

Metal elimination effect by sulfuric acid for Ag and Cu pre-treated activated carbon

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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 pore structure were investigated by SEM. X-ray diffraction patterns indicated that activated carbon containing metal species show better performance for metal and metal compound removal by post-treatment with acid. The FT-IR spectra of metal-activated carbon samples show that the acid post-treatment was consequently associated with the removal of metals 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 metal-activated carbons transformed by post-treatment with sulfuric acid, samples were analyzed by EDX.

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

Introduction

Activated carbon materials as adsorbents have substituted for most different materials in the fields of air and water purification. Their advantage compared to other materials such as zeolites is a developed surface area, microporosity, thermal stability, high sorption capacity in moist air streams, and low costs per volume of adsorber. 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 common heteroatoms in the matrix are oxygen, hydrogen, nitrogen, phosphorus and sulfur. 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]. The most popular method of modification applied for carbon used in large quantities is its impregnation with

various chemicals. To prepare modified carbon sorbent, metallic ions have been either adsorbed on or impregnated into 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]. All of the above-mentioned modifications make the cost of materials higher and, in some cases, special precautions must be exercised during the operation process. 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, which is the first part of a study 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 metal-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.

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Table 1. Nomenclatures of Metal-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
0.05 M CuSO ₄ + Activated Carbon	Cu _{0.05} -AC
0.05 M CuSO ₄ + Activated Carbon + 0.01 H ₂ SO ₄ (post treatment)	Cu _{0.05} -AC-0.01SA
0.05 M CuSO ₄ + Activated Carbon + 0.05 H ₂ SO ₄ (post treatment)	Cu _{0.05} -AC-0.05SA
0.05 M CuSO ₄ + Activated Carbon + 0.1 H ₂ SO ₄ (post treatment)	Cu _{0.05} -AC-0.1SA
0.1 M CuSO ₄ + Activated Carbon	Cu _{0.1} -AC
0.1 M CuSO ₄ + Activated Carbon + 0.01 H ₂ SO ₄ (post treatment)	Cu _{0.1} -AC-0.01SA
0.1 M CuSO ₄ + Activated Carbon + 0.05 H ₂ SO ₄ (post treatment)	Cu _{0.1} -AC-0.05SA
0.1 M CuSO ₄ + Activated Carbon + 0.1 H ₂ SO ₄ (post treatment)	Cu _{0.1} -AC-0.1SA

Experimental

Preparation procedures

Home made activated carbon used as a starting material was prepared from coconut shell based granular carbon. The carbonized coconut shell was heated first at 773 K for burn off, then physically activated with water vapor in the temperature range of 1023–1053 K. For the treatment, H₂SO₄, CuSO₄ 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 and copper sulfate 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 metal 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.

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 elemental analysis of metal contents in metal-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 metal-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 metal-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. The spectra of the samples were measured between 4000 and 500 cm⁻¹ using a FTS 3000MX (Bioered Co.) spectrophotometer.

Boehm titration

A Boehm titration method [2] 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 numbers of acidic sites of various types were calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups; Na₂CO₃, carboxylic and lactonic groups; and NaHCO₃, only carboxylic groups. The number of surface basic sites was calculated from the amount of hydrochloric acid, which reacted with the carbon.

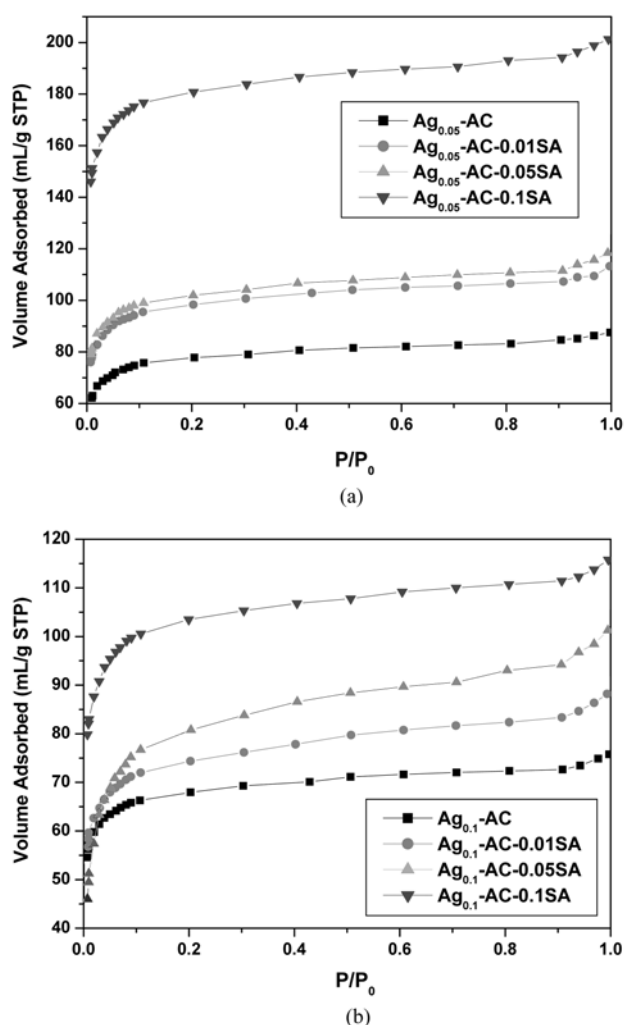


Fig. 1. Adsorption isotherm obtained from Ag-activated carbon transformed by post-treatment with sulfuric acid; (a) $\text{Ag}_{0.05}\text{-AC-SA}$ and (b) $\text{Ag}_{0.1}\text{-AC-SA}$ series.

