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## ON THE INFLECTION POINTS ON STRONTIUM IONS ADSORPTION ISOTHERMS ON CAN-7 AND CAN-8 OXIDISED ACTIVATED CARBONS

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Inflection points of strontium ion adsorption isotherms on CAN-7 and oxidized CAN-8 activated carbons were studied. The causes of inflection points on strontium ion adsorption isotherms on CAN-7 and oxidized CAN-8 activated carbons, obtained in the laboratory from walnut shells were identified. Studies have shown that the bonds between  $\text{Sr}(\text{OH})^+$  and strong and weak carboxylic groups in the micropores and supermicropores of CAN-7 activated carbon are stronger than those in mesopores and macropores. The differential heating curve (DTA) of strontium ions adsorbed on CAN-7 has two thermal effects: one endothermic and the other exothermic.

**Keywords:** *adsorption, activated carbon, inflection point, strontium ions, thermal analysis.*

### DESPRE PUNCTELE DE INFLEXIUNE PE IZOTERMELE DE ADSORBȚIE A IONILOR DE STRONȚIU PE CĂRBUNII ACTIVI CAN-7 ȘI CAN-8 OXIDAT

Au fost studiate punctele de inflexiune pe izotermele de adsorbție a ionilor de stronțiu pe cărbunii activi CAN-7 și CAN-8 oxidat, obținuți în laborator din coji de nucă. Studiile au demonstrat că legăturile dintre  $\text{Sr}(\text{OH})^+$  și grupele carboxilice puternice și slabe din microporii și supermicroporii cărbunelui activ CAN-7 sunt mai puternice decât cele din mezopori și macropori. Curba diferențială de încălzire (DTA) a ionilor de stronțiu adsorbiți pe CAN-7 prezintă două efecte termice: un efect endotermic și celălalt – exotermic.

**Cuvinte-cheie:** *adsorbție, cărbune activ, punct de inflexiune, ioni de stronțiu, analiză termică.*

### Introduction

In some publications, the adsorption isotherms of different heavy metal ions, measured at different pH values, on different adsorbents, obtained from various raw materials (especially vegetable by-products), have inflection points followed by increased adsorption values [1-9]. In these works, however, the cause of these points is not discussed, although, according to the publications, at some pH values, and also at some temperatures, the adsorption isotherms of the same adsorbate on the same adsorbent do not have inflection points.

Adsorption isotherms of zinc, cadmium and copper ions from aqueous solutions, measured at different temperatures, on different samples of activated carbon, obtained from food industry waste (almond shells), have inflection points at certain equilibrium concentrations, followed by a significant increase in adsorption values [1]. The article discusses the influence of temperature, of the radii of hydrated ions on their adsorption, but also evaluates the values of specific adsorption chemical energy, calculated from the obtained adsorption isotherms. The causes of inflection points on the adsorption isotherms of heavy metals on the adsorbents under study could ultimately lead to higher values of adsorption, which is very important when we want to remove these pollutants from surface waters, groundwater or waste waters.

The aim of the present work is to identify the causes of inflection points on the isotherms of adsorption of strontium ions on CAN-7 and CAN-8 activated carbons, obtained in the laboratory from walnut shells.

### Materials and methods

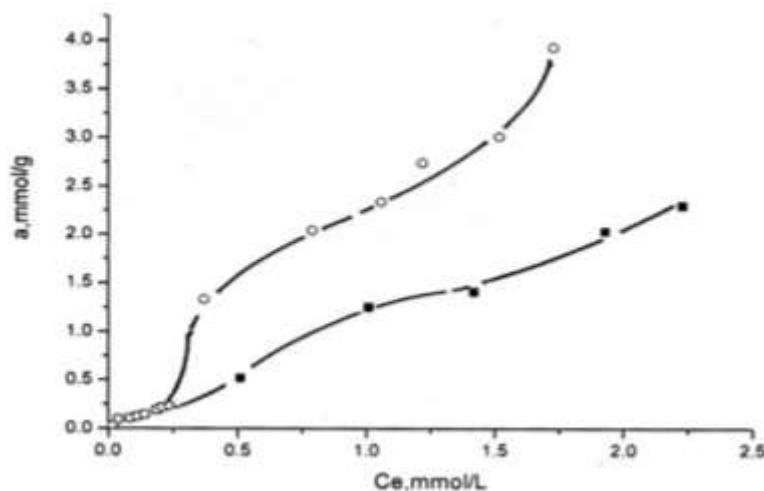
CAN-7 activated carbon was obtained from walnut shells by impregnation with orthophosphoric acid at 80°C and subsequent activation at 460°C. CAN-8 activated carbon was obtained from walnut shells by the physico-chemical method, by activation with water vapours at 960°C. Subsequently, the activated carbon thus obtained was oxidized with 20% nitric acid at 80°C [10].

