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ADSORPTION OF STRONTIUM IONS FROM AQUEOUS SOLUTIONS ON NUT SHELLS ACTIVATED CARBONS

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Abstract. The adsorption of strontium ions from aqueous solutions on nut shells activated carbons (samples CAN-7 and CAN-8) at different temperatures has been studied. The isotherm of adsorption of strontium ions from aqueous solutions on activated carbon CAN-7 has two inflection points at relatively small and high equilibrium concentrations. As the temperature increases, the adsorption values decrease, which indicates that the adsorption process is exothermic.

Keywords: activated carbon, adsorption heat, entropy, exothermic process, strontium ion.

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Introduction

It is known that the carbon adsorbents obtained from olive stones have an enhanced adsorption capacity to Pb^{2+}, and those obtained from almond shells have a competitive adsorbent capacity [1-2]. The adsorption capacity depends on the metal used, being in the following order: $Tl^{+} > Sr^{2+} > Co^{2+} > Cs^{+}$ [1-2]. Rivera-Utrilla, J. and Ferro-Garcia, M.A. stated that with increasing activation time, the adsorption of cobalt ions from solutions increases [2]. The activated carbon made from almond shells with a specific surface area of 1820 m^2/g has an enhanced adsorbent capacity to cobalt ions. In another publication the adsorption of zinc, cadmium and copper ions on activated carbon, obtained from almond shells, olive kernels and peach kernels, has been studied, which showed that the obtained activated carbons had on their surface basic acidic functional groups and high values of specific surfaces [3]. The nature of the raw material for the activated carbons production has an important role in the adsorption process of heavy metal cations from aqueous solutions. It is stated that the adsorption of Zn^{2+} and Cd^{2+} ions on these adsorbents decreases with increasing temperature (exothermic effect), while the adsorption of copper ions on the same adsorbents increases (endothermic effect) [3]. Another research team studied the adsorption of strontium ions from aqueous solutions on various adsorbents obtained from the chemically treated almond green shells [4]. The adsorbent capacity of this adsorbent was investigated in two ways: different chemical treatment and different adsorbent content and different concentration of Sr^{2+} ions in the solution. The optimal dose of adsorbent for the maximum Sr^{2+} ion adsorption was 0.3 g at 102 mg/L of solution. Removal of Sr^{2+} ions from aqueous solutions on activated carbon obtained from almond hull was studied as well [5]. The obtained experimental results demonstrate a good fitting of the points (R^2= 0.9806) into linear coordinates of the Langmuir model. Probably, the activated carbon prepared from almond shells, according to the technology presented herein, has homogeneous adsorption centres. In the paper [6], the study of the adsorption of strontium ions on activated carbon demonstrated the endothermicity of the adsorption process, the isotherm of adsorption being described by the Freundlich model.

The purpose of this paper is to present the study of the adsorption of strontium ions from aqueous solutions on two samples of activated carbons obtained from nut shells by chemical activation with phosphoric acid (CAN-7) and water vapour activation (CAN-8). Previously, this process has been studied in order to assess the possibility of using CAN-7 activated carbon for the removal of strontium ions from groundwater (Hirjauca water, Calarasi district, Republic of Moldova [7]).

Experimental

Materials

Two samples of activated carbons from nut shells were used for studies: *(i)* CAN-7, obtained by chemical activation with phosphoric acid (at 460°C) and *(ii)* CAN-8, prepared by the physico-chemical method of activation with water vapours (at 960°C). Activated carbon fractions of 0.8-1.0 mm were used for adsorption studies.

Strontium nitrate of reagent grade was used for the adsorption studies.

Methods

The adsorption isotherms of strontium ions on activated carbon were determined at various concentrations of strontium ions in solution, a constant solid/liquid ratio and different temperatures (25-65°C). The equilibrium concentration of strontium ions in solutions was determined on the AAS-1 spectrophotometer.

The *differential isosteric adsorption heat (Q)* at different values of the specific adsorption *a* was calculated based on the Clausius–Clapeyron equation (Eq.(1)).

$$Q = R\left(\frac{\partial lnC}{\partial \frac{1}{T}}\right)_a = 2.303\,R\left(\frac{\partial lnC}{\partial \frac{1}{T}}\right)_a \qquad (1)$$

The value $\partial \log C / \partial \frac{1}{T}$ was determined as the angle of inclination of the adsorption isostere at the axis 1/T.

