre-treated activated carbons are transformed using sulfuric acid. From the results of adsorption, each isotherm shows a distinct knee band, which is characteristic of microporous adsorbents with capillary condensation in micropores. In order to reveal the causes of the differences in adsorption capacity and specific surface area after the samples were washed with various strengths of sulfuric acid, surface morphology and external pore structure were investigated by SEM. X-ray diffraction patterns indicated that Ag-activated carbons show better performance for silver and silver compounds removal by post-treatment with acid. The FT-IR spectra of silver-activated carbon samples show that the acid post-treatment was consequently associated with the removal of silver with an increased surface functional group containing oxygen of the activated carbon. The type and quality of oxygen groups are determined on the method proposed by Boehm. For the chemical composition microanalysis of silver-activated carbons transformed by post-treatment with sulfuric acid, samples were analyzed by EDX.

Key words : adsorption isotherm, silver-activated carbon, SEM/EDX, XRD, Boehm titration, FT-IR

1. Introduction

Porous carbon materials as adsorbents have substituted for most different materials in the fields of air and water purification. Applications of activated carbon are governed by a high surface area, developed pore structure, and surface chemistry. Although the adsorption process onto activated carbon is mainly of the dispersive interaction type, surface chemistry plays an important role when specific interactions are considered.^{1,2} The surface chemistry determines their adsorption of polar species, catalytic properties and acid-base character.³

This is related to the presence of heteroatoms other than carbon within the carbon matrix. The most important heteroatoms in activated carbon are oxygen, which are usually bound to peripheral carbon atoms at the edges of the crystallites. Most of the chemical properties of activated carbon come from the incorporation of oxygen during its production, forming oxides like carboxylic, phenolic and lactonic groups. Activated carbon including these heteroatoms can be easily modified using various physical, chemical and electrochemical methods.^{4,5} To prepare modified carbon sorbent, metallic ions have been either adsorbed on or impregnated into

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activated carbon. The functional groups may play a role in the sorption and deposition of nonpolar molecules and metallic ions by creating obstacles for physical adsorption and stopping the molecules from occupying the most energetically favorable position on the carbon surface. Activated carbons treated with metals have been known as excellent materials for the removal of organic and toxic species,^{6,7} and antibacterial properties.⁸ The objective of this paper is to compare the surface features of two kinds of activated carbon treated with metals and the variation of their properties by acid post-treatments. The difference in the method of acid treatment results in dramatically different structural and chemical properties of sorbents.

In this paper, first part of the study focuses on the metal-activated carbon system transformed by post-treatments with sulfuric acid. The purpose is to investigate the effects of physical and textural changes of activated carbon, and chemical treatment sequences. Full characterizations of post-treatment effects for silver-activated carbon are presented by nitrogen adsorption properties, SEM-EDX analysis, XRD patterns, FT-IR results and properties of surface functional groups by Boehm titration.

2. Experimental

2.1 Preparation procedures

Home made activated carbon prepared from cocunut shell based granular was used as a starting material. The carbonized cocunut shell was heated first at 773 K for burn off, then physically activated

with water vapor in the temperature range of 1023~1053 K. H₂SO₄ and AgNO₃ were obtained from Aldrich (99+%, ACS reagent) and used as received. In order to be free from impurities, doubly distilled water was used. For pretreatment with metal, 20 g of activated carbon was dipped into 100 ml of 0.05 and 0.1 M silver nitrate solutions and stirred for 24 h at room temperature. Then, air and bubbles in the solution were removed under a vacuum pressure of about 1.33 Pa for 20 minutes, and then the solution was discarded. These samples were then dried at 383 K for 48 h in an N₂ atmosphere. For the acid post-treatment, 20 g of activated carbon treated with silver salts was dipped into 100 mL of 0.01, 0.05 and 0.1 M sulfuric acid aqueous solution and stirred for 12 h at room temperature. After removal of the liquid, samples post-treated with acid were dried completely in a vacuum oven. The nomenclature of the samples is given in *Table 1*.

