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REMOVAL OF NITRITE IONS FROM WATER IN DYNAMIC AND OXIC CONDITIONS

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Abstract
Active carbons have been found the most efficient and commonly used adsorbents in water purification all over the world.
The purpose of this work was to investigate the possibility of applying active carbons AG-5 and AG-5ox for the removal of nitrite ions from water in (i) dynamic and (ii) oxic conditions.
Obtained results reveal that the sample AG-5 is more efficient for removal of nitrite ions from water in the dynamic conditions but sample AG-5ox is more efficient in oxic conditions.
The capacity of active carbon AG-5 for nitrite ions removal from water, expressed in dynamic conditions as a ratio of the adsorbent volume to the solution volume passed through column with adsorbent, is about 1:80.
Studies show that the application of the recommended method using the AG-5ox carbonic adsorbent provides of 75% efficiency in the removal of nitrite ions from natural water and 100% of the model solution.

Keywords*: active carbon, dynamic condition, nitrite ions, oxic condition, removal*

Introduction

The treatment processes of water contaminated with nitrate ions have been studied much more widely than nitrite-contaminated water treatment processes. However, several literature procedures describe the removal of nitrite ions from water. These include: biological nitrification/denitrification (Kapoor & Viraraghavan 1997, Ng' & Stenstrom 1987, Srinu & Pydi 2012, Zubair et al 2012); chemical denitrification (Horold et al 1993, Kapoor & Viraraghavan 1997, Lemaignen et al 2002, Soares et al 2008); adsorption (Afkhami 2003, Afkhami et al 2007, Mir 2010, Öztürk & Köse 2008).
Active carbons have been found the most efficient and commonly used adsorbents in water purification all over the world (Kawamura 1991). The reason that active carbon is such an effective adsorbent material is due to its high surface area, porous structure, and high degree of surface activity. Active carbons are also highly inert, thermally stable and can be used over a broad pH range (Kawamura 1991).
For the treatment of drinking water and wastewater, it is quite common to use activated carbon in granular form.

The adsorption efficiency depends both on the type of contaminant that is adsorbed, on the porous structure and on the surface chemistry of adsorbents (Kapoor & Viraraghavan 1997, Kawamura 1991, Lupascu 2004).Therefore, chemical modification of the active carbon surface is of great interest in obtaining adsorbent materials with specific applications. More often, the surface of activated carbon is modified by oxidative methods, producing a more hydrophilic structure with a large number of oxygen-containing functional groups (Bandosz 2006, Rivera-Utrilla et al 2011).
The adsorption of ions does not depend only on the specific area of the adsorbent but also on the presence of the surface groups. The oxidation of active carbons can lead to the increase amount of the oxygen functional groups on the surface of the adsorbent, and the result of this is an increase in polarity and hydroliphilicity of the surface of the carbon adsorbent (Bandosz 2006, Rivera-Utrilla et al 2011).
In order to minimize operational problems during water treatment processes, particular attention should be draw to the size of the active carbon particles. Large particles have a small outer surface and large distances of the internal diffusion trajectory (Choma 1998). This reduces the mass transfer rate, resulting in long lasting processes of adsorption / removal of pollutants from water.
The purpose of this work was to investigate the possibility of applying active carbons AG-5 and AG-5ox for the removal of nitrite ions from water in (i) dynamic and (ii) oxic conditions**.**

