DOI: 10.17344/acsi.2024.8693 *Acta Chim. Slov.* **2025,** *72,* 24–33

Scientific paper

Walnut Shells Activated Carbons for Adsorption of Nitrite Ions

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Received: 12-14-2024

Abstract

In this paper, activated carbons obtained from walnut shells were used as adsorbents to remove nitrite ions from aqueous solutions. The novel adsorbent was obtained by modification with hydrochloric acid. The physical-chemical characteristics of activated carbons were determined from nitrogen sorption isotherms, SEM-EDX, elemental analysis, FTIR, thermal analysis, and temperature programmed decomposition (TPD). According to the results obtained, chlorine is retained on the surface in an amount of 2%. The results of batch experiments indicate that maximum adsorption/ removal of nitrite ions can be achieved at pH = 3, being of 0.2 mg/g for CAN and 4.7 mg/g for CAN-Cl. To study the adsorption of nitrite ions on activated carbons the following mathematical models were used: pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models, and Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin-Pyzhev isotherm models.

Keywords: Activated carbon, modification, adsorption, nitrite ions, theoretical models.

1. Introduction

A variety of technologies have been developed for the removal of different species of ions from water: membrane separation, ion exchange, precipitation, and adsorption; the last frequently used technique for removal of pollutants from contaminated/polluted waters.[1–4]

Activated carbons are efficient adsorbent materials for removing pollutants from water, like heavy metal ions (Pb^{2+}, Cd^{2+}, Hg^{+}, etc.) and anions (F^{-}, S^{2-}, NH_4^{+}, etc.). Furthermore, due to their highly developed porosity and internal surface activated carbons can be used in granular and powder forms, because they are porous materials.[3–6]

One of the ions that are of concern to researchers is nitrite ions because nitrite ions are pretty dangerous for the human body. They can be found almost everywhere: in water, plants, air, and soil, and they can be formed in the digestive tract which can be taken from water as well as from vegetables and fruits.[7] The high level of nitrite in water results from agricultural application of fertilizers. High concentrations of nitrite in drinking water lead to a health problem for humans (especially in infants, which can cause methemoglobinemia).[8]

The absorbed nitrite in the organism is quickly oxidized into nitrate once it has reached the blood. The nitrite that got into the blood is involved in the oxidation of hemoglobin into methemoglobin (methemoglobinemia), that is, Fe^{2+} is oxidized to Fe^{3+}, and the remaining nitrite is firmly bound to the oxidized hemoglobin. Thus, Fe^{3+} does not allow the transport of oxygen through the body due to the strong binding of oxygen.[7] Nitrites can react in the stomach with secondary and tertiary amines or amides from food to form N-nitroso compounds.[9]

Among the processes known for removing nitrite ions from water are: biological nitrification/denitrification, chemical denitrification, catalytic oxidation/reduction, and adsorption. Technologies that use the chemical removal of nitrite from water include ion exchangers, reverse osmosis, and electrodialysis.[2,3,10]

In the process of catalytic reduction of nitrites from water, the catalyst is usually composed of a noble metal such as palladium, platinum, ruthenium, rhodium, or iridium and a transition metal, for example, copper, nickel, iron, silver, indium, or tin on solid support (usually activated carbon).[11–14]

Another chemical method of removing nitrite ions by reduction to nitrogen is the oxidation of nitrite ions to nitrate ions in the presence of catalysts which can occur electrostatically in the presence of complexes with transition metals (manganese, cobalt) or in the presence of metal-modified carbon catalysts.[14,15]

In several research works, another process proposed for the removal of nitrite ions from water is adsorption on activated carbons and according to literature data, the surface of activated carbon is very important. The method of modifying the absorbent, in the case of activated carbons, by oxidizing the surface or treating it with acid, was tried.[6,16–18] Thus, after testing the activated carbons obtained from walnut shells and apple wood and modified by oxidation, the efficiency of the activated carbons decreases in series: CA-Mox > CA-Mox-u ≈ CA-Nox-u >>> CA-M ≈ CA-N.[6] In the same way, comparative studies of the process of adsorption of nitrite ions from water using two other carbonaceous adsorbents were carried out. These carbonaceous adsorbents are: CAN-7 (obtained by the chemical method with phosphoric acid) and AG-5ox (oxidized with nitric acid), they have an acidic surface that ensures a 75% efficiency in removing nitrite ions from water. The carbonaceous adsorbent have good performance for adsorption/removal of nitrite ions from water, but the method of the modification is costly.[18] Considering the high price of the modification by adsorption with nitric acid of the activated carbons used in the process of adsorption of nitrites from the waters, it was decided to find another cheaper method of modifying the carbonaceous adsorbents.

