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**EVALUATION OF THE INFLUENCE OF CARBONACEOUS
ADSORBENT SURFACE CHEMISTRY ON THE ADSORPTION
PROCESS OF POLLUTANTS**

144.01 – PHYSICAL CHEMISTRY

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CONCEPTUAL FRAMEWORK OF THE RESEARCH

Actuality and importance of the research. Activated carbons are efficient adsorbent materials for removing pollutants from water. The physical-chemical nature of the activated carbon (AC) surface plays an important role in the process of adsorption and must be considered when selecting or preparing AC for application purposes in adsorption and/or oxidation. It is proven that the high adsorption capacity of AC is due to a well-developed porous structure and their surface chemistry.

The characteristics of the surface chemistry are strongly related to the presence of heteroatoms on the surface of the AC, such as, oxygen, sulfur, nitrogen, phosphor and other atoms. The type and quantity of heteroatoms present in functional groups depend on the nature of the raw material and heteroatoms that are introduced on the carbon surface during the process of activation or modification. Functional groups on the surface (formed by heteroatoms) determine the acidic or basic nature of the AC surface. Technics of modification of AC are divided in two groups: chemical modification (including acid and base treatment, impregnation of AC) and physical modification (heteroatoms impregnation with precursors and thermal treatment). The modification of AC surface has various advantages: (i) increases the concentration of basic or acidic functional groups on the AC surface; (ii) enhances the capacity of chelation with different pollutants; (iii) enhances the AC capacity of adsorption of organic pollutants; (iv) enhances the capacity of catalytic oxidation; (v) increases the specific surface BET (Brunauer-Emmet-Teller) and to the volume growth of the pores, etc. Beyond the previously mentioned advantages, there are several disadvantages, such as: acid/base treatment sometimes may lead to the decrease of the specific surface BET and pore volume; high temperature treatment may lead to the decomposition of oxygen-containing functional groups on the surface of carbonaceous adsorbents.

The nature of the surface chemistry may be evaluated using various research techniques and methods, such as, infrared spectral methods (IR), acid-basic potentiometric titrations, Boehm titration method, pH determination method of activated carbon suspensions, pH estimation in point zero charge (pH_{pzc}), temperature programmed decomposition (TPD), X-ray photoelectron spectroscopy, thermogravimetric analysis.

The purpose of the research consists in the modification of the surface and the correlation of carbonaceous adsorbents surface chemistry with their sorption and/or catalytic properties.

To achieve this goal, the following **objectives** have been outlined:

- modification of the activated carbon surface chemistry;
- evaluation of the physical-chemical characteristics (nitrogen sorption-desorption isotherms; thermal analysis; X-ray diffraction (XRD); scanning electron microscope coupled with an element analyzer (SEM-EDX));
- assessment of the surface chemistry by:

- ✓ pH-metric titrations: (i) concretization of some methodological aspects regarding the application of pH-metric titrations for heterogeneous systems (carbonaceous adsorbents /aqueous solutions); (ii) estimation of pH_{pzc} by intersection point of the proton binding isotherms (in the presence of different concentrations of electrolytes) and by method of extrapolating the initial pH (pH_0) of suspension in function of the ions strength;
- ✓ detailing of functional groups on the surface of carbonaceous adsorbents using infrared spectroscopy (FTIR);
- ✓ determination of the functional groups on the surface of activated carbons by temperature programmed decomposition method (TPD).
- Evaluation of the redox properties by: (i) ABTS radical cation method, adaptation of the method for application in determination redox properties in heterogeneous systems (carbonaceous adsorbents/aqueous solutions); (ii) chemiluminescence method in luminol/peroxide hydrogen;
- elucidation of the particularities of interaction and/or specific sorption, the effect of porous structure and surface chemistry, in order to correlate the surface properties of carbon adsorbents with their sorbent and/or catalytic properties in order to improve the adsorption process of pollutants.

Scientific novelty and originality consists in the elucidation of the particularities of specific interaction and/or sorption depending on the pH and surface chemistry of carbonaceous adsorbents. For the first time, mechanisms of adsorptions has been proposed for a broad pH interval, by considering the pH of the medium, the ionization degree of the groups (pH_{pzc}) and the types of ions in solution. For the first time, the ABTS radical-cation method has been adapted for the evaluation of the redox properties of carbonaceous adsorbents (heterogeneous systems). A new and economical method of activated carbon oxidation with nitric acid/urea mixture has been proposed.

The **research hypothesis** consists in modifying the surface chemistry of carbonaceous adsorbents by different methods: modification with chlorine ions, by oxidation (with nitric acid, with a mixture of nitric acid/urea) and impregnation with metals (copper and manganese oxides).

The theoretical significance. The research results contribute to the development of scientific information regarding methods of the evaluation of carbon adsorbents surface chemistry. Also, this study correlates the surface properties of carbonaceous adsorbents with their sorbent and/or catalytic properties, in order to enhance the adsorption process of pollutants.

The applicative value of the work. The applied research carried out in this thesis offers the possibility to evaluate the redox properties of carbon adsorbents by the ABTS radical-cation method, and, also to optimize the known methods of modifying activated carbons that contribute to reduction of their price.

Implementation of scientific results. Modified carbonaceous adsorbents (oxidized with nitric acid and nitric acid/urea mixture) have been tested for nitrite ions removal from natural water. The ABTS radical-cation method, adapted for the evaluation of the redox properties in heterogeneous systems has been used in the research.

Practical application possibilities: (i) of the oxidation method of activated carbons with nitric acid/urea mixture allows a production of an array of carbons at low cost; (ii) of carbonaceous adsorbents modified with chlorine ions as enterosorbents for adsorption/removal of nitrite ions from the digestive system.

Approval of results. The obtained results were reported and discussed each year at the meetings of the Scientific Council of the Doctoral School of Chemical and Technological Sciences (SUDC) during the years of doctoral studies (2016-2019). Also, the obtained results were presented at various scientific forums.

Publications on research topic. The obtained results have been published in 24 scientific works: 2 articles in scientific journals (with impact factor), 2 articles in national scientific journals, 5 articles in national/international collections and 12 participations in national and international conferences, scientific symposia.

CONTENT OF THE THESIS

1. MOTIVATION AND OBJECTIFS OF THE RESEARCH

In this chapter, the structure and production methods of carbonaceous adsorbents are described. The areas of use of these adsorbents as catalysts or as supports for catalysts in adsorption and oxidation processes are also described in this section. Additionally, the chapter contains a broad analysis of different types of functional groups (basic and acidic) that are present on the surface of the activated carbon and which play an important role in the adsorption and oxidation of organic and inorganic compounds.

2. METHODOLOGY OF SCIENTIFIC RESEARCH

In this chapter, the methodology of research, used in order to achieve the purpose and the objectives, is presented as follows: the methods of modification and characterization of activated carbons (evaluation of the physical-chemical characteristics (nitrogen sorption-desorption isotherms; thermal analysis; X-ray diffraction (XRD), scanning electron microscope coupled with an element analyser (SEM-EDX)); description of evaluation methods of the surface chemistry of carbonaceous adsorbents: application of pH-metric titrations (i) concretization of some methodological aspects regarding the application of pH-metric titrations for heterogeneous systems (carbonaceous adsorbents /aqueous solutions) (ii) estimation of pH_{pzc} by intersection point of the proton binding isotherms (in the presence of different concentrations of electrolytes) and by method of extrapolating the initial pH (pH_0) of suspension in function of the ions strength; evaluation of the functional groups at the surface

of the carbonaceous adsorbents via infrared spectroscopy (FTIR); determination of functional groups at the surface of activated carbons via the Temperature Programmed Decomposition (TPD).

Additionally, the evaluation methods of redox properties of carbonaceous adsorbents are described by adapting the ABTS radical-cation method for application in the redox properties determination in heterogeneous systems (carbonaceous adsorbents/water solutions) and by determining the redox properties via the chemiluminescence method.

Furthermore, the chapter describes adsorption processes and the mathematical methods used for the experimental data processing, such as, kinetic models of pseudo-first order, pseudo-second order, intraparticle diffusion and models of theoretical isotherms of adsorption of Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich, thermodynamic calculations. The methods of modification of carbonaceous adsorbents via modification with manganese and copper oxides. For the modification of the AC surface via oxidation, a new method of oxidation with mixture of nitric acid and urea was applied for the first time.

For pH-metric titrations some *experimental conditions have been defined and are recommended*: the use of automatic titrator with propeller stirrer in order to avoid the gridding of the samples of AC; the utilization of fractions of AC range between 0.6÷1.3 mm; solid-liquid ratio; 0.2÷0.4 g/60 mL of electrolyte solution; the titrant concentration 0.01÷0.02 M; titrant debit 0.05÷0.1 mL/min; sample moistening time of 48÷72 hours; medium: argon; agitation of AC suspension about 60 min in argon medium before titration: monotonic equivalence point titration (MET).

The recommended optimal conditions have been defined for the evaluation of redox properties (antioxidant activity) via the ABTS^{•+} radical-cation method: for samples of dried AC of a mass of 0.25÷0.5 g, with a fraction of 0.63÷2.0 mm, with an automatic micropipette one adds 5.00 mL of working solution of ABTS^{•+} radical-cation, after contact through agitation during 5 min, the phases are separated via filtration with syringe and the value of the adsorption is recorded at a wavelength of 734 nm.

3. CHARACTERIZATION OF CARBONACEOUS ADSORBENTS USED IN THE RESEARCH

The explication of the influence of the AC surface ensures a more reasonable applications for detoxification of the human body, for various technologies of water purification, for different synthesis (as catalysts) etc. It is known that the presence of different functional groups and different heteroatoms in the structure of activated carbons heavily modifies their physical-chemical properties in order to ensure selective sorption and catalytic properties [1].

The research presented in this chapter includes: the determination of the physical-chemical properties of the carbonaceous adsorbents via the X-ray diffraction analysis; via the scanning electron microscopy with energy dispersive X-Ray (SEM-EDX) analysis and thermal analysis; the determination of structural properties of carbonaceous adsorbents by using nitrogen sorption-

desorption isotherms; the evaluation of the chemistry surface of AC via the infrared spectroscopy, mass spectroscopy and electrometric titrations; the evaluation of redox properties of AC via the chemiluminescence method in luminol/H₂O₂ system and via the ABTS radical-cation method [2].

3.1. Physical-chemical properties of carbonaceous adsorbents

In this thesis, a broad gamut of carbonaceous adsorbents had been used: (i) local carbon obtained from nut shells via the method of physical-chemical activation with steam (CAN, produced at P.L.C. Ecosorbent) and the sample modified with chlorine ions (CAN-Cl) [3]; (ii) activated carbon obtained from nut shells (CA-N) and from apple wood (CA-M) modified with nitric acid (CA-Mox) and with nitric acid and urea (CA-Nox-u/CA-Mox-u) [4] and (iii) activated carbons impregnated with manganese and copper oxides (from E and C series with acidic or basic surface).

The physical-chemical characteristics had been determined following multiple general indexes (ash *A*, humidity *U*, bulk density *D* and elemental analysis) (Table 3.1). According to the obtained results, carbons CAN and CAN-Cl are quite hygroscopic, with a humidity of about 8%. The content of ash decreases in CAN-Cl probe about 4 times comparing to the initial probe (Table 3.1, Figure 3.1). According to the results of the analysis of the elements for carbonaceous adsorbents CAN and CAN-Cl (Table 3.1), the nitrogen is missing in both samples of activated carbons, while chlorine was found in CAN-Cl sample in a quantity of ~2%, which confirms that the goal has been achieved. The results of the SEM-EDX analysis give an additional confirmation of the chlorine presence in the CAN-Cl sample, meanwhile, a part of the ash present in CAN is removed during the modification process (is eliminated the calcium, potassium etc.) (Table 3.1, Figure 3.1) [3, 4].