2.2. Measurement

Nitrogen isotherms were measured using an ASAP 2010 instruments (Micromeritics) at 77 K. Before each experiment, the samples were heated at 473 K and then outgassed at this temperature under a vacuum of 1.33×10^{-3} Pa to a constant pressure. The isotherms were used to calculate the specific surface area and pore volume. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the surface state and pore structure of metal-activated carbon transformed by post-treatment with sulfuric acid and the transformed metal state. For the

Table 1. Nomenclatures of silver-activated carbon samples transformed by post-treatment with sulfuric acid

Sample	Nomenclature
0.05 M AgNO ₃ + Activated Carbon	Ag _{0.05} -AC
0.05 M AgNO ₃ + Activated Carbon + 0.01 H ₂ SO ₄ (post treatment)	Ag _{0.05} -AC-0.01SA
0.05 M AgNO ₃ + Activated Carbon + 0.05 H ₂ SO ₄ (post treatment)	Ag _{0.05} -AC-0.05SA
0.05 M AgNO ₃ + Activated Carbon + 0.1 H ₂ SO ₄ (post treatment)	Ag _{0.05} -AC-0.1SA
0.1 M AgNO ₃ + Activated Carbon	Ag _{0.1} -AC
0.1 M AgNO ₃ + Activated Carbon + 0.01 H ₂ SO ₄ (post treatment)	Ag _{0.1} -AC-0.01SA
0.1 M AgNO ₃ + Activated Carbon + 0.05 H ₂ SO ₄ (post treatment)	Ag _{0.1} -AC-0.05SA
0.1 M AgNO ₃ + Activated Carbon + 0.1 H ₂ SO ₄ (post treatment)	Ag _{0.1} -AC-0.1SA

elemental analysis of metal contents in silver-activated carbon transformed by post-treatment with sulfuric acid, energy dispersive X-ray analysis (EDX) was also used. X-ray diffraction patterns were taken using an X-ray generator (Shimatz XD-D1, Japan) with Cu K α radiation. The silver-activated carbons transformed by post-treatment with sulfuric acid were examined by a KBr method using Fourier transform infrared (FT-IR) spectroscopy. Discs for the method were prepared by first mixing 1 mg of powdered silver-activated carbon with 600 mg of KBr (for FT-IR spectroscopy) in an agitate mortar, and then pressing the resulting mixture successively under a pressure of 450 Pa for 3 minutes. Spectra of the samples were measured between 4000 and 500 cm^{-1} using a FTS 3000MX (Bioered Co.) spectrophotometer.

2.3. Boehm titration

A Boehm titration method² was used for the identification of oxygenated surface groups on the carbon surfaces. One gram of carbon sample was placed in 50 ml of the following 0.05 M solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate, and hydrochloric acid. The elenmeyer flasks were sealed and shaken for 24 h and then 5 mL of each filtrate was pipetted and excess of base and acid was titrated with HCl and NaOH, respectively. The number of acidic sites of various types were calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups; Na_2CO_3 , carboxylic and lactonic groups; and NaHCO_3 , only carboxylic groups. The number of surface basic sites was calculated from the amount of hydrochloric acid, δ which reacted with the carbon.

3. Results and discussion

In order to study the variation of pore structure inside of the silver-activated carbon transformed by post-treatment with sulfuric acid, the adsorption isotherms of N_2 at 77K were measured for all carbon samples. Fig. 1 shows the adsorption isotherms on the silver-activated carbons transformed with sulfuric

