

INVESTIGATION OF THE STATE OF ADSORBED SILVER IONS ON MODIFIED ACTIVE CARBONS

A. Świątkowski*, S. Biniak, G. S. Szymański and L. Bogdan*

*Military Technical Academy, 01-489 Warsaw, Poland

Nicolaus Copernicus University, Faculty of Chemistry, 87-100 Toruń, Poland

Introduction

Some heavy and/or noble metal cations can be reduced to lower valences due to adsorption on active carbon materials (granules, powder, or fibres). The contribution of reductive properties in concentrating, separating, and recovering of metal cations in adsorption processes has not been explained yet. The ability of the carbon materials to reduce ions of relatively high standard potentials can be attributed to the possibility of oxidation of surface sites with an increased electron density (Lewis base centres). On the other hand, a carbon material surface can easily be modified by metals simply by exposing it to a solution containing the relevant metal ions [1-2]. Carbon materials with deposited metals have many applications. For example, silver is often used as an antibacterial agent in activated carbon water purifier [2].

The aim of this work is to investigate possible silver ion sorption mechanisms such as ion-exchange and/or redox reactions on carbon surface of various chemical nature.

Experimental

Three samples of deashed (with conc. HF and HCl) and chemically modified commercial active carbon D-43/1 (Carbo-Tech, Essen, Germany) were studied. Oxidation with conc. HNO₃ (D-O) as well as heating in vacuum (D-H) in an ammonia atmosphere at 1170 K (D-N) were used as modification procedures [3]. BET surface area from the N₂ adsorption at 77 K was determined. The total amounts of oxygen and nitrogen were also analysed. The chemical properties of the modified carbon surface were estimated by neutralisation with NaOH and HCl (both of 0.1 M). Additionally, the acidities (pHs) of carbon slurries in 0.1 M NaCl were determined. The values of adsorption of Ag⁺ from aq. AgNO₃ (0.05M, pH=4.70) on three modified active carbons were determined. The Ag⁺ concentration was determined by titration with KSCN using Fe³⁺ as an indicator. The kinetic curves and adsorption isotherms determined at 298 K. pH values were recorded for all experimental points. The adsorbed silver was eluted from separate samples with water, 0.01 M nitric acid, 0.1 M ammonia water and ethanol.

All experiments with silver solution were carried out in a dark chamber. The carbon samples with and without adsorbed silver ions were also studied spectroscopically (with FTIR and XPS). Transmission IR spectra of the carbon samples were obtained using a Perkin-Elmer FTIR Spectrum 2000 spectrometer. The XPS spectra were obtained with an EscaLab 210 (V.G. Scientific Ltd.) photoelectron spectrometer.

Results and Discussion

The surface modification procedures applied to the studied deashed carbon change its surface area only slightly. However, oxidation with conc. nitric acid leads to formation of many different acidic surface structures but annealing, especially in ammonia, enhances basicity of the carbons [3]. The adsorption kinetics and isotherms determined at 298 K for Ag⁺ on the modified carbon samples are shown in Figs. 1 and 2, respectively. For all studied carbons, we observed a decrease of pH values of external solution during adsorption. Silver adsorption increases (and pH decreases) rapidly especially during initial 10-20 minutes, and deposition of metallic layer on carbon grains can be observed. The amount of adsorbed silver depends strictly on the kind of surface modification and is considerably higher for carbons which exhibit basic properties (heat-treated in vacuum and ammonia atmosphere).

Because of deposition and aggregation of metallic silver on carbon surface, the samples for spectral studies were used after 15 min. time of contact with Ag⁺ solution. The IR measurement procedure applied here (KBr pellet technique) makes impossible to compare quantitatively either the FTIR spectra (Fig. 3) obtained for different carbon samples. However, the spectra recorded indicate clearly the possibility that individual surface structures may be present or absent [3]. For all IR spectra recorded in the 2000-600 cm⁻¹ range (Fig. 3), the presence of absorption bands of C=O (1750-1350 cm⁻¹) and C-O (1300-950 cm⁻¹) moieties can be observed. The spectral changes caused by Ag⁺ adsorption on D-H and D-N carbons point out possible oxidation of their surface and creation of a new oxygen-containing species according to mechanism proposed by Fu et al. [1]. If the carbon material has caused the reduction of Ag⁺ to Ag⁰, the oxidation of active-hydrogen-containing as

Table 1. Physicochemical properties of carbon samples

AC	S _{BET}	Total O/N (%wt).	pH*	Neutralization capacity (mmole/g)	
				NaOH	HCl
D-H	1133	0.6/0.1	10.7	0.13	0.42
D-O	1071	10.8/0.1	3.08	1.66	0.13
D-N	1178	0.4/1.9	10.4	0.09	0.63

Table 2. Adsorption and desorption of silver ions

AC	Adsorption data (t=15min)		Elution (%)	
	Ag ⁺ (mM/g)	pH	H ₂ O	0.01HNO ₃
D-H	0.72	2.51	-	22.3
D-O	0.44	2.55	-	41.2
D-N	0.76	3.76	-	18.7