Table 3.1. Values of humidity, ash and bulk density

Sample	<i>U</i> , %	<i>A</i> , %	<i>D</i> , g/cm ³	Elemental analysis, %			
				C	H	N	Cl
CAN	<8.12> ±0,16	1.91	<0.494> ±0,004	92.23	1.86	-	-
CAN-Cl	<7.82> ±0,11	0.53	<0.467> ±0,002	92.77	2.30	-	2.02

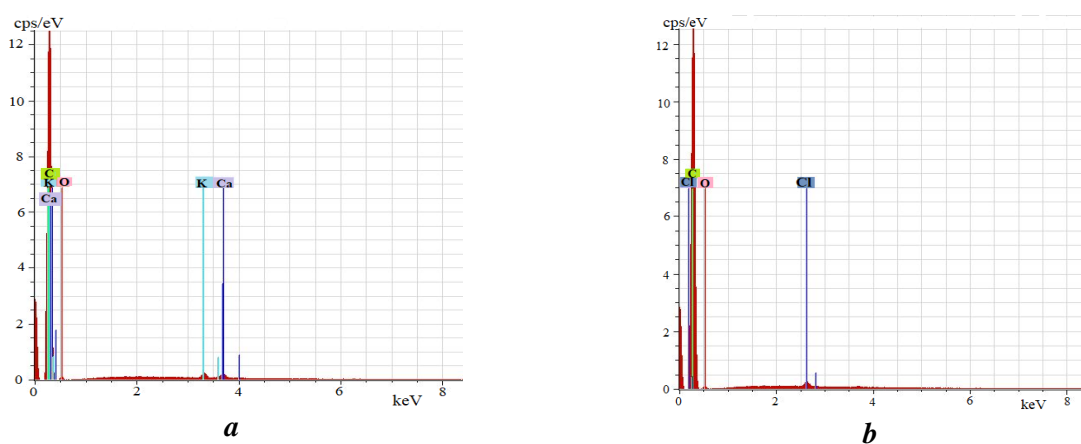


Fig. 3.1. Elemental analysis of activated carbons by SEM-EDX method (a) CAN and (b) CAN-Cl [3]

The AC samples used at impregnation with manganese and copper ions are quite various in what concerns the surface chemistry and ash content. The sample from E series has a higher

content of ash due to calcium, magnesium and iron compounds, and has a basic pH at surface (9.5), while the sample from C series has only traces of ash (0.29%) and an acidic surface (pH 4.0) [5]. Carbonaceous adsorbents impregnated with different oxides MnO, MnO₄, Mn₂O₃, MnOOH, may be obtained via this. According to literature data, at thermal decomposition of manganese and copper carbonates, only bivalent oxides, MnO and CuO are obtained [5]. For the production of AC impregnated with copper and manganese oxides (catalysts), considering the thermal behavior (determined via the thermogravimetric analysis), the samples had been treated at the temperatures of 300, 450 and 600°C. The samples from E series had been obtained with an yield of 50-60% and the quantity of manganese impregnated as oxide had constituted 1.44-1.65%, depending of the applied method. The samples from C series had been obtained with a higher yield (92-98%), but with lower quantities of impregnated manganese [1]. The quantity of impregnated oxides and their nature depends of either the composition of the solution of modification, as well as of the nature of the surface (acidic or basic) of the AC as support [6]. The graphite is identified in the composition of AC in proportion of 16-43%, via the powder X-ray diffraction method. While increasing the temperature from 300 to 600°C, the graphite content decreases from 34% to 16% in the E-3-Mn and E-3H-Mn series. Additionally, in the E-3-Mn series, apart from graphite and manganese oxide, calcium (calcite) is determined with a content which increases with the temperature increase, with a mass ratio from 35% to 63% (Figure 3.2) [7, 8].

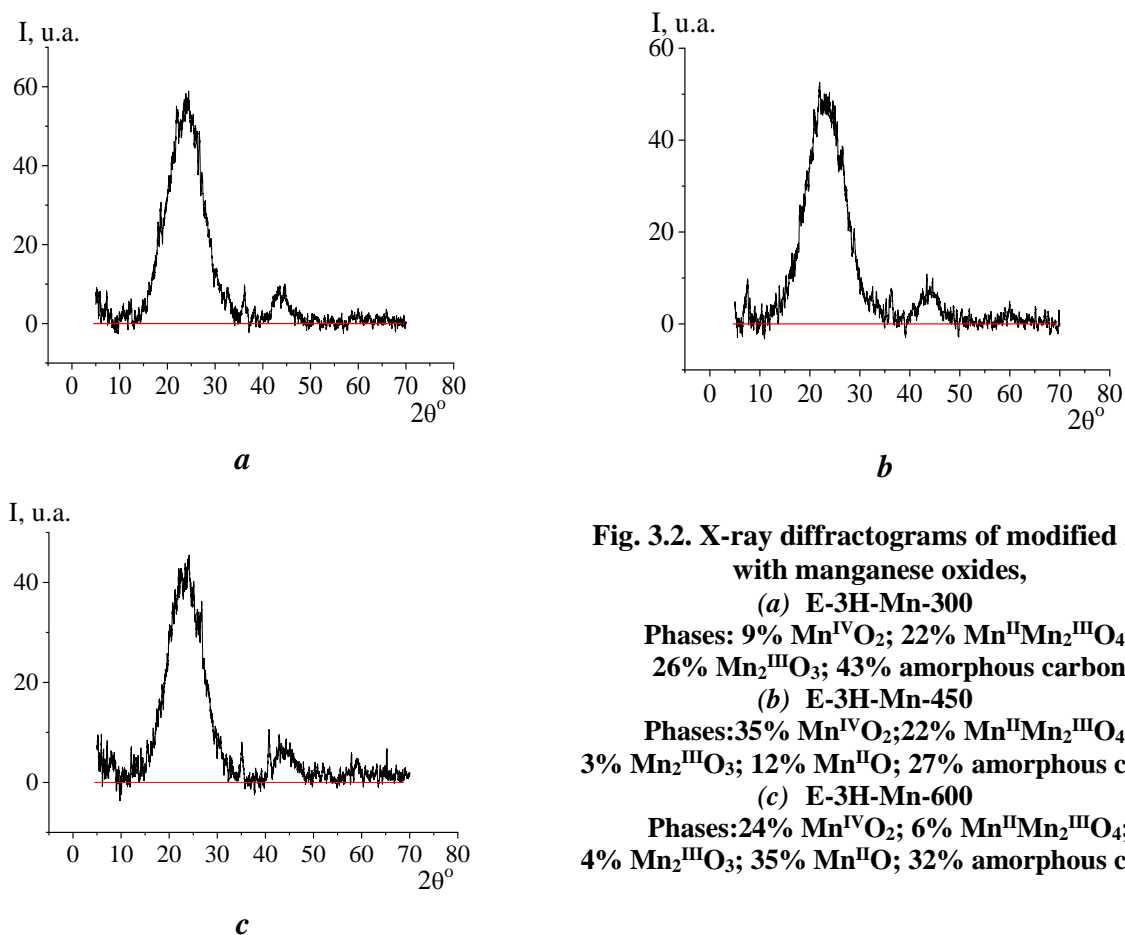


Fig. 3.2. X-ray diffractograms of modified AC with manganese oxides,
(a) E-3H-Mn-300
Phases: 9% Mn^{IV}O₂; 22% Mn^{II}Mn₂^{III}O₄; 26% Mn₂^{III}O₃; 43% amorphous carbon
(b) E-3H-Mn-450
Phases: 35% Mn^{IV}O₂; 22% Mn^{II}Mn₂^{III}O₄; 3% Mn₂^{III}O₃; 12% Mn^{II}O; 27% amorphous carbon
(c) E-3H-Mn-600
Phases: 24% Mn^{IV}O₂; 6% Mn^{II}Mn₂^{III}O₄; 4% Mn₂^{III}O₃; 35% Mn^{II}O; 32% amorphous carbon

The modification of activated carbons via oxidation with concentrated nitric acid (CA-Mox sample) and with nitric acid/urea mixture (CA-Mox-u and CA-Nox-u samples) leads to a small content of ash from ~3% to ~0.6% (Table 3.2) [4]. The content of metals determined via atomic adsorption spectroscopy AAS, and completed by the SEM-EDX results, reveals that after the oxidation process traces of metals remain, while all the manganese, sodium and iron compounds are mostly washed away [4].

Table 3.2. The description and characteristics of carbonaceous adsorbents [4]

<i>Sample</i>	<i>Sample description</i>	<i>U, %</i>	<i>A, %</i>	<i>D, g/cm³</i>
<i>CA-N</i>	Activated carbon obtained from nut shells	<13.11>±0.44	<2.94>±0.23	<0.268>±0.001
<i>CA-M</i>	Activated carbon obtained from apple wood	<8.65>±0.03	<1.06>±0.04	<0.232>±0.001
<i>CA-N_{ox-u}</i>	Oxidized with nitric acid/urea mixture	<14.76>±0.23	<0.95>±0.06	<0.272>±0.001
<i>CA-M_{ox-u}</i>	Oxidized with nitric acid/urea mixture	<15.49>±0.41	<0.87>±0.12	<0.273>±0.001
<i>CA-M_{ox}</i>	Oxidized with concentrated nitric acid	<5.26>±0.40	<0.56>±0.11	<0.268>±0.001

3.2. Characteristics of the porous structure of carbonaceous adsorbents

The structure parameters of carbonaceous adsorbents had been determined from the nitrogen sorption-desorption isotherms by using the Autosorb device at the Institute of Chemistry. After modification with chlorine ions of the CAN sample, the S_{BET} is increased with ~28 m²/g, the V_{total} – with 0.015 cm³/g and the V_{micro} – with 0.011 cm³/g. However, the radius of the micropores does not indicate any significant changes (Table 3.3) [3].

Table 3.3. Porous structure characteristics of active carbons determined from N₂ sorption isotherms

<i>Sample</i>	<i>S_{BET}, m²/g</i>	<i>V_{total}, cm³/g</i>	<i>V_{micro}, cm³/g</i>	<i>E_{micro}, kJ/mol</i>	<i>R_{micro}, nm</i>
<i>CAN-Cl</i>	608	0.318	0.203	24.7	2.5
<i>CAN</i>	580	0.303	0.192	24.3	2.5

S_{BET} – surface determined by Brunauer-Emmet-Teller equation; *V_{total}* – the total volume of pores; *V_{micro}* – the micropores volume; *E_{micro}* – the energy of adsorption in micropores; *R_{micro}* – the radius of micropores.

Regarding the samples of carbonaceous adsorbents modified with manganese and copper oxides, the porous structure characteristics determined from the nitrogen sorption-desorption isotherm, shows that the sorption properties change with the nature of the surface of the initial sample and with the temperature of the thermal treatment (Table 3.4) [1]. In the case of samples from the C series, the thermal treatment leads to the decrease of several parameters, such as S_{BET} , V_{total} , and to the increase of V_{micro} and S_{micro} (estimated via *t*-method). This trend is kept with the increase in the temperature of the carbon treatment up to 450°C [1].

For the samples from the E series, the obtained results reveal that depending on the conditions of the thermal treatment, the samples modified with manganese oxides show an increase of S_{BET} with ~13-26%, and a significant increase of V_{mezo} (twice) when compared with initial sample (Table 3.4). This effect can be explained via an additional activation at 300°C due to impregnation salts. The modified samples, obtained on support of carbonaceous adsorbent with acid surface, are more stable at thermal treatment. The insignificant decrease of S_{BET} (with 5-10%) is in a good agreement with the production efficiency of the samples [7, 8].

Table 3.4. The structural parameters of carbonaceous adsorbents modified with manganese oxides [1]

No.	Sample	Method	$S_{BET}, m^2/g$	$V_{total}, cm^3/g$	$V_{meso}, cm^3/g$	$V_{micro}, m^3/g$	R, nm
<i>Samples obtained on the basis of the active carbons with acidic surface</i>							
1	C	initial	1208	0.808	0.737	0.071	2.7
2	C-3H-Mn-300	MnCl ₂ /NH ₄ OH	1064	0.683	0.580	0.103	2.6
3	C-3H-Mn-450	MnCl ₂ /NH ₄ OH	1155	0.736	0.626	0.110	2.6
4	C-3H-Mn-600	MnCl ₂ /NH ₄ OH	1138	0.756	0.658	0.098	2.7
<i>Samples obtained on the basis of the active carbons with basic surface</i>							
5	E	initial	878	0.487	0.205	0.282	2.2
6	E-3-Mn-300	MnCl ₂ /NaOH	994	0.607	0.392	0.215	2.4
7	E-3-Mn-450	MnCl ₂ /NaOH	816	0.476	0.203	0.273	2.3
8	E-3-Mn-600	MnCl ₂ /NaOH	942	0.520	0.222	0.298	2.2
9	E-3H-Mn-300	MnCl ₂ +H ⁺ /NaOH	1105	0.658	0.404	0.254	2.4
10	E-3H-Mn-450	MnCl ₂ +H ⁺ /NaOH	920	0.506	0.204	0.302	2.2
11	E-3H-Mn-600	MnCl ₂ +H ⁺ /NaOH	954	0.520	0.218	0.302	2.2

The characteristics of the porous structure of the samples modified via oxidation (CA-M; CA-N; CA-Mox; CA-Mox-u and CA-Nox-u) determined from the nitrogen sorption-desorption, are presented in Table 3.5 [4]. The results show that after the oxidation process, there is a decrease in the values of S_{BET} of the carbonaceous adsorbents, V_{total} , V_{micro} and V_{meso} , either for AC obtained from nut shells (CA-N), as well as, for AC obtained from apple wood (CA-M) (Table 3.5) [4]. According to literature data, there is a decrease in S_{BET} and V_{total} after the oxidation process [9, 10], which in certain cases is explained by the formation of functional groups and pores are blocked.

Table 3.5. Porous structure characteristics of active carbons determined from N₂ sorption isotherms

Sample	$S_{BET}, m^2/g$	$V_{total}, cm^3/g$	$V_{micro}, cm^3/g$	$V_{meso}, cm^3/g$
CA-M	812	0.540	0.240	0.300
CA-N	782	0.505	0.235	0.270
CA-M _{ox}	670	0.361	0.225	0.136
CA-M _{ox-u}	719	0.416	0.233	0.183
CA-N _{ox-u}	696	0.411	0.230	0.181

3.3. Characterization of the surface chemistry of carbonaceous adsorbents

The surface chemistry of the activated carbons has been evaluated via the application of pH-metric titrations, infrared spectroscopy (FTIR) and temperature programmed desorption (TPD).

Infrared spectroscopy. The IR spectra of the activated carbon samples CAN (initial) and CAN-Cl (modified) are very similar. In the range of 2800-3000 cm⁻¹, the low intensity bands are attributed to the C-H bond of aliphatic groups CH, CH₂ and CH₃. For both activated carbons (CAN and CAN-Cl) there is a broad band, of superposed adsorptions, in the range 1660-1450 cm⁻¹ with shoulders at ~ 1560 and 1450 cm⁻¹ due to C=C vibrations of the activated carbon skeleton and the bond of aromatic rings with double bonds C=C or C=O, and vibrations in CH₂ and CH₃ groups in aromatic structures [11].