The *standard adsorption entropy* (ΔS^0) of strontium ions on activated carbon was determined by Eq.(2) [7].

$$\Delta S^0 = -\frac{Q^0}{T} + R\,lnK_2 \qquad (2)$$

where, ΔS^0 is the standard variation of entropy;

Q^0 means the standard isosteric heat of adsorption;

K_2 is the equilibrium adsorption constant.

Results and discussion

The structure parameters of activated carbons obtained from nut shells by various activation methods are shown in Table 1. The parameters W_0, E_0 and X_0 were determined on the basis of the benzene vapour adsorption isotherm using the Dubinin–Radushkevich equation. The specific surface area (S_{sp}) of the activated carbon CAN-8 is 708 m^2/g. If we compare the structure parameters of these two activated carbons, then we find that the activated carbon CAN-8 has a much smaller share of very small pores (X_0= 0.44 nm), while on CAN-7 sample X_0= 2.18 nm, where X_0 is the half-width of micropores.

Figure 1 shows the adsorption isotherm of strontium ions from aqueous solutions on the activated carbon CAN-7. As shown in Figure 1, the presented isotherm has inflection points even at higher values of the equilibrium concentrations. The isotherm of adsorption of strontium ions in the coordinates of $log(C_{ads}/C_e)$ *vs.* $f(C_e)$ is shown in Figure 2. The $logK_{ads}$ value was graphically obtained by extrapolating the curve $log(C_{ads}/C_e)= f(C_e)$ to $C_e= 0$.

Table 1

Structure parameters of activated carbons determined from benzene sorption-desorption isotherms, by Dubinin–Radushkevich equation*.

Sample	W_0, cm^3/g	E_0, kJ/mol	X_0, nm	S_{me}, m^2/g	V_{me}, cm^3/g	S_{sp}, m^2/g
CAN-7	0.24	15.72	2.18	210	0.24	725
CAN-8	0.35	22.77	0.44	166	0.23	708

**W_0- micropore volume;*
E_0- adsorption energy in micropores;
X_0- half width of micropore;
S_{me}- surface of mesopores;
V_{me}- mesopores volume;
S_{sp}- specific surface area.

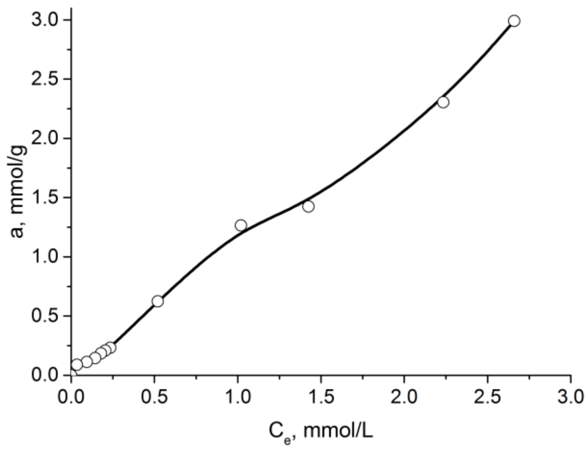

Figure 1. Adsorption isotherm of strontium ions from aqueous solutions on the activated carbon CAN-7.

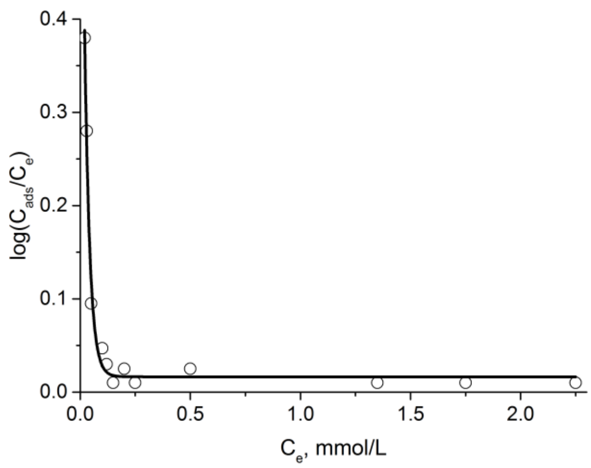

Figure 2. The isotherm of adsorption of strontium ions from aqueous solutions on the activated carbon CAN-7, in the coordinates of *$log(C_{ads}/C_e)$ vs. C_e*, at t= 25°C.