The aim of the work is the use of modified activated carbon for the elimination of nitrite ions from aqueous solutions.

2. Materials and Methods

2. 1. Materials

All the reagents used in this research were of analytical grade. As activated carbons with a fraction of 0.8÷1.3 mm were used local activated carbon obtained from walnut shells via the physical-chemical method of activation with steam CAN (produced at LLC Ecosorbent, Republic of Moldova), and modified with chlorine ions, CAN-Cl.[19] Some general characteristics of the activated carbons samples are presented in Table 1.[19]

Table 1. General characteristics of activated carbons.[19]

Sample	U, %	A, %	D, g/cm^3	Elemental analysis, %			
				C	H	N	Cl
CAN	8.12	1.91	0.494	92.23	1.86	–	–
CAN-Cl	7.82	0.53	0.467	92.77	2.30	–	2.02

U – humidity; A – ash content; D – bulk density.

2. 2. Characterization Methods

The morphological analysis (SEM-EDX) of the samples was performed using the scanning electron microscope, SEM model VEGA II LSH, produced by TESCAN Czech Republic, coupled with an EDX detector type QUANTAX QX2, produced by BRUKER/ROENTEC Germany. The Quantax QX2 instrument is an EDX detector used to perform qualitative and quantitative micro-analysis.

Thermal analysis measurements were performed using a Derivatograph Q-1000 analyzer. The samples were heated from room temperature up to 1000 °C in a flowing air atmosphere (100 mL/min) at a heating rate of 10 °C/min.

The *structure parameters* of activated carbons were determined from nitrogen adsorption-desorption isotherms, on the Autosorb 1- MP.[20]

Infrared (FTIR) spectra of activated carbons were recorded on the FT-IR Spectrometer Spectrum 100 (Perkin-Elmer, USA), using KBr pellets.

The *Temperature Programmed Decomposition (TPD)* profiles of the activated carbons samples were obtained on the thermogravimetric analyzer coupled with a mass spectrometer, TPD-SM. TPD-MS measurements were performed using a control system, which is based on an MX-7304A mass spectrometer (Sumy, Ukraine).

2. 3. Adsorption Experiments

Determination of adsorption from aqueous solutions. Adsorption isotherms were determined from aqueous solutions by contacting the dry activated carbons with a solution of the adsorbate of different concentrations (in ascending order) at the same solid: liquid ratio.[19,21] Adsorption equilibrium time was determined from the kinetic curves. The equilibrium concentration was determined after equilibrium was established, and the adsorption value, expressed in mg/g, was calculated from equation 1:[22]

$$a = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where, C_0 – is the initial adsorbate concentration, mg/L; C_e – the equilibrium concentration of the adsorbate, mg/L; V – is the volume of contact solution, L; m – the mass of the dry adsorbent, g.

The *pH value* of the solutions was measured with a HANNA HI 121 pH meter, and the *conductivity* of the solutions was measured on the multiparameter Consort C535 (Belgium).

Nitrite ion determination method. The determination of nitrite ions in the solution was performed by the colorimetric method with the Griess reagent, at a wavelength of 520 nm, using the KFK-3 spectrophotometer.[23]

2. 4. Mathematical Models

The adsorption process was kinetically analyzed using the following models: the pseudo-first-order kinetic model (Lagergren),[24] the pseudo-second-order kinetic model (Ho and McKay),[25] and the intraparticle diffusion

kinetic model (Weber-Morris).[26] The general expressions of the theoretical models are presented in equations 2–4 and Table S1.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

$$q_t = k_i t^{1/2} \quad (4)$$

Adsorption processes were described with the help of several theoretical models: Langmuir I.,[27] Freundlich H.,[28] Dubinin M. M. and Radushkevich L. V.[29] and Temkin M. and Pyzhev V.[30] The isotherms are presented by equations 5–11 and Table S2.

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (5)$$

The essential characteristic of the Langmuir isotherm can be expressed using the parameter known as the separation factor (R_L).[31]

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

where, C_0 – initial concentration, mg/L; K_L – Langmuir constant, L/mg.

$$q_e = K_F C_e^{1/n} \quad (7)$$

The values of the empirical parameter 1/n range from 0 to 1; the closer the value of 1/n is to 0, the more heterogeneous the surface is. These constants refer to the relative adsorption capacity of the adsorbent and to the adsorption intensity.

$$q_e = (q_s)\, exp - k_{ads}\varepsilon^2 \quad (8)$$

where, q_s – the saturation capacity of the theoretical isotherm; k_{ads} – constant of the Dubinin-Radushkevich isotherm. ε – constant of the Dubinin-Radushkevich isotherm which can be obtained from equation 9.

$$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right] \quad (9)$$

where, R – gas constant, 8.314 J/molK; T – absolute temperature, K; C_e – equilibrium concentration of adsorbate, mg/L.

