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Adsorption properties and metal growth aspects on the surface of activated carbon monolith electrochemically deposited with Ag

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Abstract The electrochemical adsorption of the Ag ions from aqueous solution on pelletized activated carbon monolith was investigated over wide range of operation time. The adsorption capacities of pelletized activated carbon monolith are associated with their internal porosity and are related properties such as surface area, pore size distribution. The chemical industry generates wastewater that contains toxic matters like heavy metals in small concentrations so that their economic recovery is not feasible. But, the method using activated carbon monolith can be used to withdrawal of heavy metals in waste water. After the electrochemical treatment, the quantitative properties in Ag ion solutions are also examined by pH concentration and studied elemental analysis by ICP-Atomic Emission Spectrometer and Energy Disperse X-ray (EDX) spectra. It is consider that the pH is very important factor at the reason of water pollutant with increasing acidity in industrial field. The result of quantitative analysis using Inductively Coupled Plasma-Atomic Emission Spectrometer of metal after electrochemical reaction in Ag ions solution depending on time are shown that the amount of Ag ions deposited was decreased with growth of Ag particles on the carbon surfaces as increasing electrochemically treated time. And, surface morphologies are investigated by scanning electron microscopy (SEM) to explain the changes in adsorption properties.

Key words Adsorption, Surface area, Pore size distribution, ICP, EDX, SEM

1. Introduction

Activated carbons are widely used in different branches of industry, for adsorption of unwanted substances from both gas and liquid phase, as catalyst supports and catalysts in technologies characterized by requirements for very high quality products [1]. Adsorption properties play a important role in the modern industries, especially in the field of environmental treatment for large scale chemical, electrochemical, biochemical, and environmental recovery and purification and protection engineering [2]. Adsorption processes in the industrial field are being employed widely in liquid-solid, gas-solid and gas-gas operation such as the decolorization of petroleum products, and the removal of pollutants from aqueous or gaseous effluents. Most metals and metal salts present in industrial wast water are toxic, poorly retrieve and not easily biodegradable. Adsorption on activated carbon is an attractive alternative to eliminate these contaminants from industrial effluents and water sources. However, the effect of process conditions on the electrochemical adsorption of metals and their salts must be fully understood in order to optimize the use of activated carbon on an industrial scale. We have found in our previous work that the preparation method of metal treated activated carbon for adsorption were remarkably distinguishable [3]. To wide their application, the adsorption of transition metals on activated carbon and activated carbon fiber has been introduced using chemical [4] and electrochemical methods [5]. Such a metal treated activated carbon and fiber can be used for antibacterial agent, catalysts and electrode of metal retrieve.

This paper deal with the electrochemical adsorption of Ag ions at much lower concentration. This study is aimed to test a home made pelletized activated carbon electrode, for example, is able to remove Ag ions from aqueous solutions. The variations in the surface properties, such as adsorption isotherms, surface areas and pore size distribution of electrochemically metal treated activated carbon are investigated as a function of electrochemical deposition time. After the electrochemical treatment, the quantitative properties in Ag ion solutions are also examined by pH concentration and studied elemental analysis by ICP-Atomic Emission Spectrometer and EDX. Finally, surface morphologies are investigated by SEM to explain the changes in adsorption properties.

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2. Experimental

2.1. Preparation of activated carbon monolith

For the preparation of activated carbon monolith, a powder activated carbon has been chosen from a series of chemically activated carbons prepared using KOH as the activating agent and a Indonesian coconut shell as the raw material. After preparing a large quantity of this activated carbon, novolac phenolic resin (PR) as the binder material could be used for the preparation of the activated carbon monoliths. The amount of PR for the preparation was 15~20 wt%. For the binding effect, bentonite as the additive material could be also used for the preparation. The amount of that was 5~10 wt%. The binder/bentonite/activated carbon mixtures were dried to a powder and then pressed into 9.95×39.5×5.95 mm hexagonal pellets in a mould. The curing temperature of the pelletized activated carbon monoliths was about 150°C. The cured sample were then pyrolyzed at 750°C for 3 h in order to completely carbonized the binder. Nomenclature and preparation methods of activated carbon monoliths are listed in Table 1.

2.2. Electrochemical characteristics

The pelletized activated carbon monolith of test electrodes was consist of the size of 9.95(b)×39.5(h)×5.95(t) mm of pellet type activated carbon. The counter electrode was artificial graphite rod. The electrolyte was 0.01 M silver nitrate solution. The electrode preparation were investigated by electrochemically deposited metal ion measurements at 0.5 $mAcm^{-2}$ at room temperature. The measured voltage was set to 4.5 V.

2.3. Measurements and analysis

After electrochemical reaction in Ag ion solution depending on operation time, characterization of all porous Ag-treated activated carbons was carried out by the physical adsorption of gases (N_2 at 77 K) using an automatic adsorption system (Degisorb 2500, Micrometric Instrument Corp, USA). The micropore volume has been calculated from the application of the Dubinin-Radushkevich (DR) equation to the N_2 adsorption at 77 K. Scanning electron microscopy (SEM, JSM-5200 JOEL, Japan) was used to observe the surface state and pore structure of electrochemically metal treated activated carbon and the grown metal state on the surface. For the elemental analysis of metal contents in activated carbon, EDX was also used. For the quantitative analysis in Ag ion solutions after electrochemical deposition, Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, Jovin Yvon Ultima-C) were used to obtain elemental properties. A combination pH electrode (EYELA Model AR 10) was used to measure the solution pH.