The calculation of the adsorption equilibrium constant for strontium ions has been done based on the concept presented in paper [5], from which it follows that the adsorption equilibrium constant equals to 2 and, respectively, the ΔG_0 value is 0.5 kJ/mol ($\Delta G_0 = RTlnK_{ads}$). According to the data presented in the paper [7] for the carbonic adsorbent - water interface ΔG_0 for H_2O is equal to 2.3 kJ/mol. The adsorbent with a lower standard molar differential free energy of adsorption (ΔG_0) less than the solvent (water) cannot displace it from the surface of the adsorbent (from its pores), however strontium ions are adsorbed at relatively high equilibrium concentrations, the value of adsorption of these ions being considerable (Figure 1). This phenomenon is explained by the fact that at low equilibrium concentrations strontium ions interact with the water molecules in the porous structure of activated carbon CAN-7 forming the $Sr(OH)^+$ ions. The formation and diffusion processes of $Sr(OH)^+$ in the microporous structure of carbonic adsorbent were reported earlier [6].

At relatively higher equilibrium concentrations, the water molecules will not be displaced by strontium ions that are bound to activated carbon by the interaction with carboxylic groups (-COOH) and also with phosphate and polyphosphate groups (P=O, C-O-P).

Figures 3 and 4 show the adsorption isotherms of strontium ions from aqueous solutions on the CAN-7 and CAN-8 activated carbons, respectively, at different temperatures. From the data presented, it is seen that with the increase in temperature, the adsorption values on the both CAN-7 and CAN-8 activated carbon samples are diminishing, but just the shape of adsorption isotherms of strontium ions on the CAN-8 activated carbon at low equilibrium concentrations differs from that on the CAN-7 activated carbon. At somewhat higher equilibrium concentrations, we also distinguish a difference in the shape of strontium ion adsorption isotherms on the CAN-8 activated carbon sample compared to that of the CAN-7 activated carbon.

Figures 5 and 6 show the adsorption isosteres of strontium ions from aqueous solutions on the CAN-7 and CAN-8 activated carbons at different specific adsorption values.

The differential isosteric adsorption heats Q at different values of the specific adsorption a were calculated based on the Clausius–Clapeyron equation (Eq.(1)). Figures 7 and 8 show the values of isosteric adsorption heat (Q_{is}) as function of a, assuming the linearity of the correlation up to $a = 0$. Thus, one can determine the standard Q^0 adsorption heat by extrapolation.

The data presented in Figures 7 and 8 show that the standard adsorption heat values of strontium ions on the CAN-7 and CAN-8 activated carbons are different. The Q^0 value of CAN-7 is higher than that of the CAN-8 activated carbon, equal to 8.6 kJ/mol and 6.8 kJ/mol, respectively.

In order to evaluate the degree of mobility of strontium ions in the adsorbent layer, having determined the values of standard heat adsorption Q^0 of strontium ions on activated carbon, Eq.(2) has been used. The value of standard adsorption entropy (ΔS^0) of strontium ions on the CAN-7 activated carbon is equal to 0.023 kJ/mol·grad at T= 298.15 K. This absolute value is small, indicating that the mobility of strontium ions in the adsorbent layer is high. Most likely, in this case a located adsorption does not take place.

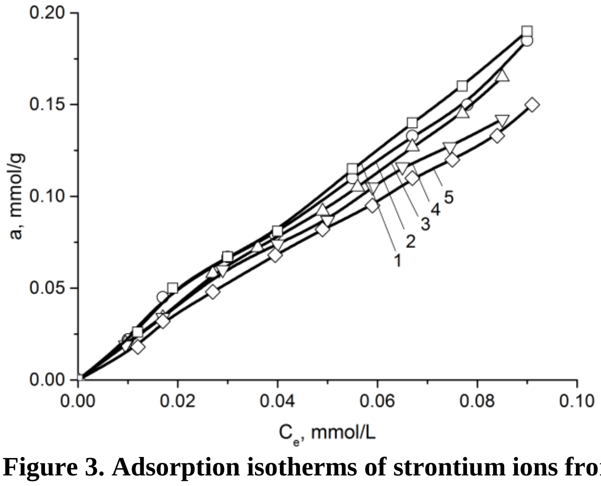

Figure 3. Adsorption isotherms of strontium ions from aqueous solutions on activated carbon CAN-7, at different temperatures: *(1)*- 25°C, *(2)*- 35°C, *(3)*- 45°C, *(4)*- 55°C, *(5)*- 65°C.