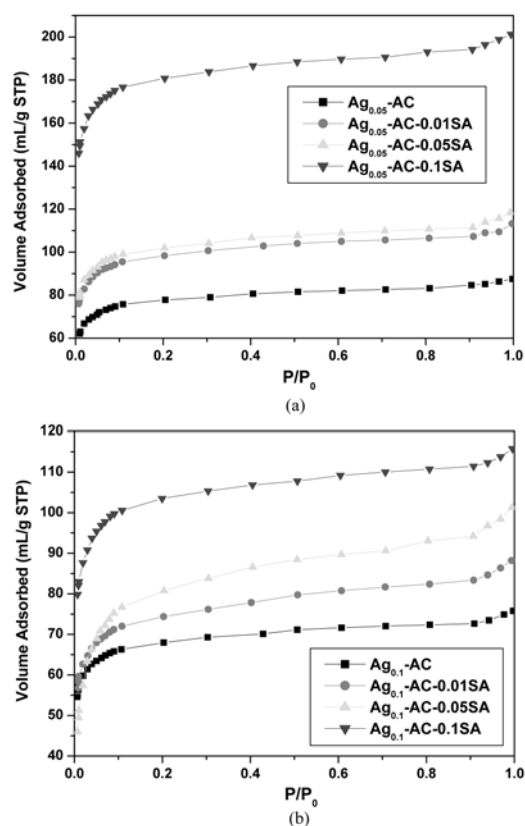
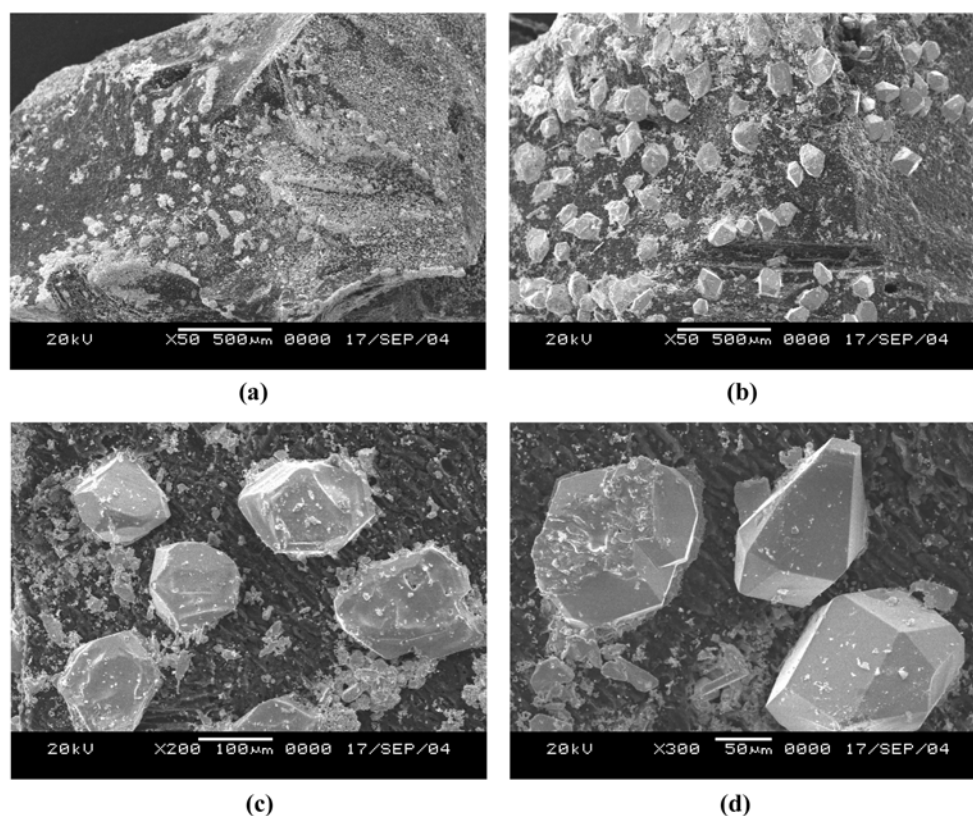


Fig. 1. Adsorption isotherm obtained from Ag-activated carbon transformed by post-treatment with sulfuric acid; (a) Ag_{0.05}-AC-SA and (b) Ag_{0.1}-AC-SA series.

acid. In general, they exhibit a mixed-type I + II of the Brunauer, Demming, Demming, Teller (BDDT) classification with a small increase at higher relative pressures. This indicates that the oxidized carbons studied were mainly micro- and mesoporous in character with a minor presence of wider pores where capillary condensation occurred. A sharp increase of adsorption was observed at relative pressures lower than 0.1. Each isotherm shows a distinct knee band, which is characteristic of microporous adsorbents. This phenomenon is associated with capillary condensation in micropores. The end of the knee band in each isotherm approximately occurs at a relative pressure of 0.1. Generally, one can find that the isotherm shapes are similar for all carbon samples. However, an increase of adsorbed volumes is observed for the samples

Table 2. Comparison of physical parameters of silver-activated carbon samples transformed by post-treatment with sulfuric acid

Sample	Parameter			
	$S_{\text{BET}}(\text{m}^2/\text{g})$	Micropore Volume (mL/g)	External Surface Area (m^2/g)	Average Pore Diameter (Å)
Ag _{0.05} -AC	1121	0.454	432.7	15.11
Ag _{0.05} -AC-0.01SA	1022	0.428	396.7	15.11
Ag _{0.05} -AC-0.05SA	1181	0.433	415.2	15.14
Ag _{0.05} -AC-0.1SA	1343	0.463	433.4	15.15
Ag _{0.1} -AC	992.3	0.453	325.8	14.95
Ag _{0.1} -AC-0.01SA	988.5	0.451	315.9	15.06
Ag _{0.1} -AC-0.05SA	996.9	0.455	328.4	15.08
Ag _{0.1} -AC-0.1SA	1023	0.458	393.3	15.11

Fig. 2. SEM images obtained for Ag_{0.05}-AC-SA samples; (a) Ag_{0.05}-AC, (b) Ag_{0.05}-AC-0.01SA, (c) Ag_{0.05}-AC-0.05SA and (d) Ag_{0.05}-AC-0.1SA

obtained by successive removal of external layers of treated silver from the carbon surfaces. The values of parameters characterizing the porous structure of studied activated carbon samples are summarized in Table 2.

