Supplementary material:

Walnut shells activated carbons for adsorption of nitrite ions

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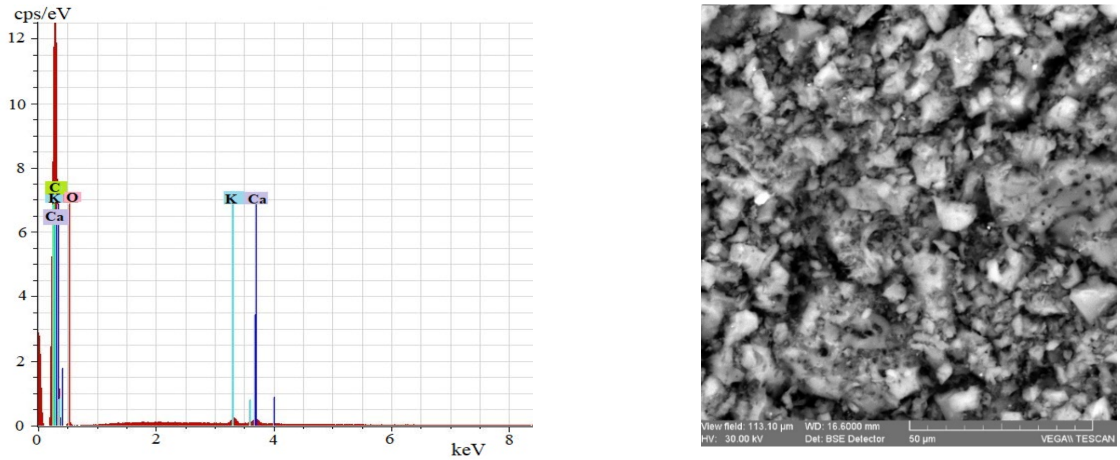
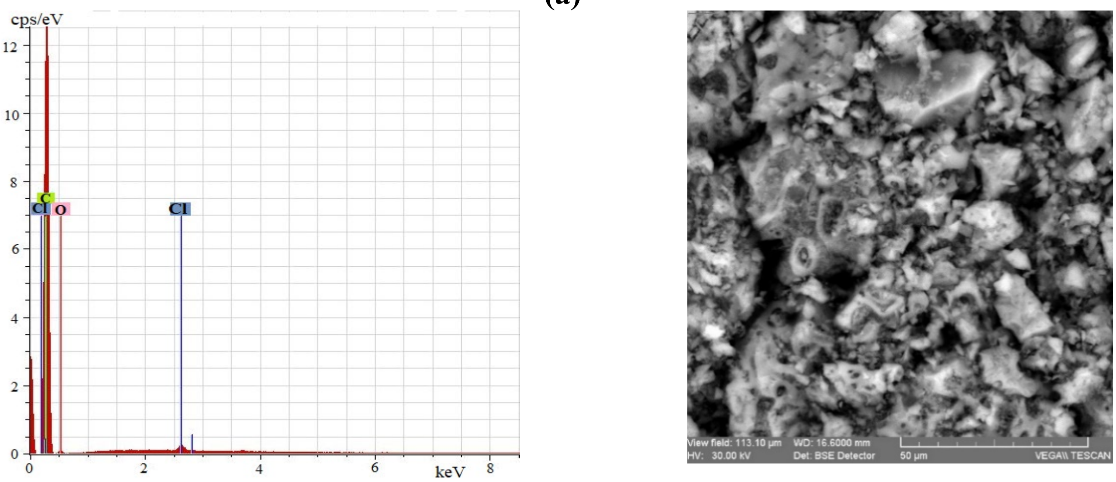


(a)



(b)

Figure S1. Elemental analysis and the morphology of the granules of activated carbons by EDX method **(a)** CAN and **(b)** CAN-Cl [1].

1. Ginsari, I.; Nastas, R. Modification and characterization of activated carbon from walnut shells. International Scientific Conference "Perspectives and Problems of Integration in the European Space of Research and Education", Cahul, Republic of Moldova, 07 06 2017. (In Romanian)

Table S1. Linear expressions, graphs and constants of kinetic models.