Materials and Methods

In this work, were used two active carbon samples: (I) AG-5 commercially available activated carbon, obtained from coal (Russia) and (II) oxidized sample with concentrated nitric acid AG-5ox (Goreacioc 2015). The physico-chemical characteristics of active carbons were evaluated by a series of general indices, including humidity, ash content, and elemental analysis, pH of active carbon slurry, granulation and bulk density (Table 1) (Goreacioc 2015).
The activated carbon samples are predominantly microporous, according to the results obtained from nitrogen adsorption isotherms (Goreacioc 2015). Infrared spectroscopy and Boehm titration method results revealed that AG-5 sample has a basic surface and AG-5ox sample has acidic surface (Table 1); after oxidation process the acidic functional group are formed on the surface of the activated carbon AG-5ox; the concentration of acidic groups on the surface of AG-5ox follows the series: strong carboxylic groups > weak carboxylic groups > phenolic groups (Goreacioc 2015).
The process of nitrite ions removing from water under dynamic conditions has been studied in a system with two parallel-mounted columns filled with AG-5 active carbon and AG-5ox oxidized activated carbon (30 g, working fraction 0.8-2.0 mm) on the installation shown in Figure 1.
The removal of nitrite ions from water in oxic conditions (by adsorption/oxidation processes) was performed on the laboratory installation provided with an air bubbler and recovery flask (Figure 2). Tests have been done on the model solutions as well as on natural underground water from the village Isacova, district Orhei, Republic of Moldova (Table 2).

Table 1. Description of active carbon samples

Sample	Bulk density, g/cm^3 (fraction 0.8-2.0 mm)	pH of slurry	The character of surface groups, meq/g	
			Acidic	Basic
AG-5	<0.578>±0.005	6.65	0.38	0.48
AG-5ox	<0.553>±0.004	3.30	2.33	0.13

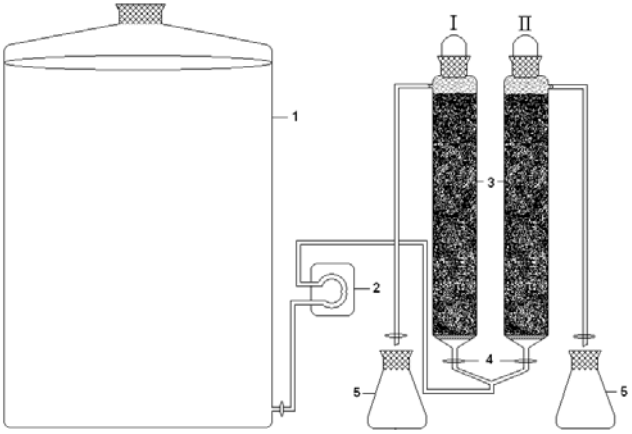

Figure 1. Scheme of the installation for removal of nitrite ions in dynamic conditions. 1 - water tank containing nitrite ions, 2 - pump, 3 – columns with activated carbon, 4 - taps, 5 - sample collection vessel, I – AG-5, II – AG – 5ox.

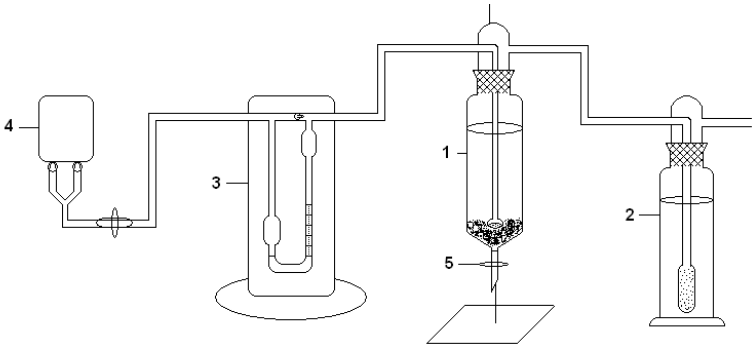

Figure 2. Scheme of the installation for removal of nitrite ions in oxic conditions. 1-Reactor; 2- recovery flask for nitrogen oxides; 3- flow meter; 4- air pomp; 5- sample port

Adsorption capacity (a) of active carbons has been determined by Eq. 1 and removal efficiency (R) of nitrite ions from water by Eq. 2.

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

where C_0 and C_e are the initial and equilibrium concentration of nitrite ions (mg/L), V is the solution volume passed through the column (mL), m is the amount of adsorbent (g).

$$R = \frac{C_0 - C_e}{C_0}\cdot 100\% \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentration of nitrite ions (mg/L).