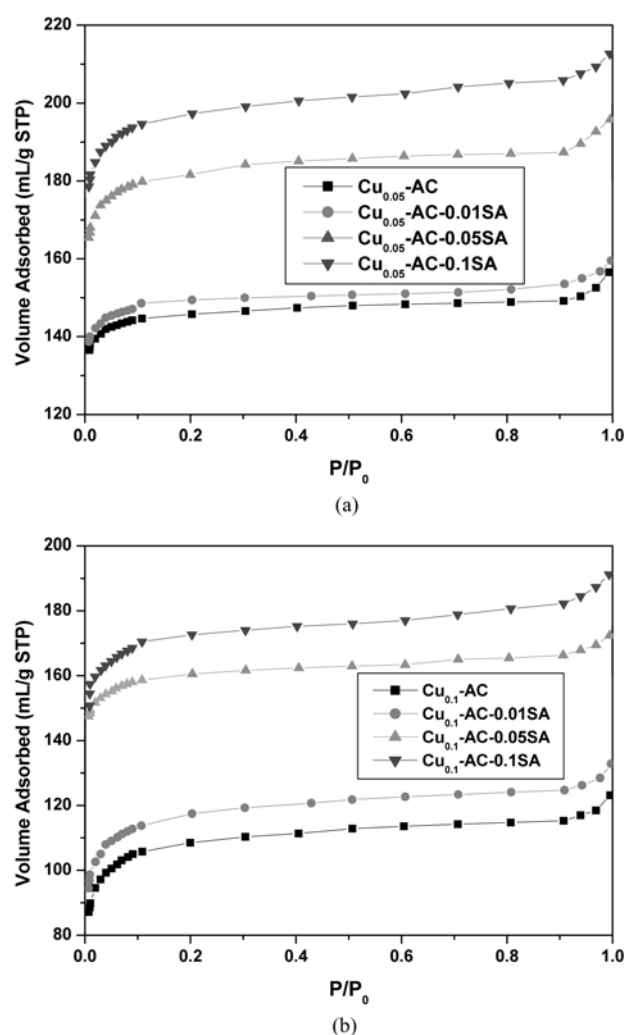


Fig. 2. Adsorption isotherms obtained from Cu-activated carbon transformed by post-treatment with sulfuric acid; (a) $\text{Cu}_{0.05}\text{-AC-SA}$ and (b) $\text{Cu}_{0.1}\text{-AC-SA}$ series.

Results and Discussion

In order to study the variation of pore structure inside of the metal-activated carbon transformed by post-treatment with sulfuric acid, the adsorption isotherms of N_2 at 77 K were measured for all carbon samples obtained. Figures 1 and 2 show the adsorption isotherms on the metal-activated carbons transformed with sulfuric 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. The sharp increase of adsorption is 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 also 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 obtained by successive removal of external layers of treated metal from the carbon surfaces. The values of parameters characterizing the porous structure of studied activated carbon samples are summarized in Table 2.

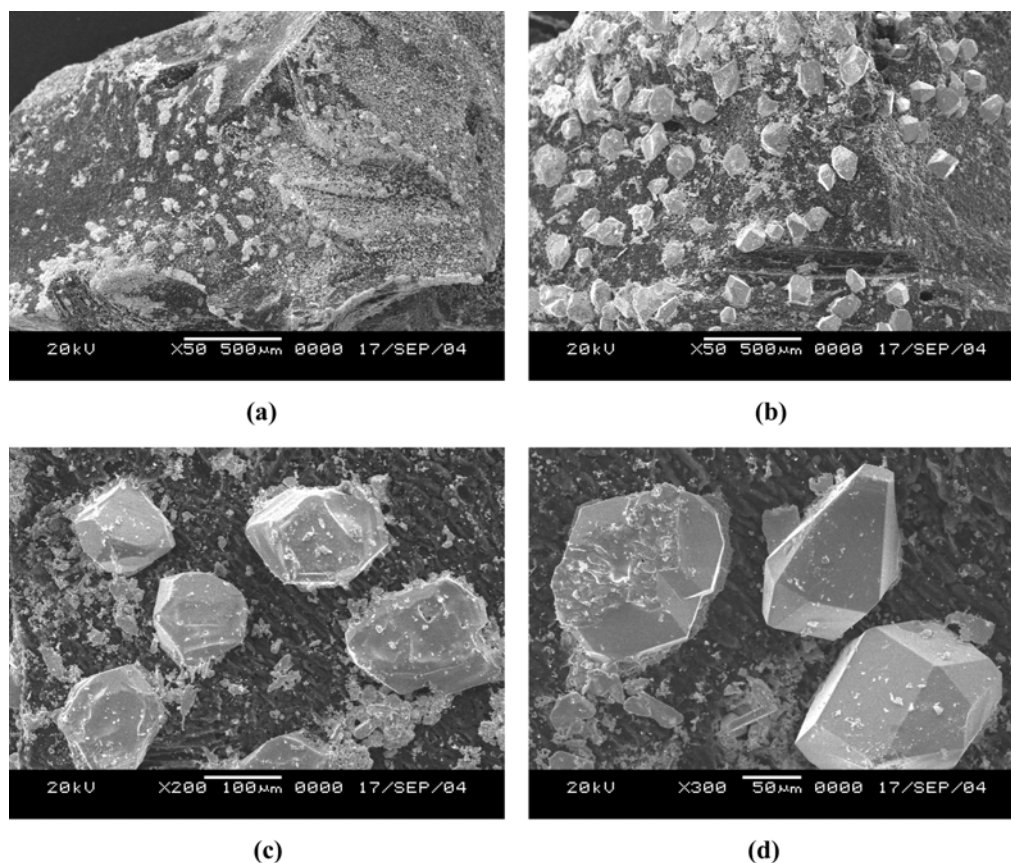
To reveal the causes of the differences in adsorption capacity and specific surface area after the samples were washed with different strengths of sulfuric acid, surface morphology and pore structure were investigated by SEM. Figures 3 and 4 show the surface morphologies of the Ag-activated carbons before and after post-treatment with sulfuric acid. In 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 treat-

Table 2. Comparison of Physical Parameters of Metal-Activated Carbon Samples Transformed by Post-Treatment with Sulfuric Acid