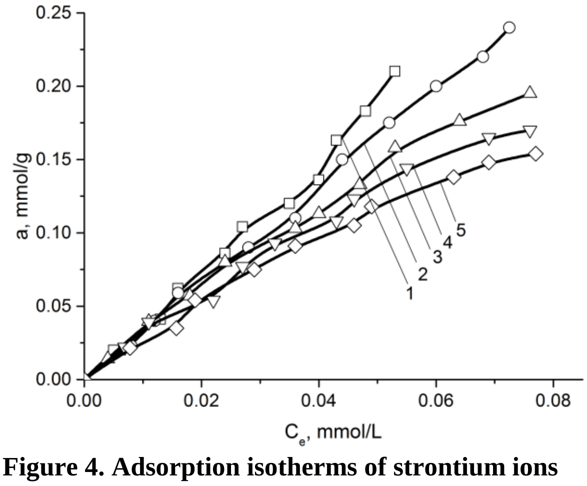

Figure 4. Adsorption isotherms of strontium ions from aqueous solutions on the activated carbon CAN-8, at different temperatures: *(1)*- 25°C, *(2)*- 35°C, *(3)*- 45°C, *(4)*- 55°C, *(5)*- 65°C.

Figures 9 and 10 show the adsorption isotherms of strontium ions in coordinates of *log(*C_{ads}/C_e*) vs.* *(*C_e*)* on the activated carbons CAN-7 and CAN-8, at 35°C, 45°C and 55°C. The values of *log*K_{ads} were plotted as a result of the extrapolation of curves *log(*C_{ads}/C_e*)= f(*C_e*)* to $C_e=0$. From the data presented in Figures 9 and 10, we note that these values do not differ significantly. Thus, the interaction of $Sr(OH)^+$ ion with the functional polar groups on the surface of the activated carbons CAN-7 and CAN-8, being however relatively low, based on the obtained data, determines the adsorption process of strontium ions at low equilibrium concentrations.

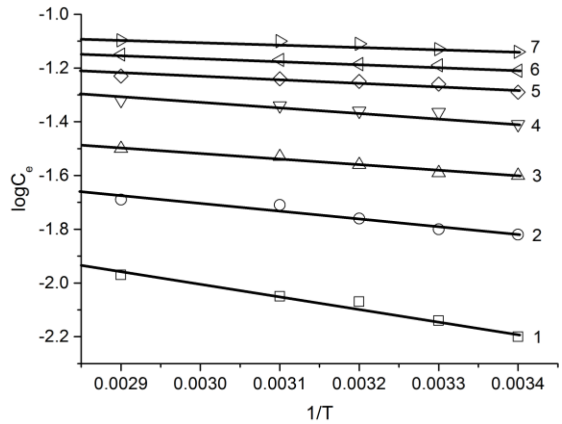

Figure 5. Isosteres of strontium ion adsorption from aqueous solutions on activated carbon CAN-7, at specific adsorption values: *(1)*- 0.02 mmol/g, *(2)*- 0.04 mmol/g, *(3)*- 0.06 mmol/g, *(4)*- 0.08 mmol/g, *(5)*- 0.1 mmol/g, *(6)*- 0.12 mmol/g, *(7)*- 0.14 mmol/g.

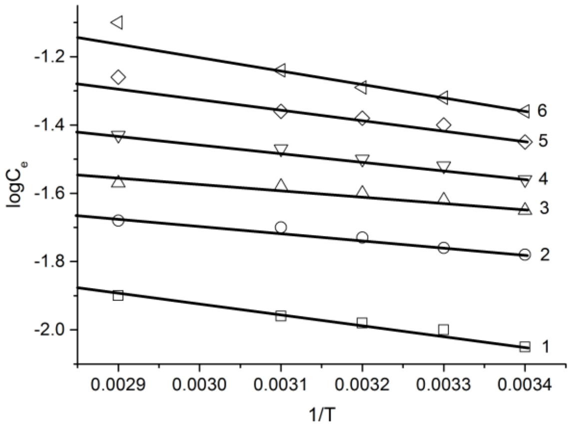

Figure 6. Isosteres of strontium ion adsorption from aqueous solutions on activated carbon CAN-8, at specific adsorption values: *(1)*- 0.025 mmol/g, *(2)*- 0.05 mmol/g, *(3)*- 0.075 mmol/g, *(4)*- 0.1 mmol/g, *(5)*- 0.125 mmol/g, *(6)*- 0.15 mmol/g.

