

# Adsorption of Cobalt and Strontium ions on Plant-derived Activated Carbons. The Suggested Mechanisms

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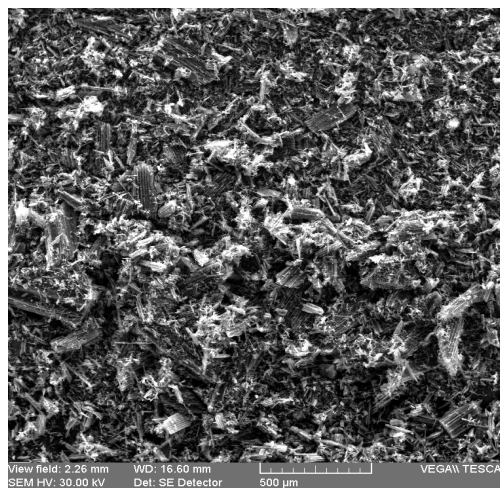
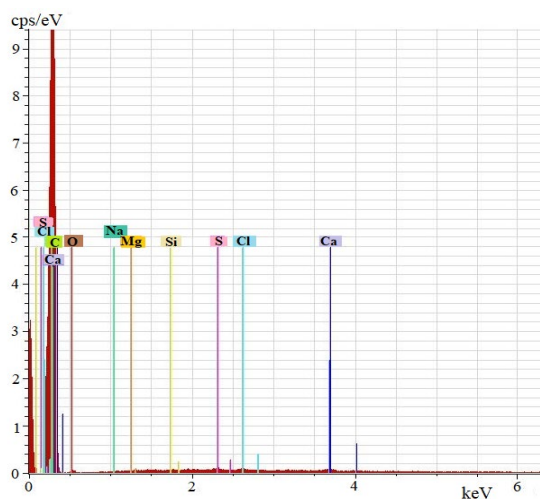
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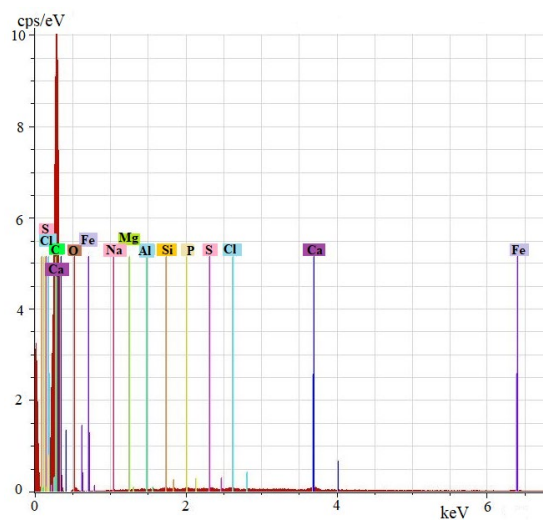
\* Correspondence: [raisa.nastas@ichem.md](mailto:raisa.nastas@ichem.md)

**Table S1.** The metal quantity (%) in activated carbons, recalculated to oxides.

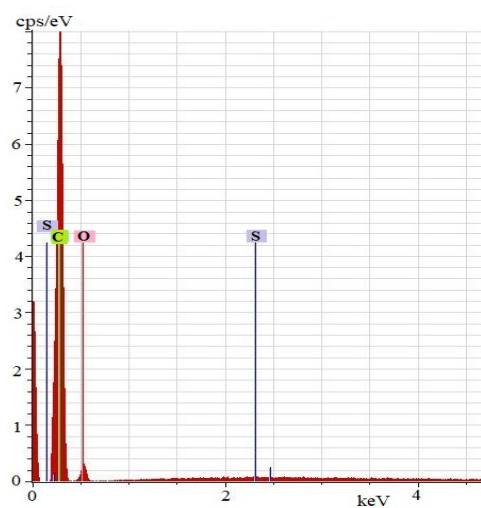
Sample	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	MnO <sub>2</sub>	CuO	ZnO
CA-N	0.071	0.433	2.426	0.104	0.285	0.051	0.002	0.061
CA-M	0.067	0.237	2.102	0.079	0.060	0.034	0.002	0.002
CA-Nox-u	0.035	0.018	0.007	0.022	0.065	0.009	0.002	0.002
CA-Mox-u	0.032	0.034	0.038	0.178	0.013	0.009	0.001	0.001
CA-Mox	0.022	0.024	0.044	0.052	0.028	0.004	0.001	0.006