Sample	Parameter			
	S_{BET} (m^2/g)	Micropore Volume (mL/g)	External Surface Area (m^2/g)	Average Pore Diameter ($\text{\AA}$)
$\text{Ag}_{0.05}\text{-AC}$	1121	0.454	432.7	15.11
$\text{Ag}_{0.05}\text{-AC-0.01SA}$	1022	0.428	396.7	15.11
$\text{Ag}_{0.05}\text{-AC-0.05SA}$	1181	0.433	415.2	15.14
$\text{Ag}_{0.05}\text{-AC-0.1SA}$	1343	0.463	433.4	15.15
$\text{Ag}_{0.1}\text{-AC}$	992.3	0.453	325.8	14.95
$\text{Ag}_{0.1}\text{-AC-0.01SA}$	988.5	0.451	315.9	15.06
$\text{Ag}_{0.1}\text{-AC-0.05SA}$	996.9	0.455	328.4	15.08
$\text{Ag}_{0.1}\text{-AC-0.1SA}$	1023	0.458	393.3	15.11
$\text{Cu}_{0.05}\text{-AC}$	1111	0.456	445.9	15.22
$\text{Cu}_{0.05}\text{-AC-0.01SA}$	1142	0.453	421.1	15.19
$\text{Cu}_{0.05}\text{-AC-0.05SA}$	1167	0.459	434.7	15.20
$\text{Cu}_{0.05}\text{-AC-0.1SA}$	1389	0.459	433.4	15.23
$\text{Cu}_{0.1}\text{-AC}$	1187	0.451	446.1	14.86
$\text{Cu}_{0.1}\text{-AC-0.01SA}$	1042	0.454	398.2	14.76
$\text{Cu}_{0.1}\text{-AC-0.05SA}$	1261	0.455	429.3	15.32
$\text{Cu}_{0.1}\text{-AC-0.1SA}$	1339	0.460	453.2	15.45

ment. 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 metals 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 particles and silver compounds, and then larger size silver particles are obtained as the reduction is continued. Figures 5 and 6 show the surface morphologies of the Cu-activated carbons before and after post-treatment with sulfuric acid. It is noted that the size of aggregated particles obtained from samples post-treated with acid is smaller than that obtained from non-treated samples. Before the samples were post-treated with acid, most of the aggregated Cu salt particles form islands which block the external and internal surfaces of the activated carbon, while the small particles remaining after post-treatment with acid block the pores on the carbon surface. After the samples are post-treated with acid, aggregated particles become smaller. From the SEM results, it was observed that the more number of small copper salt particles were heterogene-

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

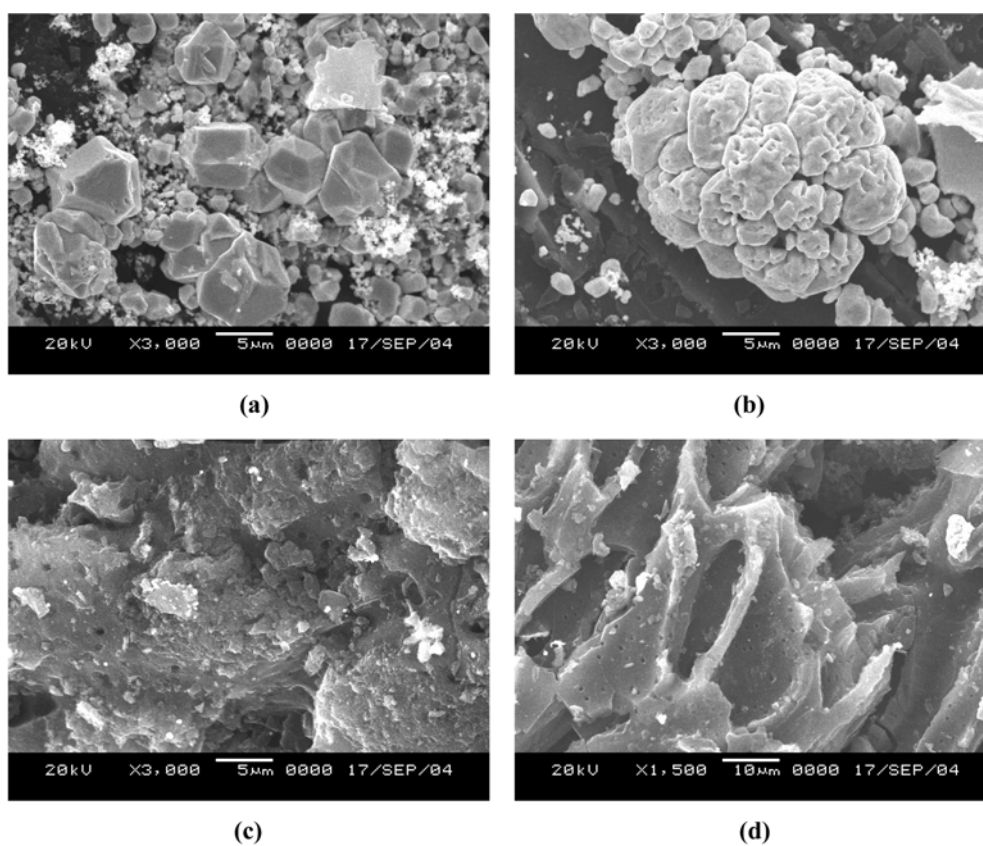


Fig. 4. SEM images obtained from the $\text{Ag}_{0.1}\text{-AC-SA}$ series; (a) $\text{Ag}_{0.1}\text{-AC}$, (b) $\text{Ag}_{0.1}\text{-AC-0.01SA}$, (c) $\text{Ag}_{0.1}\text{-AC-0.05SA}$ and (d) $\text{Ag}_{0.1}\text{-AC-0.1SA}$