To reveal the causes of the differences in

adsorption capacity and specific surface area after the samples were washed with different strengths of sulfuric acid, surface morphology and pore structure were investigated by SEM. Fig. 2 and 3 show the surface morphologies of the Ag-activated carbons before and after post-treatment with sulfuric acid. In

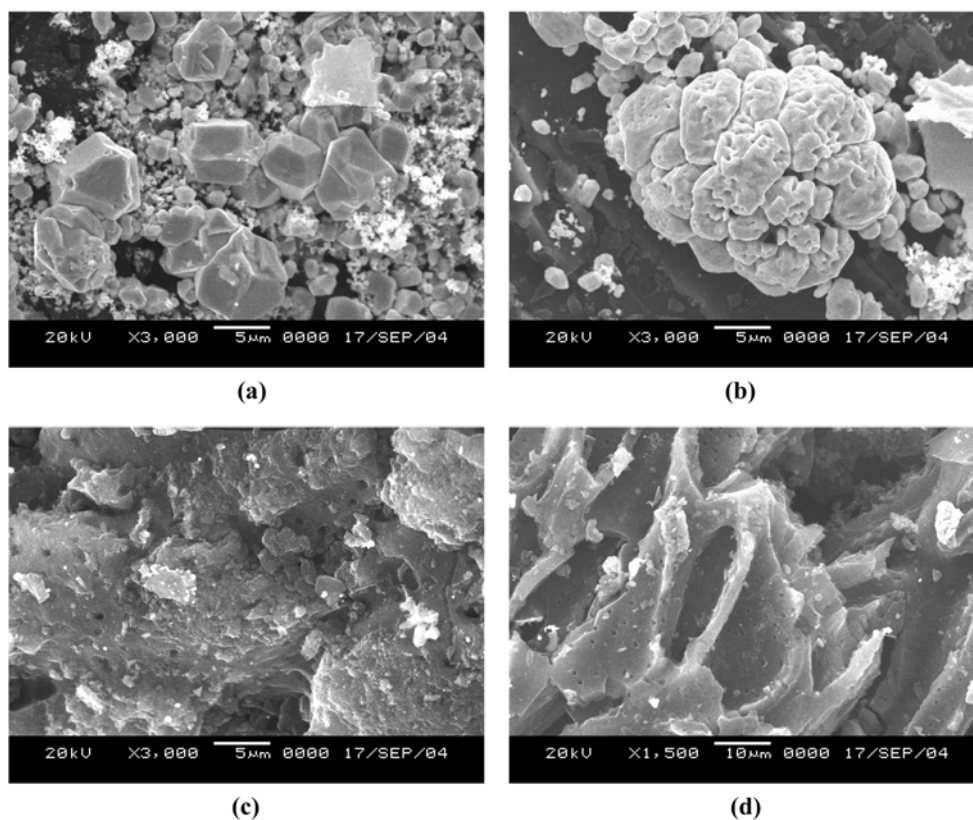


Fig. 3. SEM images obtained for the $\text{Ag}_{0.1}\text{-AC-SA}$ samples; (a) $\text{Ag}_{0.1}\text{-AC}$, (b) $\text{Ag}_{0.1}\text{-AC-0.01SA}$, (c) $\text{Ag}_{0.1}\text{-AC-0.05SA}$ and (d) $\text{Ag}_{0.1}\text{-AC-0.1SA}$

these figures, one can clearly see the highly developed porous structure and homogeneous distribution and growth state of metals on the surface of Ag-activated carbon before being treated with acid. It is also noted that a number of micropores are blocked by metals before the treatment. Differences in the degree of blocking effects depend on the type of treated metals. It is considered that the metal distributed and its crystal particles affect the pore structures in terms of S_{BET} , micropore volume and pore radius. In the case of the $\text{Ag}_{0.05}\text{-AC-SA}$ series, the growth state of metal compounds and particle size on the surface of Ag-activated carbon after treatment with acid increase with increasing mole ratio of sulfuric acid. In the case of silver, as reported by Oh and co-workers,^{5,8} silver adsorbed on activated carbon is known to be initially reduced to form silver metal nuclei which migrate and aggregate to form silver

compounds, and then larger size silver compound particles are obtained as the reduction by bonding of sulfate ion is continued.