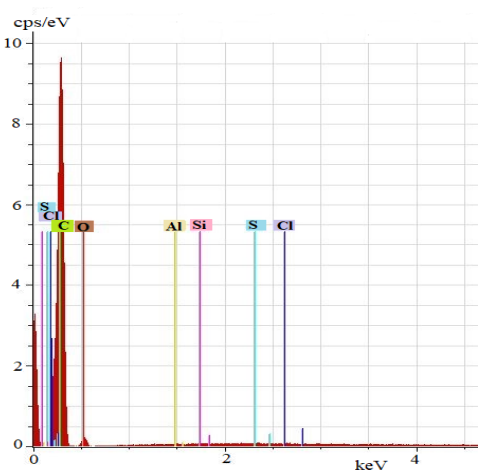
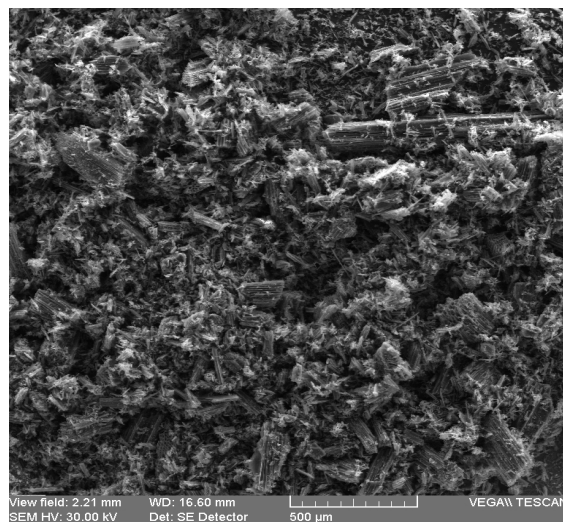
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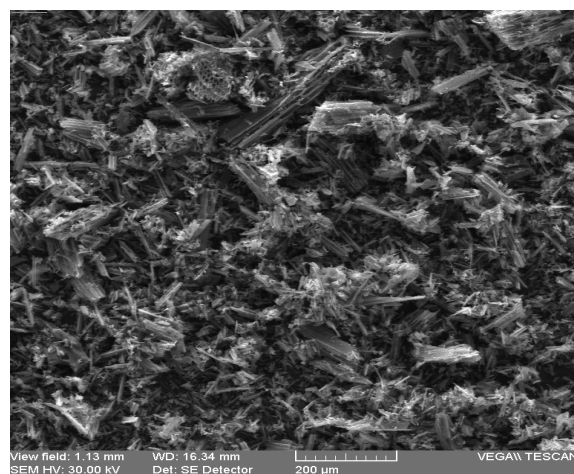
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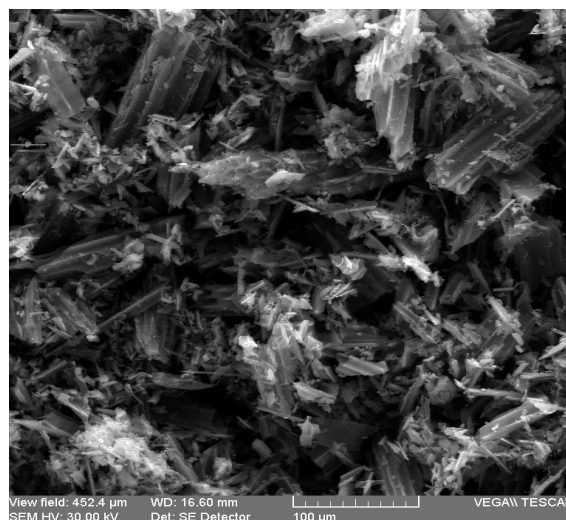
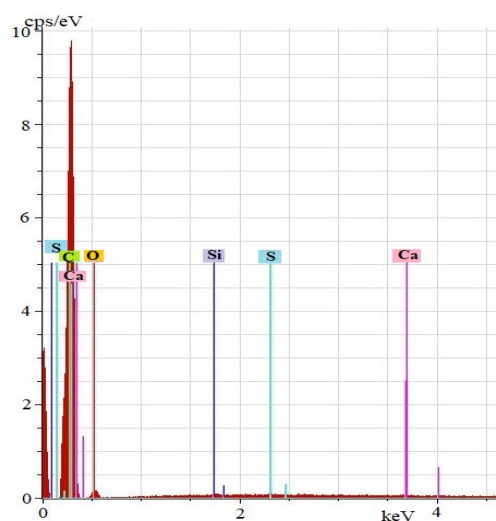


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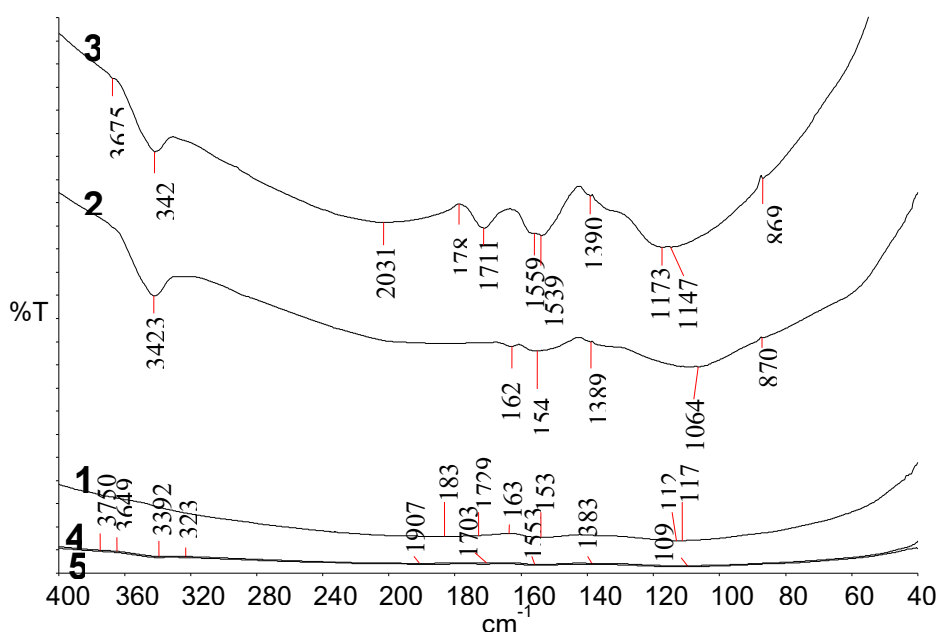
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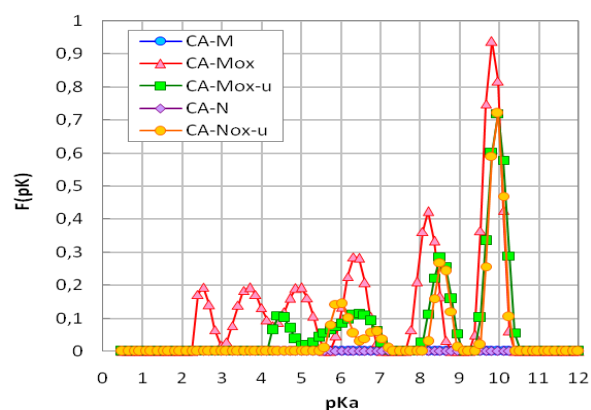