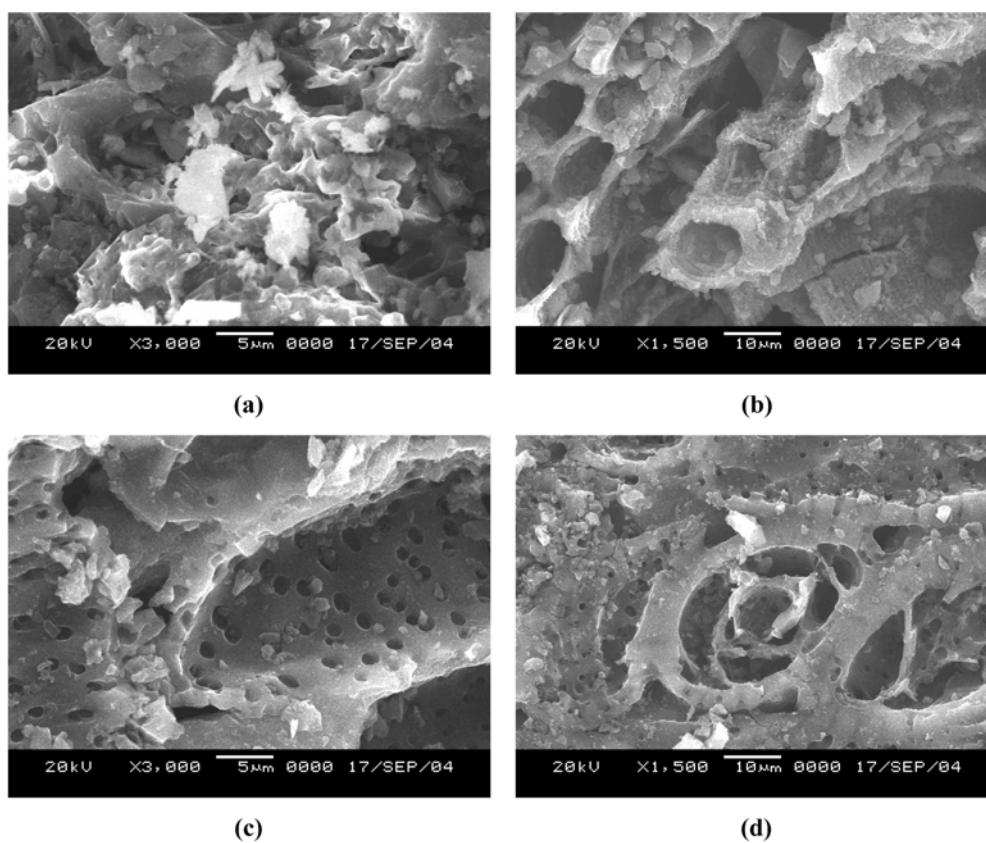


Fig. 5. SEM images obtained from the $\text{Cu}_{0.05}\text{-AC-SA}$ series; (a) $\text{Cu}_{0.05}\text{-AC}$, (b) $\text{Cu}_{0.05}\text{-AC-0.01SA}$, (c) $\text{Cu}_{0.05}\text{-AC-0.05SA}$ and (d) $\text{Cu}_{0.05}\text{-AC-0.1SA}$

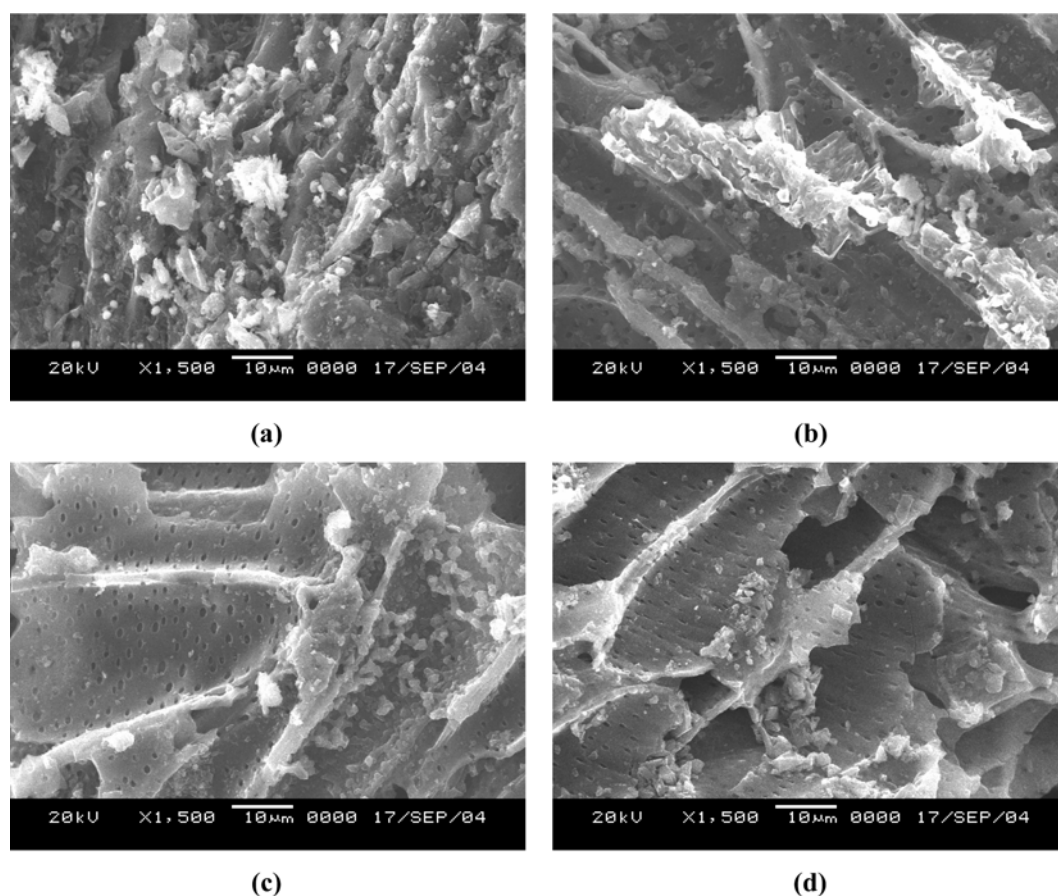


Fig. 6. SEM images obtained from the $\text{Cu}_{0.1}\text{-AC-SA}$ series; (a) $\text{Cu}_{0.1}\text{-AC}$, (b) $\text{Cu}_{0.1}\text{-AC-0.01SA}$, (c) $\text{Cu}_{0.1}\text{-AC-0.05SA}$ and (d) $\text{Cu}_{0.1}\text{-AC-0.1SA}$.