3. Results and Discussion

The N_2 (at 273 K) adsorption isotherms of Ag-treated samples were obtained in a volumetric system. Figure 1 and Fig. 2 present the nitrogen adsorption isotherms corresponding to the Ag-binder/bentonite/activated carbon after electrochemically treated. All the isotherms are Type I isotherms, characteristics of microporous solids and they show a plateau isotherm reflecting a minimum presence of mesopores. Thus, it can be said that the

Table 1
Nomenclature and preparation methods of AC1s and AC2s

Preparation method	Nomenclature
AC(80%) + BT(5%) + PR(15%); 30 sec. operation in Ag soln.	AC1-30S
AC(80%) + BT(5%) + PR(15%); 1 min. operation in Ag soln.	AC1-1M
AC(80%) + BT(5%) + PR(15%); 3 min. operation in Ag soln.	AC1-3M
AC(80%) + BT(5%) + PR(15%); 5 min. operation in Ag soln.	AC1-5M
AC(80%) + BT(5%) + PR(15%); 7 min. operation in Ag soln.	AC1-7M
AC(80%) + BT(5%) + PR(15%); 10 min. operation in Ag soln.	AC1-10M
AC(80%) + BT(10%) + PR(10%); 30 sec. operation in Ag soln.	AC2-30S
AC(80%) + BT(10%) + PR(10%); 1 min. operation in Ag soln.	AC2-1M
AC(80%) + BT(10%) + PR(10%); 3 min. operation in Ag soln.	AC2-3M
AC(80%) + BT(10%) + PR(10%); 5 min. operation in Ag soln.	AC2-5M
AC(80%) + BT(10%) + PR(10%); 7 min. operation in Ag soln.	AC2-7M
AC(80%) + BT(10%) + PR(10%); 10 min. operation in Ag soln.	AC2-10M

*AC : Activated Carbon.
**BT : Bentonite.
***PR : Phenolic Resin.

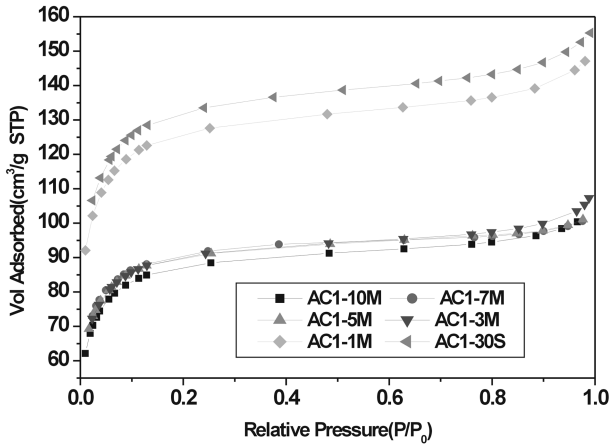


Fig. 1. Adsorption isotherm plotted on the relative pressure scale for the porous AC1s at 77.3 K.

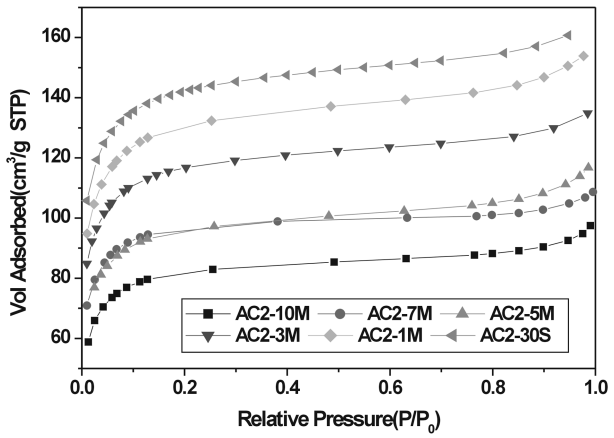


Fig. 2. Adsorption isotherm plotted on the relative pressure scale for the porous AC2s at 77.3 K.

preparation process of the pelletized activated carbon monoliths does not produce mesoporosity. In these Figs., it can be seen that nitrogen adsorption capacity have a decrease with growth of Ag metal particles as increasing electrochemical operation time. It is consider that the formed macropore, mesopore and wider micropore on the surface before electrochemical treatment are transformed to micropore and narrow micropore. The isotherms are characteristic of predominantly micropores solids with some contribution by the micropores. The adsorption isotherms presented in these Figs. that the total sorption uptake decreases with increasing operation time. Comparing the isotherms for these samples (AC1s and AC2s), it can be presented that the AC1s obtained under 30s and 1m treatment exhibit higher adsorption volume than that of any other samples. As shown in Fig. 2, the amounts of adsorbed volume decrease with prolonged operation time for the electrochemical treatments. It can be observed that the nitrogen adsorption capacity is very similar in both cases. It can be considered that formed wider micropore, mesopore and macropore on the surface before electrochemical operation are transformed to micropores and narrow micropores.