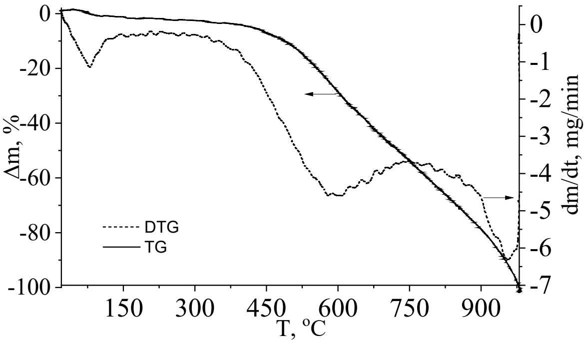
Types	***Linear expressions***	***Graphical expressions***	***A – slope***	***B - intersection with the Y axis***	k_1	q_e ***calc.***
Pseudo-first order	$\ln(q_e - q_t) = \ln(q_e) - k_1 t$	$\ln(q_e - q_t)$ *depending on* t	$-k_1$	$\ln(q_e)$	-A	e^B
Pseudo-second order	$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}$	$\frac{t}{q_t}$ *depending on* t	$\frac{1}{q_e}$	$\frac{1}{k_2 q_e^2}$	$\frac{A^2}{B}$	$\frac{1}{A}$
Intraparticle diffusion	$q_t = k_i t^{1/2}$	q_t *depending on* $t^{1/2}$	k_i	B = 0	A	-

Table S2. Linear expressions, graphs and constants of isotherm models.

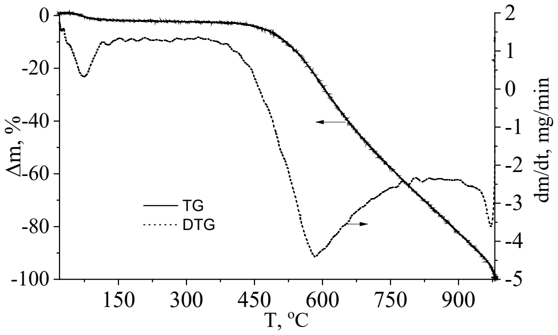
Types	***Linear expressions***	***Graphical expressions***	***A – Slope***	***B - intersection with the Y axis***	***K***	Q_0
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0}$	$\frac{C_e}{q_e}$ *depending on* C_e	$\frac{1}{Q_0}$	$\frac{1}{K_L Q_0}$	$\frac{A}{B}$	$\frac{1}{A}$
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$\ln(q_e)$ *depending on* $\ln(C_e)$	$\frac{1}{n}$	$\ln(K_F)$	$K_F = e^B$	$n = \frac{1}{A}$
D-R	$\ln(q_e) = \ln(q_s) - k_{ads}\varepsilon^2$	$\ln(q_e)$ *depending on* ε^2	$-K_{ads}(RT)^2$	$\ln(q_s)$	$K_{ads} = \frac{-A}{(RT)^2}$	e^B
Temkin-Pyzhev	$q_e = B_T \ln(K_T C_e)$	q_e *depending on* $\ln(C_e)$	B_T	$B_T \ln(K)$	$K_T = K_T = e^{B/A}$	$B_T = A$

Table S3. Linear expression, graphical expression and thermodynamic constants.

Linear expression	***Graphical expression***	***A – slop***	***B - intersection with the Y axis***	***Calculated values***
$\ln K_L = -\frac{\Delta H^o}{RT} \cdot \frac{1}{T} + \frac{\Delta S^o}{R}$	$\ln K_L$ depending on $\frac{1}{T}$	$-\frac{\Delta H^o}{R}$	$\frac{\Delta S^o}{R}$	$\Delta H° = -A \cdot R$ $\Delta S° = B \cdot R$



(a)



(b)

Figure S2. DTG and TG curves of the activated carbon samples **(a)** CAN and **(b)** CAN-Cl.

Table S4. Porous structure characteristics of actived carbons determined from nitrogen sorption isotherms.

Sample	*S_{BET}, m^2/g*	*V_{total}, cm^3/g*	*V_{micro}, cm^3/g*	*E_{micro}, kJ/mol*	*R_{micro}, nm*
CAN-Cl	608	0.318	0.203	24.7	2.5
CAN	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.