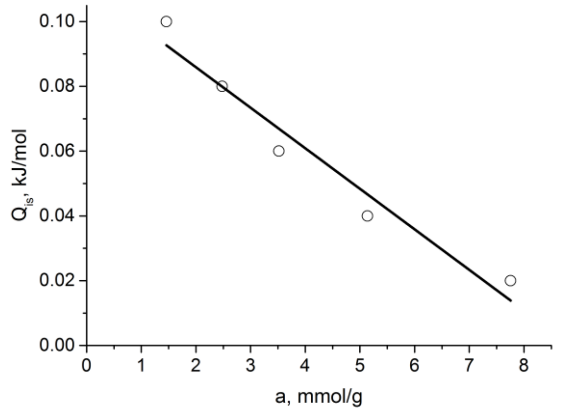

Figure 7. Correlation of the adsorption isosteric heat (*Q_{is}*) of strontium ions on the activated carbon CAN-7 and the specific adsorption *a*.

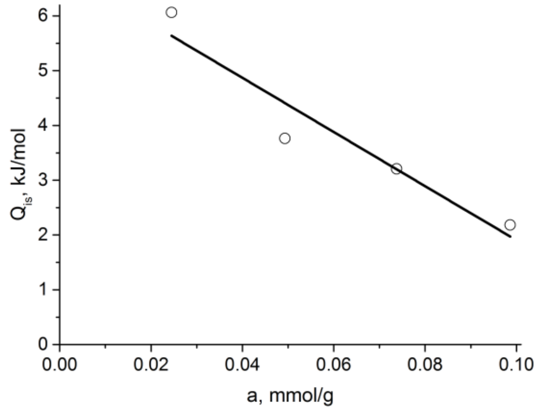

Figure 8. Correlation of the adsorption isosteric heat (*Q_{is}*) of strontium ions on the activated carbon CAN-8 and the specific adsorption *a*.

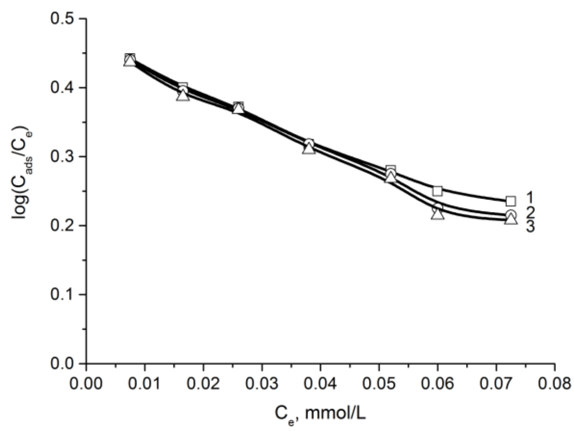

Figure 9. Adsorption isotherms of strontium ions from aqueous solutions on the activated carbon CAN-7 in the coordinates of *log(*C_{ads}/C_e*) vs.* C_e, at *(1)*- 35°C, *(2)*- 45°C and *(3)*- 55°C.

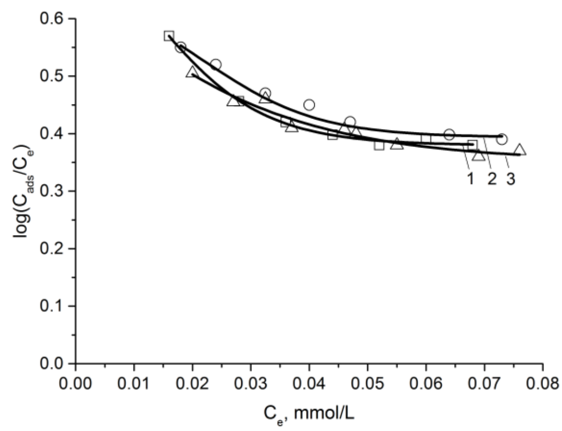

Figure 10. Adsorption isotherms of strontium ions from aqueous solutions on activated carbon CAN-8 in the coordinates of *log(*C_{ads}/C_e*) vs.* C_e, at *(1)*- 35°C, *(2)*- 45°C and *(3)*- 55°C.

Conclusions

The isotherm of adsorption of strontium ions from aqueous solutions on the activated carbon CAN-7 has two inflection points, even at relatively low concentrations of equilibrium concentrations.

As the temperature rises, the adsorption values decrease, indicating that the adsorption process is exothermic. The values of standard heats of adsorption of strontium ions on the activated carbons CAN-7 and CAN-8 are different. The Q^0 value of activated carbon CAN-7 is higher than that for the sample CAN-8, equal to 8.6 kJ/mol and 6.8 kJ/mol, respectively.

The absolute value of the standard entropy variation of adsorption for strontium ions on the activated carbon CAN-7 is small, which is related to the high mobility of strontium ions in the adsorbent, consequently, the adsorption may be of non-located type.

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