The broad band 1000-1300 cm⁻¹ in the spectra of both activated carbons can be attributed to the vibrations of C-OH from alcohols, phenols and acids; to the vibrations of simple C-O bonds from ethers, esters and lactones; as well as to the vibrations of O-H bond from phenol [12, 13].

The IR spectra of CA-M and CA-N initial samples contain absorptions characteristic to unmodified activated carbons. Whilst the samples oxidized with nitric acid (CA-Mox) and nitric acid/urea mixture (CA-Mox-u and CA-Nox-u), in the IR spectra, display additional absorption bands, which are attributed to the OH group from alcohols, phenols and carboxylic acids, moreover, the adsorption increases in intensity at $\sim 1700\text{ cm}^{-1}$ due to vibrations in the C=O bond of the carboxylic, ketones and aldehydes groups [14].

Temperature programmed decomposition (TPD) implies the thermal decomposition of activated carbon samples and the analysis of the eliminated gases via mass spectroscopy. The mass spectra of the activated carbons samples CAN and CAN-Cl (Figure 3.3) reveal that at the temperature lower 400°C , the most unstable functional groups are decomposed and eliminated as CO_2 , which shows the presence of carboxylic functional groups on the surface. The CO released from CAN and CAN-Cl active carbons beyond 600°C shows the presence of phenolic groups, carbonyl groups and quinones [15]. Meanwhile, the elimination of C_2H_6 and CH_4 from the samples CAN and CAN-Cl, suggests on the uncompleted (partial) activation of the activated carbon. The species evolved for chlorine groups were mainly mass 36 (HCl^{35}); this means that the groups decompose mainly to HCl (Figure 3.3 b) [15].

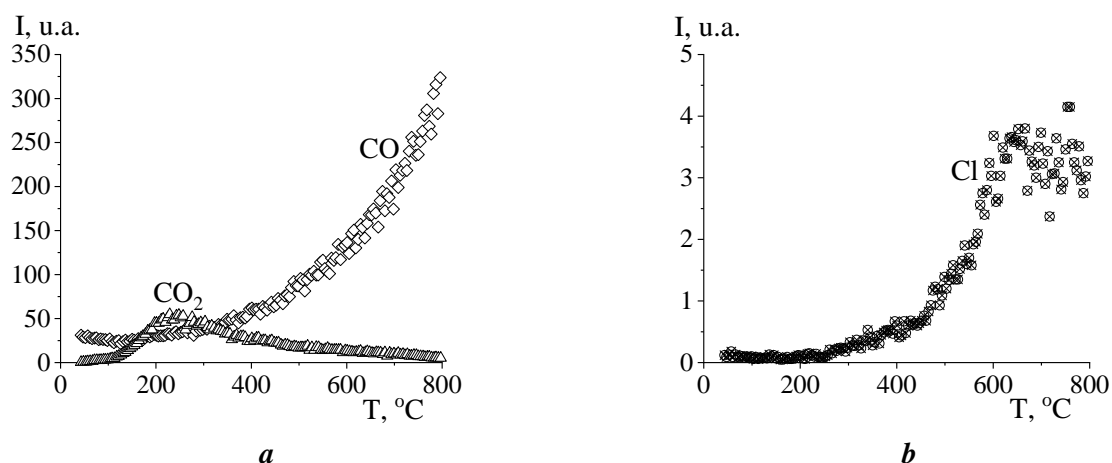


Fig. 3.3. CO and CO_2 (a) and (b) chlorine evolution from active carbon CAN-Cl [15]

The acid-basic properties of activated carbons have been studied by applying the pH-metric titrations (integral curve, differential curve). The pH-metric titration curves of the activated carbon CAN-Cl, helped identify the functional groups with equivalence point at $\text{pH} \sim 8.7\text{--}8.8$ (differential curve), attributed to surface functional groups and pH_{pzc} value of ~ 5.75 has been determined (Figure 3.4) [16]. The obtained value is comparable and in agreement with the results reported by other authors, pH_{pzc} of 5.3 for the same quantity of chlorine on the surface.

The pH_{pzc} and dissociation constants of the functional groups (pK) of carbonaceous adsorbents modified via oxidation with nitric acid and nitric acid/urea (CA-N, CA-M, CA-Mox, CA-Mox-u, CA-Nox-u) were determined from the pH-metric titrations. The obtained results show that for the initial AC sample CA-M, the charge on surface is null in the pH range 4.58-9.15, while the value of

pH_{pzc} via the extrapolation method is 6.84-6.89. For the modified sample CA-Mox, the pH_{pzc} is ~ 2.3 , determined via both methods. The value of pH_{pzc} for the sample CA-Mox-u is ~ 3.3 [18].

The curves of distribution of functional groups according to the pK value (Figure 3.5) show that for both initial activated carbon samples (CA-N and CA-M) have only basic functional groups of 0.98 meq/g for the activated carbon CA-M and 0.75 meq/g for the activated carbon CA-N. In addition, it should be noted, that most of the peaks belong to the CA-Mox sample (basic functional groups 0.45 meq/g and acid functional groups 1.33 meq/g) [18]. Four peaks are distinguishable for each of the activated carbon samples: CA-Mox-u (basic functional groups 0.58 meq/g and acidic functional groups 0.75 meq/g) and for CA-Nox-u (basic functional groups 0.60 meq/g and acidic functional groups 0.55 meq/g) [18].

The acidic or basic character of the functional groups on the surface of activated carbons determined by pH-metric titrations is in a good agreement with the type of functional groups determined via the Boehm method (Table 3.6) [17, 18]. The small discrepancies in values can be explained by different approaches in the determination of functional groups via these two methods.

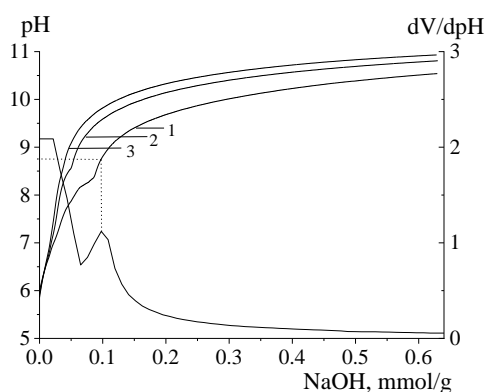


Fig. 3.4. pH-metric titration curve with NaOH of active carbon CAN-Cl in the presence of the electrolyte NaCl:
1 – 0,10 M; 2 – 0,01 M and 3 – 0,05 M

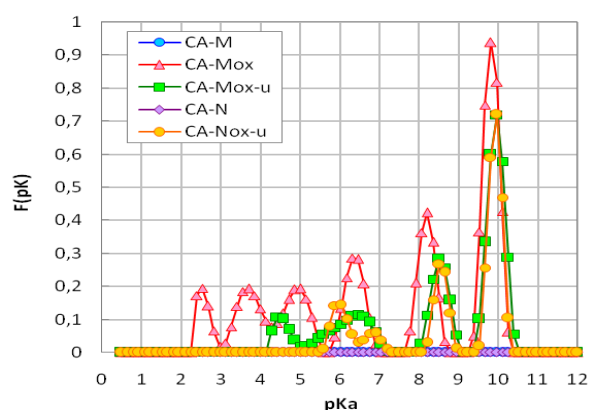


Fig. 3.5. Distribution of surface groups according to the dissociation constants pK [18]

Table 3.6. The quantity and character of functional groups (meq/g) on the surface of active carbons, determined by the Boehm method [17, 18]

Sample	Susp. pH	The amount of functional groups, meq/g				Character of functional groups, meq/g			
		Titrant				Carboxylic		Phenolic	Basic
		0.05 N NaHCO ₃	0.1 N Na ₂ CO ₃	0.05 N NaOH	0.05 N HCl	Strong acidic	Weak acidic		
CA-N	7.8	0.02±0.03	0.07±0.02	0.29±0.03	0.92±0.02	0.02	0.05	0.22	0.92
CA-M	7.7	0	0.35±0.01	1.09±0.01	0.98±0.02	0	0.35	0.74	0.98
CA-N _{ox-u}	5.62	0.32±0.05	0.54±0.01	0.86±0.03	0.60±0.02	0.32	0.22	0.32	0.60
CA-M _{ox-u}	5.56	0.44±0.04	0.77±0.01	1.09±0.05	0.55±0.05	0.44	0.33	0.32	0.55
CA-M _{ox}	4.71	0.95±0.01	1.78±0.02	1.9±0.01	0.45±0.03	0.95	0.83	0.12	0.45

3.4. The evaluation of redox properties of carbonaceous adsorbents

The redox properties of AC have been established via the *chemiluminescence method* in the hydrogen peroxide-luminol system and the *ABTS radical-cation method* [19]. The results reveal that the samples CAN and CAN-Cl possess antioxidant activity evaluated by chemiluminescence method (Figure 3.6 a). Also, the comparative analysis of the results indicate that the sample CAN possesses reducing properties (captures free radicals generated in the system), whilst the CAN-Cl sample has pro-oxidant properties against CAN (Figure 3.6 a). The redox activity evaluated by the *ABTS radical-cation method* shows that both samples (CAN and CAN-Cl) possesses comparable antioxidant activity towards ABTS radical-cation; about 49% for the CAN and 47% for the CAN-Cl.

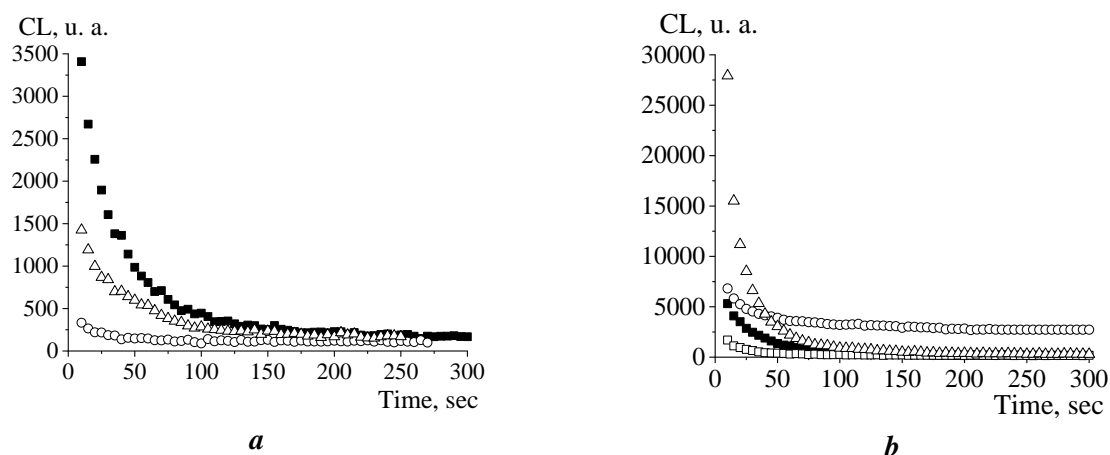


Fig. 3.6. The chemiluminescence curves for the (a) blank sample (■), activated carbons CAN (○) and CAN-Cl (Δ) and (b) blank sample (■); E (□); E-Cu-Na₂CO₃ (○); E-Mn-Na₂CO₃ (Δ)

The redox activity of adsorbents modified with metal oxides evaluated by the chemiluminescence method (chemiluminescence curves (Figure 3.6 b) and the antioxidant activity, calculated at 30 sec of reaction) reveal that the modification with manganese oxides amplifies the pro-oxidant activity of AC. The sample E-Mn-Na₂CO₃ possesses pro-oxidant activity in the first 25 sec (about 5.5 times greater compared to the blank sample), after which the chemiluminescent signal decreases (Figure 3.6 b). Although the activity of the sample E-Cu-Na₂CO₃ in the first seconds is comparable to that of the blank, its pro-oxidant activity doesn't decrease over time, but remains relatively constant during the experiment thus revealing the achievement of balance: formation and capture of free radicals (Figure 3.6 b) [20].

According to the characteristics of AC structure (well-activated/graphitized structure, functional groups, π electrons, quinone/hydroquinone couple, etc.) under different conditions AC has a dualistic behavior: on the one hand it captures free radicals from different systems, and under other special conditions the AC itself can contribute to formation of free radicals. Activated carbon, through the redox couple quinone/hydroquinone on the surface, in the luminol/hydrogen peroxide system, contributes to the formation of free radicals that react with hydrogen peroxide, thus generating hydroxyl radicals OH[•] analogous to the Fenton reaction.

The redox activity of carbonaceous adsorbents (catalysts) evaluated by the ABTS radical-cation method, reveals that for the E series of AC samples modified with manganese and copper oxides, the activity for ABTS radical-cation reduction is between 40÷70%. The ABTS radical-cation reduction activity of the samples from E series decreases: E-Mn-Na₂CO₃>E-3-Mn-600>>E-3H-Mn-600>E-3-Mn-450>E-3-Mn-300>E-3-Mn-450>E>E-3H-Mn-450>>E-Cu-Na₂CO₃>>E-3H-Mn-300>E-3-Mn-300 [20].

For the C series of carbonaceous adsorbents modified, with manganese and copper oxides, the activity for ABTS radical-cation reduction is between 60-72%. The ABTS radical-cation reduction activity of the samples from C series decreases: C-3-Mn-Na₂CO₃>C-3Ac-Mn-300>>C-3Ac-Mn-450>C>C-3Ac-Mn-600>>C-3H-Mn-600>C-1-Cu-Na₂CO₃>C-3H-Mn-450>>C-3H-Mn-300 [20].