X-ray diffraction patterns shown in Fig. 4 indicate that activated carbon containing metal species show a better performance for metal and metal compound removal by post-treatment with acid. The samples treated with different metals show different diffraction patterns. From the sharp XRD peaks, the existence of metals and metal compounds on the surface is confirmed. After post-treatment with acid, diffraction peaks of metallic silver and silver sulfate strongly decrease and some peaks of metallic silver appear (Fig. 4). From the above results, it is considered that a small quantity of silver sulfate is produced by chemical reaction with strong acid on the carbon surface. It is also believed that metallic silver and silver compounds are removed by acid treatments.

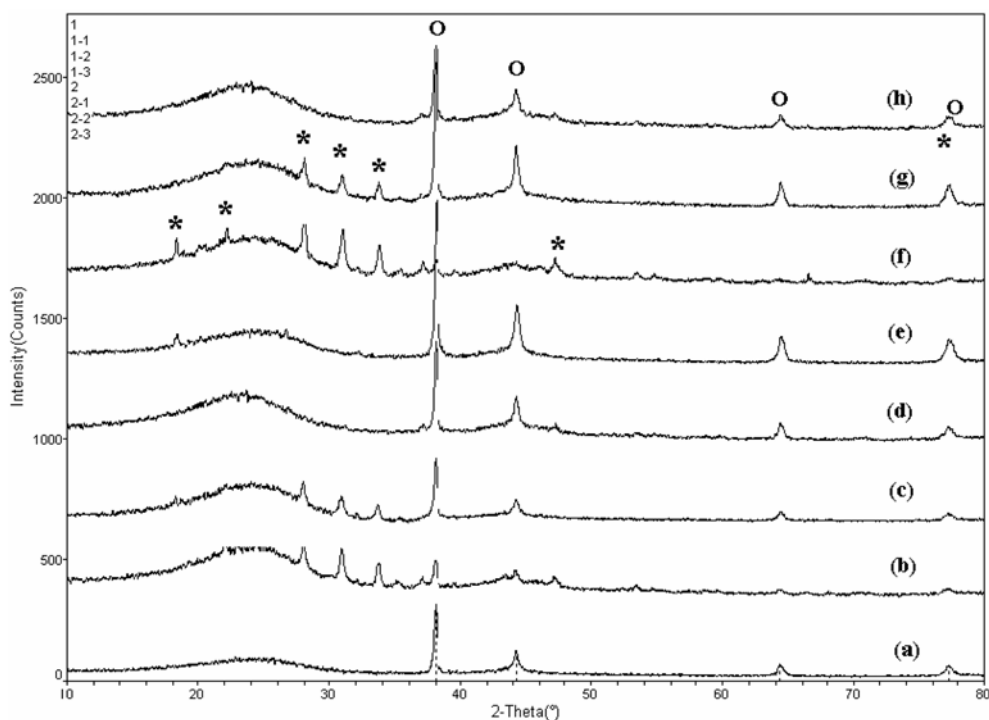


Fig. 4. XRD patterns for the Ag_{0.05}-AC-SA and Ag_{0.1}-AC-SA series (O: metallic Ag, *: Ag₂SO₄); (a) Ag_{0.05}-AC, (b) Ag_{0.05}-AC-0.01SA, (c) Ag_{0.05}-AC-0.05SA, (d) Ag_{0.05}-AC-0.1SA, (e) Ag_{0.1}-AC, (f) Ag_{0.1}-AC-0.01SA, (g) Ag_{0.1}-AC-0.05SA and (h) Ag_{0.1}-AC-0.1SA.

In the FT-IR spectra (Fig. 5) of the carbon materials the O-H bond stretching vibrations (3400 cm⁻¹) are due to surface hydroxyl group and chemisorbed water. The asymmetry of this band at lower wave numbers indicates the presence of strong hydrogen bonds. The band observed at 2360 cm⁻¹ is usually ascribed to the presence of aliphatic compounds. The presence of bands at 1730 cm⁻¹, 1620 cm⁻¹, 1550 cm⁻¹ can be attributed to the stretching vibrations of C=O moieties in carboxylic, ester, lactonic or anhydride groups (1730 cm⁻¹), quinone, enol, cyclic β-ketones and/or ion-radical structures (1620 cm⁻¹), and conjugated systems like diketones, keto-esters and keto-enol structures, respectively.⁹ These results indicate that acid post-treatment gave rise to a greater increase in C=O bonds in carboxylic acid and lactone groups. According to Oh and Yum,³ the *u* (C-O) mode of the methoxy groups depends on the chemical structure of the adsorption sites. Absorption of C-O followed