The adsorption isotherms of strontium ions from aqueous solutions were determined under static conditions, at different initial concentrations of strontium nitrate and at the same amount of adsorbent, at a temperature of 20°C. Pure chemical strontium nitrate was used. Equilibrium concentrations of strontium ions were determined on the AAS-1 spectrophotometer.

The structural parameters of CAN-7 and oxidized CAN-8 activated carbons have been previously determined [10]. Thermal curves were measured on the derivatograph of the Paulik system.

### Results and discussions

Figure 1 shows the adsorption isotherms of strontium ions from aqueous solutions on CAN-7 and oxidized CAN-8 activated carbons.



**Fig.1.** Adsorption isotherms of  $\text{Sr}^{2+}$  ions from aqueous solutions on CAN-7 (■) and oxidized CAN-8 (○) activated carbons.

The presented data show the presence of inflection points on the adsorption isotherms of  $\text{Sr}^{2+}$  ions, followed by an increase of the adsorption values on both activated CAN-7 and oxidized CAN-8 carbons.

This paper [3] showed that the adsorbent obtained from pecans, although it has a small specific surface area, still has a fairly high adsorption capacity of bivalent metals and that it depends largely on the pH value. The allure of the isotherms also depends on the pH, but also the presence or absence of inflection points.

It should be noted here that the jumps on both adsorption isotherms are very clear and start on CAN-7 and oxidized CAN-8 at about the same equilibrium concentrations of strontium ions in solutions. The structural parameters of these two activated carbon samples differ significantly, in particular, the volume of micropores, the volume of supermicropores, but also the surface of mesopores [10]. Probably, an important role in the adsorption process of strontium ions from aqueous solutions on these two activated carbons is played by the chemistry of the surface of these adsorbents, and the possibility of the formation of polyionic layers on the surface of the adsorbents. In [10] it was found that the surface heterogeneity of CAN-7 activated carbon is higher than the surface heterogeneity of oxidized CAN-8 activated carbon. If the surface of the adsorbent is more inhomogeneous, then each stage of the adsorption isotherm must be replaced by the plurality of stages, each one corresponding to the formation of the monolayer on homogeneous surface sectors [11]. At a plurality of steps, the isotherm becomes smoother, which can be seen by comparing the adsorption isotherms of strontium ions from aqueous solutions on CAN-7 and oxidized CAN-8 activated carbons.

The paper [12] presents the adsorption isotherms of nitrogen, argon and oxygen on graphitized carbon adsorbents (Sterling MT 3100) at 77K. Note that the nitrogen adsorption isotherm on Sterling MT 3100 has inflection points at both, low equilibrium and higher concentrations. The oxygen adsorption isotherm on the same adsorbent has no inflection points throughout the studied P/Ps values. Inflection points are also observed on the adsorption isotherms of strontium ions from aqueous solutions on CAN-7 and oxidized CAN-8 activated carbons (Fig.1).

In our opinion, the appearance of inflection points on strontium ion adsorption isotherms on CAN-7 and oxidized CAN-8 activated carbons is related to the interaction of strontium ions with the inhomogeneous surface of CAN-7 and oxidized CAN-8 activated carbons (mainly with phosphate groups, weak and strong carboxylic groups) with the subsequent formation of the polyionic adsorption layer, due to the hydrogen bonds formed between the  $\text{Sr}(\text{OH})^+$  ions, and also the collateral interactions between the strontium ions adsorbed at the interface.