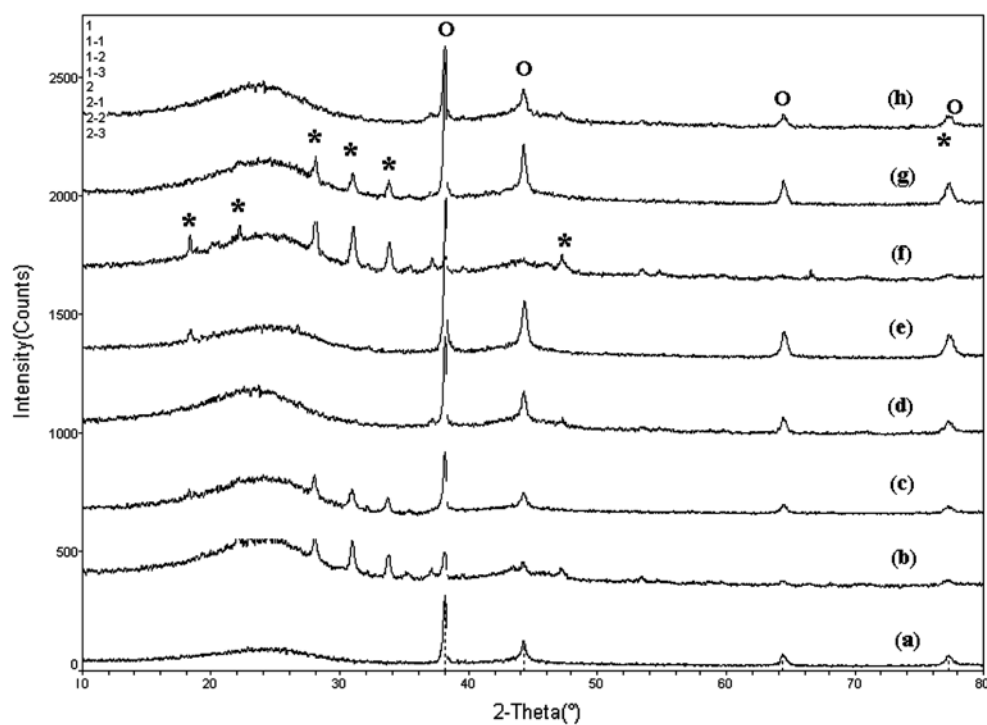


Fig. 7. XRD patterns for the $\text{Ag}_{0.05}\text{-AC-SA}$ and $\text{Ag}_{0.1}\text{-AC-SA}$ series (O: metallic Ag, *: Ag_2SO_4); (a) $\text{Ag}_{0.05}\text{-AC}$, (b) $\text{Ag}_{0.05}\text{-AC-0.01SA}$, (c) $\text{Ag}_{0.05}\text{-AC-0.05SA}$, (d) $\text{Ag}_{0.05}\text{-AC-0.1SA}$, (e) $\text{Ag}_{0.1}\text{-AC}$, (f) $\text{Ag}_{0.1}\text{-AC-0.01SA}$, (g) $\text{Ag}_{0.1}\text{-AC-0.05SA}$ and (h) $\text{Ag}_{0.1}\text{-AC-0.1SA}$.

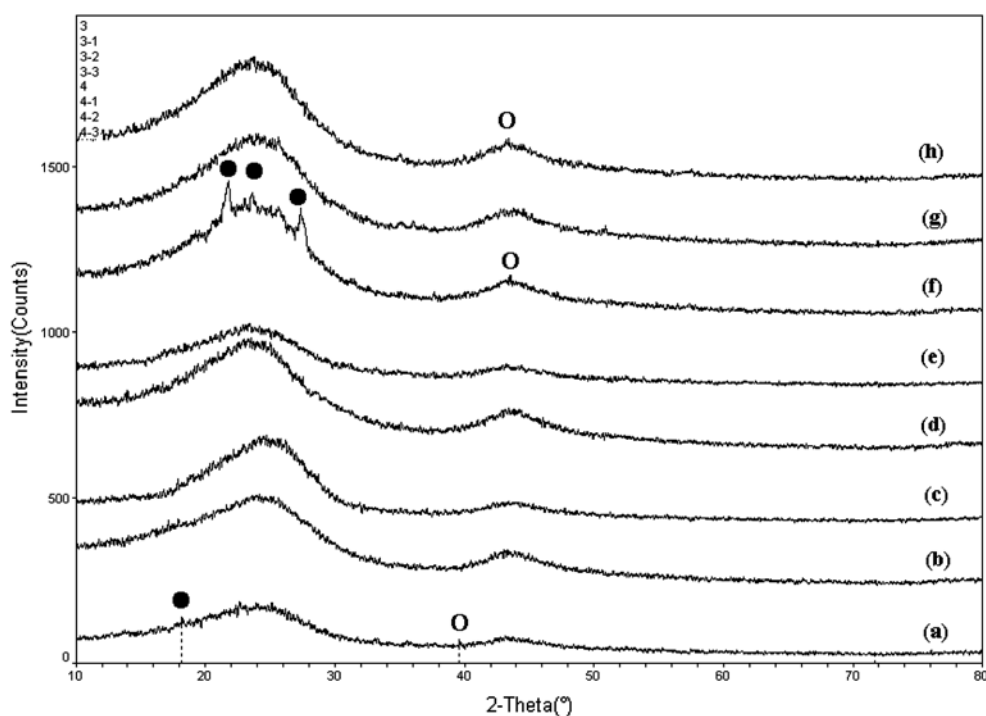


Fig. 8. XRD patterns for the $\text{Cu}_{0.05}\text{-AC-SA}$ and $\text{Cu}_{0.1}\text{-AC-SA}$ series (● : CuSO_4 , ○ : Cu) (a) $\text{Cu}_{0.05}\text{-AC}$, (b) $\text{Cu}_{0.05}\text{-AC-0.01SA}$, (c) $\text{Cu}_{0.05}\text{-AC-0.05SA}$, (d) $\text{Cu}_{0.05}\text{-AC-0.1SA}$, (e) $\text{Cu}_{0.1}\text{-AC}$, (f) $\text{Cu}_{0.1}\text{-AC-0.01SA}$, (g) $\text{Cu}_{0.1}\text{-AC-0.05SA}$ and (h) $\text{Cu}_{0.1}\text{-AC-0.1SA}$.

ously dispersed both outside micropores and on the surface of Cu-activated carbons by post-treatment with acid. It may be believed that the discrepancies in adsorption and surface properties before and after the acid treatment are mainly due to different pore opening effects. Also the effects depend on the means of distribution, the shape of metal salts, the size of particles, and the pattern of aggregates on the carbon surface. It is considered that the acid post-treatment alters not only the morphologies of metal salts on the carbon surface but the physicochemical properties of the surface of the carbon itself.