4. THE PROCESS OF ADSORPTION OF POLLUTANTS FROM WATER

The sorption that takes place at the liquid/solid interface plays an important role in many processes. The sorption of substances from the liquid phase to the solid is based on van der Waals forces or Lewis-type acid-base interactions acting between sorbent and sorbate. Thus, the parameters determined from the kinetics and isotherms of the adsorption process will provide a lot of information about the type and mechanism of adsorption [21].

4.1. Evaluation of the adsorption process of nitrite ions on activated carbons

To evaluate the adsorption process of nitrite ions on activated carbons CAN and CAN-Cl, the adsorption *kinetic curves* at 3 initial sorbent concentrations and 4 temperatures (278, 288, 303, 313 K) were determined. The concentration of nitrite ions, pH and electrical conductivity were determined in the solutions [22]. For the processing of experimental data the pseudo-first order kinetic, the pseudo-second order kinetic and the intraparticle diffusion models were applied. These models allow the determination of the reaction order, the reactions rate constants and calculation adsorption value. For the both carbons (CAN and CAN-Cl) the experimental adsorption values ($q_e(exp)$) are in good agreement with the calculated adsorption values ($q_e(calc)$) by the pseudo-second order kinetic model (Table 4.1) [21]. This fact shows that chemisorption predominates [23, 24].

In order to determine the diffusion in the pores and the transport of the sorbate from the liquid phase on the free active sites on the AC, the intraparticle diffusion model was applied [23]. According to the obtained data, the diffusion velocity of NO₂⁻ in the pores of CAN-Cl carbon is small (14·10⁻¹⁴ m²/s), similar values of diffusion coefficients for nitrite ions in the AC pores have been reported in the literature [23]. Meanwhile, in the case of adsorption of NO₂⁻ in the pores of AG-5ox and CAN-7 ACs, the value of the diffusion is by order of magnitude higher, which can be explained by the utilization of a higher fraction of ACs in the investigated systems. Analysis of the obtained data shows that the diffusion velocity in pores increases with the temperature (313K).

Table 4.1. Kinetic parameters and q_e values of the nitrite ions adsorption process on activated carbon CAN-Cl at different temperatures. The pseudo-second order kinetic model

T, K	$C_0, mg/L$	$q_e(exp), mg/g$	<i>Kinetic parameters</i>		
			$K_2, g/mg\ min$	$q_e(cal), mg/g$	R^2
278	5	0.434	0.09038	0.447	0.999
	11	0.898	0.09754	0.887	0.999
	15	1.208	0.02222	1.229	0.999
288	5	0.472	0.05356	0.478	0.999
	11	1.004	0.04214	1.009	0.999
	15	1.290	0.01407	1.290	0.996
303	5	0.453	0.08729	0.464	0.995
	11	0.871	0.04762	0.882	0.996
	15	1.055	0.02047	1.093	0.976
313	5	0.473	0.09959	0.473	0.999
	11	0.953	0.05803	0.959	0.999
	15	1.305	0.02197	1.296	0.998

The intraparticle diffusion model (Weber-Morris model) has been applied in order to determinate the influence of mass transfer on the process of nitrite ions adsorption on activated carbons CAN and CAN-Cl. The adsorption dependence as function of the square root of contact time ($q_t=f(t^{1/2})$), presents three linear regions, thus demonstrating that the adsorption process occurs in three stages (Figure 4.1). From the values of adsorption, pH (and conductivity), can be observed a decrease of diffusion velocity with increasing contact time (1st stage), the other two stages are due to the adsorption and transfer from mezopores to micropores.

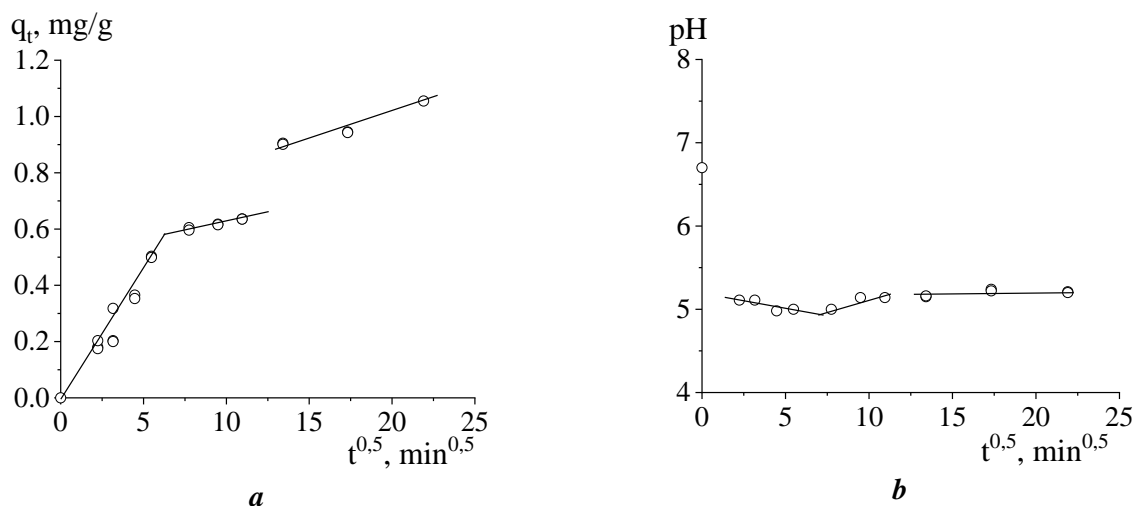


Fig. 4.1. Intraparticle diffusion kinetic model (Weber-Morris model) for nitrite ions adsorption on activated carbon CAN-Cl, $T = 303K$. Dependence of nitrite ion adsorption (a), pH value of solutions at equilibrium (b) vs the square root of contact time

The adsorption isotherms of nitrite ions on CAN and CAN-Cl activated carbons had been determined as functions of temperature, pH and electrolyte presence. For the description of experimental data, the theoretic models of Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich have been applied, which allowed the estimation of sorption parameters (Table 4.2 and Figure 4.3). The obtained results show that nitrite ion adsorption on CAN and

CAN-Cl (for different temperatures and pH values) is best described by the Langmuir model, R_L validates that the process is favorable. This fact is also confirmed by the Freundlich isotherm model ($1/n$). The investigated values of the free energy (Dubinin-Radushkevich model) demonstrate that the process is dominated by the chemical adsorption (Tables 4.2-4.4 and Figures 4.2-4.3).

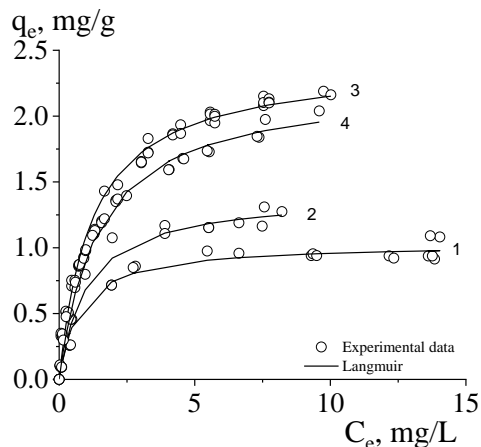


Fig. 4.2. Nitrite ions adsorption isotherms on activated carbon CAN-Cl, at different temperatures: (1) 283K, (2) 288K, (3) 298K and (4) 313K

Table 4.2. Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich isotherm constants for the adsorption of nitrite ions on activated carbon CAN-Cl at different temperatures

Isotherm model	T, K	283	288	298	313
	Langmuir	Parameters			
	K_L (L/mg)	1.318	0.976	0.828	0.694
	Q_0 (mg/g)	1.031	1.404	2.411	2.248
	R^2	0.988	0.984	0.989	0.989
R_L		0.02 ÷ 0.41	0.04 ÷ 0.047	0.03 ÷ 0.56	0.04 ÷ 0.58
Freundlich	K_f (mg/g)	0.406	0.520	0.912	0.718
	n	2.470	1.986	2.061	1.842
	R^2	0.849	0.893	0.959	0.909
Temkin-Pyzhev	K_T (L/g)	21.226	15.856	17.902	12.268
	B_T	0.182	0.264	0.405	0.414
	R^2	0.917	0.932	0.934	0.995
Dubinin-Radushkevich	K_{ads} (mol ² /kJ ²)	7.10×10^{-8}	5.90×10^{-8}	3.71×10^{-8}	6.78×10^{-8}
	Q_0 (mg/g)	0.878	1.054	1.452	1.667
	E (kJ/mol)	2653.72	2911.11	3671.11	2715.62
	R^2	0.910	0.834	0.825	0.966

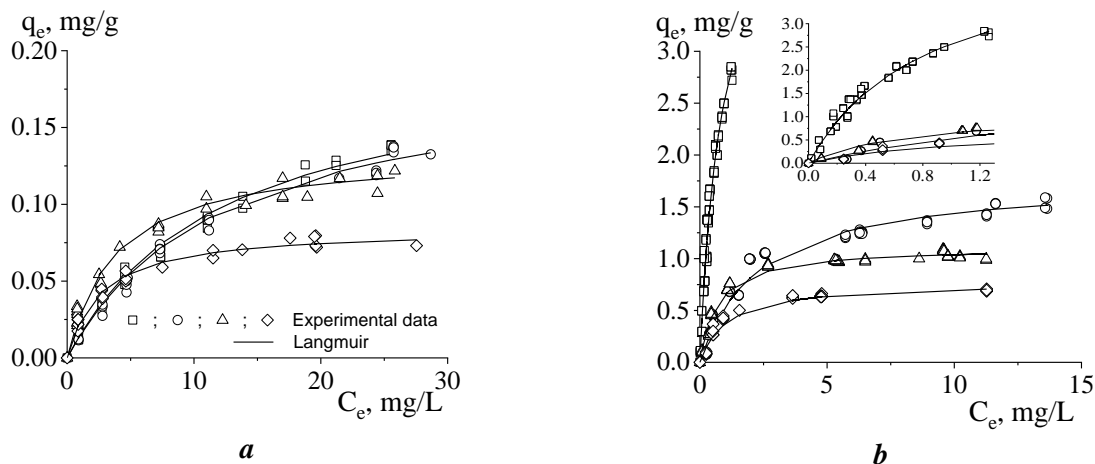


Fig. 4.3 Adsorption isotherms of nitrite ion on activated carbons (a) CAN and (b) CAN-Cl obtained at different values of pH: 3 (□); 5 (○); 7 (Δ) and 10 (◇)

Table 4.3. Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich isotherm constants for the adsorption of nitrite ions on activated carbon CAN, at different initial values of pH

Isotherm model	pH Parameters	3	5	7	10
		<i>Langmuir</i>	K_L (L/mg)	0.083	0.082
	Q_0 (mg/g)	0.196	0.130	0.134	0.080
	R^2	0.941	0.947	0.983	0.991
R_L		0.30 ÷ 0.92	0.28 ÷ 0.92	0.12 ÷ 0.78	0.08 ÷ 0.72
<i>Freundlich</i>	K_f (mg/g)	0.018	0.019	0.032	0.026
	n	1.546	1.628	2.300	2.665
	R^2	0.969	0.965	0.950	0.925
<i>Temkin-Pyzhev</i>	K_T (L/g)	1.320	1.227	3.330	4.500
	B_T	0.035	0.036	0.027	0.017
	R^2	0.932	0.930	0.970	0.969
<i>Dubinin-Radushkevich</i>	K_{ads} (mol ² /kJ ²)	5.19×10^{-7}	5.15×10^{-7}	3.26×10^{-7}	3.11×10^{-7}
	Q_0 (mg/g)	0.085	0.085	0.097	0.064
	E (kJ/mol)	981.52	985.32	1238.44	1267.95
	R^2	0.775	0.702	0.854	0.846

Table 4.4. Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich isotherm constants for the adsorption of nitrite ions on activated carbon CAN-Cl, at different initial values of pH

Isotherm model	pH Parameters	3	5	7	10
		<i>Langmuir</i>	K_L (L/mg)	1.192	0.430
	Q_0 (mg/g)	4.717	1.773	1.111	0.723
	R^2	0.856	0.955	0.995	0.987
R_L		0.02 ÷ 0.43	0.07 ÷ 0.69	0.03 ÷ 0.41	0.05 ÷ 0.51
<i>Freundlich</i>	K_f (mg/g)	2.992	0.480	0.493	0.302
	n	1.267	1.831	2.503	2.094
	R^2	0.956	0.790	0.828	0.786
<i>Temkin-Puzhev</i>	K_T (L/g)	26.687	6.353	23.185	11.356
	B_T	0.691	0.348	0.200	0.158
	R^2	0.885	0.969	0.940	0.940
<i>Dubinin-Radushkevich</i>	K_{ads} (mol ² /kJ ²)	3.56×10^{-8}	1.75×10^{-7}	6.58×10^{-8}	1.29×10^{-7}
	Q_0 (mg/g)	2.194	1.262	0.944	0.665
	E (kJ/mol)	3747.65	1690.30	2756.58	1968.74
	R^2	0.922	0.942	0.921	0.988

The sites on the activated carbon surface, where adsorption took place, can be classified as: (i) hydrophobic surface constituted by graphene layers and (ii) oxygen-containing functional groups that are hydrophilic. This fact offers two possibilities of nitrite ion adsorption: adsorption via interaction between the π orbitals of the graphene layers and anions, or the ion-exchange mechanism, which implies oxygen-containing functional groups. For activated carbon CAN, the nitrite ions quantity had barely changed within the pH interval 5÷10, therefore, one suppose that the adsorption takes place among the free electrons of anions with delocalized π electrons from Lewis basic sites. Hence, the acidic medium is favoring the process of nitrite ion adsorption on both activated carbon samples (CAN and CAN-Cl), which is in agreement with data described in the literature [25]. The results show that the modification with chlorine ions leads to an increase of the adsorption capacity of nitrite ions by about 50 times [21].