Table 2
Comparison of physical properties for porous AC1s and AC2s

Sample	S_{BET} (cm^3/g)	Average pore diameter (Å)
AC1-30S	499.7	29.47
AC1-1M	484.7	25.29
AC1-3M	342.5	30.23
AC1-5M	339.1	25.51
AC1-7M	349.8	26.19
AC1-10M	329.7	25.87
AC2-30S	544.3	23.63
AC2-1M	502.3	25.89
AC2-3M	448.3	24.89
AC2-5M	370.0	30.54
AC2-7M	375.5	24.24
AC2-10M	317.7	27.63

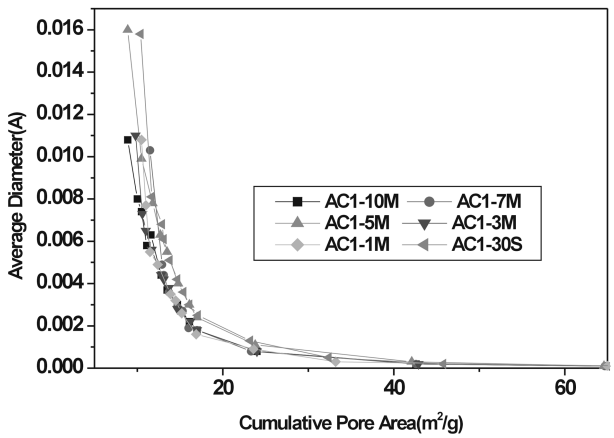


Fig. 3. Pore size distributions obtained from the activated carbon electrodes (AC1s).

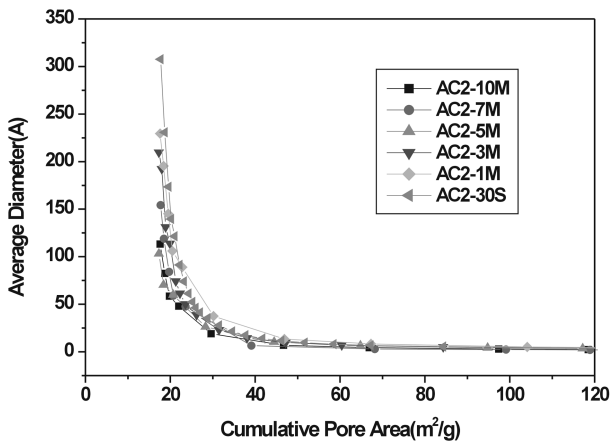
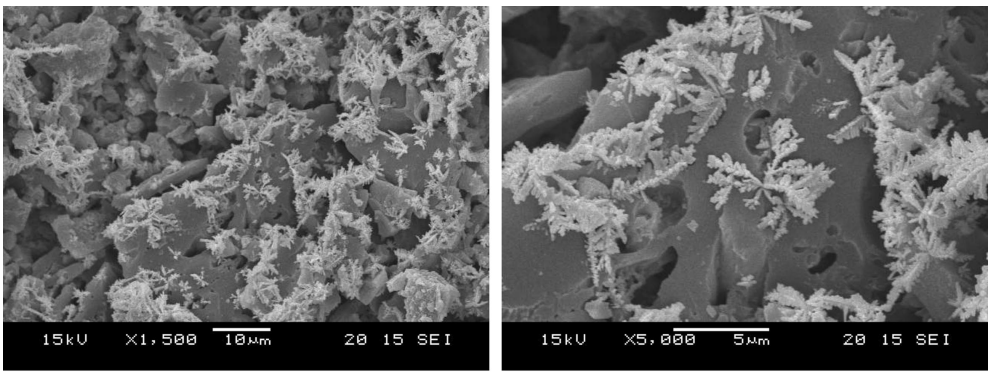


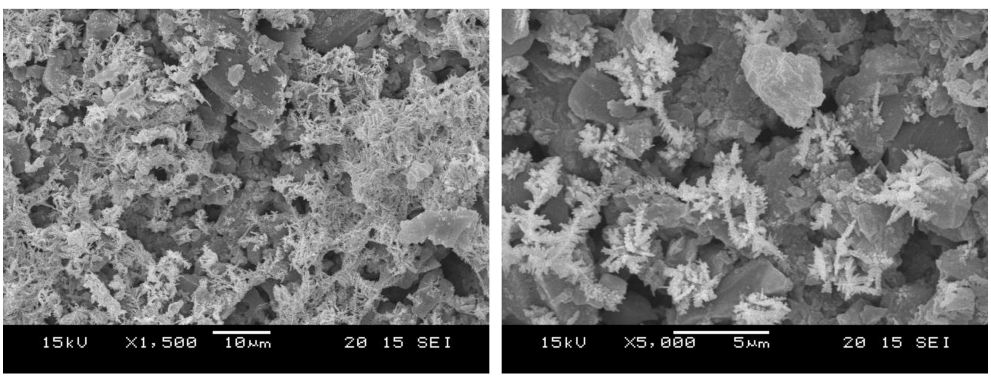
Fig. 4. Pore size distributions obtained from the activated carbon electrodes (AC2s).

Table 2 shows the specific surface area (S_{BET}) and average pore diameter from BET method and the application of the DR equation of the Ag treated samples obtained. The areas of Ag-treated activated carbons are in the range of 329.7~499.7 m^2/g for AC1s and 317.7~544.3 m^2/g for AC2s. The surface area decrease by factor of operation time. And average pore diameters are distributed to the range of 25.29~30.23 Å for AC1s and 23.63~30.54 Å for AC2s, respectively. The average pore diameter is almost constant for samples treated to operation time. The biggest difference not exists among samples.