Table S5. FTIR spectra of activated carbon samples CAN and CAN-Cl [2].

Domain	***Bond***	***Assignments***	***ν, cm^{-1}***	
			CAN	***CAN–Cl***
3500-3200	bonding vibrations in the group O-H, connection of -H	alcohols, phenols, carboxylic acids	3411	3405
3000-2800	C-H (CH, CH_2, CH_3)	aliphatics	2970 2944 2865	-
1740-1720	bond C=O	aldehydes, ketones, carboxylic acids	1721	1720
1660-1450	-C=C-, -C=O C-H	vibrations of rings in extended aromatic structures or valence vibrations of the C=O component in conjugated systems (diketones, ketoesters, ketoenols) alkenes, aromatics	1626 1563 1452	1658 1564 1455
1300-1000	vibrations C-OH simple bond C-O O-H	alcohols, phenols, acids ethers, esters, lactones phenol	wide band (1171)	wide band (1169)

2. Ginsari, I.; Nastas, R. IR Spectral Analysis of Chlorine Modified Activated Carbon. Scientific Conference of Doctoral Students (with international participation), 6th edition, Contemporary trends in the development of science: views of young researchers, Chisinau, Republic of Moldova, 15 06 2017. (In Romanian)

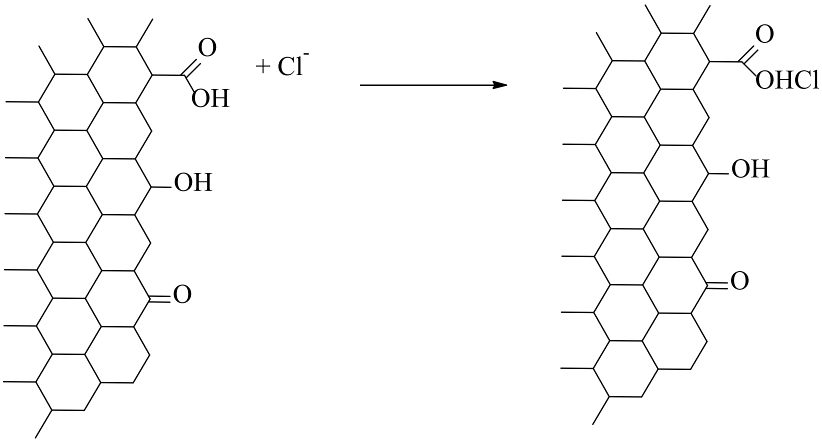


Figure S3. Scheme of the bond formation between the hydrogen atom and the chlorine atom (adapted [3]).

3. Zhu, J.; Liang, H.; Fang, J.; Zhu, J.; Shi, B. Characterization of Chlorinated Tire-Derived Mesoporous Activated Carbon for Adsorptive Removal of Toluene. *Clean – Soil, Air, Water* **2011,** *39,* 557–565. [10.1002/clen.201000265]

Table S6. Kinetic parameters and q_e values of nitrite ions adsorption process on activated carbon CAN, at different temperatures. The pseudo-first order kinetic model. Solid: liquid ratio – 1:100, pH 5.

T, K	**C_0, mg/L**	***Kinetic parameters***			
		q_e(exp) (mg/g)	**k_1 (min^{-1})**	**q_e(cal) (mg/g)**	**R^2**
278	5	0.115	0.003	0.168	0.917
	11	0.324	0.004	0.403	0.934
288	5	0.012	0.007	0.008	0.784
	11	0.035	0.009	0.029	0.904
303	5	0.033	0.002	0.032	0.962
	11	0.079	0.002	0.074	0.973
313	5	0.062	0.002	0.030	0.777
	11	0.159	0.002	0.102	0.915

Table S7. Kinetic parameters and q_e values of nitrite ions adsorption process on activated carbon CAN-Cl, at different temperatures. The pseudo-first order kinetic model. Solid: liquid ratio – 1:100, pH 5.