Considering the characteristics of activated carbons modified with chlorine ions (sample CAN-Cl) for adsorption of nitrite ions at low pH values (the low ash content is also an advantage), its using as enterosorbent for nitrite ions adsorption/elimination from human body (the stomach pH varies from 1-2 to 4-5) *is recommended*.

The presence of *electrolytes* in the process of ions adsorption on activated carbons often has a significant influence [25]. According to obtained results, the presence of NaCl and NaClO₄ electrolytes in the process of nitrite ions adsorption on investigated carbonaceous adsorbents (CAN and CAN-Cl) decreases the adsorption value. It seems that activated carbons possess a higher affinity for chlorine and perchlorate ions than for nitrite ions [25]. In the case of carbonaceous adsorbent modified by chlorine CAN-Cl the nitrite ions adsorption value (a, mg/g) decreased ~10 times in the presence of electrolyte NaCl and ~60 times in the presence of electrolyte NaClO₄, when compared to the adsorption value in the absence of electrolyte.

Thermodynamic parameters (ΔG° , ΔH° and ΔS°) have been determined from the constants of the Langmuir theoretical model. The negative values of ΔG° , obtained for the activated carbon CAN-Cl highlights that the equilibrium of the adsorption process is reached faster at higher temperatures and that the adsorption process is spontaneous. The entropy (ΔS°) positive value shows that structural modification appear in the adsorbent and that the surface heterogeneity increases during the adsorption process. This process is characteristic for the activated carbon CAN-Cl, one of reasons is the release of water molecules as a consequence of the exchange between the nitrite ions and functional groups on the carbon surface.

Table 4.5. Thermodynamic constants calculated for activated carbon CAN

<i>T, K</i>	$\Delta G^\circ, J/mol$	$\Delta H^\circ, kJ/mol$	$\Delta S^\circ, J/(mol \cdot K)$
283	969.3635	-0.0143	-3.4375
288	993.4261		
298	1024.364		
313	1079.364		

Table 4.6. Thermodynamic constants calculated for activated carbon CAN-Cl

<i>T, K</i>	$\Delta G^\circ, J/mol$	$\Delta H^\circ, kJ/mol$	$\Delta S^\circ, J/(mol \cdot K)$
283	-14561.6	0.1477	51.6372
288	-14923.0		
298	-15387.8		
313	-16213.9		

The testing of copper and manganese oxides catalysts (on the activated carbon as support) for removal (adsorption/oxidation) of nitrite ions from water highlights the samples modified with copper oxides from the E series and the samples modified with manganese from the C series [21]. Meanwhile, the removal capacity of nitrite ions from water in presence of catalysts modified with copper oxides (E-Cu-Na₂CO₃, C-1-Cu-Na₂CO₃) reaches ~90% and is in agreement with the redox activity of the catalysts evaluated via the chemiluminescence method [21].

The testing of local activated carbons (LLC Ecosorbent, Republic of Moldova) obtained from nut shells and apple wood (CA-N and CA-M), modified via oxidation with nitric acid (CA-Mox) and with nitric acid/urea mixture (CA-Mox-u and CA-Nox-u) for the nitrite ions removal has been performed on natural water from Valea Morilor spring (Chisinau). The results demonstrates the necessity of use of oxidized AC in the process of nitrite ions removal from water in oxic conditions. The AC efficiency decreases in the order: CA-Mox>CA-Mox-u~CA-Nox-u>CA-M~CA-N [17].

4.2. Evaluation of the adsorption process of metal ions on activated carbons

The adsorption process of toxic metal ions (Co, Sr, Cd, Pb, Hg, Cs) on activated carbons (CA-M, CA-N, CA-Mox, CA-Mox-u, CA-Nox-u) has been investigated as function of pH, concentration and temperature. The pH and conductivity values had been recorded in solutions. The comparative analysis of activated carbon adsorption capacity for toxic metal ions from solutions highlights the samples modified via oxidation for adsorption of Co, Pb, Cd and Sr ions [4].

Kinetics of metal ions adsorption process. For the in-depth study of the metal ions adsorption process on activated carbons, salts of (Co(NO₃)₂ and Sr(NO₃)₂) have been selected. The adsorption process has been described using the following kinetic models: pseudo-first order, pseudo-second order, intraparticle diffusion models (Weber-Morris model). The cobalt and strontium ions adsorption on initial and oxidized activated carbons is very well described by the pseudo-second order kinetic model (Tables 4.7 and 4.8) [26, 27]. The applicability of the pseudo-second order kinetic model suggests that the adsorption of cobalt and strontium ions on initial and oxidized activated carbons is based on chemisorption, implying an electron exchange among the adsorbate and the adsorbent whereas the cobalt and strontium ions are attached on the surface by chemical bond.

Table 4.7. Kinetic parameters and q_e values of the adsorption process of cobalt ions ($C_0= 2$ mmol/L) on oxidized activated carbons. Pseudo-second kinetic model (Ho and McKay)

Sample	$q_e(exp), mmol/g$	$K_2, g/mmol \cdot min$	$q_e(cal), mmol/g$	R^2
CA-Mox	0.085	0.91398	0.087	0.999
CA-Mox-u	0.056	0.76945	0.058	0.999
CA-Nox-u	0.041	1.32650	0.043	0.999

Table 4.8. Kinetic parameters and q_e values of the adsorption process of strontium ions ($C_0= 1$ mmol/L) on oxidized activated carbons. Pseudo-second kinetic model (Ho and McKay)

Sample	$q_e(exp), mmol/g$	$K_2, g/mmol \cdot min$	$q_e(cal), mmol/g$	R^2
CA-M	0.032	2.37233	0.033	0.999
CA-N	0.034	2.13791	0.035	0.991
CA-Mox	0.076	1.56193	0.077	0.999
CA-Mox-u	0.041	1.47768	0.043	0.999
CA-Nox-u	0.034	1.89445	0.035	0.999

The prediction of the velocity limitation stage is a factor that should be considered in the adsorption process. The dependence of cobalt(II) and strontium(II) ions adsorption as function of square root of contact time, according to Weber-Morris model, on activated carbons is multilinear and contains three stages, the first two stages of intraparticle diffusion suggest that the adsorption

process occurs via the phase of adsorption on the surface of the AC particle and intraparticle or pores diffusion. The third stage is the stage when adsorption equilibrium is established (Figure 4.4).

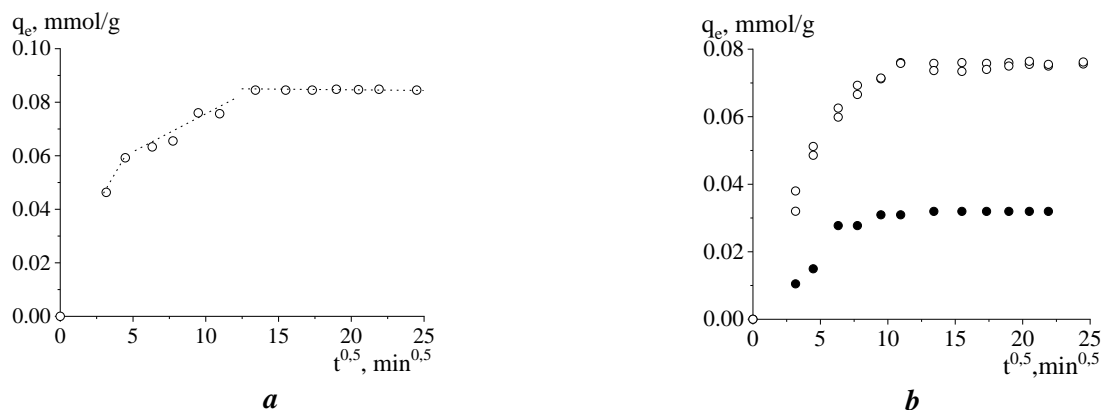


Fig. 4.4. Intraparticle diffusion kinetic model (Weber-Morris) for cobalt ions adsorption on oxidized activated carbons CA-Mox (a) and for strontium ions adsorption on activated carbons CA-M (●) and CA-Mox (○) (b)

Adsorption isotherms of metal ions on activated carbons. The process of cobalt(II) and strontium(II) ions adsorption has been described by applying the theoretical isotherm models of Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich. The experimental data for cobalt ions adsorption on the oxidized activated carbons (CA-Mox, CA-Mox-u, CA-Nox-u) are best described by the Langmuir model (Figure 4.5, Table 4.9).

The separation factor (R_L) estimated from the Langmuir constant, demonstrates that the process of strontium(II) and cobalt(II) ion adsorption onto oxidized activated carbons is favorable. Which, is also confirmed by the empiric parameter $1/n$, estimated for the Freundlich theoretic model ($1/n$ ranges from 0 to 1). The free energy estimated from the Dubinin-Radushkevich model determined that chemical sorption takes place for the modeled system.

Table 4.9. Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich isotherm constants for the adsorption of cobalt ions on oxidized activated carbons

<i>Isotherm model</i>	<i>Parameters</i>	<i>CA-Mox</i>	<i>CA-Mox-u</i>	<i>CA-Nox-u</i>
<i>Langmuir</i>	K_L (L/mmol)	8.096	3.768	7.357
	Q_0 (mmol/g)	0.075	0.069	0.040
	R^2	0.989	0.979	0.999
R_L		$6.1 \times 10^{-6} \div 1.6 \times 10^{-5}$	$1.2 \times 10^{-5} \div 1.6 \times 10^{-5}$	$6.1 \times 10^{-6} \div 0.00022$
<i>Freundlich</i>	K_f (mmol/g)	0.059	0.057	0.031
	n	3.883	2.075	4.120
	R^2	0.941	0.935	0.891
<i>Temkin-Pyzhev</i>	K_T (L/g)	974.728	56.759	298.501
	B_T	0.009	0.013	0.006
	R^2	0.970	0.923	0.938
<i>Dubinin-Radushkevich</i>	K_{ads} (mol ² /kJ ²)	9.23×10^{-9}	2.24×10^{-8}	1.67×10^{-8}
	Q_0 (mmol/g)	0.067	0.051	0.037
	E (kJ/mol)	7360.107	4724.556	5471.756
	R^2	0.955	0.870	0.922

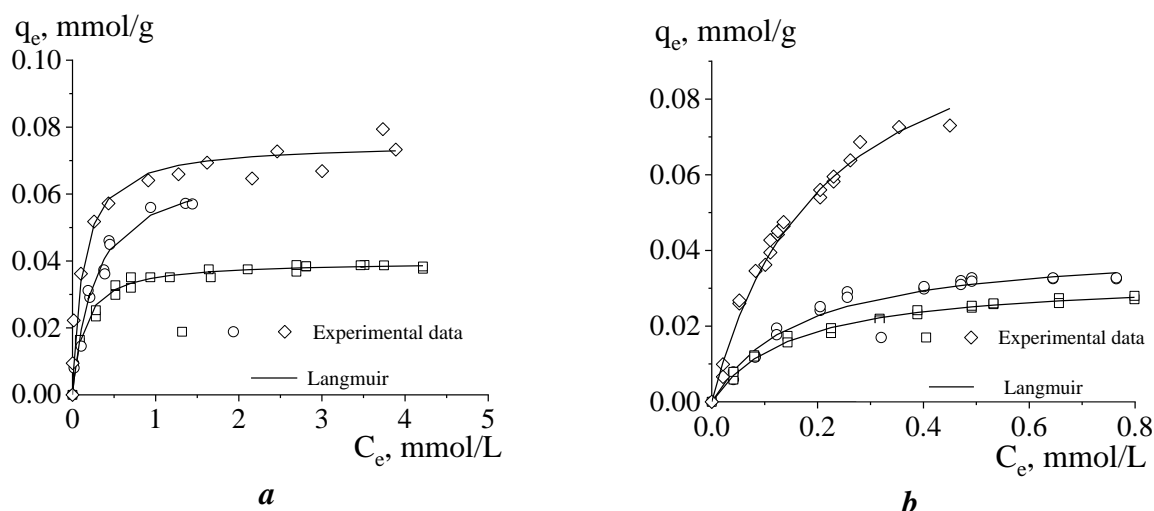


Fig. 4.5. Adsorption isotherms of (a) cobalt ions and (b) strontium ions on oxidized activated carbons: (\diamond) CA-Mox, (\circ) CAMox-u and (\square) CA-Nox-u. Solid:liquid ratio - 1:100, pH 4

According to literature data, the radius of hydrated ions of cobalt(II) and strontium(II) is very close as value (0.412 nm and 0.423 nm); the hydration free energy is lower for cobalt(II) ions and the electronegativity is higher, which means that cobalt(II) ions may have a higher affinity for the activated carbon surface. Under the experimental conditions of the current work, the adsorption capacity for cobalt(II) ions is comparable with the one for strontium(II).