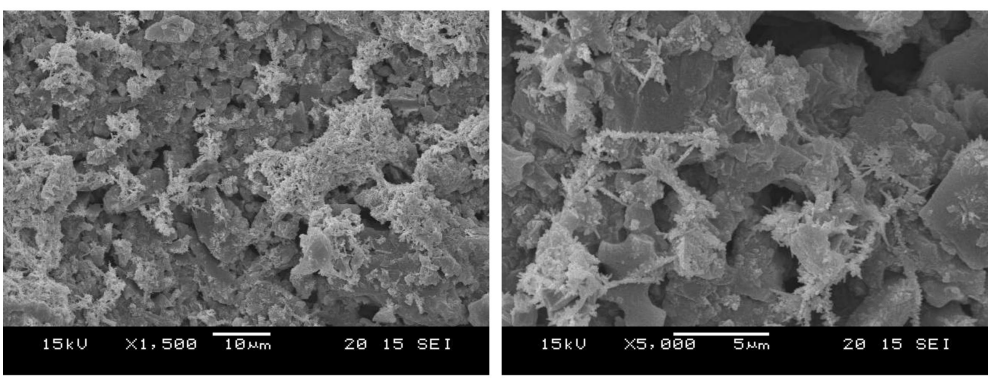
The pore size distributions(PSDs) calculated for our materials using the density functional theory are shown in Fig. 3 and 4. The developments of micropores for AC1s and micro- and mesopores for AC2s are observed with increasing operation time. For the pore analysis of Ag-treated activated carbons, it is believe that treatment time produces a significant increase in number of micropore and small mesopores along with a decrease in number of mesopores. Consequently, the AC2s have a border pore size distribution, the AC1s have obviously



(a) ACI-30S

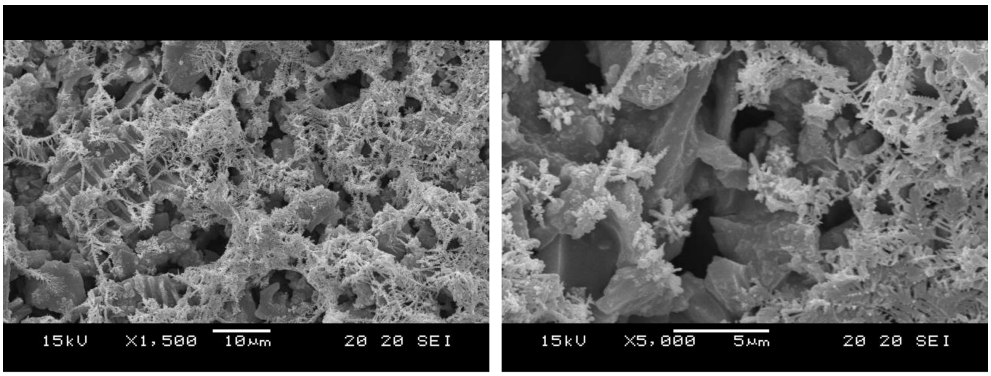


(b) ACI-1M

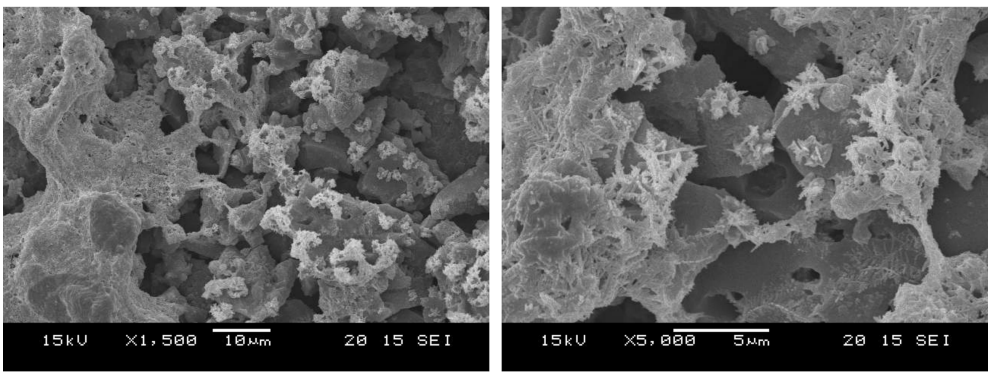


(c) ACI-3M

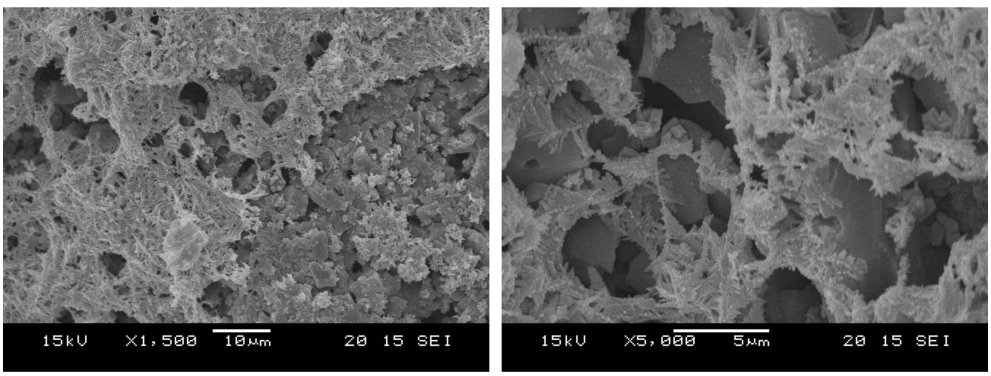
Fig. 5. SEM images of activated carbon electrodes (AC1s).