by measuring IR spectra has been used to characterize treated and non-treated metal catalysts. The frequency of *u* (C-O) of adsorbed carbon monoxide is often treated as an indicator characterizing the local coordination. This is also suitable for examining the state of metal ions situated differently on the solid surface. The post-treatment with acid is consequently associated with the homogeneous removal of metal ions and their compounds with increased surface acidity of the activated carbons. When H₂O is adsorbed on the surface of activated carbons, specific interaction like hydrogen bonds, chemisorption due to surface oxide hydration and non-specific interactions like physical adsorption occur. The absorption bands in the 1600-1500 cm⁻¹ region can be described by OH bending vibrations. Few of the complicated absorption bands in the 1650-1500 cm⁻¹ region correspond to that aromatic ring bands and C=C vibrations overlap the above mentioned C=O stretching vibration bands

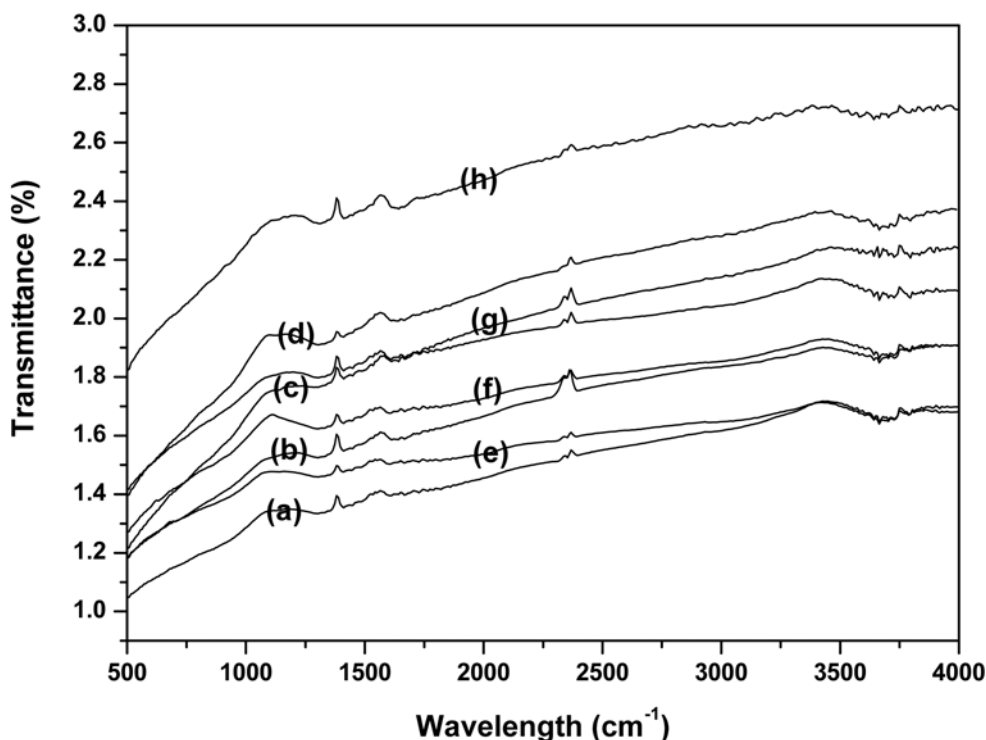


Fig. 5. Infrared spectra recorded from Ag-activated carbon transformed by post-treatment with sulfuric acid; (a) Ag_{0.05}-AC, (b) Ag_{0.05}-AC-0.01SA, (c) Ag_{0.05}-AC-0.05SA, (d) Ag_{0.05}-AC-0.1SA, (e) Ag_{0.1}-AC, (f) Ag_{0.1}-AC-0.01SA, (g) Ag_{0.1}-AC-0.05SA and (h) Ag_{0.1}-AC-0.1SA.