The pH influence on the process of metal ions adsorption on activated carbons. The pH value is an important parameter for the adsorption of metal ions from aqueous solutions, because it affects the metal ions solubility, the concentration of ions associated to the adsorbent functional groups and the ionization degree of functional groups during the reaction. In case when the solution pH is higher than the adsorbent pH_{pzc} , the negative charge from the surface ensures favorable electrostatic interactions for the cationic species adsorption. For the samples of activated carbons used in the Co(II) and Sr(II) ions adsorption from aqueous solutions, the pH_{pzc} value decreases as follows: CA-Mox (2,3) > CA-Mox-u (3,3) > CA-Nox-u (3,9) > CA-M (6,9) > CA-N (8,3).

The pH influence on the adsorption (removal) of cobalt(II) and strontium(II) ions from the solution in the presence of activated carbons is represented in Figure 4.6. It should be noted that the values of pH and electrical conductivity of final solutions is different than of the initial solutions. In case of cobalt(II) ions removal, the pH of initial solutions varies from 1 to 10 (the conductivity value ranges from 118 to 128 $\mu S cm^{-1}$), while pH at equilibrium varies in steps. As shown in Figures 4.6-4.7, for the removal rate of cobalt(II) ions (variation of pH and conductivity at equilibrium), the behavior of initial activated carbons CA-M and CA-N, and the oxidized ones CA-Mox-u and CA-Nox-u is similar: nothing happens on the pH range from 1 to 2, the pH value is constant and the cobalt ions removal rate is null. This fact is also demonstrated by the conductivity of the solutions.

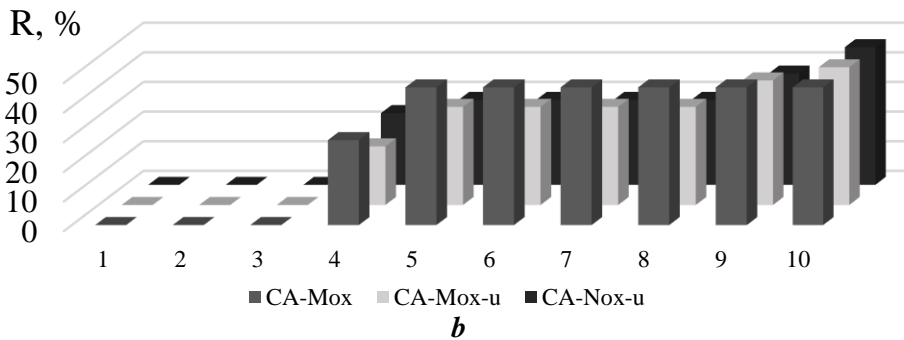
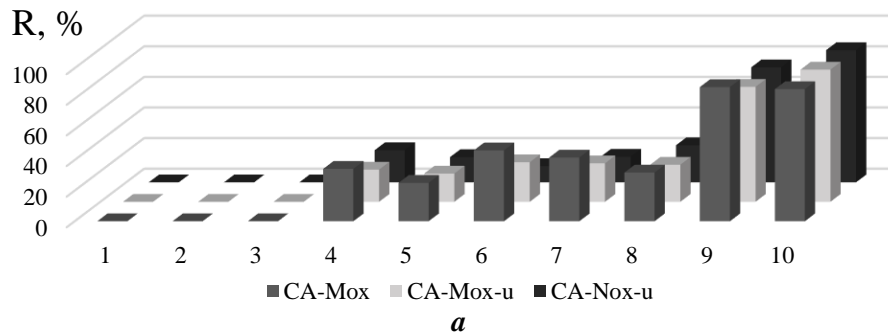


Fig. 4.6. The pH influence on the adsorption (removal) of cobalt(II) and strontium(II) ions from the solution in the presence of oxidized activated carbons.
Removal rate (R, %) of cobalt(II) ions (a) and strontium(II) ions (b) from solutions

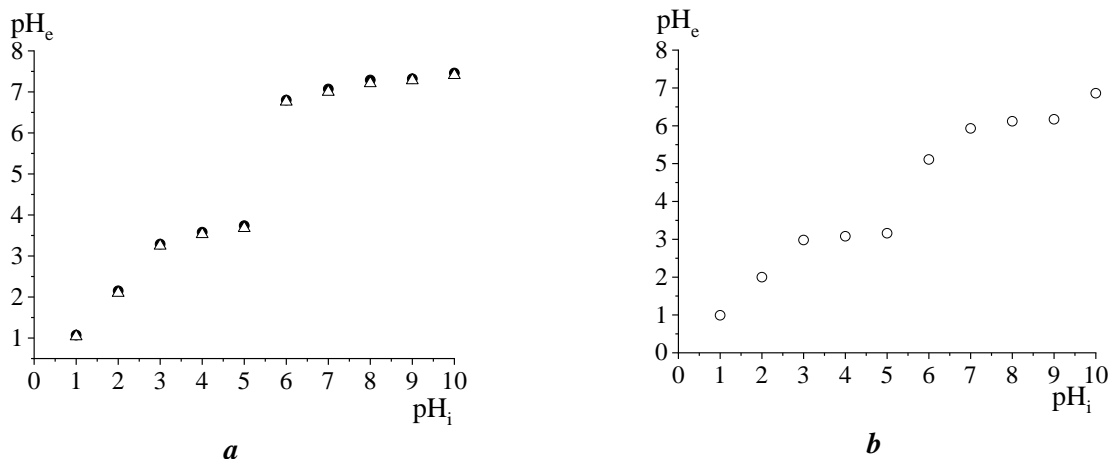


Fig. 4.7. The pH influence on the adsorption (removal) of cobalt(II) ions from solutions in the presence of oxidized activated carbons:
(a) and (b) pH variation in equilibrium solutions Δ CA-Nox-u, \bullet CA-Mox-u, \circ CA-Mox

The second stage is on the pH interval 3-5; within this range, the equilibrium pH varies between 3.25-3.70. On the same interval, one observes an increase of the removal rate of cobalt ions, comparable values for these four types of AC (CA-M, CA-N, CA-Mox-u, CA-Nox-u). It is unclear if acidic functional groups from the carbon surface were involved for the cobalt ions adsorption. The pH_{pzc} value for the oxidized samples is 3.3 (CA-Mox-u) and 3.9 (CA-Nox-u), for the pH of solutions, some acid functional groups from the oxidized activated carbon surface should be ionized. For solutions with initial pH 6, the value of pH at equilibrium suddenly increases up to ~6.8. This phenomenon can be explained by the presence of various forms of cobalt ions in solution, e.g.,

Co(OH)^+ , Co(OH)_2 , Co(OH)_3^+ , at pH near 8, therefore, the effect of cobalt ions removal is decreased. For the next stage, the initial pH of the solutions (7-10) decreases down to 7.0-7.5 at equilibrium. On this interval, most probably, the precipitation of cobalt ions take place but not the adsorption, because the conductivity value is nearly constant in these solutions (Figure 4.7). On the diagram of cobalt ions removal from solution, at pH 9 and 10 the removal rate increases until ~85%. However, this is due to the precipitation of the cobalt ions in the hydroxide form (Figure 4.6 a).

The influence of the solution pH on cobalt ions adsorption on various adsorbents had been studied by several researchers. Nevertheless, the pH interval when cobalt ions adsorption occurs is different and some have reported that maximum adsorption occurring in the pH interval 3-5; 6.5; 7.

The oxidized activated carbon CA-Mox, when compared to other samples, behaves slightly different in solution. On the pH interval 1-2, the pH value at equilibrium remain constant, the removal rate of cobalt ions is null (Figure 4.7). With the increase of initial solution pH, i.e., pH interval 3-5, the pH at equilibrium decreases to ~3 (2.98-3.16). This pH interval is higher than the pH_{pzc} of this activated carbon (2.3) and the cobalt ions adsorption depends of the dissociation state of weak acidic functional groups. At pH higher than 5, the number of competitive hydrogen ions is lower and more functional groups are dissociated, the charge on surface of the activated carbon CA-Mox becomes more negative and, therefore, contributes to the cobalt ions adsorption via ion exchange. For the solution with initial pH 6, in the case of sample CA-Mox, the solution pH at equilibrium (Figure 4.7) does not increase, instead it decreases to 5.1, also, the increase of the adsorption rate of cobalt ions is observed. This can be explained by two effects: (i) at pH 6, the dissociation of strong acidic functional groups from the surface of CA-Mox begins, hydrogen ions are released in solution (solution pH decreases) and adsorption of cobalt cations occurs; (ii) $\text{pH } 6 > \text{pH}_{\text{pzc}}$ of activated carbon CA-Mox; the surface is more negatively charged and attracts positively charged cobalt ions. From the Figure 4.7, the variation of the pH value at equilibrium (and of the conductivity), it is highlighted that cobalt ions adsorption occurs up to pH 8 of the initial solutions (equilibrium pH of 5.9-6.1).

Generally, functional groups from the activated carbons surface possess affinity and adsorption capacity for heavy metal ions, because they are able to donate a pair of electrons, thus bonding the metal via chelation or complexation. The adsorption mechanism is explained by surface complexation, diffusion in adsorbent micropores, chemisorption, ion exchange and electrostatic interactions, which may occur in singular or complex modes.

The obtained results show that acidic functional groups formed on the activated carbon surface CA-Mox (via oxidation with nitric acid) had led to the increase of the ion exchange capacity among the cobalt(II) ions and the following functional groups: hydroxyl (-OH), carboxyl (-COOH), carbonyl (-C=O). Other researchers have also tried to explain a dependence between the point of zero charge (PZC), solutions pH and the character of surface functional groups. The studies have revealed that

the modification of the solution pH leads to the change of the activated carbon surface charge, which is different for different solution pH values. It is also mentioned that carboxylic and lactone groups dissociate in aqueous solutions, the H^+ ions transfer in solution and the activated carbon surface remains negative charged $-COO^-$.

In case of strontium(II) ions adsorption onto activated carbons CA-M, CA-N, CA-Mox-u, CA-Nox-u and CA-Mox, the adsorption capacity depends on the solutions pH value. At initial solution $pH < 3$, the value of pH at equilibrium is not modified for all the investigated samples, the strontium ions adsorption does not occur, which suggests the complete protonation of the functional groups from the activated carbon surface (Figure 4.6 b). For higher pH values (4-7), the removal rate of strontium ions from solution is increased; this observation is in agreement with the conductivity value at equilibrium for this pH range. On the pH interval 8-10 of initial solution, the removal rate of strontium ions slightly increases, but the pH value at equilibrium remain constant around 6 for CA-M, CA-N, CA-Mox-u and CA-Nox-u carbons and in the range of 4 and 5 for CA-Mox. For the all activated carbons, the solution conductivity at equilibrium tends to decrease. In aqueous solutions, strontium is found as Sr^{2+} ions and $SrOH^+$ species on a broad pH interval but $SrOH^+$ as the main form at $pH > 12.8$. The strontium ions removal capacity at pH higher than 7 is due to a combined effect of adsorption and precipitation on the activated carbon surface.

The proposed mechanisms for the adsorption of different species on activated carbons

By corroborating the obtained results regarding the characterization of carbonaceous adsorbents surface chemistry and the pollutants adsorption capacity as function of the solution pH and temperature, mechanisms of pollutants adsorption are proposed.

- ***Initial activated carbons***, which are poor in functional groups on surface, in the adsorption process C_π sites participate. These sites or adsorption centers (C_π) are strongly influenced by the solution pH value, in the acidic domain, protons (H^+) are concentrated on C_π sites and the positively charged graphitic structure of activated carbon attracts the nitrite ions.

- ***Modified activated carbons***. Adsorption via the mechanism of protonation of hydroxyl groups (-OH) on the activated carbon surface. On the surface of initial activated carbons, with a weak basic surface, there are few hydroxyl groups from alcohols and phenols, while on the surface of oxidized activated carbons there are more hydroxyl groups from alcohols, phenols and carboxylic acidic.

In the basic domain, OH^- ions are competitive with the nitrite ions, the graphitic surface of activated carbon becomes negatively charged and, consequently, rejects the nitrite ions.

For the metal ions adsorption onto activated carbons, at $pH < 3$ there is a competition between the H^+ and Me^{2+} ions for the same adsorption site.

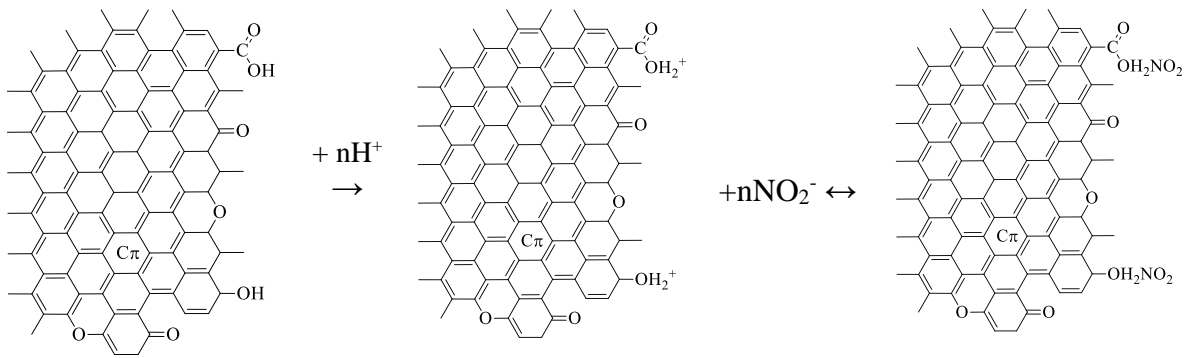


Fig. 4.8. Schematic presentation of the nitrite ions adsorption on the surface of the modified activated carbon. (1) - protonation of functional groups on the surface of activated carbon; (2) - adsorption of nitrite ions by electrostatic interaction

- **On the interval $pH < pH_{pzc}$ of activated carbons.** Generally, at values of $pH < pH_{pzc}$, the metal ions adsorption on activated carbons may occur via the complexation mechanism (between the oxygen atoms from C=O groups from the activated carbon surface and the metal ions) and electrostatic interactions.