(d) ACI-5M



(e) ACI-7M



(f) ACI-10M

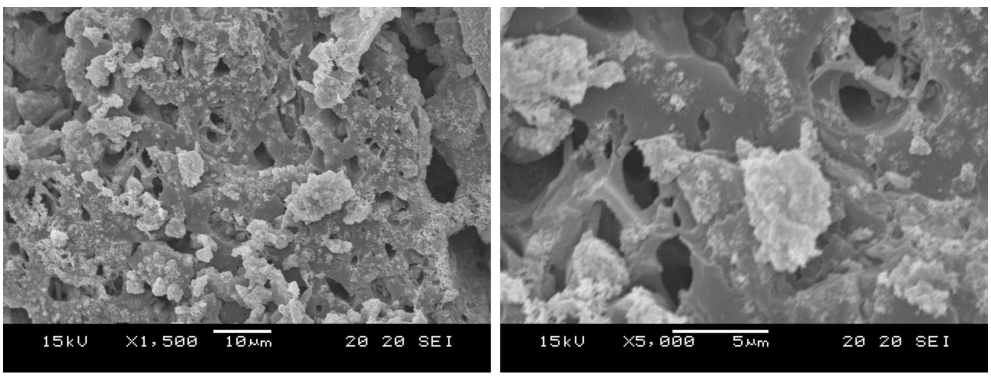
Fig. 5. Continued.

mesopores.

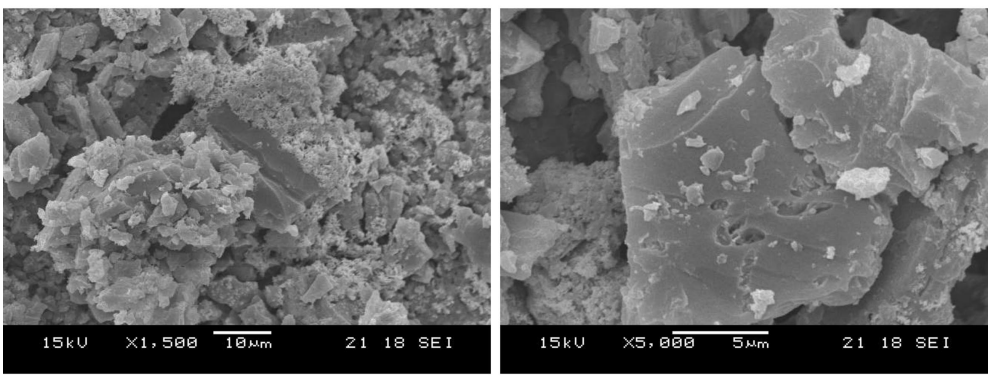
The SEM micrographs of AC1s and AC2s samples with different metal loading time are present in Fig. 5 and 6. The all samples seem as a porous metal-activated carbon with any visible pores, cavities and bulk solid on the surface. At the same time, the measure specific surface area of the samples is very low and ranged from 317.7 m^2/g to 544.3 m^2/g. This fact is well correlated with previous works [3, 4, 6]. The results were shown unique microporous structure of metal-treated activated carbon; activated carbon contain mainly micropores with narrow size distribution between 1 and 2 m invisible in the images presented in Fig. 5(a) and (b), and 6 (a) and (b). The effect of increasing electrochemical operation time on the Ag-treated activated carbon surface morphology is clearly observed by the SEM images (Fig. 5 and 6). The image of activated carbon electrochemically treated for 30 s in Ag solution is much the same as that of original activated carbon. This observation indicated that practically all the Ag introduced is located inside the micropores and consequently, it is dispersed into very small crystallites with growth of Ag metals. Ag contents above operation time 3 m in Ag solution lead to drastic morphology changes:

large grown Ag particles on the activated carbon outer surface are clearly visible and presented in the Fig. 5(e) and (f), and 6 (e) and (f) for the operation time 7 m and 10 m, respectively. The increasing time of large Ag particles on the activated carbon surface resulted in clogging and blocking of micropores and this fact is well considered with specific surface area measurements. Finally, the metallic Ag grown is located between micropores and out side surfaces of activated carbon and the Ag treated to above 3 m is distributed on the out side surface in the form of metallic crystal and aggregates. So, in this study, it is consider that two types of Ag/activated carbon were prepared and investigated; first one is that all Ag is sited in micropores, another one is that the Ag is located both in micropores and on the out side surface of activated carbon.