Table 3. Number of surface species (meq/g) obtained from Boehm titration

Sample	Functional Group (meq/g)				
	Carboxylic	Lactonic	Phenolic	Acidic	Basic
Ag _{0.05} -AC	0.32	0.61	0.76	1.72	0.98
Ag _{0.05} -AC-0.01SA	0.34	0.61	0.78	1.76	0.13
Ag _{0.05} -AC-0.05SA	0.38	0.65	0.80	1.83	0.12
Ag _{0.05} -AC-0.1SA	0.42	0.68	0.82	1.92	0.11
Ag _{0.1} -AC	0.30	0.56	0.72	1.58	0.96
Ag _{0.1} -AC-0.01SA	0.30	0.62	0.74	1.66	0.12
Ag _{0.1} -AC-0.05SA	0.32	0.78	0.80	1.90	0.11
Ag _{0.1} -AC-0.1SA	0.42	0.78	0.88	2.08	0.11

and deformed O-H band. Another sharp band near the 1400 cm⁻¹ consists of a series of in-plane vibrations of C-H in various C=C-H structures. The additional band observed at 1250 cm⁻¹ in all the samples may be due to the stretching surface nitrate or carbonitrate structures derived from raw carbon. The main goal of oxidation by acid treatment is to obtain a more hydrophilic surface with a relatively

large number of functional groups containing oxygen and to control metal contents onto the carbon surfaces.

The results of the chemical investigations after the carbon surface modification are presented in Table 3. As described above, the FT-IR spectra transformations are due to an alteration of the carbon surface via introduction of oxygen groups and removal of few of

Table 4. EDX Elemental microanalysis of silver-activated carbon samples transformed by post-treatment with sulfuric acid

Sample	O	Si	S	K	Cu	Ag
Ag _{0.05} -AC	46.7					53.4
Ag _{0.05} -AC-0.01SA	74.2		5.97			19.9
Ag _{0.05} -AC-0.05SA	76.2	1.92	6.48			15.4
Ag _{0.05} -AC-0.1SA	94.3		1.48			4.18
Ag _{0.1} -AC	32.8					67.2
Ag _{0.1} -AC-0.01SA	88.3					11.7
Ag _{0.1} -AC-0.05SA	88.3		1.41			10.3
Ag _{0.1} -AC-0.1SA	90.61		5.98			3.41