Table 2. Quality indices of underground water from Isacova village (Orhei district)

No.	Determined parameters* (selective)	Values	MAC**
1	Hardness, mol/m^3, max.	0.9	7.0
2	Dry residue (110º C), mg/L	1309	1500
3	NH_4^+, mg/L	4.10	0.50
4	Nitrate ions (NO_3^-), mg/L	5.90	50
5	Iron (Fe) total, mg/L	0.38	0.3
6	Chloride ions (Cl^-), mg/L	63.01	250
7	Sulphate ions (SO_4^{2-}), mg/L	208.08	250
8	Fluoride ions (F^-), mg/L	4.40	1.5
9	Sodium (Na^+), mg /L	503.01	200
10	Potassium (K^+), mg/L	9.10	-
11	Nitrite ions (NO_2^-), mg/L	7.35	0.5
12	pH value	8.3	≥6.5 and ≤9.5
13	RedOx, mV	97-109	-
14	O_2, mg O_2/L	0.05	-
15	Conductivity, mS	2.28	-
16	Temperature, ºC	14.5	-

**Quality indices were determined by standard methods.*

***Maximal allowable concentrations regulated by Government of Republic of Moldova. Official Monitor No. 276-280 from 29.11.2013. Art. No. 1037.*

Results and Discussion

The process of nitrite ions removing from water under dynamic conditions has been studied in a system with 2 parallel-mounted columns filled with AG-5 active carbon and AG-5ox oxidized activated carbon (Figure 1). The concentration of nitrite ions in the initial solution varied between 1.5 and 10 mg/L and the flow rate was between 5.5 and 50 mL/min. In the eluates the concentration of nitrite ions, the pH value and the conductivity of the solution were determined. Selective results are shown in Figures 3 and 4. Since activated carbon AG-5 exhibited greater adsorption capacity of nitrite ions under dynamic conditions, it was used for further researches. A research team from Poland reported results regarding the dynamic adsorption of nitrate, nitrite and ammonium ions on AG-5 active carbon AG-5 and oxidized sample with hydrogen peroxide (Gierak & Lazarska 2017), but the purpose of their work was to extract these ions from the mixture (the concentration of nitrite ions was 1 mg/L and the flow rate of the solution was 3 mL/min). According to their results, the efficiency of the removal/adsorption process of nitrate ions under dynamic conditions does not depend on surface chemistry of active carbons.

The process of removing nitrite ions from water in dynamic conditions using initial active carbon AG-5 was studied at the initial concentration of nitrite ions of 10 mg/L

and the flow rate of the 5.5 mL/min (Figures 5 and 6). The capacity of active carbon AG-5 for nitrite ions removal from water, expressed in dynamic conditions as a ratio of the adsorbent volume to the solution volume passed through column with adsorbent, is about 1:80.

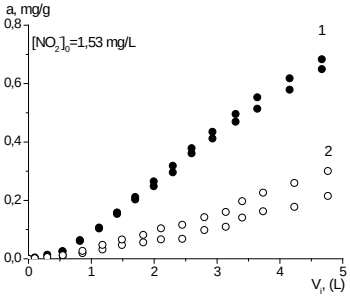

Figure 3. Capacity of active carbons for nitrite ions removal in dynamic conditions. C_0 =1.53 mg/L, (1) column with AG-5, (2) column with AG-5ox

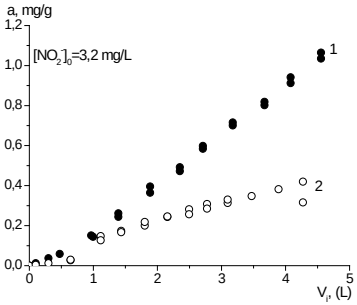

Figure 4. Capacity of active carbons for nitrite ions removal in dynamic conditions. C_0 =3.2 mg/L, (1) column with AG-5, (2) column with AG-5ox