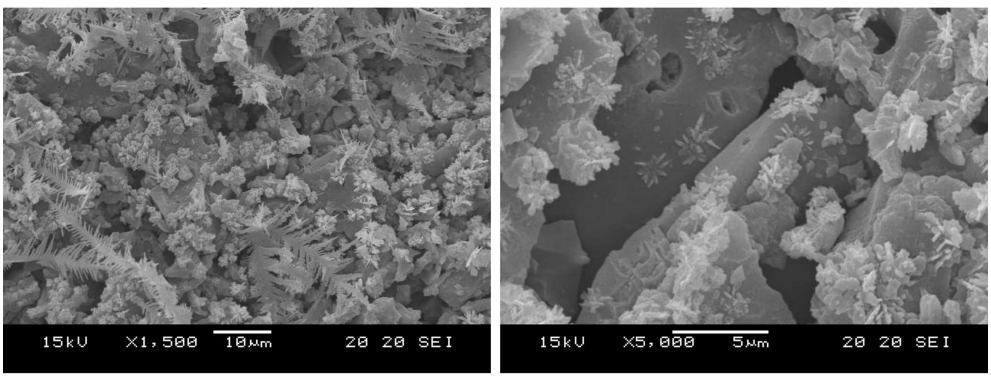
In order to know how pH properties are affected by the amount of additive material (bentonite), pelletized activated carbons with different percentage of additive material were prepared. The pH variation during the electrochemical deposition on activated carbon pellet in Ag solution is shown in Fig. 8. From the Fig. 8, it is observed that the pH concentrations for the both samples (AC1s and AC2s) were slowly decreased in the



(a) AC2-30S

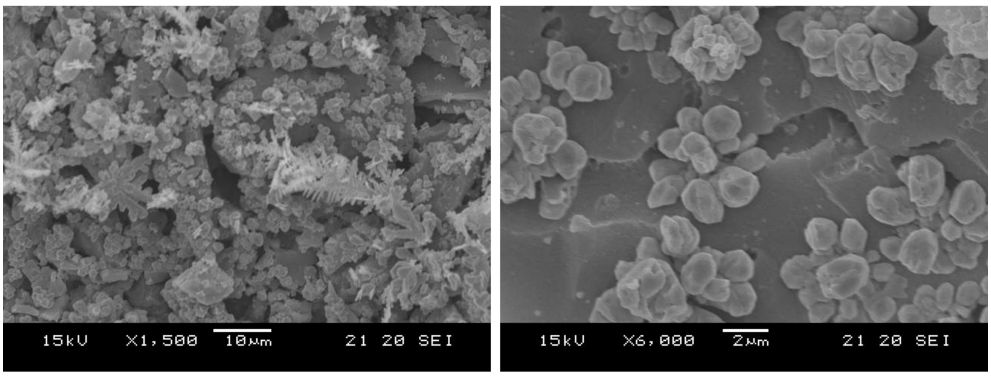


(b) AC2-1M

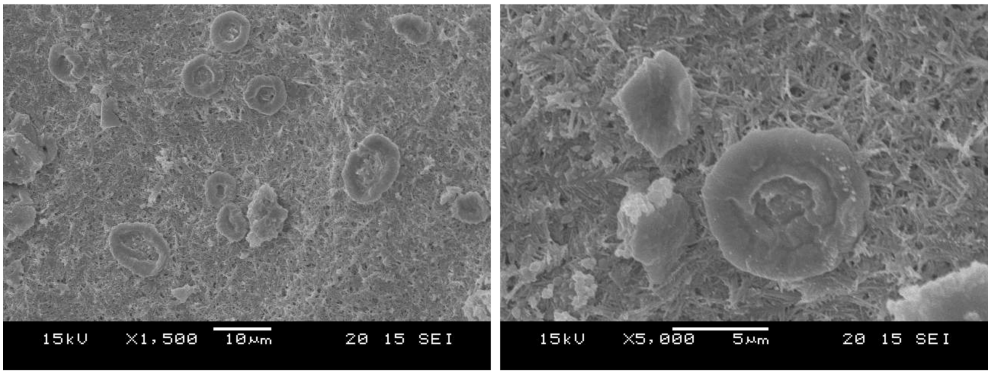


(c) AC2-3M

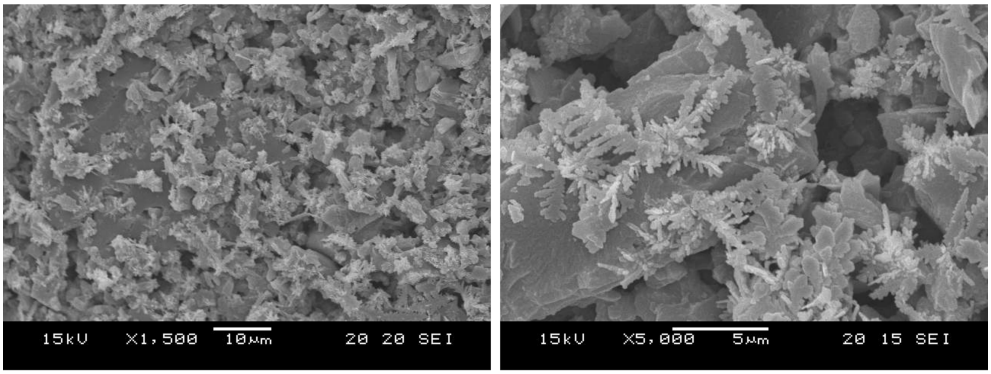
Fig. 6. SEM images of activated carbon electrodes (AC2s).