The relationship between the Dubinin-Radushkevich isotherm constant (k_{ads}) and the average free energy (E) per mole of adsorbent is expressed by the mathematical equation 10:

$$E = \left[\frac{1}{\sqrt{2k_{ads}}}\right] \quad (10)$$

Based on the value of the free energy of adsorption, the Dubinin-Radushkevich model allows the identification of the type of sorption occurring in the modeled systems:

- physical adsorption (1–8 kJ/mol);
- ion exchange adsorption (9–16 kJ/mol);
- chemical adsorption (>16 kJ/mol).[31,32]

$$q_e = \left(\frac{RT}{b}\right) ln\,(K_T C_e) \quad (11)$$

where, RT/b = B_T; R – gas constant (8,31 J/mol K); T – absolute temperature, K.

Thermodynamic studies are important as they can determine what kind of adsorption mechanism occurs (chemical or physical adsorption). The Gibbs energy calculation equation (ΔG°) is represented in equation 12 and Table S3:[33]

$$\Delta G^o = -RTlnK_c \quad (12)$$

where, ΔG° – the Gibbs energy, J/mol; $H°$ – enthalpy, J/mol; ΔS° – entropy, J/(mol·K); R – the universal gas constant (8.314 J/(mol·K)); T – the temperature at which the process was carried out, K.

3. Results and Discussions

3. 1. Characterization of Activated Carbons Samples

The physical-chemical characteristics of the studied samples (CAN, CAN-Cl) are presented in Table 1 and Figure S1. According to the obtained results, nitrogen is missing in both samples of activated carbons, while chlorine was found in the CAN-Cl sample in a quantity of ~2%. The results of the 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 S4, Figure S2).[6,19]

The thermal stability of CAN and CAN-Cl activated carbons was evaluated by the thermogravimetric method (Figure S2). A slow decrease in the mass of the CAN sample was observed with increasing temperature up to 450 °C, which is due to the elimination of water and some volatile species from the activated carbon structure. At temperatures higher than approx. 450 °C activated carbon burns. After modification with chlorine ions, the CAN-Cl activated carbon sample becomes more thermally unstable (Figure S2 b).

The surface chemistry of the activated carbons has been evaluated via the application of infrared spectroscopy (FTIR) and temperature programmed decomposition (TPD). 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 (Figures 1 and 3) reveal that at a temperature lower 400ºC, 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.[34] Meanwhile, the elimination of C_2H_6 and CH_4 from the samples CAN and CAN-Cl, suggests the uncompleted (partial) activation of the activated carbon. The species that evolved for chlorine groups were mainly mass 36 (HCl^{35}); this means that the groups decompose mainly to HCl (Figure 3).[14,34,35]

The IR spectra of the activated carbon samples CAN

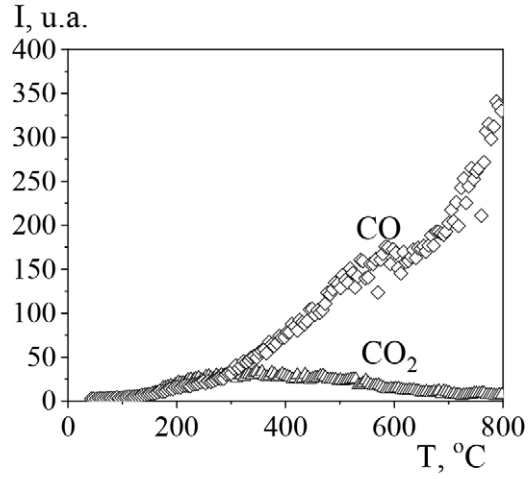

Fig. 1. CO and CO_2 evolution profiles from activated carbon CAN.

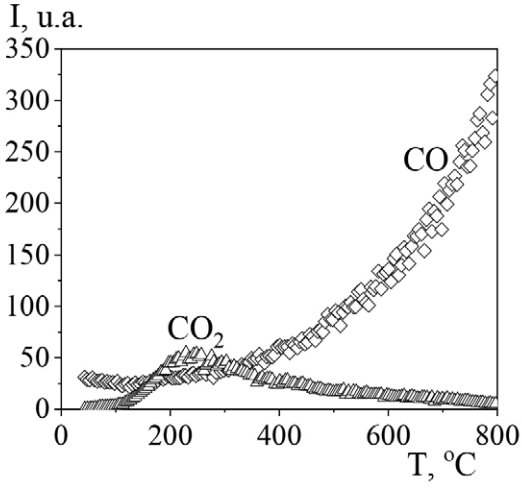

Fig. 2. CO and CO_2 evolution profiles from activated carbon CAN-Cl.