e

**Figure S1.** SEM-EDX profiles for activated carbons: (a) CA-N; (b) CA-M; (c) CA-Nox-u; (d) CA-Mox-u; (e) CA-Mox.



**Figure S2.** FTIR spectra of activated carbons: (1) CA-M; (2) CA-N; (3) CA-Mox; (4) CA-Mox-u; (5) CA-Nox-u.

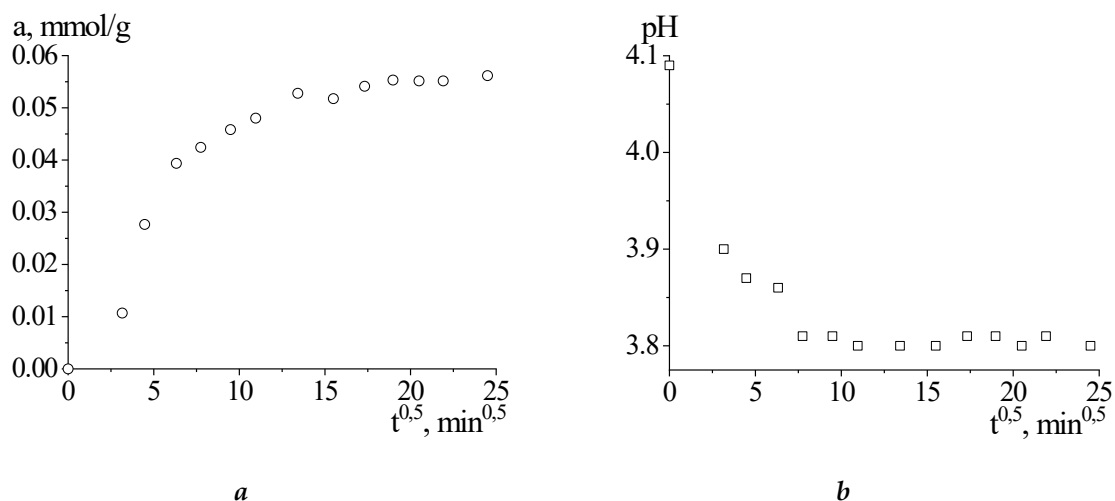


**Figure S3.** Distribution of surface groups according to the dissociation constants pK [1]

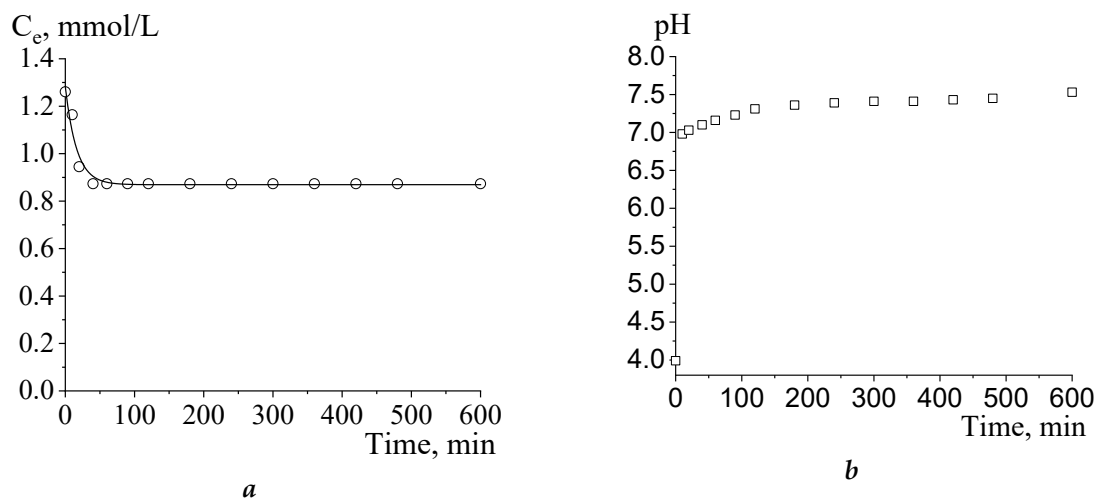
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**Table S2.** Kinetic parameters and  $q_e$  values of the adsorption process of cobalt ions ( $C_0 = 2$  mmol/L) on oxidized activated carbons.

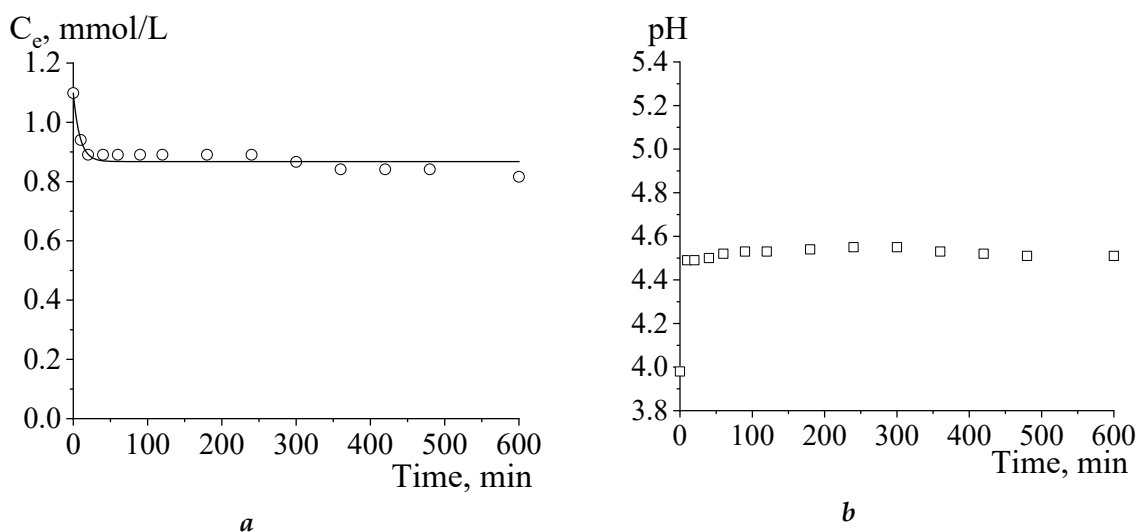
Sample	<i>Pseudo-first-order kinetic model (Lagergren)</i>			
	$q_e(\text{exp})$ (mmol/g)	$k_1$ (min <sup>-1</sup> )	$q_e(\text{cal})$ (mmol/g)	$R^2$
CA-Mox	0.085	0.00005	0.078	0.575
CA-Mox-u	0.056	0.00741	0.021	0.921
CA-Nox-u	0.041	0.0160	0.026	0.906