(d) AC2-5M



(e) AC2-7M



(f) AC2-10M

Fig. 6. Continued.

overall of electrochemical reaction. The pH values of the $AgNO_3$ solution after electrochemically 30 s operated were 6.7 for the AC1 and 5.2 for the AC2, respectively. It can be seen that the change in the pH concentration with the amount of additive material is very important. Activated carbon and activated carbon fiber have been used to remove trace metal ions from liquid and drinking water and mixed industrial effluents [7]. In this study, it is reveal that the pH in procedure of removing the trace metal ions in solution is decreased with increasing adsorbed metal contents on pelletized activated carbon monoliths. On the other hand, in Fig. 7 and 8 it can be observed that an increase in the amount of additive material form 5 to 10 wt% produces a decrease in the pH concentration and the residue concentration (ppm) of Ag ions, which is very important for electrochemical metal ion deposition applications.

Energy disperse X-ray (EDX) spectra of Ag-treated activated carbon of AC1s are shown in Fig. 9. And, the results of typical EDX elemental microanalysis of metallic Ag supported activated porous carbons are shown in Table 3. Fig. 9(a) shows a typical EDX spectrum taken on a non-treated AC1 sample. It shows the presence of C, Ca, K, O and Si. The sample is richer in carbon and

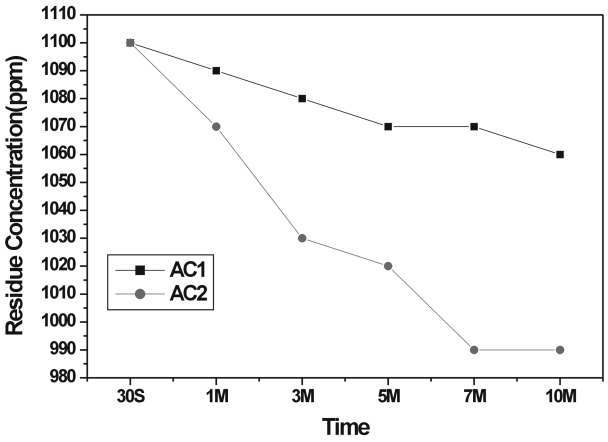


Fig. 7. Result of ICP analysis after electrochemical reaction in Ag solution.

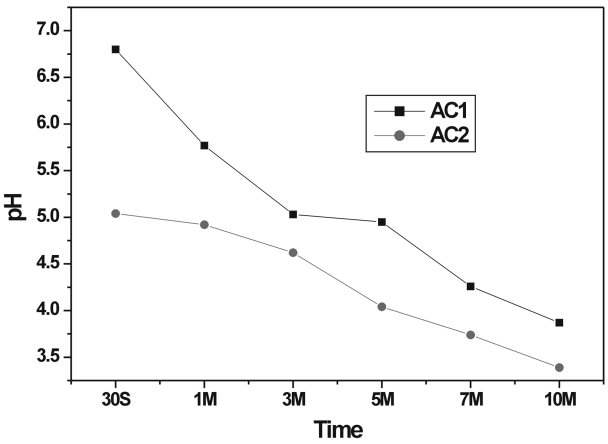
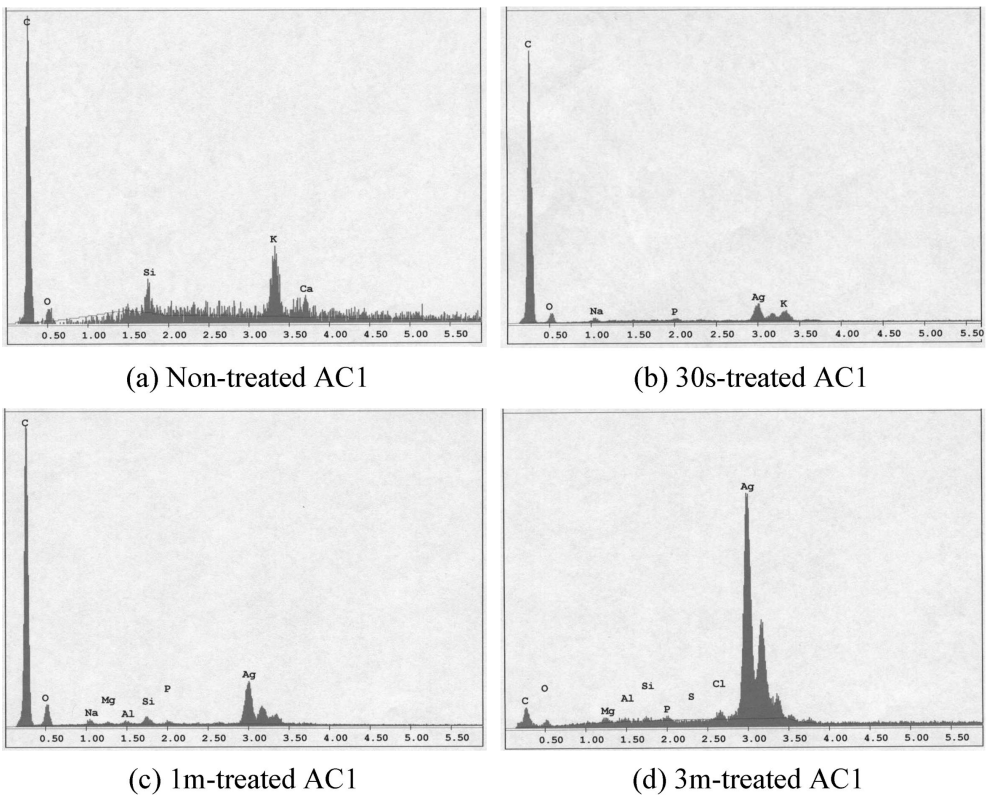


Fig. 8. pH variation after electrochemical reaction in Ag solution.