T, K	***C_0, mg/L***	***q_e(exp), mg/g***	***Kinetic parameters***		
			k_1, min^{-1}	***q_e(cal), mg/g***	***R^2***
278	5	0.434	0.003	0.107	0.934
	11	0.898	0.001	0.065	0.518
	15	1.208	0.003	0.367	0.961
288	5	0.472	0.003	0.223	0.913
	11	1.003	0.003	0.319	0.933
	15	1.290	0.004	0.737	0.911
303	5	0.453	0.007	0.248	0.845
	11	0.871	0.008	0.527	0.957
	15	1.055	0.007	0.809	0.931
313	5	0.473	0.003	0.185	0.899
	11	0.953	0.003	0.367	0.898
	15	1.305	0.002	0.693	0.870

Table S8. Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich isotherm constants for the adsorption of nitrite ions on activated carbon CAN at different temperatures. Solid: liquid ratio – 1:100, pH 5.

Isotherm model	*T, K* / *Parameters*	*283*	*288*	*298*	*313*
Langmuir	K_L (L/mg)	0.048	0.059	0.183	0.090
	Q_0 (mg/g)	0.063	0.044	0.040	0.041
	R^2	0.874	0.936	0.974	0.967
R_L		0.44 ÷ 0.95	0.42 ÷ 0.93	0.14 ÷ 0.35	0.28 ÷ 0.91
Freundlich	K_f (mg/g)	0.003	0.005	0.008	0.004
	n	1.323	1.450	1.575	1.522
	R^2	0.961	0.994	0.998	0.934
Temkin-Pyzhev	K_T (L/g)	0.988	0.968	2.231	1.309
	B_T	0.001	0.122	0.009	0.008
	R^2	0.942	0.934	0.965	0.969
Dubinin-Radushkevich	K_{ads} (mol^2/kJ^2)	7.88×10^{-7}	7.27×10^{-7}	3.39×10^{-7}	6.14×10^{-7}
	Q_0 (mg/g)	0.022	0.028	0.025	0.022
	E (kJ/mol)	7.965	8.293	1.214	9.020
	R^2	0.743	0.659	0.882	0.886

Table S9. Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich isotherm constants for the adsorption of nitrite ions on activated carbon CAN-Cl at different temperatures. Solid: liquid ratio – 1:100, pH 5.

Isotherm model	**T, K** / **Parameters**	**283**	**288**	**298**	**313**
Langmuir	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)	2.653	2.911	3.671	2.715
	R^2	0.910	0.834	0.825	0.966

Table S10. 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. Solid: liquid ratio – 1:100, T 298K.

Isotherm model	pH / Parameters	3	5	7	10
Langmuir	K_L (L/mg)	0.083	0.082	0.267	0.378
	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
Freundlich	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
Temkin-Pyzhev	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
Dubinin-Radushkevich	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)	0.981	0.985	1.238	1.267
	R^2	0.775	0.702	0.854	0.846

Table S11. 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. Solid: liquid ratio – 1:100, T 298K.

Isotherm model	pH / Parameters	3	5	7	10
Langmuir	K_L (L/mg)	1.192	0.430	1.419	0.930
	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
Freundlich	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
Temkin-Puzhev	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
Dubinin-Radushkevich	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)	3.747	1.690	2.756	1.968
	R^2	0.922	0.942	0.921	0.988

Table S12. Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich isotherm constants for the adsorption of nitrite ions on activated carbon CAN-Cl, in the presence of supporting electrolytes. Solid: liquid ratio – 1:100, pH 5, T 298K.

Isotherm model	*Parameters*	*NaCl*	*$NaClO_4$*
Langmuir	K_L (L/mg)	0.011	0.013
	Q_0 (mg/g)	1.177	0.088
	R^2	0.165	0.287
R_L		0.73 ÷ 0.98	0.69 ÷ 0.98
Freundlich	K_f (mg/g)	0.014	0.001
	n	1.115	1.148
	R^2	0.965	0.982
Temkin-Pyzhev	K_T (L/g)	0.656	0.704
	B_T	0.078	0.007
	R^2	0.870	0.782
Dubinin-Radushkevich	K_{ads} (mol^2/kJ^2)	6.79×10^{-7}	7.6×10^{-7}
	Q_0 (mg/g)	0.109	0.015
	E (kJ/mol)	0.858	0.811
	R^2	0.494	0.708

Table S13. Langmuir, Freundlich, Temkin-Pyzhev and Dubinin-Radushkevich isotherm constants for the adsorption of nitrite ions on activated carbon CAN, in the presence of sodium perchlorate. Solid: liquid ratio – 1:100, pH 5, T 298K.