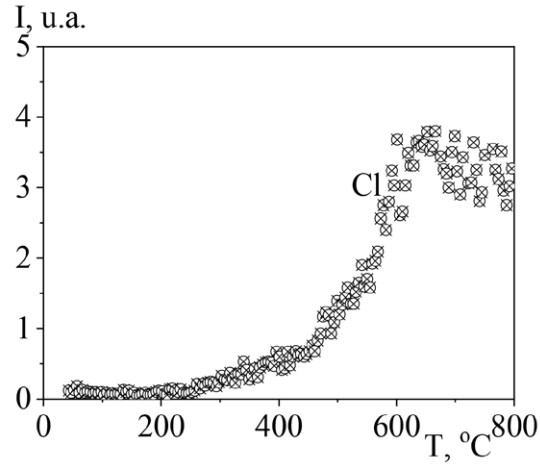

Fig. 3. Chlorine evolution profiles from activated carbon CAN-Cl.

(initial) and CAN-Cl (modified) are very similar (Table S5). In the range of 2800–3000 cm^{-1}, the low intensity bands are attributed to the C-H bond of aliphatic groups CH, CH_2, and CH_3. For both activated carbons (CAN and CAN-Cl) there is a broadband, 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 CH_2 and CH_3 groups in aromatic structures.[35,36] In the infrared spectrum of activated carbon CAN, the presence of carboxylic groups can be demonstrated by absorptions at 1720 cm^{-1} (C=O bond) and the broadband at approx. 1170 cm^{-1} where several overlapping absorptions are found, including vibrations in the bond C-OH and single bond C-O, O-H. Additionally, the presence of oxygen in the structure of the activated carbon CAN is demonstrated in the EDX profile of its. A broad band of low intensity attributed to carbon dioxide is found in the TPD profile of the CAN sample. This suggests the presence of a small amount of carboxylic groups on the surface of the activated carbon CAN.[19,37]

Carboxylic groups have a complex structure with π bonds, which leads to charge transfer from the oxygen atom to the carbon atom in the O-H structure and the positive charge of the hydrogen atom. Chlorine's electronegativity is 3.16 and the strong positive charge of the hydrogen atom will attract the electronegative chlorine and form an electrostatic interaction.[38]

The main factor in forming the bond between the hydrogen atom and the chlorine atom is the carboxyl group.[38] Reviewing the results obtained regarding the carboxylic groups on the surface of the activated carbon CAN and the results from the literature, the scheme (Figure S3) of the formation of the bond between the chloride ion and the carboxylic group on the surface of the activated carbon CAN is proposed. According to literature data, the acidity of activated carbons after chlorination increases with the increase of chlorine content on the surface of carbon

adsorbents.[36] This fact has been attributed to the inductive effect of chemisorbed chlorine[39] leading to increased Brönsted acidity, weakly acidic oxide sites, and increased hydrogen ion concentration.[40] Chlorine covalently bound to the surface of activated carbon has two opposite effects: inductive and resonance responsible for withdrawing and releasing electrons to/from the surface of activated carbon.[41,42] The inductive effect leads to the increase of Brönsted acidity and the creation of Lewis acid sites.[43]

3. 2. The Adsorption Studies

The influence of various experimental parameters (pH value, amount of adsorbent, initial concentration, contact time, and effect of electrolytes for adsorption of nitrite ions on activated carbons) was evaluated in batch experiments.

The sorption that takes place at the liquid/solid interface plays an essential 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.[44]

The kinetics of the adsorption process of nitrite ions on CAN and CAN-Cl activated carbons have been investigated by applying the following models: pseudo-first order kinetic, pseudo-second order kinetic, and intraparticle diffusion models.

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 was determined in the solutions. For the processing of experimental data the pseudo-first order kinetic, the pseudo-second order kinetic and the intraparticle diffusion models were applied (Tables 2–4 and Tables S6–7).

Table 2. Kinetic parameters and q_e values of the nitrite ions adsorption process on activated carbon CAN at different temperatures. The pseudo-second order kinetic model. Solid: liquid ratio – 1:100, pH 5.

T, K	C_0, mg/L	q_e(exp), mg/g	Kinetic parameters		
			K_2, g/mg min	q_e(cal), mg/g	R^2
278	5	0.115	0.046	0.125	0.975
	11	0.324	0.008	0.398	0.972
288	5	0.012	1.427	0.013	0.983
	11	0.035	0.488	0.039	0.996
303	5	0.033	0.032	0.045	0.931
	11	0.079	0.009	0.123	0.918
313	5	0.062	0.237	0.063	0.998
	11	0.159	0.034	0.174	0.981

These models allow the determination of the reaction order, the reaction rate constants, and the calculation of the adsorption value. For 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 (Tables 2 and 3). This fact shows that chemisorption predominates.[45,46]

Table 3. 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. Solid: liquid ratio – 1:100, pH 5.