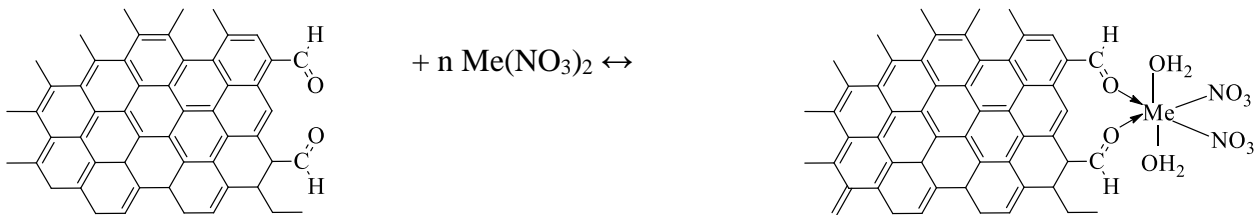


Fig. 4.9. Schematic presentation of the adsorption of metal ions on activated carbons by complexation

Generally, $C_{\pi} - Me^{n+}$ (cation) interactions are attributed to electrostatic interactions between the aromatic rings of carbonaceous adsorbents (with basic surface) and metal cations. On the activated carbon surface, according to some authors, the π (C_{π}) electrons possess weak negative charge properties. The positions with C_{π} electronic density could correspond to the basic functional groups determined via the Boehm method (chromene, ketones and pyrones structures).

- **On the interval of $pH 3 \div 5$. Oxidized activated carbons**

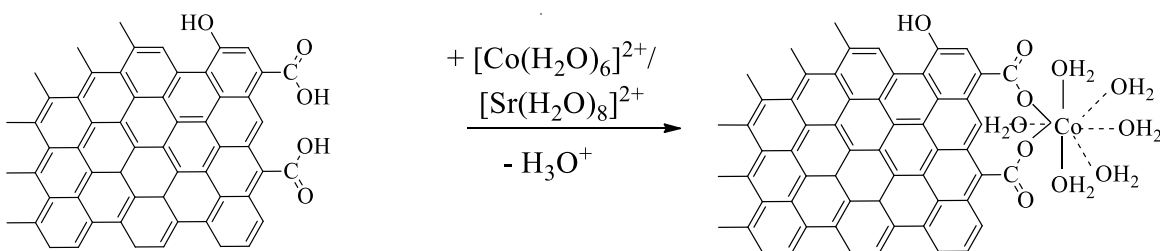


Fig. 4.10. Schematic presentation of the adsorption of metal ions on oxidized activated carbons by ion exchange and the formation of metal-ligand complexes on the surface

- **On the pH interval 5÷7.** For oxidized activated carbon, within this interval the weak acidic functional groups dissociate, e.g., lactones. At the same time, the species of Co(II) , Co(OH)^+ , Co(OH)_2 , Co(OH)_3^+ begin to form in the solution.

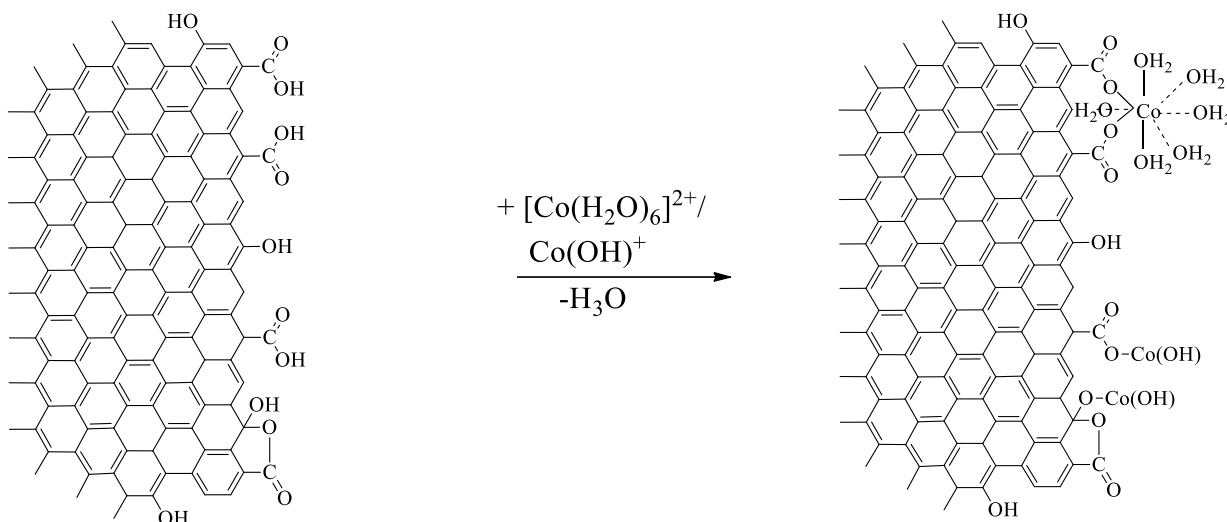


Fig. 4.11. Schematic presentation of the adsorption of Co(II) ion species on the surface of oxidized activated carbon by ion exchange and complexation

- **On the pH > 7 interval.** For oxidized activated carbons, within this interval the dissociation of hydroxyl groups (from phenols and alcohols, $-\text{OH}$; $\text{pK} \sim 9\text{-}13$) begins, also in this interval $\text{Co(OH)}_2\downarrow$ and $\text{Sr(OH)}_2\downarrow$ hydroxides are formed. Moreover, the increase of the removal rate of Co(II) and Sr(II) ions is mostly due to the precipitate formation of these hydroxides in solution or on the activated carbon surface. In conclusion, under the modeled conditions, for the studied metal ions, hydroxyl groups do not participate in the adsorption process.

4.3. The estimation of activated carbons price

The estimative price of 1 kg of activated carbon modified with chlorine ions CAN-Cl is **601.31 lei**. In the calculation, it was considered the raw material (455.28 lei), electricity (9.45 lei) and other costs (136.58 lei). Comparative analysis reveals that the CAN-Cl price is about 3.5 times lower than the price of AG-5ox carbons – recommended for nitrite ions adsorption from solutions.

The estimative price of 1 kg of activated carbon oxidized with nitric acid/urea mixture (samples CA-Nox-u/CA-Mox-u) is **685.66 lei**. Meanwhile, according to the methodology, the oxidation mixture (nitric acid/urea) can be reused for the oxidation of another quantity of activated carbon. The estimative price of 1 kg of activated carbon oxidized with nitric acid (sample CA-Mox) is **2138.65 lei**.

By comparison, the oxidation methods of activated carbon, it was established that the price of oxidized activated carbons obtained by nitric acid/urea mixture (samples CA-Nox-u/CA-Mox-u) is ~ 3 times lower than the price of activated carbons oxidized with nitric acid (CA-Mox).

CONCLUSIONS AND RECOMMENDATIONS

1. New carbonaceous adsorbents had been obtained by modifying the surface with chlorine ions; metal oxides (of copper and manganese) and oxidation. The parameters of activated carbon structure have been determined from the nitrogen sorption isotherms. According to the obtained results, all the carbonaceous adsorbents are mostly microporous.
2. The surface chemistry of the studied activated carbons has been investigated by complementing the pH-metric titration and the Boehm technique, in order to establish the acidic-basic properties of the adsorbents, whilst the IR spectroscopy and temperature programmed decomposition (TPD-MS) were used to detail the surface functional groups.
3. The results reveal the importance of surface chemistry in the process of impregnation with copper and manganese oxides, and that the basic surface of carbonaceous adsorbents favors the metal oxides bond. Depending on the temperature and treatment medium, manganese oxides $\text{Mn}^{\text{IV}}\text{O}_2$, $\text{Mn}^{\text{II}}\text{Mn}_2^{\text{III}}\text{O}_4$, $\text{Mn}_2^{\text{III}}\text{O}_3$, $\text{Mn}^{\text{II}}\text{O}$ can be formed in various ratio and quantity.
4. The presence of chlorine in the CAN-Cl sample (with a quantity of ~2%) has been demonstrated via elemental analysis and scanning electron microscopy technique (SEM-EDX). The application of IR spectroscopy, pH-metric titrations and temperature programmed decomposition (TPD) highlights the formation of oxygen-containing functional groups onto the surface of activated carbon and the decrease of pH_{pzc} value down to 5.75.
5. The presence of functional groups onto the surface of activated carbons obtained from nut shells and apple wood have been determined by IR spectroscopy, pH-metric titrations and the Boehm method. The following carboxylic groups have been identified onto the surface of activated carbon: strongly acidic groups (CA-Mox, 0.95 meq/g; CA-Mox-u, 0.44 meq/g; CA-Nox-u, 0.32 meq/g), weakly acidic and phenolic groups, while the pH_{pzc} value of the studied activated carbons decreases as follows: CA-Mox (2.3) > CA-Mox-u (3.3) > CA-Nox-u (3.9) > CA-M (6.9) > CA-N (8.3).
6. The kinetics of the adsorption process of nitrite ions on CAN and CAN-Cl activated carbons has been investigated by applying the following models: pseudo-first order kinetic, pseudo-second order kinetic, intraparticle diffusion models. The results reveal that the nitrite ions adsorption onto activated carbons CAN and CAN-Cl follows the pseudo-second order kinetic model, and, also corresponds to the intraparticle diffusion model suggesting that the adsorption process is governed by chemical adsorption.
7. The theoretical isotherm models of Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich have been applied. The experimental data is best described by the Langmuir adsorption model showing that the adsorption process is dominated by chemisorption on the energetically homogenous surface. For both carbons (CAN and CAN-Cl) the separation factor (R_L) value was found within the limits ($0 < R_L < 1$) meaning that the adsorption process of nitrite ions is favorable. This is also confirmed by the obtained values of the Freundlich isotherm model ($1/n$). The values of the adsorption free energy (E), obtained from the Dubinin-Radushkevich model, demonstrates that the process is governed by chemical adsorption.
8. The comparative analysis of the kinetic curves and isotherms of nitrite ions adsorption onto CAN and CAN-Cl activated carbons, reveals that the modification of the activated carbon surface with chlorine ions contributes to the increase of the velocity and adsorption capability for nitrite ions by ~50 times.
9. The thermodynamic parameters, i.e., Gibbs energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), have been determined for the adsorption process of nitrite ions onto CAN and CAN-Cl activated carbons. The obtained data reveal that the adsorption process for CAN-Cl activated carbon is spontaneous and endothermic, whilst for the CAN activated carbon, the value of ΔG° has a negative effect on the stability of the bond between the nitrite ions and the activated carbon, and the process is exothermic.
10. The adsorption process of strontium(II) and cobalt(II) ions on activated carbons has been studied by applying the following models: pseudo-first order model, pseudo-second order model and intraparticle diffusion model, as well as theoretic isotherms models of Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich. The experimental data are best described by the pseudo-second kinetic model suggesting that the adsorption of metal ions (cobalt(II), strontium(II)) onto oxidized activated carbons is based on chemisorption. The constants determined for the Freundlich and Langmuir modes and the energy values estimated by Dubinin-Radushkevich, demonstrate that the adsorption

process of strontium(II) and cobalt(II) ions onto oxidized activated carbons is favorable and dominated by chemisorption of the energetically homogenous surface in the modeled system.

11. The investigations highlight the important role of the solution pH, of the functional groups from the activated carbons surface and the pH_{pzc} value for the adsorption process of cobalt(II) and strontium(II) ions. It should be noted that depending on the surface chemistry and solution pH, the adsorption of strontium(II), cobalt(II) and nitrite ions occurs via different mechanisms:

- In the process of nitrite ions adsorption on initial activated carbons (which are scarce in functional groups on surface, for $pH(3\div 5) < PZC$), between the protonated C_π sites and nitrite ions, a mechanism of electrostatic interaction has been proposed. For modified activated carbons, the mechanism of protonation of hydroxyl groups (-OH) from the activated carbon surface has been proposed.
- For $pH < pH_{pzc}$ values, the adsorption of metal ions on activated carbons may occur through the complexation mechanism (between oxygen atoms from C=O groups from the activated carbon surface and metal ions) and electrostatic interactions.
- For the adsorption of metal ions on initial activated carbons (with basic surface, on the pH interval $3\div 5$), has been proposed the mechanism of adsorption via electrostatic interactions between the C_π sites and metal ions. For oxidized activated carbons, has been proposed the mechanism of ion exchange between the carboxylic groups and metal ions and formation of metal-ligand complexes on surface.
- On the pH interval $5\div 7$, for the oxidized activated carbon (within this interval, the weak acidic functional groups of lactone type dissociate), the mechanism of adsorption of cobalt(II) ion species on the surface of the oxidized activated carbon via ion exchange and complexation has been proposed. On the interval of $pH > 7$ (for oxidized activated carbons), dissociation of hydroxyl groups begins (from phenols and alcohols, -OH; $pK \sim 9-13$). Also on this domain, cobalt(II) and strontium(II) hydroxides ($Co(OH)_2 \downarrow$ and $Sr(OH)_2 \downarrow$) are formed.