X-ray diffraction patterns shown in Figs. 7 and 8 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. 7). From the results of Fig. 8, the X-ray diffraction peaks of Cu-treated activated carbons are very similar to those of non treated raw activated carbons except for some peaks obtained with metals. In the case of $\text{Cu}_{0.1}\text{-AC-0.01SA}$, many peaks corresponding to metallic Cu and CuSO_4 were present. The formation of bulky Ag_2SO_4 and CuSO_4 can be explained by the fact that pretreated metallic silver and copper, as active sites, take part in the oxidation of SO_2 derived from sulfuric acid.

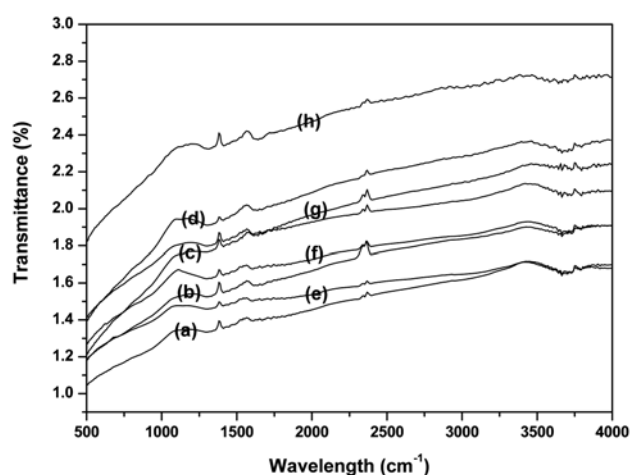


Fig. 9. Infrared spectra recorded from Ag-activated carbon transformed by post-treatment with sulfuric acid; (a) $\text{Ag}_{0.05}\text{-AC}$, (b) $\text{Ag}_{0.05}\text{-AC-0.01SA}$, (c) $\text{Ag}_{0.05}\text{-AC-0.05SA}$, (d) $\text{Ag}_{0.05}\text{-AC-0.1SA}$, (e) $\text{Ag}_{0.1}\text{-AC}$, (f) $\text{Ag}_{0.1}\text{-AC-0.01SA}$, (g) $\text{Ag}_{0.1}\text{-AC-0.05SA}$ and (h) $\text{Ag}_{0.1}\text{-AC-0.1SA}$.

In the FT-IR spectra (Figs. 9, 10) of the carbon materials the bond O-H stretching vibrations (3400 cm^{-1}) were due to surface hydroxyl groups 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 respectively attributed to the stretching vibrations of C=O moieties in carboxylic, ester, lactonic or

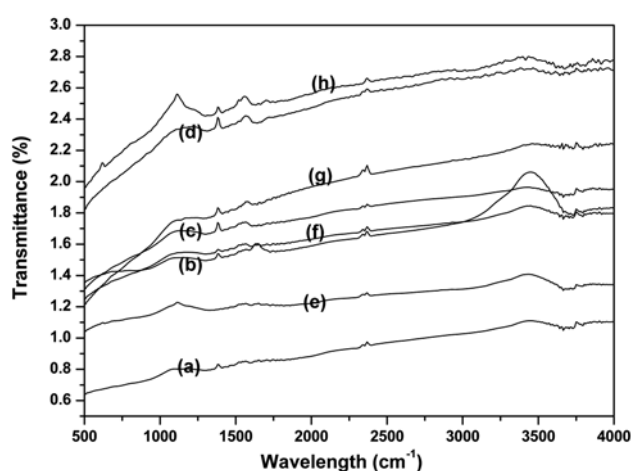


Fig. 10. Infrared spectra recorded from Cu-activated carbon transformed by post-treatment with sulfuric acid; (a) $\text{Cu}_{0.05}\text{-AC}$, (b) $\text{Cu}_{0.05}\text{-AC-0.01SA}$, (c) $\text{Cu}_{0.05}\text{-AC-0.05SA}$, (d) $\text{Cu}_{0.05}\text{-AC-0.1SA}$, (e) $\text{Cu}_{0.1}\text{-AC}$, (f) $\text{Cu}_{0.1}\text{-AC-0.01SA}$, (g) $\text{Cu}_{0.1}\text{-AC-0.05SA}$ and (h) $\text{Cu}_{0.1}\text{-AC-0.1SA}$.

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 [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 $\nu(\text{C-O})$ 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 $\nu(\text{C-O})$ 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 H_2O is adsorbed on the surface of activated carbons with the participation of both specific interaction like hydrogen bonds, chemisorption due to surface oxide hydration and non-specific interactions like physical adsorption, the absorption bands in the $1600\text{--}1500\text{ cm}^{-1}$ region can also be described by OH bending vibrations. Some complicated absorption bands in the $1650\text{--}1500\text{ cm}^{-1}$ region suggests that aromatic ring bands and C=C vibrations overlap the above mentioned C=O stretching vibration bands and deformed OH bands. 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 FT-IR spectra for the Ag-AC-SA series are very similar to that of the Cu-AC-SA series. The main goal of oxidation by acid treatment is to obtain a more hydrophilic surface with a relatively

Table 3. Number of Surface Species (meq/g) Obtained from Boehm Titration

Sample	Functional Group (meq/g)				
	Carboxylic	Lactonic	Phenolic	Acidic	Basic
$\text{Ag}_{0.05}\text{-AC}$	0.32	0.61	0.76	1.72	0.98
$\text{Ag}_{0.05}\text{-AC-0.01SA}$	0.34	0.61	0.78	1.76	0.13
$\text{Ag}_{0.05}\text{-AC-0.05SA}$	0.38	0.65	0.80	1.83	0.12
$\text{Ag}_{0.05}\text{-AC-0.1SA}$	0.42	0.68	0.82	1.92	0.11
$\text{Ag}_{0.1}\text{-AC}$	0.30	0.56	0.72	1.58	0.96
$\text{Ag}_{0.1}\text{-AC-0.01SA}$	0.30	0.62	0.74	1.66	0.12
$\text{Ag}_{0.1}\text{-AC-0.05SA}$	0.32	0.78	0.80	1.90	0.11
$\text{Ag}_{0.1}\text{-AC-0.1SA}$	0.42	0.78	0.88	2.08	0.11
$\text{Cu}_{0.05}\text{-AC}$	0.30	0.58	0.84	1.72	0.54
$\text{Cu}_{0.05}\text{-AC-0.01SA}$	0.34	0.66	0.88	1.88	0.12
$\text{Cu}_{0.05}\text{-AC-0.05SA}$	0.42	0.72	0.88	2.02	0.10
$\text{Cu}_{0.05}\text{-AC-0.1SA}$	0.46	0.78	0.90	2.14	0.12
$\text{Cu}_{0.1}\text{-AC}$	0.30	0.66	0.84	1.80	0.55
$\text{Cu}_{0.1}\text{-AC-0.01SA}$	0.34	0.72	0.84	1.90	0.12
$\text{Cu}_{0.1}\text{-AC-0.05SA}$	0.40	0.74	0.88	2.02	0.11
$\text{Cu}_{0.1}\text{-AC-0.1SA}$	0.42	0.74	0.88	2.04	0.16