Table 3. Binding energies (B.E.) and peak relative ratio (p.r.r.) from Ag_{3d} XPS spectra after adsorption

AC	Ag _{3d} 5/2		Ag _{3d} 3/2	
	B.E. (eV)	p.r.r. (%)	B.E. (eV)	p.r.r. (%)
D-H	367.9	100	373.9	100
D-O	367.8	88	373.8	91
	366.4	12	372.3	9
D-N	367.9	100	373.9	100

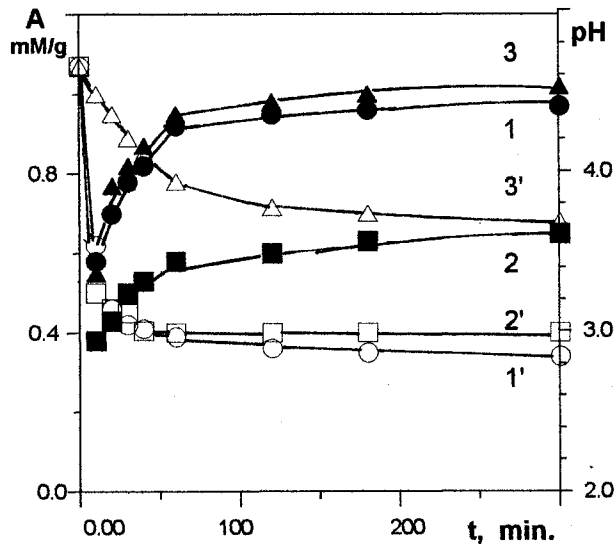


Figure 1. Kinetics of Ag⁺ ion adsorption from 0.05 m AgNO₃ solution (curves 1-3) and pH changes (1'-3') during adsorption on carbons: 1,1' - D-H; 2,2' - D-O; 3,3' - D-N

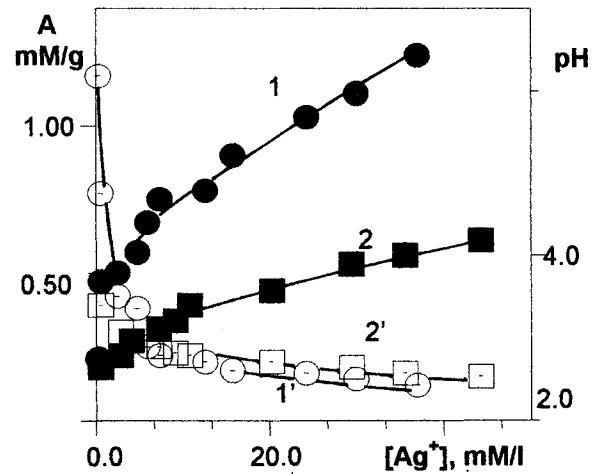


Figure 2. Isotherms of Ag⁺ adsorption from AgNO₃ solutions and pH changes (see Figure 1)

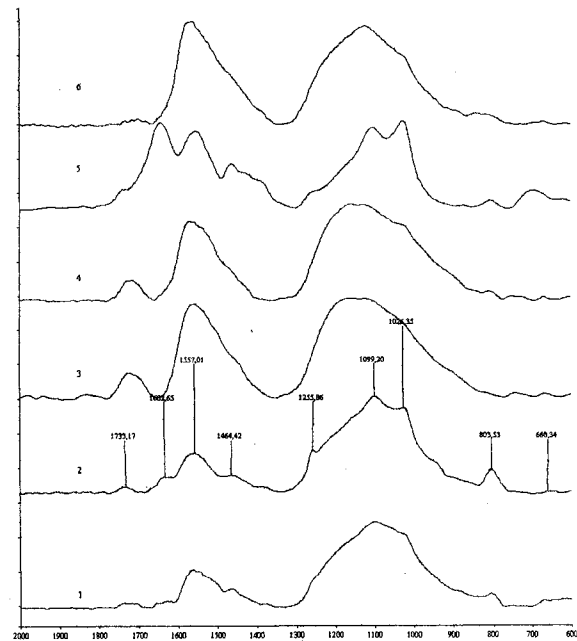


Figure 3. FTIR spectra of carbons (1,2- D-H; 3,4- D-O; 5,6-D-N) before (1,3,5) and after (2,4,6) Ag⁺ adsorption

well as an iono-radical surface centers must be considered. Preliminary XPS results shown in Table 3 indicate that adsorbed silver cations may be partially reduced to metallic silver (on D-H and D-N) or even oxidized to Ag²⁺ (on D-O).

References

- [1] Fu, R., Zeng, H. and Lu, Y., *Carbon* 1994, 32, 593
- [2] Oya, A., Yoshida, S., Alcaniz-Monge, J. and Linares-Solano, A., *Carbon* 1996, 34, 53
- [3] Biniak, S., Szymanski, G., Siedlewski, J. and Swiatkowski, A., *Carbon* (in press)