After contacting 100mL of  $\text{Sr}(\text{NO}_3)_2$  solution with a concentration of 1g/L with 100mg of activated carbon CAN-7, after 3 hours of mixing, the pH value became 5.05. Without coal the pH was 7.05.

An important role is played by acidic functional groups on the surface of CAN-7 activated carbon, but also by the fact that  $\text{Sr}(\text{NO}_3)_2$  probably forms  $\text{Sr}(\text{OH})^+$  ions that interact with the porous structure of the adsorbent – a fact known in the literature [13].



It should be noted that the dissociation constant of nitric acid is  $4 \cdot 10^{-4}$  mol/L, and of strontium hydroxide –  $1,5 \cdot 10^{-1}$  mol/L. The higher the dissociation constant, the more easily the electrolyte dissociates. In this context, we cannot speak of the hydrolysis of strontium nitrate, but the formation of the  $\text{Sr}(\text{OH})^+$  ion is possible in solution (1), and also in the porous structure of the carbon adsorbent. According to the Brensted-Loury theory, all hydrated ions in solutions are more or less acidic [14].

The interaction between hydrated strontium ions ( $\text{Sr}^{2+}$ ) and the supermicroporous and microporous surface of CAN-7 and oxidized CAN-8 adsorbents (Table) [10] will be totally different from that of mesopores.

Table

Structural parameters of CAN-7 and oxidized CAN-8 activated carbons

Type of activated carbon	W <sub>01</sub>	W <sub>02</sub>	E <sub>01</sub>	E <sub>02</sub>	X <sub>01</sub>	X <sub>02</sub>	V <sub>s</sub>	V <sub>me</sub>	S <sub>me</sub>	S <sub>sp</sub>
	cm <sup>3</sup> /g		kJ/mol		nm		cm <sup>3</sup> /g		m <sup>2</sup> /g	
CAN-7 intact	0.24	0.16	15.72	6.49	0.64	1.54	0.64	0.24	210	725
CAN-8 oxidized	0.17	0.06	25.08	9.09	0.40	1.10	0.42	0.19	90	650

In micropores and supermicropores, due to the relatively high values of characteristic adsorption energies - 15.72 kJ/mol and 6.49 kJ/mol for CAN-7 activated carbon and 25.08 kJ/mol and 9.09 kJ/mol for the oxidized CAN-8 activated carbon (Table), water molecules will probably be adsorbed as well. The interaction of these water molecules thus adsorbed with the  $\text{Sr}^{2+}$  ions, adsorbed in these porous structures, will be different from the interaction of strontium ( $\text{Sr}^{2+}$ ) ions and the water molecules adsorbed in the mesopores.

