

Surface Complexes on Activated Carbons for Removal of Metal Ions from Water

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Introduction

In a previous paper we have found that activated carbons from almond shells can be used as adsorbents to remove, in more or less extent, some metal ions, such as Cs⁺, Tl⁺, Sr²⁺ and Co²⁺, from aqueous solutions (1). Pore size distributions in the carbons play an important role in this process; so, the adsorption capacity of these carbons increases with increasing their porosity.

It is known that other parameter affecting adsorptive properties of carbons is their chemical nature. Therefore, it is interesting to know the influence of some surface complexes on the removal of above-mentioned cations. In this way, in the present work we have studied the effect of carbon-oxygen and carbon-nitrogen surface complexes on the adsorption of Na⁺, Cs⁺, Ag⁺, Sr²⁺ and Co²⁺ on an activated carbon obtained from almond shells.

Experimental

The activated carbon used in this study (A-8) was prepared using almond shells as raw material and following the method described elsewhere (1). Its activation time was 8 h. This carbon sample shows the following characteristics: N₂ apparent surface area= 837 m²/g, CO₂ apparent surface area= 1150 m²/g, micropore volume= 0.470 cm³/g, total open pore volume= 0.628 cm³/g, pore volume contained in pores greater than 7.5 nm= 0.269 cm³/g, porosity percentage= 56.14 and ash content= 0.20%.

This activated carbon sample was given oxidative treatment with dry air at 573K, concentrated HNO₃ and hydrogen peroxide (H₂O₂) following the procedure described elsewhere (2). The samples so obtained will be denominated as A-air, A-HNO₃ and A-H₂O₂. Carbon-nitrogen surface complexes were also formed on A-8 sample by flowing NH₃ during 3 h at 773K and 973K [samples A-NH₃(773) and A-NH₃(973)].

In order to know the surface acidity of each sample, selective neutralization techniques have been carried out using NaHCO₃, Na₂CO₃ and NaOH. The pH values of aqueous suspensions of

these samples have also measured; for that, 1 g of sample was mixed with 20 cm³ CO₂-free distilled water, the suspension was shaken for 48 h and then its pH value was determined.

The adsorption of cations by these samples was studied by adding 0.1 g of carbon sample to a vial containing 4 cm³ of a 10⁻⁷ M aqueous solution of the corresponding radioisotope (²²Na, ¹³⁷Cs/^{137m}Ba, ^{110m}Ag, ⁹⁰Sr/⁹⁰Y and ⁶⁰Co). The vials were kept in a thermostat shaker bath at 298K. The percentage adsorption was calculated by comparing the initial radioactivity of the solution with that corresponding to the solution after adding the carbon. Details of this procedure are given in reference (1).

Results and discussion

Table 1 shows the elemental analysis of all samples, and Table 2 their base neutralization capacities and pH values. These latter results indicate, as expected, that while samples A-8, A-NH₃(773) and A-NH₃(973) show predominance of basic functional groups, A-air, A-HNO₃ and A-H₂O₂ samples show predominance of acidic groups.

Since, according to Boehm (3), NaHCO₃ neutralizes carboxylic groups, Na₂CO₃ neutralizes carboxylic and lactonic groups and NaOH neutralizes carboxylic, lactonic and phenolic groups, the total surface acidity of our acidic surface samples increases in the order A-H₂O₂ < A-air < A-HNO₃. On the other hand, as indicated in Table 2, the percentage of each acidic group varies from a sample to another; thus, for example, whereas A-H₂O₂ has 1.3% of carboxylic groups with relation to its total acidic groups, A-HNO₃ sample has 42.7%. All these results might agree the elemental analysis data.

Table 1. Elemental analysis of the carbon samples (wt%)

Sample	C	H	N	O (by diff.)
A-8	94.73	0.57	0.51	4.19
A-air	81.97	0.94	0.00	17.09
A-HNO ₃	68.89	1.99	0.76	28.36
A-H ₂ O ₂	86.71	1.11	0.00	12.18
A-NH ₃ (773)	91.81	0.55	0.81	6.83
A-NH ₃ (973)	93.29	0.53	1.44	4.74

Table 2. Base neutralization capacities (meq/g) and pH values of carbons

Sample	pH	NaHCO ₃	Na ₂ CO ₃	NaOH	Amount (%) of Total Acidic Groups		
					Carboxylic	f-Lactones	Phenolic
A-8	8.56						
A-air	6.08	0.20	0.62	1.72	11.6	24.4	64.0
A-HNO ₃	4.92	1.70	2.26	3.98	42.7	14.1	43.2
A-H ₂ O ₂	5.00	0.01	0.06	0.74	1.3	6.8	91.9
A-NH ₃ (773)	10.44						
A-NH ₃ (973)	11.63						

Following, the procedure indicated, the adsorption of Na⁺, Cs⁺, Ag⁺, Sr²⁺ and Co²⁺ on all samples was investigated as a function of equilibration time. In general, at the beginning the adsorption increases sharply with increasing equilibration time, around 500 min the percentage adsorption attains a constant value. Percentage adsorption values at the equilibrium for all cases are summarized in Table 3. These results indicate that both Na⁺ and Cs⁺ are not significantly adsorbed by A-8, A-NH₃(773), A-NH₃(973) and A-H₂O₂; however, A-air sample adsorbs more than 50% of the Na⁺ and Cs⁺ amounts added, and A-HNO₃ sample adsorbs almost the total amount (>90%). The small adsorption capacity of some of these samples against Na⁺ and Cs⁺ might be because of the low polarising power of these cations; hence, the carbon-cation interaction forces must be too weak and therefore these cations need a high density of negative charge on the carbon surface to be adsorbed. So, A-HNO₃, which has the highest surface acidity, shows the greatest capacity to remove not only Na⁺ and Cs⁺ but also Ag⁺, Sr²⁺ and Co²⁺.

It is interesting to note that Ag⁺, Sr²⁺ and Co²⁺ can be extensively removed by carbons containing acidic functional groups as well as by those with basic groups on their surface. Except in the case of sample A-H₂O₂, all samples containing surface complexes show a higher adsorption capacity than the original activated carbon, A-8.

Table 3. Percentage adsorption of cations by carbons

Sample	Na ⁺	Cs ⁺	Ag ⁺	Sr ²⁺	Co ²⁺
A-8	none	7	81	44	25
A-air	51	78	88	84	84
A-HNO ₃	95	99	95	98	98
A-H ₂ O ₂	none	none	80	43	6
A-NH ₃ (773)	none	none	88	43	50
A-NH ₃ (973)	none	none	90	53	81

Data of Table 3 point out that by means of some of these processes it is possible to separate such cations of each other from an aqueous solution where they are present in trace amounts. Moreover, these adsorption processes might be used to preconcentrate the mentioned cations.

References

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