12. The price of oxidized activated carbon obtained by different methods has been estimated. The price of activated carbons oxidized with nitric acid/urea mixture is ~ 3 times lower than the price of activated carbons oxidized with concentrated nitric acid.

13. Considering the low price and the characteristics of activated carbons modified with chlorine ions (CAN-Cl sample) for adsorption of nitrite ions at low pH values (the low contain of ash is also an advantage), it is recommended the use of this type activated carbon as an enterosorbent for adsorption/elimination of nitrite ions from the human body (pH of the stomach varies from 1-2 to 4-5).

14. The testing of the local activated carbons obtained from nut shells and apple wood (CA-N and CA-M), modified by oxidation (CA-Mox, CA-Mox-u and CA-Nox-u) for the removal of nitrite ions from natural water (Valea Morilor spring, Chisinau), demonstrates the necessity of the use of oxidized activated carbon for such applications. The activated carbons efficiency decreases in the order: CA-Mox > CA-Mox-u ~ CA-Nox-u > CA-M ~ CA-N.

Practical recommendations

1. A mixture of nitric acid and urea (at $t=95^\circ C$) is proposed for the modification of the activated carbon surface. The advantage of this method consists in avoiding the formation of humic or fulvic acids, therefore the process does not require stage of activated carbon washing with alkaline solutions. The price of activated carbons oxidized with nitric acid/urea mixture is ~ 3 times lower than the price of activated carbons oxidized with concentrated nitric acid.

2. For pH-metric titrations of activated carbon suspensions, the following experimental conditions are recommended: the use of automatic titrator with propeller stirrer in order to avoid the grinding of activated carbon samples; the use of as homogenous as possible fraction of activated carbon; the solid-liquid ratio ($0.2\div 0.4$ g/60 mL); a titrant concentration of $0.01\div 0.02$ M; a titrant debit of $0.05\div 0.1$ mL/min; a sample moistening time of $48\div 72$ hours; titration medium: argon; agitation of the carbon suspension for ~ 60 min in argon medium before titration: monotonic equivalence point titration (MET).

3. The use of ABTS radical-cation method adapted for heterogeneous systems is recommended for the evaluation of redox properties of the carbonaceous adsorbents.

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ADNOTARE

Gînsari Irina, „Evaluarea influenței chimiei suprafeței adsorbanților carbonici în procesul de adsorbție a poluanților”, teză de doctor în științe chimice, Chișinău, 2021

Structura tezei. Teza include introducere, patru capitole, concluzii generale și recomandări, bibliografia din 334 surse, volumul total de pagini 214, 45 tabele, 82 figuri și 9 anexe. Rezultatele obținute sunt publicate în 24 de lucrări științifice.

Cuvinte-cheie: cărbuni activi, modificare, chimia suprafeței, adsorbție, ioni de nitrit, ioni de cobalt, ioni de stronțiu, cinetică, izoterme.

Domeniul de studiu: 144.01 – chimie fizică

Scopul tezei: constă în modificarea suprafeței și corelarea chimiei suprafeței adsorbanților carbonici cu proprietățile lor sorbtive și/sau catalitice.

Obiectivele de cercetare: ● modificarea chimiei suprafeței cărbunilor activi; ● evaluarea caracteristicilor fizico-chimice (izoterme de sorbție-desorbție a azotului; analiza termică; difracție cu raze X (XRD); studiul cu microscopia electronică de baleiaj cuplat cu un analizator de elemente (SEM-EDX)); ● evaluarea chimiei suprafeței (titrări electrometrice, pH_{pzs} , spectroscopia FTIR); ● evaluarea proprietăților redox (metoda chemiluminiscenței, metoda cation-radical ABTS); ● elucidarea particularităților de interacțiune și/sau sorbției specifice, efectului structurii poroase și a chimiei suprafeței, în vederea corelării proprietăților de suprafață ale adsorbanților carbonici cu proprietățile lor sorbtive și/sau catalitice pentru eficientizarea procesului de adsorbție a poluanților.

Noutatea și originalitatea științifică rezidă în elucidarea particularităților de interacțiune și/sau sorbției specifice în funcție de pH și chimia suprafeței adsorbanților carbonici. Pentru prima dată au fost propuse mecanisme de adsorbție a ionilor pe un interval larg de pH luând în considerare pH-ul mediului, gradul de ionizare al grupelor funcționale (pH_{pzs}) și forma ionilor în soluție. Pentru prima dată a fost adaptată și propusă metoda cation-radical ABTS pentru evaluarea proprietăților redox a adsorbanților carbonici (sisteme eterogene). A fost propusă o metodă nouă, mai economă, de oxidare a cărbunilor activi cu amestec de acid azotic/uree.

Problema științifică soluționată constă în identificarea mecanismelor de adsorbție a ionilor de nitrit și metale bivalente pe adsorbanți carbonici modificați în funcție de chimia suprafeței și pH.

Semnificația teoretică. Rezultatele cercetării contribuie la lărgirea informației științifice privind metodele de evaluare a chimiei suprafeței adsorbanților carbonici. De asemenea, acest studiu corelează proprietățile de suprafață ale adsorbanților carbonici cu proprietățile lor sorbtive și/sau catalitice în scopul eficientizării procesului de adsorbție a poluanților.

Valoarea aplicativă. Cercetările aplicative derulate în cadrul acestei teze oferă posibilitatea evaluării proprietăților redox a adsorbanților carbonici prin metoda cation-radical ABTS, dar și optimizarea metodelor cunoscute de modificare a cărbunilor activi, care contribuie la micșorarea prețului de cost al acestora.

Implementarea rezultatelor științifice. Adsorbanții carbonici modificați (oxidați cu acid azotic și amestec de acid azotic/uree) au fost testați pentru eliminarea ionilor de nitrit din apă naturală. Metoda cation-radical ABTS, adaptată pentru evaluarea proprietăților redox în sisteme eterogene a fost utilizată în cercetare.

Posibilități de aplicare în practică: (i) a metodei de oxidare a cărbunilor activi cu amestec de acid azotic/uree, ce permite obținerea sortimentelor de cărbuni cu un preț de cost mic; (ii) a adsorbanților carbonici modificați cu ioni de clor în calitate de enterosorbanți pentru adsorbția/eliminarea ionilor de nitrit din sistemul digestiv.

АННОТАЦИЯ

Гынсарь Ирина, «Оценка влияния химии поверхности углеродных адсорбентов в процессе адсорбции загрязняющих веществ», докторская диссертация по химическим наукам, Кишинэу, 2021

Структура диссертации: Диссертация включает введение, четыре главы, общие выводы и практические рекомендации, библиографию из 334 источников, общий объем страниц 214, таблиц 45, рисунков 82 и 9 приложений. Полученные результаты опубликованы в 24 научных работах.

Ключевые слова: активированные угли, модификация, химия поверхности, адсорбция, нитрит-ионы, ионы кобальта, ионы стронция, кинетика, изотермы.

Область исследования: 144.01 – Физическая химия

Цель данной работы состоит в модификации поверхности и корреляции химического состава поверхности углеродных адсорбентов с их сорбционными и/или каталитическими свойствами.

Задачи исследования: • изменение химии поверхности активированного угля; • оценка физико-химических характеристик (изотермы адсорбции-десорбции азота; термический анализ; рентгеноструктурный анализ (XRD); электронный микроскоп с элементным анализатором (SEM-EDX)); • оценка химии поверхности (рНметрическое титрование, $pH_{тнз}$, FTIR); • оценка редокс свойств (хемилюминесцентный метод, катион-радикал ABTS метод); • выяснение особенностей взаимодействия и/или специфической сорбции, влияния пористой структуры и химии поверхности с целью сопоставления поверхностных свойств углеродных адсорбентов с их сорбционными и/или каталитическими свойствами для улучшения адсорбции загрязняющих веществ.

Научная новизна и оригинальность: заключается в выяснении особенностей взаимодействия и/или специфической сорбции в зависимости от рН и химии поверхности углеродных адсорбентов. Впервые предложены механизмы адсорбции ионов в широком диапазоне рН с учетом рН среды, степени ионизации функциональных групп ($pH_{тнз}$) и формы ионов в растворе. Впервые, был адаптирован и предложен катион-радикал ABTS метод для оценки редокс свойств углеродных адсорбентов (гетерогенных систем). Предложен новый, более экономный метод окисления активированного угля смесью азотной кислоты и мочевины.

Решенная научная проблема состоит в выяснение механизмов адсорбции нитрит-ионов и двухвалентных металлов на модифицированных углеродных адсорбентах, в соответствии с химией поверхности и рН.

Теоретическое значение: Результаты исследования способствуют распространению научной информации о методах оценки химии поверхности углеродных адсорбентов. Кроме того, это исследование коррелирует поверхностные свойства углеродных адсорбентов с их сорбционными и/или каталитическими свойствами, чтобы улучшить процесс адсорбции загрязнителей.

Внедрение научных достижений. Прикладные исследования, проведенные в этой диссертации, дают возможность оценить редокс свойства углеродных адсорбентов катион-радикал ABTS методом, а также оптимизировать известные методы модификации активированных углей, которые способствуют снижению их себестоимости.

Прикладная ценность работы: Модифицированные углеродные адсорбенты (окисленные азотной кислотой и смесью азотная кислота мочевины) были испытаны для удаление нитрит-ионов из природной воды. В исследовании использовался катион-радикал ABTS метод, адаптированный для оценки редокс свойств в гетерогенных системах.

Возможности практического применения: (i) метод окисления активированных углей смесью азотной кислоты и мочевины, позволяющий получать ассортимент угля по невысокой себестоимости; (ii) углеродные адсорбенты, модифицированные хлорид ионами, в качестве энтеросорбентов для адсорбции/удаления нитрит-ионов из пищеварительной системы.

ANNOTATION

Ginsari Irina, „Evaluation of the influence of carbonaceous adsorbent surface chemistry on the adsorption process of pollutants”, PhD thesis in chemical sciences, Chisinau, 2021

Structure of the thesis. The thesis includes introduction, four chapters, general conclusions and recommendations, References contains 334 titles, total volume of 214 pages, 45 tables, 82 figures and 9 annexes. The obtained results have been published in 24 scientific papers.

Keywords: activated carbons, modification, surface chemistry, adsorption, nitrite ions, cobalt ions, strontium ions, kinetics, isotherms.

Field of investigation: 114.01 – physical chemistry

The purpose of the research consists in the modification of the surface chemistry and the correlation of carbonaceous adsorbents surface chemistry with their sorption and/or catalytic properties.

Objectives of the thesis:

- modification of the activated carbon surface chemistry;
- evaluation of the physical-chemical characteristics (nitrogen sorption-desorption isotherms; thermal analysis; X-ray diffraction (XRD); scanning electron microscope coupled with an element analyser (SEM-EDX));
- assessment of the surface chemistry (electrometric titrations, pH_{pzc} , FTIR);
- evaluation of the redox properties (chemiluminescence method, ABTS radical cation method);
- elucidation of the particularities of interaction and/or specific sorption, the effect of porous structure and surface chemistry, in order to correlate the surface properties of carbon adsorbents with their sorbent and/or catalytic properties in order to improve the adsorption process of pollutants.

Scientific novelty and originality consists in the elucidation of the particularities of specific interaction and/or sorption depending on the pH and surface chemistry of carbonaceous adsorbents. For the first time, mechanisms of adsorptions has been proposed for a broad pH interval, by considering the pH of the medium, the ionization degree of the groups (pH_{pzc}) and the types of ions in solution. For the first time, the ABTS radical-cation method has been adapted for the evaluation of the redox properties of carbonaceous adsorbents (heterogeneous systems). A new and economical method of activated carbon oxidation with nitric acid/urea mixture has been proposed.

The **research hypothesis** consists in modifying the surface chemistry of carbonaceous adsorbents by different methods: modification with chlorine ions, by oxidation (with nitric acid, with a mixture of nitric acid/urea) and impregnation with metals (copper and manganese oxides).

The **solved scientific problem** consists in identifying the adsorption mechanisms of nitrite ions and bivalent metals on modified carbonaceous adsorbents depending on the surface chemistry and pH.

The **theoretical significance.** The research results contribute to the development of scientific information regarding methods of the evaluation of carbon adsorbents surface chemistry. Also, this study correlates the surface properties of carbonaceous adsorbents with their sorbent and/or catalytic properties, in order to enhance the adsorption process of pollutants.

The **applicative value of the work.** The applied research carried out in this thesis offers the possibility to evaluate the redox properties of carbon adsorbents by the ABTS cation-radical method, and, also to optimize the known methods of modifying activated carbons that contribute to decrease of their price.

Implementation of scientific results. Modified carbonaceous adsorbents (oxidized with nitric acid and nitric acid/urea mixture) have been tested for nitrite ions removal from natural water. The ABTS radical-cation method, adapted for the evaluation of the redox properties in heterogeneous systems has been used in the research.

Practical application possibilities: (i) of the oxidation method of activated carbons with nitric acid/urea mixture allows a production of an array of carbons at low prices; (ii) of carbonaceous adsorbents modified with chlorine ions as enterosorbents for adsorption/removal of nitrite ions from the digestive system.

GINSARI IRINA

**EVALUATION OF THE INFLUENCE OF CARBONACEOUS
ADSORBENT SURFACE CHEMISTRY ON THE ADSORPTION
PROCESS OF POLLUTANTS**

144.01 – PHYSICAL CHEMISTRY

Summary of the doctoral thesis in chemical sciences

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