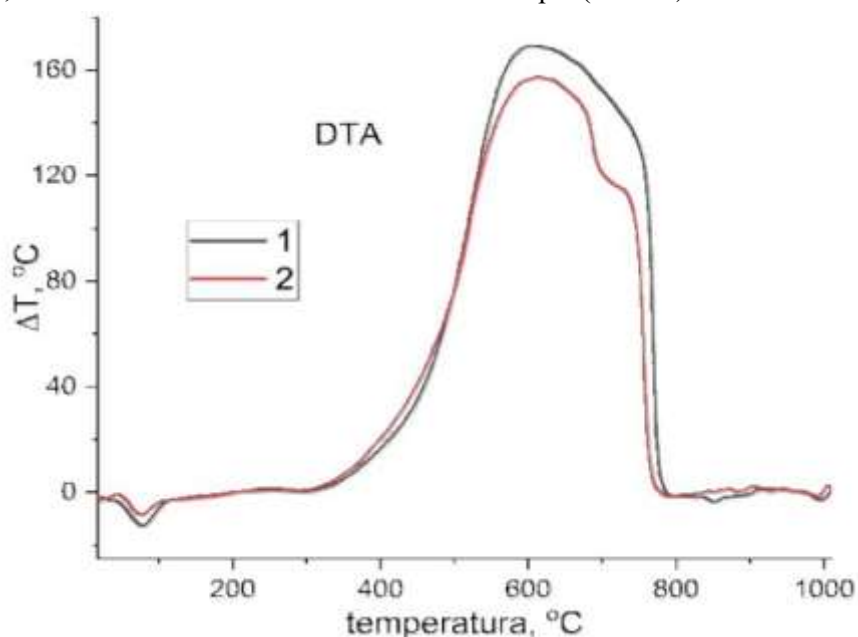
These different modes of interaction, and not only between the solvent and adsorbed molecules in the porous structures of these two activated carbon samples, but also the side interactions between  $\text{Sr}(\text{OH})^+$  ions, which probably form in micropores and supermicropores, can lead to the appearance of those two inflection points on the adsorption isotherms of strontium ions ( $\text{Sr}^{2+}$ ) on the activated carbons CAN-7 and oxidized CAN-8. Probably, here we can talk about the important role of hydrogen bonds. The strength of the hydrogen bonds formed between the  $\text{Sr}(\text{OH})^+$  ions in micropores, but also the strength of the hydrogen bonds formed between the  $\text{Sr}(\text{OH})^+$  ions and the functional groups on the surface of both activated carbon samples, will probably be stronger in the range of equilibrium concentrations, at which the first inflection point appears on the isotherms. This is due to the strong adsorption field in the micropores. In supermicropores, the overlap of the adsorption field from the walls of these pore categories is less pronounced compared to the adsorption field in micropores and, consequently, a second inflection point appears on the adsorption isotherms of strontium ions, both on CAN-7 and on oxidized CAN-7 activated carbons, followed by an increase in the value of adsorption. Regarding the adsorption in mesopores, here there is no overlap of the adsorption field from the pore walls, due to the relatively large pore size and the interactions between the  $\text{Sr}(\text{OH})^+$  ions between them, and also with the functional groups on the surface of the adsorbents is ordinary and the value of adsorption in such pores is already included in the second jump, so that a new jump does not occur.

It should be noted that the equilibrium concentrations at which the jumps begin on the strontium ion adsorption isotherms on CAN-7 and oxidized CAN-8 activated carbons are practically the same. The values of the characteristic adsorption energies of these two activated carbon samples (Table) are close, so that the appearance of these two inflection points on the activated carbons under study is related to the state of  $\text{Sr}(\text{OH})^+$  ions in very fine porous structures with very strong potential adsorption fields. In addition, the  $\text{Sr}(\text{OH})^+$  ion, which has been adsorbed, is in the force field created by several molecules (ions) already adsorbed.

In addition to these interactions, the presence in the porous structure of CAN-7 activated carbon of the phosphate ( $P = O$ ) and polyphosphate (COP) functional groups must be taken into account, and in the porous structure of oxidized CAN-8 activated carbon, of the groups  $C = O$  and  $COOH$  groups. When we discuss the interaction between  $Sr(OH)^+$  and the porous surface of the adsorbent, we first consider these functional groups. It should be noted here that the walls of the micropores are subjected to enormous pressures due to intermolecular forces.

Thermal analysis of the activated carbon sample (CAN-7) adsorbed with water and another sample of the same activated carbon with adsorbed strontium ions, can probably offer useful information regarding the appearance of inflection points on the adsorption isotherms of strontium ions from aqueous solutions on this adsorbent.

Figure 2 shows the heating curves (DTA) of the activated carbon samples CAN-7 adsorbed with water (1) and CAN-7 adsorbed with strontium ions (2). The differential thermal curve (DTA) represents the temperature difference ( $\Delta T$ ), which is recorded between the adsorbent sample (CAN-7) and the inert substance (standard).

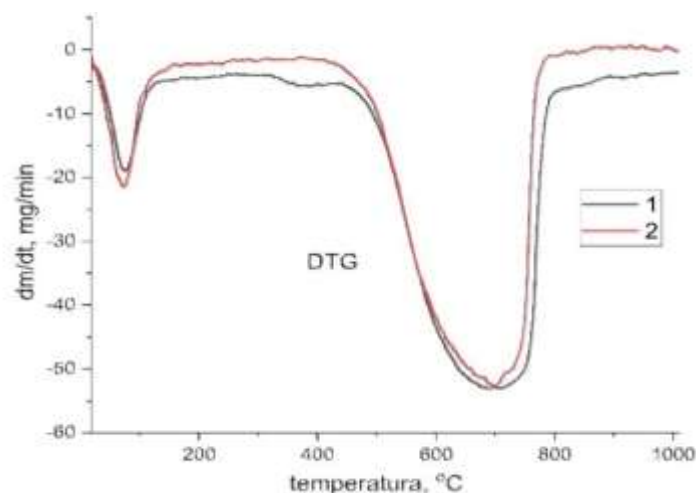


**Fig.2.** Heating curves (DTA) of water-adsorbed CAN-7 activated carbon samples (1) and strontium-ion adsorbed CAN-7 (2).