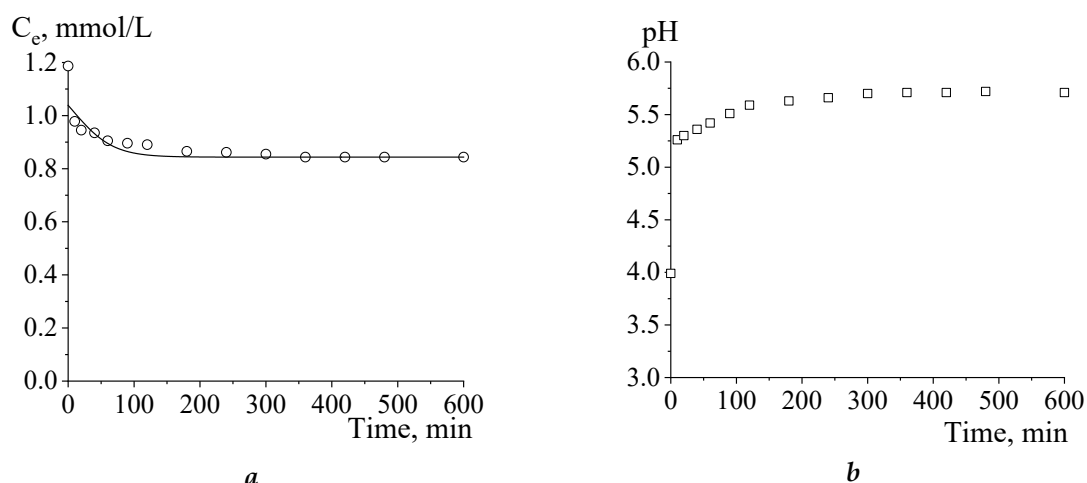
**Figure S4.** Intraparticle diffusion kinetic model (Weber-Morris) for cobalt ions adsorption on oxidized activated carbon CA-Mox-u. (a) The the plot of  $a_i$  versus  $t^{1/2}$ , (b) the plot of  $pH_i$  versus  $t^{1/2}$ .



**Figure S5.** Kinetics of strontium ions adsorption on initial activated carbon CA-N. (a) The variation of strontium ions concentration in solution with time; (b) The pH value of solutions after adsorption of strontium ions on activated carbon. Solid:liquid ratio - 1:100, pH=4.



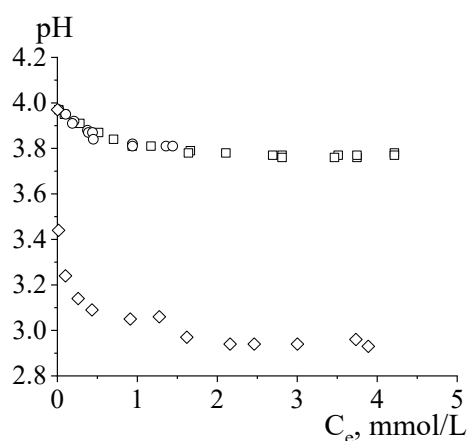
**Figure S6.** Kinetics of strontium ions adsorption on oxidized activated carbon CA-Mox-u. (a) The variation of strontium ions concentration in solution with time; (b) The pH value of solutions after adsorption of strontium ions on activated carbon. Solid:liquid ratio - 1:100, pH=4.



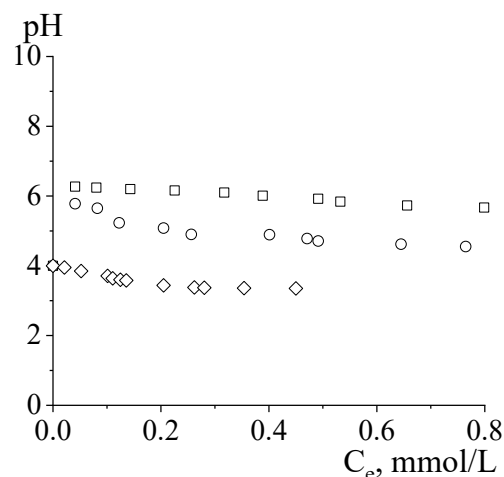
**Figure S7.** Kinetics of strontium ions adsorption on oxidized activated carbon CA-Nox-u. (a) The variation of strontium ions concentration in solution with time; (b) The pH value of solutions after adsorption of strontium ions on activated carbon. Solid:liquid ratio - 1:100, pH=4.

**Table S3.** Kinetic parameters and  $q_e$  values of the adsorption process of strontium ions on activated carbons.

Mostra	<i>Pseudo-first-order kinetic model (Lagergren)</i>			
	$q_e(\text{exp})$ (mmol/g)	$k_1$ (min <sup>-1</sup> )	$q_e(\text{cal})$ (mmol/g)	$R^2$
CA-M	0.032	0.02948	0.023	0.884
CA-N	0.034	0.13984	0.118	-
CA-Mox	0.077	0.00636	0.011	0.524
CA-Mox-u	0.041	0.01497	0.024	0.915
CA-Nox-u	0.034	0.00636	0.011	0.524



**Figure S8.** The pH value of solution at equilibrium for adsorption isotherms of cobalt ions on oxidized activated carbons: ( $\diamond$ ) CA-Mox and ( $\square$ ) CA-Nox-u. Solid:liquid ratio - 1:100, pH 4.



**Figure S9.** The pH value of solution at equilibrium for adsorption isotherms of strontium ions on oxidized activated carbons: (◊) CA-Mox, (○) CAMox-u and (◻) CA-Nox-u. Solid:liquid ratio - 1:100, pH 4.

**Table S4.** Ions properties (selectiv) [1].

	$Sr^{2+}$	$Co^{2+}$
Electronegativity (Pauling)	0.95	1.88
Radius of ion (nm)	0.125	0.084
Radius of hydrated ion (nm)	0.412	0.423
Hydration-free energy (kJ/mol)	-1380	-1996

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**Table S5.** Comparison of the adsorption capacity of the studied activated carbons with other carbonaceous adsorbents used for the removal of Co(II) and Sr(II) ions.