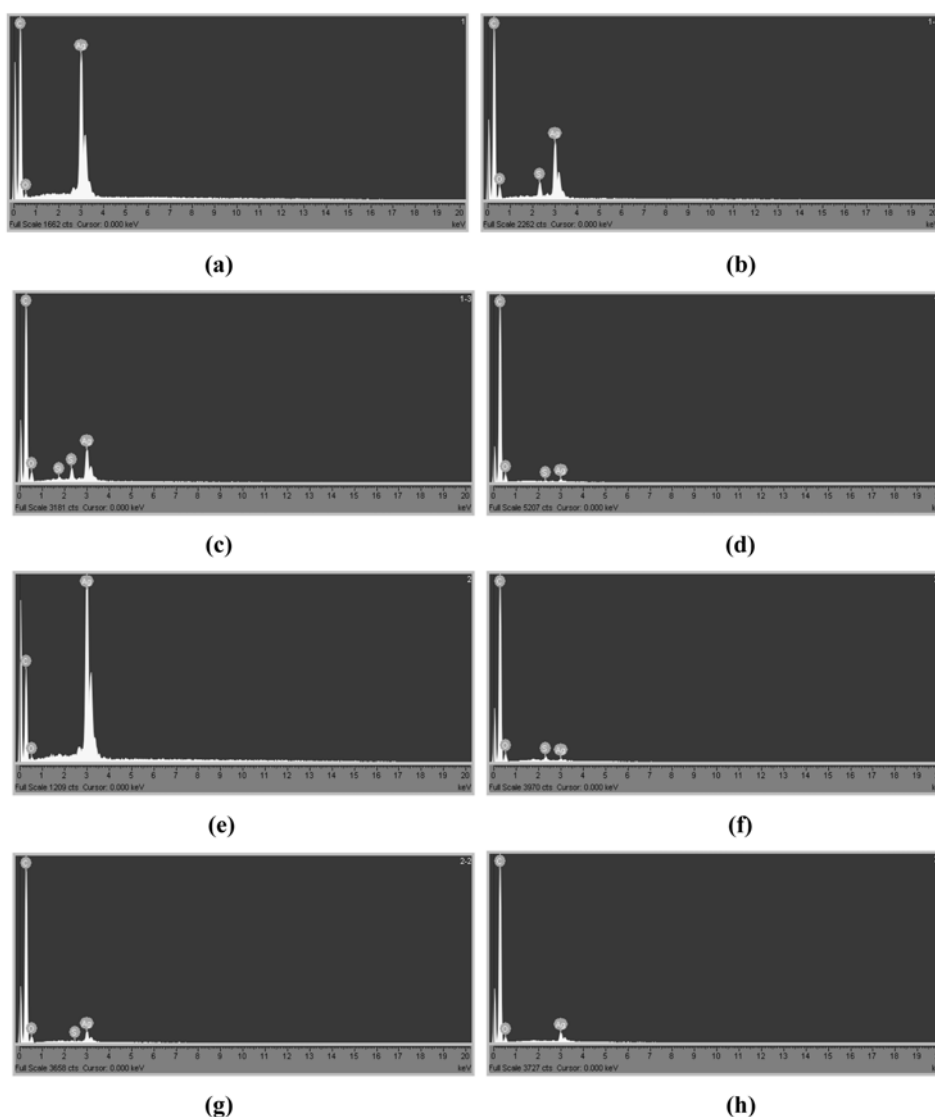


Fig. 6. EDX elemental micro-analysis spectra obtained from Ag-activated carbon samples transformed by post-treatment with sulfuric acid; (a) Ag_{0.05}-AC, (b) Ag_{0.05}-AC-0.01SA, (c) Ag_{0.05}-AC-0.05SA, (d) Ag_{0.05}-AC-0.1SA, (e) Ag_{0.1}-AC, (f) Ag_{0.1}-AC-0.01SA, (g) Ag_{0.1}-AC-0.05SA and (h) Ag_{0.1}-AC-0.1SA.

the carbon atoms from the matrix by post-treatment with acid. The type and quality of oxygen groups were determined from the method proposed by Boehm.² The surface chemical structure of the materials tested was highly diverse. Strongly oxidized carbon samples have acidic groups at different acidic strength and neutral surface oxides. The effect of surface acidity and basicity was evaluated from correlations as a function of NaOH, NaHCO₃ and Na₂CO₃ uptake have very different values. The surface acidity increases with an increase of the amount of acid post-treated, while basicity decreased with increase of the amount of acid post-treated. The titration results for the silver-activated carbons confirm the observation that an increase of the acidity and a decrease of the basicity are independent on the amount of pre-treated silver contents. The results obtained may contribute to the lowest local pH of this carbon surface with removal of silver and silver compounds due to the acid treatment. A reasonable influence of the acidic groups on the carbon surface by acid treatment is also demonstrated by the proper control of the contents of metallic silver with an increase of acidic groups calculated from Boehm titration.

For the chemical composition microanalysis of metal-activated carbons transformed by post-treatment with sulfuric acid, samples were analyzed by EDX. The EDX spectra for metal-activated carbons transformed by post-treatment with sulfuric acid are shown in Fig. 6. It shows the presence of C, S, Si, Ag and O. In the case of most of the samples, carbon and silver are present as major elements in the Ag-activated carbons transformed by post-treatment with sulfuric acid. However, the results presented for each sample show spectra corresponding to almost all samples rich in oxygen with a decrease of the silver content with an increase of the amount of acid post-treated. In the case of the Ag_{0.05}-AC-0.1SA, an increase of the amount of O content with a decrease of the Ag content is observed and the maximum value (ca. 50% excluded C contents) compared with the O content for the Ag_{0.05}-AC-0.01SA (Fig. 6(d)), which becomes more homogeneous as the carbon surface is

oxidized. From the spectra corresponding to almost all the samples rich in oxygen a decrease of copper content with an increase of the amount of acid post-treated was noticed.

4. Conclusions

From the study of adsorption isotherms, all of the samples tested gave mixed Type I+II isotherms characterized by plateau that are nearly horizontal to the p/p₀ axis. Micrographs of the surfaces by SEM inform that the acid post-treatment alters not only the morphologies of metal salts on the carbon surface but the physicochemical properties of the surfaces of the carbon itself. X-ray diffraction patterns indicate that activated carbon containing silver species show better performances for metallic silver and silver compounds removal by post-treatment with acid. FT-IR spectra of metal-activated carbon samples show that the acid post-treatment is consequently associated with the removal of silver with the increased surface functional group containing oxygen of the activated carbon. According to the Boehm titration, the surface acidity increases with an increase of the amount of acid post-treated, while the basicity decreases with an increase of the amount of acid post-treated. From the results of EDX elemental microanalysis, samples rich in oxygen contents are shown to have a decrease of metal content with an increase of the amount of acid post-treated.

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