T, K	C_0, mg/L	q_e(exp), mg/g	Kinetic parameters		
			K_2, g/mg min	q_e(cal), mg/g	R^2
278	5	0.434	0.090	0.447	0.999
	11	0.898	0.098	0.887	0.999
	15	1.208	0.022	1.229	0.999
288	5	0.472	0.054	0.478	0.999
	11	1.004	0.042	1.009	0.999
	15	1.290	0.014	1.290	0.996
303	5	0.453	0.087	0.464	0.995
	11	0.871	0.048	0.882	0.996
	15	1.055	0.020	1.093	0.976
313	5	0.473	0.099	0.473	0.999
	11	0.953	0.058	0.959	0.999
	15	1.305	0.022	1.296	0.998

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 activated carbon, the intraparticle diffusion model was applied.[45] According to the data obtained and presented in Table 4, the diffusion speed of nitrite ions in the pores is small for activated carbon CAN-Cl, and close values of the diffusion coefficients for nitrite ions in the pores of activated carbons have been reported in the literature.[45] Meanwhile, in the case of the adsorption of nitrite ions in the pores of AG-5ox and CAN-7 activated carbons, the value of the diffusion is by an order of magnitude higher, which can be explained by the utilization of a higher fraction of activated carbons in the investigated systems. Analysis of the obtained data shows that the diffusion velocity in pores increases with the temperature (313K).

The intraparticle diffusion model (Weber-Morris model) has been applied in order to determine the influence of mass transfer on the process of nitrite ions adsorption on activated carbons CAN and CAN-Cl. The adsorption dependence as a 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 (Table 4 and Figure 4). 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 mesopores to micropores (Figure 4 a,b).

Table 4. Kinetic parameters and q_e values of the nitrite ions adsorption process on activated carbon CAN-Cl at different temperatures. The intraparticle diffusion kinetic model. Solid: liquid ratio – 1:100, pH 5.

T, K	C_0, mg/L	Kinetic parameters		
		K_i, mg/g min$^{1/2}$	R^2	$\bar{D}$ m^2/s
278	5	0.011	0.887	$1.83 \cdot 10^{-11}$
	11	0.027	0.563	$1.83 \cdot 10^{-11}$
	15	0.026	0.827	$1.83 \cdot 10^{-11}$
288	5	0.005	0.701	$9.18 \cdot 10^{-12}$
	11	0.034	0.779	$2.75 \cdot 10^{-11}$
	15	0.014	0.678	$9.18 \cdot 10^{-12}$
303	5	0.010	0.751	$1.83 \cdot 10^{-11}$
	11	0.017	0.885	$1.83 \cdot 10^{-11}$
	15	0.005	0.925	$4.59 \cdot 10^{-12}$
313	5	0.024	0.763	$3.30 \cdot 10^{-9}$
	11	0.031	0.656	$1.65 \cdot 10^{-9}$
	15	0.026	0.781	$1.10 \cdot 10^{-9}$

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 (Tables S8–13 and Figures 5–7). 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

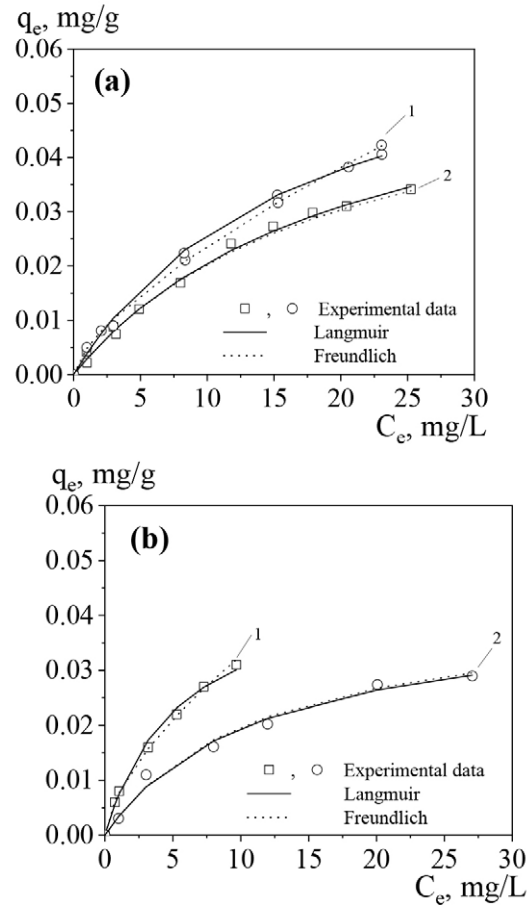

Fig. 5. Nitrite ions adsorption isotherms on activated carbon CAN, at different temperatures: **(a)** 1 – 283K, 2 – 288K, and **(b)** 3 – 298K, 4 – 313K. Solid: liquid ratio – 1:100, pH 5.