Metal ion	Carbonaceous adsorbent, characterization	Adsorption capacity, mmol/g	Reference
$Co^{2+}$	COSAC, olive stones activated carbon prepared by chemical activation using phosphoric acid	0.174	[1]
	COSAC(HNO <sub>3</sub> ), olive stones activated carbon oxidized with nitric acid	0.329	[1]
	COSAC(O <sub>3</sub> ), olive stones activated carbon oxidized with ozone	0.275	[1]
	HSAC, activated carbon prepared from hazelnut shells	0.235	[2]
	XSA(H <sub>3</sub> PO <sub>4</sub> ), Xanthoceras Sorbifolia Bunge hull activated carbon	2.136	[3]
	TPC, activated carbon prepared from Thespesia Populnea bark	0.16	[4]



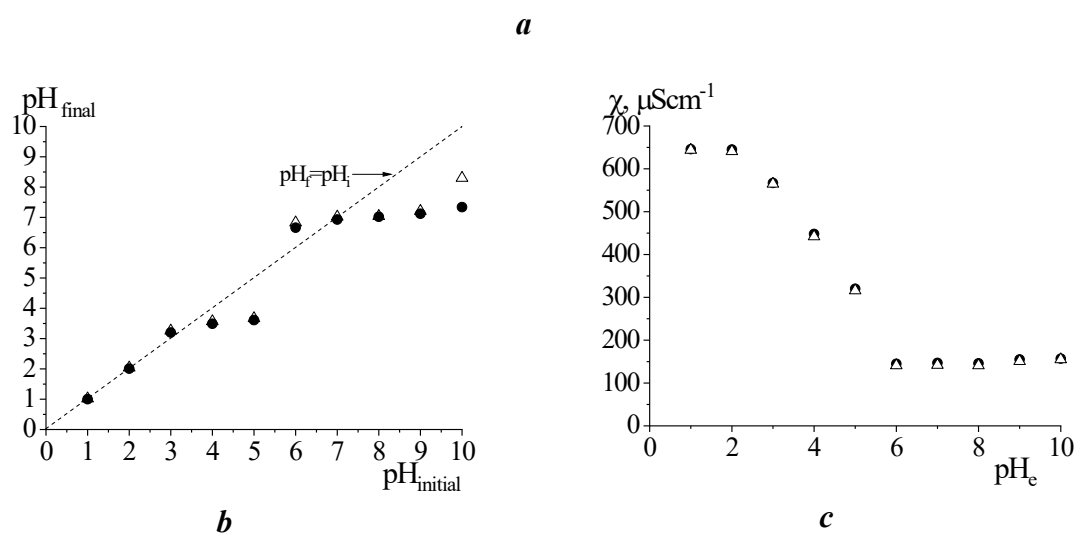
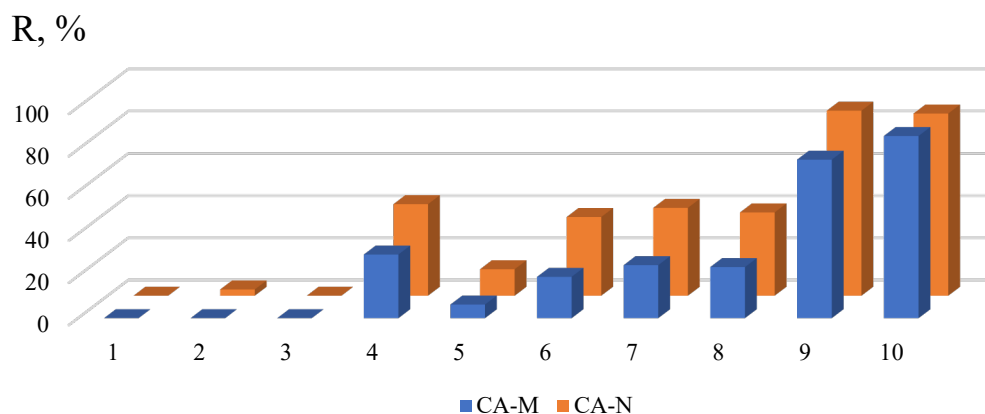
	CG, carbon gel	0.098	[5]
	CG-0.5GIC, carbon gel doped with 0.5 wt% of GIC (graphite intercalation compound)	0.137	[5]
	CA-Mox, activated carbon from apple wood, oxidized with nitric acid	0.085	This work
	CA-Mox-u, activated carbon from apple wood, oxidized with nitric acid/urea mixture	0.056	This work
	CA-Nox-u, activated carbon from walnut shells, oxidized with nitric acid/urea mixture	0.041	This work
Sr <sup>2+</sup>	Granular activated carbon, supplied by Merck, Germany	0.507	[6]
	Activated carbon, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China	0.012	[7]
	AC-Fe, activated carbon doped with iron oxide (Fe <sub>2</sub> O <sub>3</sub> ) nanoparticles.	0.109	[8]
	CAN-7, activated carbon from nut shells by chemical activation with phosphoric acid	~ 0.19	[9]
	CAN-8, activated carbon from nut shells, physico-chemical method of activation with water vapours	~ 0.22	[10]
	RS1, activated carbon from rice straw	0.145	[11]
	PS276a, carbon material from pecan shells by impregnation with phosphoric acid solution	2.055	[12]
	CA-Mox, activated carbon from apple wood, oxidized with nitric acid	0.076	This work
	CA-Mox-u, activated carbon from apple wood, oxidized with nitric acid/urea mixture	0.040	This work
	CA-Nox-u, activated carbon from walnut shells, oxidized with nitric acid/urea mixture	0.034	This work