Isotherm model	*Parameters*	*$NaClO_4$*
Langmuir	K_L (L/mg)	0.043
	Q_0 (mg/g)	0.033
	R^2	0.473
R_L		0.59 ÷ 0.95
Freundlich	K_f (mg/g)	0.002
	n	1.289
	R^2	0.959
Temkin-Pyzhev	K_T (L/g)	1.009
	B_T	0.005
	R^2	0.862
Dubinin-Radushkevich	K_{ads} (mol^2/kJ^2)	7.18×10^{-7}
	Q_0 (mg/g)	0.010
	E (kJ/mol)	0.834
	R^2	0.670

Table S14. Thermodynamic constants calculated for activated carbon CAN-Cl. Solid: liquid ratio – 1:100.

T, K	*ΔG°, J/mol*	*ΔH°, kJ/mol*	*ΔS°, J/(mol·K)*
283	-14561.6	0.1477	51.6372
288	-14923.0		
298	-15387.8		
313	-16213.9		

Appendix 1

The estimation of activated carbons price

The cost price of a product is calculated from direct costs, and direct costs are those expenses that are identified on a specific calculation object (product, service, work, order, phase, activity, function, etc.), from the moment of execution and as such are included directly in the cost of the respective objects and include: the cost of purchasing raw materials and direct materials consumed, energy consumed for technological purposes, direct labor (salaries, insurance and social protection, etc.), other direct expenses.[1,2]

In a simplified version, the estimated cost price of a product can be calculated from the total cost of raw materials, electricity consumption and the salary of employees serving the installation, which do not exceed 30% of the cost of raw materials [3,4].

Calculating the price of chlorine ion modified activated carbon

The amount and price of raw materials required to produce one kilogram of activated carbon modified with chlorine ions CAN-Cl are shown in table S15.

Table S15. Consumption of raw materials needed to obtain CAN-Cl activated carbon.

No.	**Raw materials**	**Unit of measurement**	**Price/unit, MDL**	**The quantity consumed**	**Total price, MDL**
1	Activated carbon obtained from walnut shells (CAN) produced at Ecosorbent LLC, RM	kg	60	0.3	18.00
2	Distilled water	L	5	20	100
3	Hydrochloric acid (concentrated)	L	60	0.31	18.60
TOTAL					**136.60**

To calculate the specific energy consumption required for the production of activated carbon modified with chlorine ions (CAN-Cl) the equation was used:

$$Q = N \cdot \tau \cdot k \quad (1)$$

where, Q – the specific consumption of energy, kW·h;

N – element power, kW;

τ – running time, h;

k – the coefficient of energy use (its value was considered to be 0.9 or 90%).

Drying was carried out in an oven with a power of 1 kW and a duration of operation of 7 h:

$$Q = 1 \cdot 7 \cdot 0.9 = 6.3 \text{ (kWh)}.$$

The price of electricity consumed was calculated according to the relationship:

$$P = Q_t \cdot p \quad (2)$$

where, P – the price of electricity expenses, kWh lei;

Q_t – total specific energy consumption, kWh;

p – the price of 1 kWh of electricity, equal to 1.50 MDL.

When producing one kg of activated carbon modified with CAN-Cl chlorine ions, the expenses for electricity amounted to 9.45 MDL.

Other expenses, including the salary of the employees serving the installation, do not exceed 30% of the cost of raw materials (137.22 MDL).

1. Busmachiu, E.; Gumovschi, A. *Prices and tariffs,* Publisher: ASEM, Republic of Moldova, 2005. (In Romanian)

2. Ceausescu, AI.; Vaduva, C. Using the target costing method in setting prices, *Annals of the University ―Constantin Brancuşi from Targu Jiu*, 2010, pp. 160-167. (In Romanian)
3. Goreacioc, T. Study of water treatment processes contaminated with nitrite ions. PhD Dissertation, Institute of Chemistry, 07 09 2018. (In Romanian).
4. Marchitan, N. Separation of tartaric acid from wine by-products using impregnated anionites. PhD Dissertation, Moldova State University, Chisinau, 2013. (In Romanian)