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 physical adsorption (Tables S8–13 and

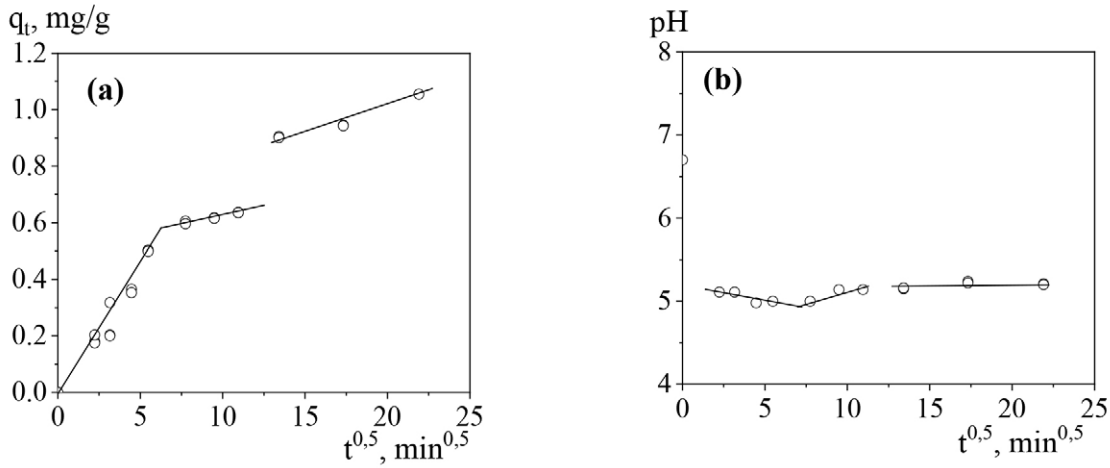

Fig. 4. Intraparticle diffusion kinetic model (Weber-Morris model) for nitrite ions adsorption on activated carbon CAN-Cl, T = 303K. Dependence of nitrite ion adsorption **(a)**, pH value of solutions at equilibrium **(b)** *vs* the square root of contact time. Solid: liquid ratio – 1:100, pH 5.

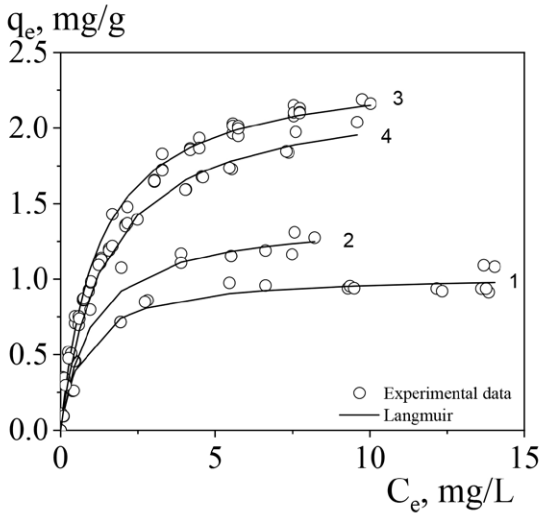

Fig. 6. Nitrite ions adsorption isotherms on activated carbon CAN-Cl, at different temperatures: (1) 283K, (2) 288K, (3) 298K, and (4) 313K. Solid: liquid ratio – 1:100, pH 5.

Figures 5–7).

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 supposes 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 the data described in the literature.[47] The results show that the modification with chlorine ions leads to an increase of the adsorption capacity of activated carbons for nitrite ions by about 50 times.[48]

The presence of electrolytes in the process of ions adsorption on activated carbons often has a significant influence.[47] According to obtained results, the presence of NaCl and $NaClO_4$ electrolytes in the process of nitrite ions adsorption on investigated carbonaceous adsorbents (CAN and CAN-Cl) decreases the adsorption value (Tables S12 and S13). It seems that activated carbons possess a higher affinity for chloride and perchlorate ions than for nitrite ions.[47] In the case of carbonaceous adsorbent modified by chlorine CAN-Cl the nitrite ions adsorption value (q_e, mg/g) decreased ~10 times in the presence of electrolyte NaCl and ~60 times in the presence of electrolyte $NaClO_4$, 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 (Table S14). The negative values of ΔG°, obtained for the activated carbon CAN-Cl highlight that the equilibrium of the adsorption process is reached faster at higher temperatures and that the adsorption process is spontaneous (Table S14 and Figure 8). The entropy (ΔS°) positive value shows that structural modification appears in the adsorbent and that the surface heterogeneity increases during the adsorption process. This process is characteristic of the activated carbon CAN-Cl, one of the reasons is the release of water molecules as a consequence of the exchange between the nitrite ions and functional groups on the carbon surface.