From the data presented in Figure 2 two thermal effects are observed: one endothermic ( $70^{\circ}C$ ) and another one – exothermic ( $620^{\circ}C$ ). Note that both activated carbon samples were kept in the oven at  $35^{\circ}C$  for 5 hours prior to derivatograph measurements. The endothermic effect is caused by the presence of water molecules between the granules of activated carbon, but possibly also in its macropores. The exothermic effect is the result of burning of CAN-7 activated carbon. The appearance of the combustion curves in the temperature range  $525-780^{\circ}C$  on both adsorbent samples is different. On the CAN-7 activated carbon sample, on which strontium ions were adsorbed, the two effects are more clearly outlined and the peak area is smaller than on the CAN-7 activated carbon sample on which only water molecules were adsorbed.

The surface area of the peak is proportional to the thermal effect of the combustion process. This result indicates that, probably, when the combustion process of CAN-7 activated carbon with adsorbed strontium ions begins (exothermic effect), the bonds between  $Sr(OH)^+$  and the strong and weak carboxylic functional groups in the microporous and supermicroporous structure of activated carbon are broken in the same temperature range, requiring energy consumption. As a result, the surface area of the peak, which is proportional to the thermal effect of the process [15], is also smaller. In this order of ideas, it is not excluded the fact of breaking the hydrogen bonds formed between the  $Sr(OH)^+$  ions and the water molecules from the microporous and supermicroporous structure of the adsorbent under study.

Figure 3 shows the DTG curves of CAN-7 activated carbon on which water was adsorbed and CAN-7 on which strontium ions were adsorbed.



**Fig.3.** DTG curves of CAN-7 activated carbon samples adsorbed with water (1) and CAN-7 adsorbed with strontium ions (2).

As we can see from the data presented in Figure 3, two endothermic effects are present on curve (1), the first one (70°C) being related to the elimination of water between the adsorbent granules and, probably, from macropores, but also from large mesopores. The second one (350°C) is related to the removal of water from micropores and supermicropores. There is no endothermic effect on the CAN-7 activated carbon sample on which strontium ions were adsorbed at 350°C, it is probably shifted to higher temperatures, which is included in the loss of mass conditioned by the burning of CAN-7 activated carbon, thus decreasing its value.

The results obtained show that the bonds between the  $\text{Sr}(\text{OH})^+$  ions and the strong and weak carboxylic groups in the micro- and supermicroporous structure of CAN-7 activated carbon are stronger than those in mesopores and macropores. The bonds between  $\text{Sr}(\text{OH})^+$  ions and water molecules in the microporous and supermicroporous structure of the adsorbent are also stronger than in meso- and macropores. These effects cause the appearance of two inflection points on the adsorption isotherms of strontium ions on CAN-7.

### Conclusions

1. It has been shown that on the CAN-7 activated carbon sample, on which water molecules were adsorbed, an endothermic effect appears on the DTG curve, at 350°C, which is related to the removal of water from micropores and supermicropores.
2. From the DTG curve for the CAN-7 activated carbon sample on which strontium ions were adsorbed at 350°C there is no endothermic effect, this being shifted to higher temperatures, and included in the loss of mass conditioned by the combustion of CAN-7 (exothermic effect), thus decreasing its value.
3. The inflection points on the adsorption isotherms are the result of  $\text{Sr}(\text{OH})^+$  interactions with strong and weak carboxylic groups in the micro- and supermicroporous structure of CAN-7 and oxidized CAN-8 activated carbon, and a result of interactions between  $\text{Sr}(\text{OH})^+$  and water molecules in these porous structures, as well.

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