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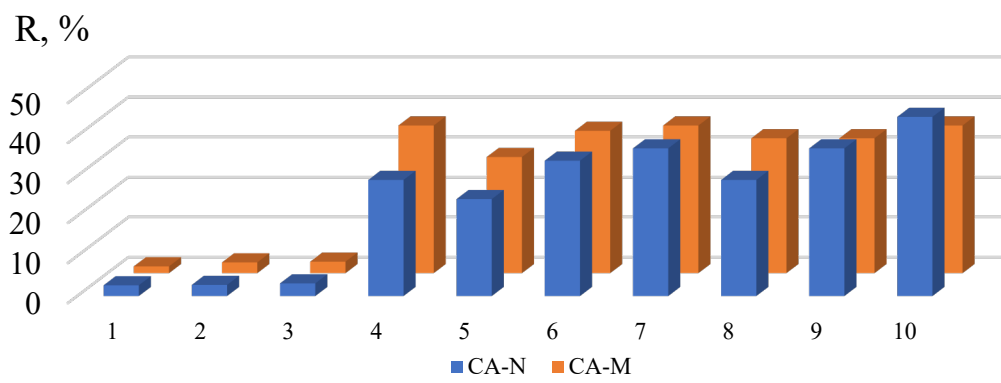
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12. Shawabkeh, R.A.; Rockstraw, D.A.; Bhada, R.K. Copper and strontium adsorption by a novel carbon material manufactured from pecan shells. *Carbon* **2002**, Volume 40, no. 5, pp. 781–786.

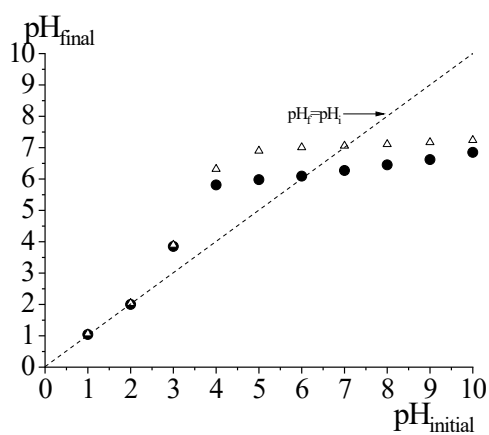


**Figure S10.** The pH influence on the adsorption (removal) of cobalt(II) ions from the solution in the presence of initial activated carbons.

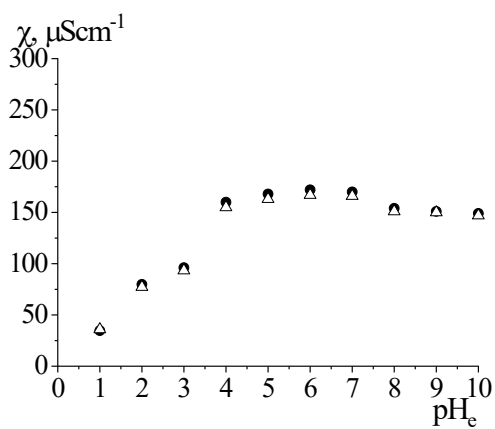
- a) Removal rate (%);
- b) pH of equilibrium solutions for  $\bullet$  CA-M and  $\Delta$  CA-N;
- c) conductivity of equilibrium solutions for  $\bullet$  CA-M and  $\Delta$  CA-N.



*a*



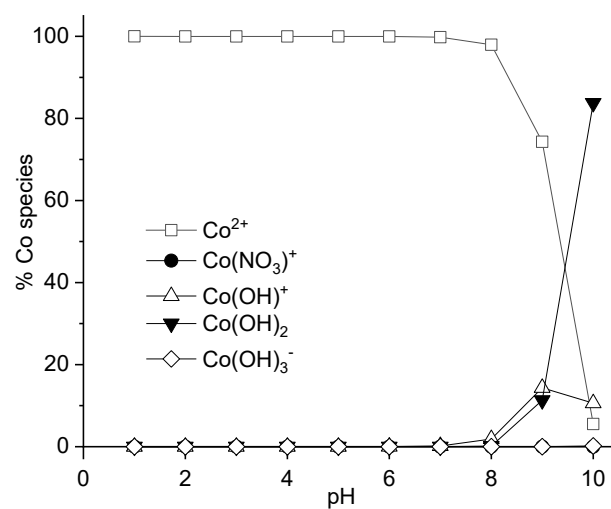
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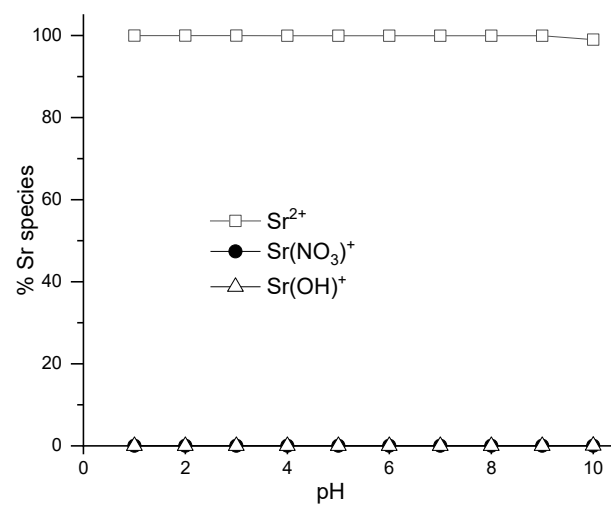
*c*

**Figure S11.** The pH influence on the adsorption (removal) of strontium(II) ions from the solution in the presence of initial activated carbons.

- a) Removal rate (%);
- b) pH of equilibrium solutions for ● CA-M and Δ CA-N;
- c) conductivity of equilibrium solutions for ● CA-M and Δ CA-N.



**Figure S12.** Equilibrium mass distribution of Co species as a function of pH.  
 $C_0(\text{Co}(\text{NO}_3)_2)=0.05$  mmol/L, temperature 25°C.



**Figure S13.** Equilibrium mass distribution of Sr species as a function of pH.  
 $C_0(\text{Sr}(\text{NO}_3)_2)=0.05$  mmol/L, temperature 25°C.