Based on the results obtained for the adsorption of nitrite ions on the studied adsorbents according to the concentration of nitrite ions in the solution, the pH value, and temperature, the adsorption mechanism can be proposed.

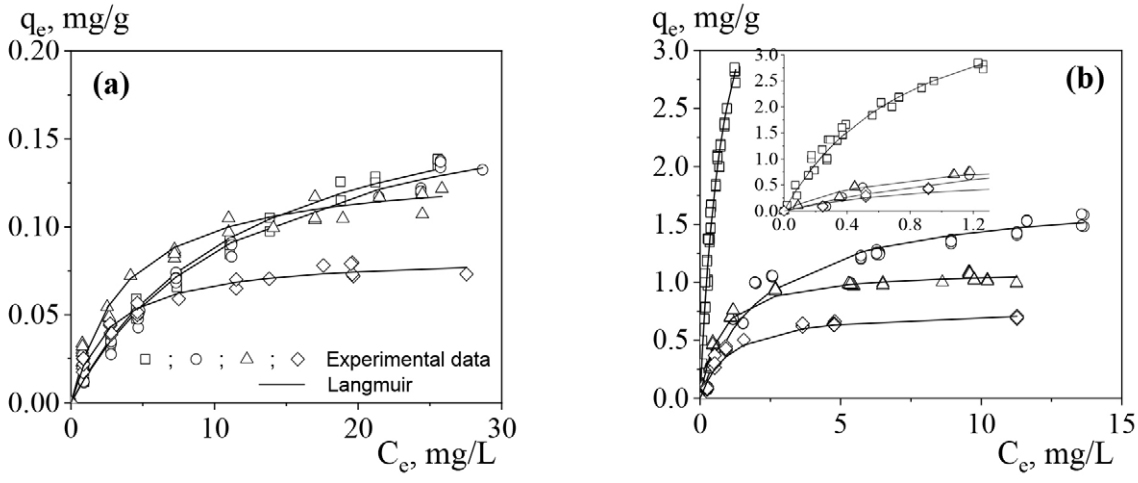

Fig. 7. Adsorption isotherms of nitrite ions on activated carbons **(a)** CAN and **(b)** CAN-Cl obtained at different values of pH: 3 (□); 5 (○); 7 (Δ) and 10 (◊). Solid: liquid ratio – 1:100, T 298K.

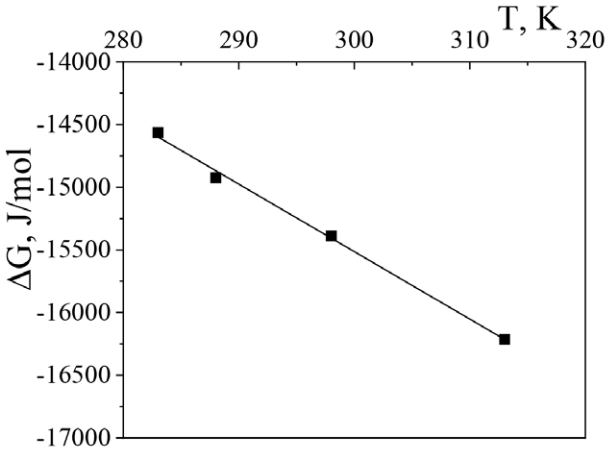

Fig. 8. Variation of Gibbs energy as a function of temperature, for the adsorption process of nitrite ions on the sample CAN-Cl.

The correspondence of the experimental data with the pseudo-second-order kinetic model suggests that the determining step in this process is chemisorption. And the Langmuir isotherm model, which best approximates the experimental data, suggests that the adsorption process is dominated by chemisorption on energetically homogeneous surfaces, and the process is favorable (according to the R_L value). The value of the free energy of adsorption (E) calculated from the Dubinin-Radushkevich equation, proves that in the modeled systems physical adsorption occurs.