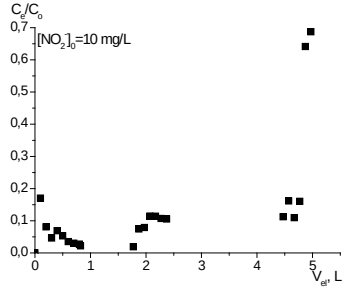

Figure 5. The variation of nitrite ions concentration in the eluates.
Column with AG-5, C_0=10mg/L, inflow 5.5 mL/min.

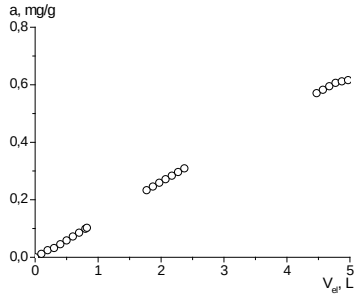

Figure 6. Capacity of AG-5 active carbon for nitrite ions removal in dynamic conditions.

Active carbons AG-5 and AG-5ox have been tested in order to choose the most efficient one for nitrite ions removal from water by adsorption/oxidation processes (in oxic conditions) using laboratory installation provided with an air bubbler and recovery flask (Figure 2). Tests have been done on the model solutions as well as on natural underground water (Table 2) under same conditions: room temperature, solid/liquid ratio equal to 1/200, air flow rate of 1.4 L/min, contact/treatment time of water was of 5 hours. For comparison, experiments were performed at two pH values, 8 and 6. Some researchers proposed an acidic environment for denitrification

of waters contaminated with nitrate/nitrite ions (Mir 2010). The efficiency of adsorbents was estimated by studying the kinetics of the process, being monitored the concentration of nitrite and nitrate ions, as well as pH value.
Depending on the pH of the medium, nitrogen oxides can be formed according to the reactions (Burgot 2012):

$pH < 3.3$ $\quad 3HNO_2 \rightarrow 2NO_{(g)} + NO_3^- + H^+ + H_2O$

$3.3 < pH < 5$ $\quad 3NO_2^- + 2H^+ \rightarrow 2NO_{(g)} + NO_3^- + H_2O$

$pH \geq 5$ $\quad NO_2^- + ½O_2 \rightarrow NO_3^-$.

The formed oxides are retained in the recovery flask (Figure 2). Comparative analysis of research results demonstrates the need of acidulation of treated water in order to optimize the nitrite ion removal process (Table 3). The studies proved that the application of the recommended procedure using the AG-5ox active carbon provides 75% efficiency in removing nitrite ions from natural water and 100% of the model solution (Table 3).

Table 3. Experimental results of nitrite ions removal from water

Sample	Natural water/model solution	pH (initial)	NO_2^- residual, mg/L	R, %	NO_2^-/NO_3^- oxidated, %	NO_2^- aerated, %	Adsorbed on active carbon
AG-5ox	Model solution	6.1	0.52	95.15	26.91	4.05	64.19
Without active carbon	Natural underground water, Isacova (Orhei)	5.7	7.20	2.04	0.85	0	1.19
AG-5		8.3	7.35	-	-	-	-
AG-5ox			6.5	12.16	9.46	0	2.70
AG-5ox		5.7	1.80	75.51	20.07	2.89	52.55

Conclusions

The capacity of active carbon AG-5 for nitrite ions removal from water, expressed in dynamic conditions as a ratio of the adsorbent volume to the solution volume passed through column with adsorbent, is about 1:80.
Comparative studies of efficiency of active carbons to remove nitrite ions in oxic conditions highlight the adsorbent AG-5ox modified by oxidation with nitric acid. The results showed that the recommended process, by using active carbon AG-5ox, ensures 100% efficiency for the removal of nitrite ions from model solution and 75% from underground water.

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