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

The results of the chemical investigations following carbon surface modification are set out 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 some 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 evaluated from correlations as a function of NaOH, NaHCO_3 and Na_2CO_3 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 metal-activated carbons confirm the observation that an increase of the acidity and a decrease of the basicity are independent of the amount of pre-treated metal contents. The results obtained may contribute to the lowest local pH of this carbon surface with removal of metal and metal 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 and copper 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 Figs.

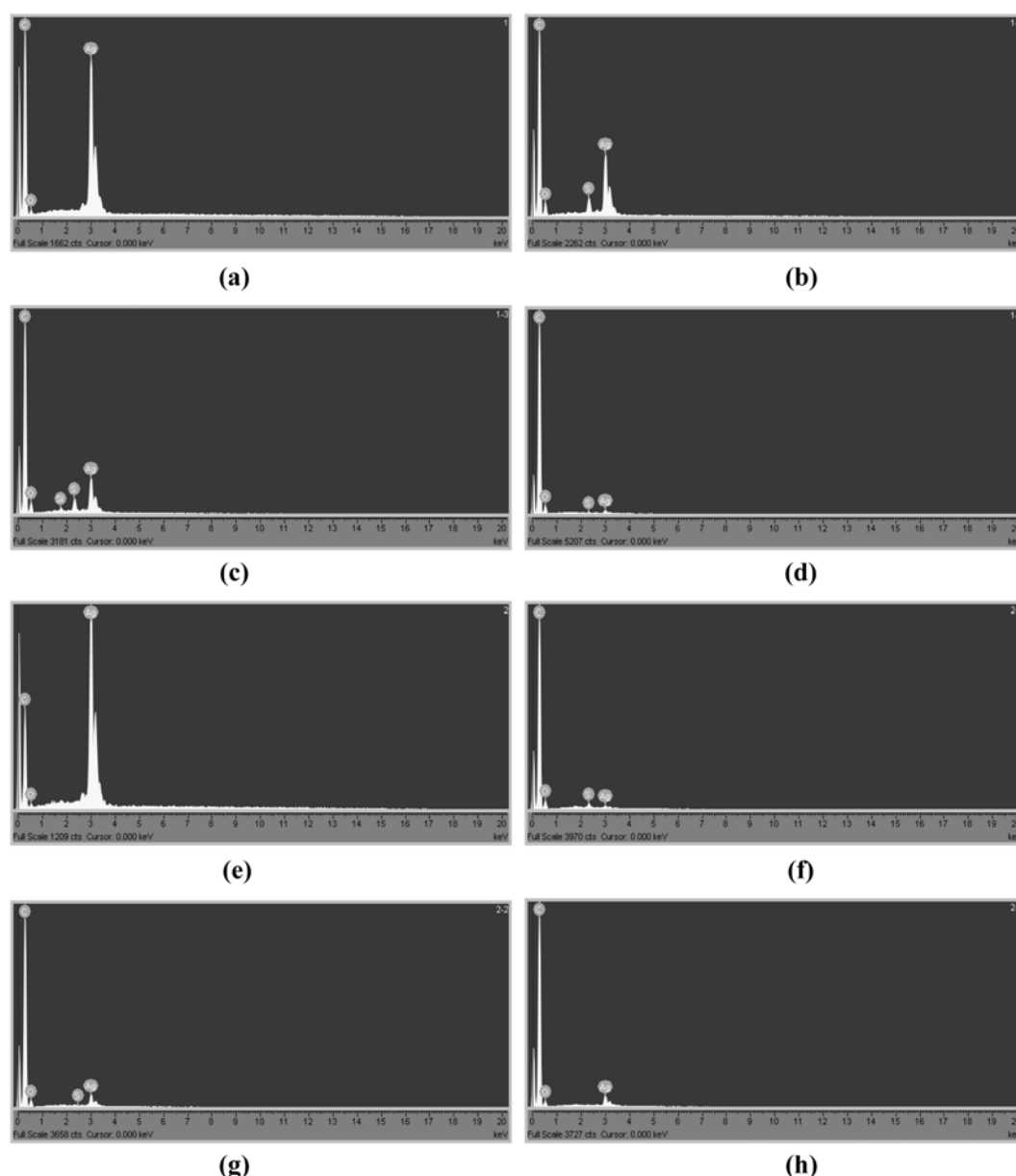


Fig. 11. EDX elemental micro-analysis spectra obtained from Ag-activated carbon samples transformed by post-treatment with sulfuric acid; (a) $\text{Ag}_{0.05}\text{-AC}$, (b) $\text{Ag}_{0.05}\text{-AC-0.01SA}$, (c) $\text{Ag}_{0.05}\text{-AC-0.05SA}$, (d) $\text{Ag}_{0.05}\text{-AC-0.1SA}$, (e) $\text{Ag}_{0.1}\text{-AC}$, (f) $\text{Ag}_{0.1}\text{-AC-0.01SA}$, (g) $\text{Ag}_{0.1}\text{-AC-0.05SA}$ and (h) $\text{Ag}_{0.1}\text{-AC-0.1SA}$.