## Appendix S1

*The scheme of the activated carbon oxidation installation*

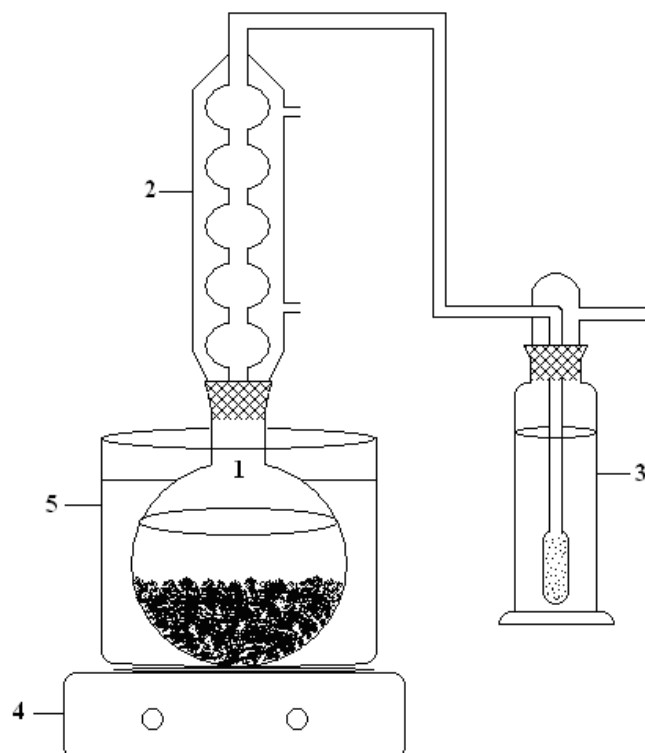


Figure A1. Scheme of the activated carbon oxidation installation.

1- Glass flask; 2- refrigerator; 3- gas capture vessel; 4- electrical heater; 5- water bath.

## Appendix S2

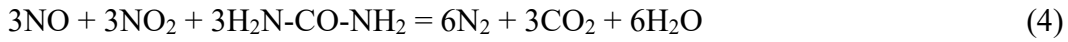
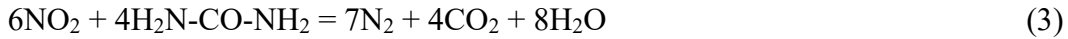
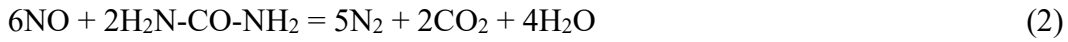
*The explanation of the urea role in the oxidation process of activated carbons with the mixture nitric acid/urea [1]*

In the oxidation process with nitric acid, such conditions as nitric acid concentration, temperature and time are of particular importance, as they influence the oxidation process and the ratio of groups on the surface of the activated carbon. Schematically, the oxidation process of activated carbon with nitric acid can be represented by equation 1.



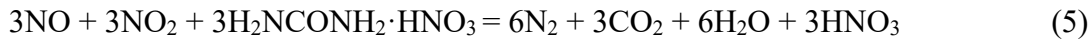
Through the classical method of oxidation with nitric acid (in the absence of urea), activated carbon by absorbing nitrogen oxides released during oxidation forms humic and fulvic acids, which are unstable and soluble in alkaline solutions and can be removed from the surface of activated carbon by washing. This reduces the adsorption capacity of activated carbon by 2-3 times.

In the process of oxidation with nitric acid in the presence of urea, the formation of nitrogen oxides and humic acids does not occur. Nitric acid in combination with urea forms a soluble complex  $\text{H}_2\text{NCONH}_2 \cdot \text{HNO}_3$ , in which the oxidation capacity of nitric acid is lower than that of the free acid in an aqueous solution. When nitrogen oxides are formed (according to reaction 1) they interact with urea through the reactions (2 – 4).



The role of urea is simple because, in combination with nitric acid, it reacts with nitrogen oxides formed in parallel reactions. The reaction products are carbon dioxide, water and nitrogen which do not influence the properties of activated carbons (equation 4).

When nitrogen oxides interact with urea, the complex is destroyed, and nitric acid is released (equation 5). Thus, urea acts as a buffer that in the initial process binds the excess of nitric acid and then releases it as a result of reactions with nitrogen oxides. It has been shown that a small amount of urea significantly reduces the content of nitrogen oxides in the exhaust gases and excess urea leads to complete neutralization of nitrogen oxides. In this method, the step of washing oxidized activated carbons with alkaline solutions to remove humic and fulvic acids is not necessary.



1. Patent RU2105715 C1, Method for production of carbon cation exchanger. Trikhleb VA (UA), Trikhleb LM (UA), published 27.02.1998. (in Russian)

### Appendix S3

#### *Boehm selective neutralization technique [1]*

According to this method, activated carbon sample (0.5g) was equilibrated with 50 mL of each of three bases 0.05N NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH, sealed and shaken for 72 h, and then 10 mL of each filtrate was back-titrated with 0.05N HCl. The surface concentrations of each acidic groups: strong-carboxyl, weak-carboxyl and phenolic; have been determined by differences between the amounts reduced by each of the bases. The schematic neutralization reactions are presented in Figures A1-A3. The total basic surface oxides have been determined with a similar titration technique using 0.05 N HCl and back-titrating with 0.05 N NaOH [2] (Figure A4).

The concentrations of surface acidic groups ( $N^A$ , meq/g) have been calculated by Eq.(1):

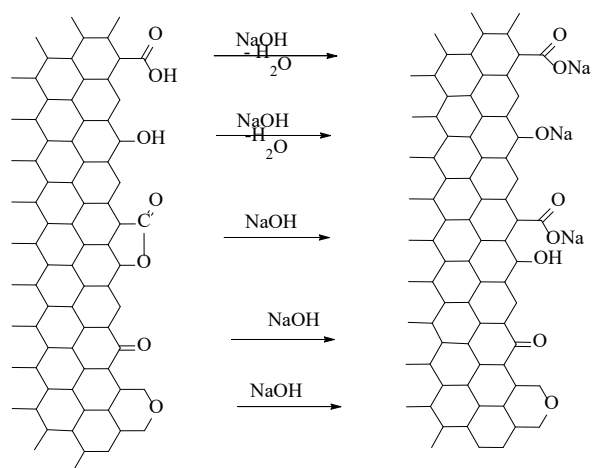
$$N^A = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where,  $C_0$  and  $C_e$  are initial and equilibrium concentrations of bases NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH;  $V$  – volume of bases added to active carbon sample, in mL;  $m$  – mass of active carbon sample, in g.