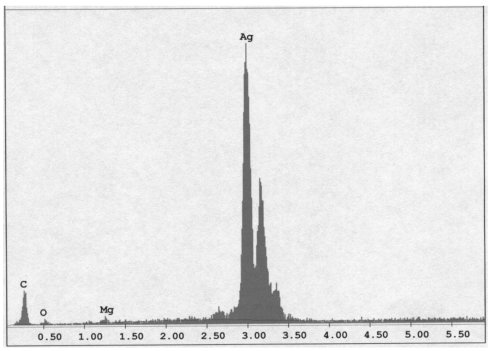
potassium than any other elements. And, the Fig. 9(b) (g) show the spectra corresponding to almost all samples rich in silver with increasing operation time. Note that for the electrochemically 30 s-treated activated carbon sample (Fig. 9(b)) a nonhomogeneous distribution of Ag is obtained, which becomes more homogeneous as the carbon surface is oxidized (Fig. 9(c) (g)). These change seem to indicate that the functionality of activated carbon surface affects the dispersion of the Ag, which is enhanced with increasing of concentration of (+) charges on the activated carbon monoliths on the condition of increasing of acidity in solution. The results from Fig. 9 seem to corroborate those obtained by pH variation (Fig. 8). Oxidation of the carbon surface is the principal vehicle for achieving high Ag dispersion by introducing (–) charged oxygen functional groups that serve as anchoring sites for the metal. The access of silver anions to these sites is, therefore, favored by attrac-



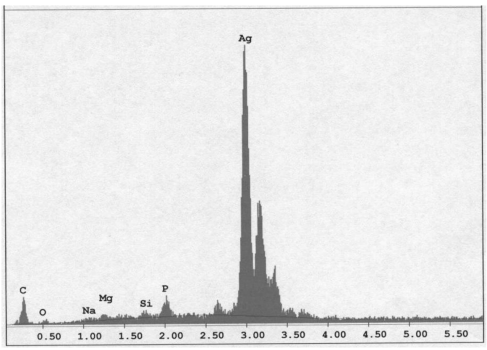
(a) Non-treated AC1 (b) 30s-treated AC1

(c) 1m-treated AC1 (d) 3m-treated AC1

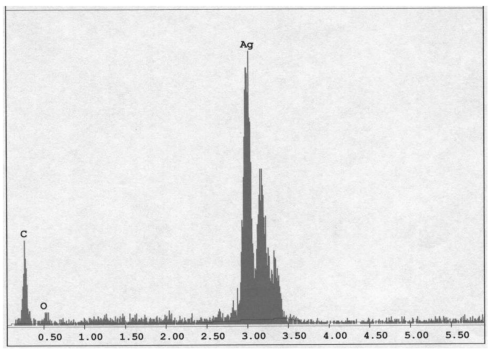
Fig. 9. Typical EDX microanalysis of the AC1s.



(e) 5m-treated AC1



(f) 7m-treated AC1



(g) 10m-treated AC1

Fig. 9. Continued.

Table 3
Comparison of EDX elemental micro-analysis for AC1s and AC2s

	Elements (%)			
	C	Ag	O	Others
AC1-30S	82.66	7.01	6.36	3.97
AC1-1M	73.95	12.75	9.91	3.39
AC1-3M	57.32	33.68	6.26	2.74
AC1-5M	15.78	81.34	1.25	1.63
AC1-7M	4.47	85.33	7.87	2.33
AC1-10M	2.87	88.23	6.45	2.45
AC2-30S	82.11	7.44	5.25	3.20
AC2-1M	71.34	22.09	3.96	2.61
AC2-3M	20.14	73.84	3.88	2.14
AC2-5M	10.96	83.24	4.41	2.39
AC2-7M	5.74	86.68	4.34	3.24
AC2-10M	2.14	89.33	4.76	3.77

tive electrostatics forces. One could expect that very low treatment pH values, when the interactions between the activated carbon and the Ag ions are favorable, could be appropriate to achieve high Ag dispersion. The problem of an insensible metal to the changes produced on the surface functionality of carbon seems to stem from the conflict that exists between active site creation and surface accessibility [8].

4. Conclusion

In this study, the electrochemical deposition of the Ag ions from aqueous solution on pelletized activated carbon monolith was investigated over wide range of operation time. The results obtained show that adsorption capacities of Ag-binder/bentonite/activated carbon are associated with their internal porosity and are related properties such as surface area, pore size distribution. The S_{BET}s of Ag-treated activated carbons are in the range of 329.7~499.7 m^2/g for AC1s and 317.7~544.3 m^2/g for AC2s. And their average pore diameters are distributed to the range of 25.29~30.23 Å and 23.63~30.54 Å, respectively. From results of PSDs and SEM micrographs, the all samples seem as a microporous metal treated activated carbon with any visible pores, cavities and bulk solid on the surface. In pH properties, it is reveal that the pH in procedure of removing the trace metal ions in solution is decreased with increasing adsorbed metal contents on pelletized activated carbon monoliths. Finally, from EDX data, Ag-binder/bentonite/activated carbons show the spectra corresponding to almost all samples rich in silver with increasing operation time.

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