11 and 12. Figure 11 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 $\text{Ag}_{0.05}\text{-AC-0.1SA}$, 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 $\text{Ag}_{0.05}\text{-AC-0.01SA}$ (Fig. 11(d)), which becomes more homogeneous as the carbon surface is oxidized. The

results of EDX elemental microanalyses of metal-activated carbon samples transformed by post-treatment with sulfuric acid are listed in Table 4. Figure 12 shows the presence of C, S, Si, Cu and O. In the case of these samples, carbon and copper are present as major elements in the Cu-activated carbons transformed by post-treatment with sulfuric acid. As mentioned above, an increase of the S content can be explained that the pretreated metallic copper, as active sites, take part in the oxidation of SO_2 derived from sulfuric acid. It is also observed that 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.

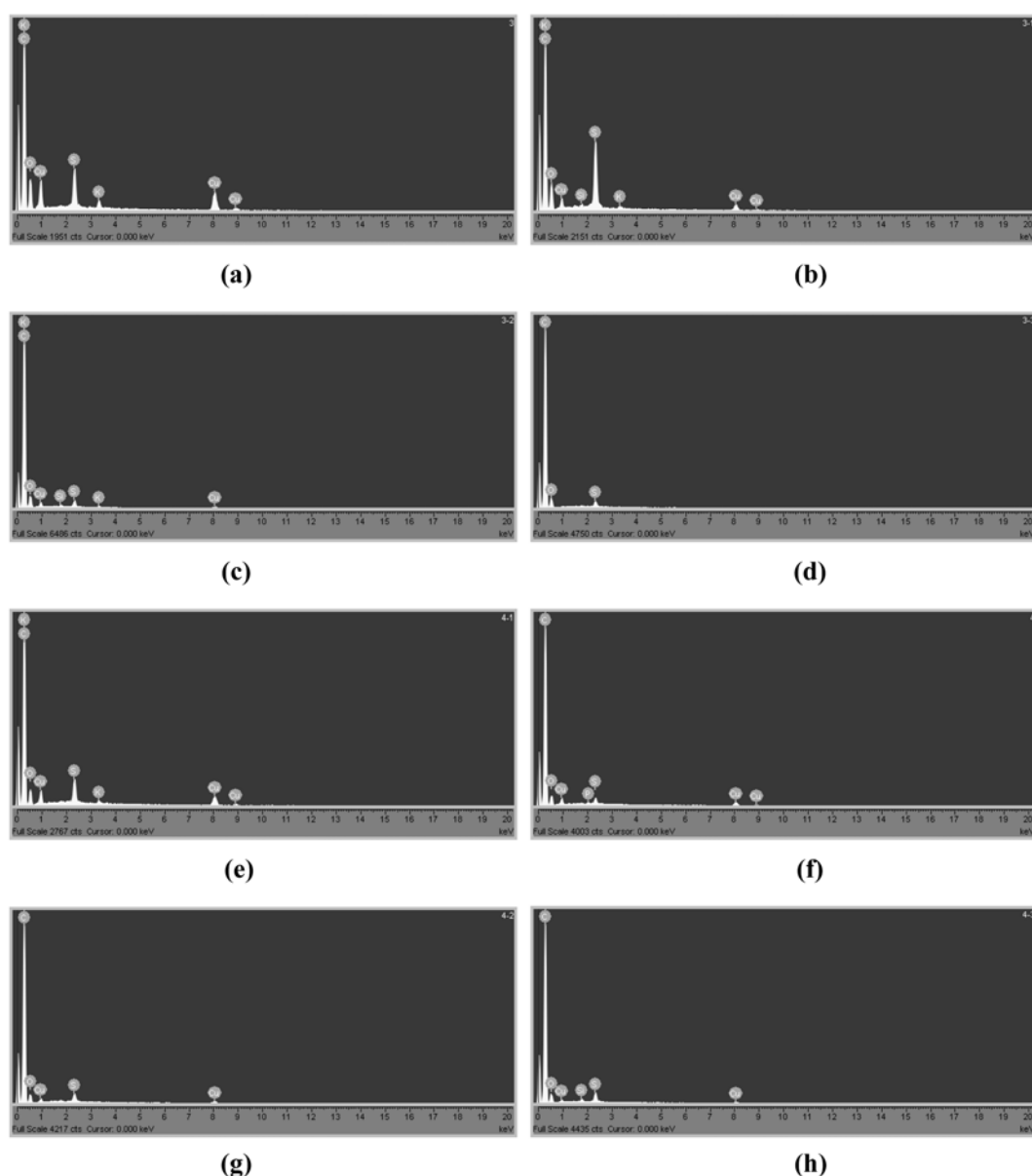


Fig. 12. EDX elemental micro-analysis spectra obtained from Cu-activated carbon samples transformed by post-treatment with sulfuric acid; (a) $\text{Cu}_{0.05}\text{-AC}$, (b) $\text{Cu}_{0.05}\text{-AC-0.01SA}$, (c) $\text{Cu}_{0.05}\text{-AC-0.05SA}$, (d) $\text{Cu}_{0.05}\text{-AC-0.1SA}$, (e) $\text{Cu}_{0.1}\text{-AC}$, (f) $\text{Cu}_{0.1}\text{-AC-0.01SA}$, (g) $\text{Cu}_{0.1}\text{-AC-0.05SA}$ and (h) $\text{Cu}_{0.1}\text{-AC-0.1SA}$.

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/p_0 axis. Micrographs of the surfaces by SEM are shown 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 metal species show better performances for metal and metal compound removal by post-treatment with acid. The FT-IR spectra of metal-activated

carbon samples show that the acid post-treatment is consequently associated with the removal of metals 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. The results of EDX elemental microanalysis for each sample are show the spectra corresponding to almost all the samples are rich in oxygen with a decrease of metal content with an increase of the amount of acid post-treated.

Table 4. EDX Elemental Microanalysis of Metal-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
Cu _{0.05} -AC	66.0		13.4	2.60	18.01	
Cu _{0.05} -AC-0.01SA	69.6	1.03	22.3	0.99	6.16	
Cu _{0.05} -AC-0.05SA	81.3	1.98	9.15	1.40	6.13	
Cu _{0.05} -AC-0.1SA	88.5		11.5			
Cu _{0.1} -AC	74.2		11.3		14.6	
Cu _{0.1} -AC-0.01SA	70.6		11.2	1.69	15.04	
Cu _{0.1} -AC-0.05SA	76.5		13.9		9.47	
Cu _{0.1} -AC-0.1SA	76.9	4.04	14.8		4.25	

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