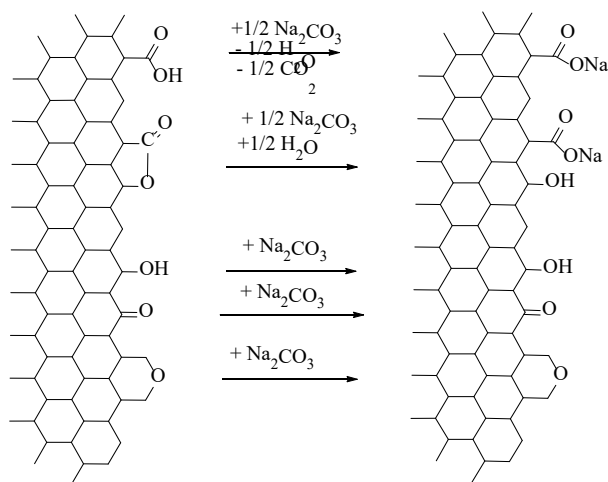
The quantity of the basic functional groups ( $N^B$ , meq/g) has been calculated by Eq.(2):

$$N^B = \frac{(C_0 - C_e)V}{m} \quad (2)$$

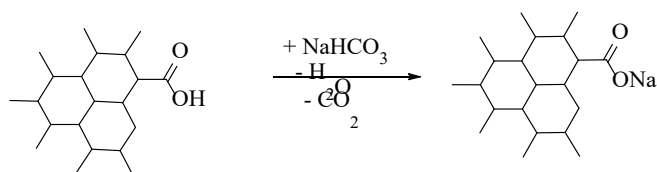
where,  $C_0$  and  $C_e$  are initial and equilibrium concentrations of HCl;  $V$  – volume of HCl added to active carbon sample, in mL;  $m$  – mass of active carbon sample, in g.



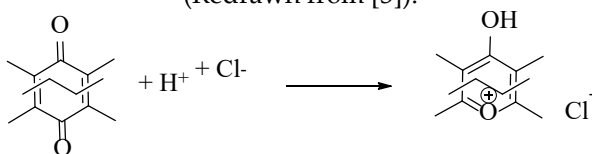
**Figure A1.** Schematic representation of acidic groups neutralisation with 0.05N NaOH solution (Redrawn from [3]).



**Figure A2.** Schematic representation of acidic groups neutralisation with 0.05N  $\text{Na}_2\text{CO}_3$  solution (Redrawn from [3]).



**Figure A3.** Schematic representation of acidic groups neutralisation with 0.05N  $\text{NaHCO}_3$  solution (Redrawn from [3]).



**Figure A4.** Schematic representation of basic groups neutralisation with 0.05N HCl solution (Redrawn from [3]).

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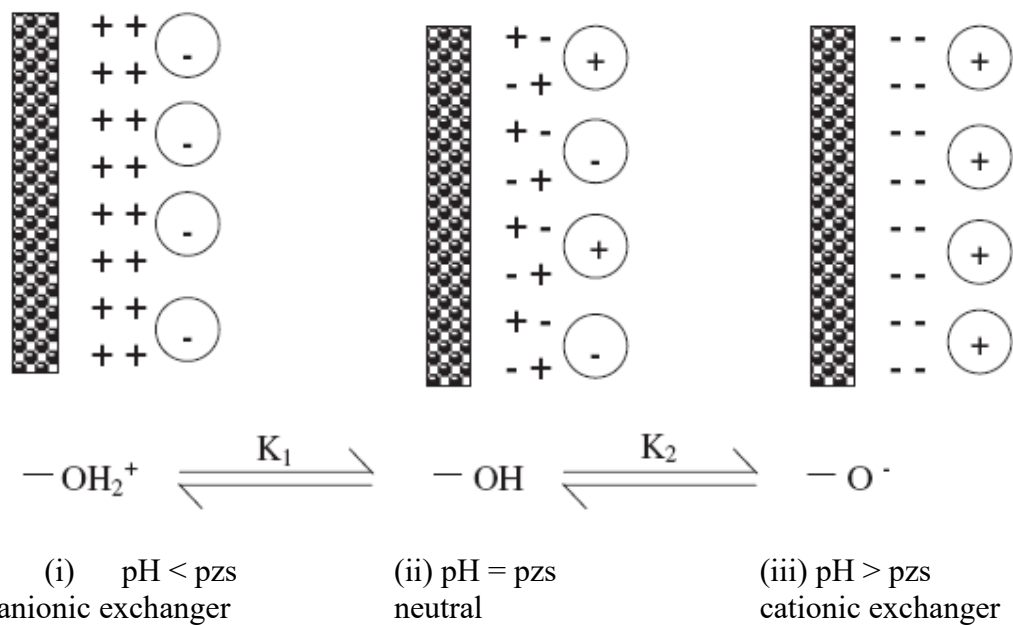
## Appendix S4

### Acid-base properties [1]

Acid-base properties of activated carbons were investigated by potentiometric titration [2] performed in a thermostatic vessel at 25 °C using a 672 Titroprocessor combined with 655 Dosimat (Metrohm, Herisau, Switzerland). To prevent contamination with CO<sub>2</sub>, the flow of pure argon was used throughout the titration. The proton concentration was monitored using an LL pH glass electrode (Metrohm, Herisau, Switzerland). Before experiments, the electrode electromotive force was calibrated to proton concentration by blank titration. Solution equilibria and a correction for possible carbonate and silicate contaminations were calculated using EST software [3]. Proton affinity distributions, F(pK<sub>a</sub>), were calculated from proton-binding isotherms by solving the adsorption integral equation using the CONTIN method [4-7].

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The pH of point zero charge (PZC) is the value of pH at which the components of surface charge are equal to zero for specified conditions of temperature, pressure, and aqueous solution components. When the pH is lower than the pH<sub>pzc</sub> value, the surface of the adsorbent is positively charged (attracts anions). Conversely, above pH<sub>pzc</sub> the surface is negatively charged (attracting cations/repelling anions) [1,2].



**Figure A1.** Schematic representation of the protonation/deprotonation process of the adsorbent surface [2].

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