For the initial activated carbons, which are poor in functional groups on the surface, the C_π positions participate in the adsorption process. These positions or centers of adsorption (C_π) are strongly influenced by the pH value of the solution. In the acidic domain, protons (H^+) are concentrated on C_π positions and the graphitic structure of the positively charged activated carbon attracts nitrite ions. In the basic range, the OH^- ions are competitive with the nitrite ions, and the graphitic surface of the activated carbon becomes negatively charged, and consequently repels the nitrite ions.[49]

Comparatively, for both active carbons (CAN, CAN-Cl) in the adsorption of nitrite ions, the pH value of the solution is of great importance, but not as significant as the surface chemistry of the active carbons and pH_{pzs}.[1,18]

By reviewing the results obtained in the given work with those reported in the literature, the mechanism of electrostatic adsorption of nitrite ions on activated carbons is proposed. Through the protonation of hydroxyl groups (equation 13) on the surface of activated carbons, positively charged adsorption centers are formed, which ensure an increase in the electrostatic adsorption of nitrite ions (equation 14).

$$\equiv C\text{–}OH + H^+ \leftrightarrow \equiv C\text{–}OH_2^+ \quad (13)$$

$$\equiv C\text{–}OH_2^+ + NO_2^- \leftrightarrow \equiv C\text{–}OH_2\,NO_2^- \quad (14)$$

The difference in the adsorption capacity of the studied adsorbents (CAN and CAN-Cl) for nitrite ions is explained by different pH_{pzs} values (CAN-Cl 5.75 and CAN 8.25).

Resulting from the characteristics of activated carbons modified with chloride ions (CAN-Cl sample) to adsorb nitrite ions at low pH values (low ash content is also an advantage) and low price cost it is recommended to use this activated carbon as an enterosorbent for the adsorption/removal of nitrite ions from the human body (stomach pH ranges from 1–2 to 4–5). The estimative price of 1 kg of activated carbon modified with chloride ions CAN-Cl is about 30 euros (Appendix 1, Table S15). Comparative analysis reveals that the CAN-Cl price is about 3.5 times lower than the price of the activated carbons AG-5ox (obtained by oxidation with nitric acid)– recommended for nitrite ions adsorption from solutions.[18]

4. Conclusions

New activated carbons had been obtained from walnut shells and by modifying the surface with hydrochloric acid. The surface chemistry of activated carbons has been evaluated by jointing IR spectroscopy, SEM-EDX, and temperature programed decomposition (TPD). The following functional groups have been identified on the surface of activated carbons: carboxylic, phenolic, carbonyl groups, and quinone. Meanwhile, on the chlorine modified activated carbon, the chlorine groups were identified by decomposition and elimination as HCl (by TPD method).

The adsorption process of nitrite 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 and Langmuir model, suggesting that the adsorption of nitrite ions on activated carbons is based on chemisorption.

Funding

This research was funded by the subprogram "Advanced research in computational and ecological chemistry, identification of technological procedures for treatment, formation of water quality and quantity" (code 010603) of the Institute of Chemistry of Moldova State University and Horizon Europe MSCA-RISE-2022-SE-01/ CLEANWATER Project, grant number 101131382.

Acknowledgments

Authors thank to: O. Petuhov (Institute of Chemistry, Chisinau, R. Moldova) for nitrogen sorption-desorption isotherms and thermal analysis measurements; T. Gromovoy (O. Chuiko Institut of Surface Chemistry,

Kyiv, Ukraine) for temperature programmed decomposition measurement; V. Vasilache (A.I. Cuza University of Iasi, Romania) for SEM-EDX analysis; M. Rusu (Institute of Chemistry, R. Moldova) for recording of FTIR spectra recording of FTIR spectra.

Conflicts of Interest

The authors declare no conflict of interest.

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Povzetek

V študiji so kot adsorbent za odstranjevanje nitritnih ionov iz vodnih raztopin uporabili aktivno oglje, pridobljeno iz orehovih lupin. Nov adsorbent je bil pridobljen z modifikacijo s klorovodikovo kislino. Fizikalno-kemijske lastnosti aktivnega oglja so bile določene iz sorpcijskih izoterm dušika, SEM-EDX, elementne analize, FTIR, termične analize in temperaturno programirane razgradnje (TPD). Iz rezultatov sklepajo, da se klor na površini zadržuje v količini 2 %. Rezultati šaržnih eksperimentov kažejo, da je mogoče doseči največjo adsorpcijo/odstranitev nitritnih ionov pri pH = 3, ki znaša 0,2 mg/g za CAN in 4,7 mg/g za CAN-Cl. Za proučevanje adsorpcije nitritnih ionov na aktivnem oglju so bili uporabljeni naslednji matematični modeli: psevdoprvi, psevdodrugi red in kinetični modeli difuzije znotraj delcev ter Langmuir, Freundlich, Dubinin-Radushkevich in Temkin-Pyzhev izotermni modeli.