

TESTING OF CARBONACEOUS ADSORBENTS FOR REMOVAL OF POLLUTANTS FROM WATER

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ABSTRACT. – Testing of carbonaceous adsorbents for removal of pollutants from water. Relevant direction for improving of quality of potable water is application of active carbons at various stages of water treatments. This work includes complex research dealing with testing of a broad spectrum of carbonaceous adsorbents for removal of hydrogen sulfide and nitrite ions from water. The role of the surface functional groups of carbonaceous adsorbents, their acid-basic properties, and the influence of the type of impregnated heteroatom (N, O,) or metals (Fe, Cu, Ni,) on removal of hydrogen sulfide species and nitrite ions have been researched. The efficiency of the catalyst obtained from peach stones by impregnation with Cu^{2+} ions of oxidized active carbon was established, being recommended for practical purposes to remove the hydrogen sulfide species from the sulfurous ground waters. Comparative analysis of carbonaceous adsorbents reveals the importance of surface chemistry for oxidation of nitrite ions.

Keywords: active carbons, adsorption, oxidation, hydrogen sulfide, nitrite ions.

1. INTRODUCTION

In Republic of Moldova water supply is covered by 85% from surface water (the rivers Dniester and Prut) and 15% from groundwater. Groundwater is an important source of water supply for about 85-90% of rural population (***, 2007). Many of underground sources of water do not follow the requirements of standards for drinking water, being detected high concentrations of F⁻, Fe total, NH_4^+ , hydrogen sulfide, NO_2^- etc. (Garaba, 2005; Mirza, 2005; ***, 2007). Relevant direction for improving of quality of potable water is application of active carbons at various stages of water treatments. Activated carbons are well known as versatile adsorbents for many different applications (Lupascu, 2004; Marsh and Rodriguez-Reinoso, 2006; Rodriguez-Reinoso, 1998).

The purpose of this work was to test vegetal carbonaceous adsorbents, with a broad spectrum of physical-chemical characteristics, for removal of hydrogen sulfide and nitrite ions from water.

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2. EXPERIMENTAL

A broad spectrum of carbonaceous adsorbents, obtained from vegetable raw materials (fruit stones and nutshells), have been tested for removal of hydrogen sulfide, and nitrite ions from water, to chose the more efficient adsorbents. Methods with different agents for activation and oxidation of carbons have been applied (Lupascu et al., 2006; Lupascu and Nastas, 2004; Nastas et al., 2007) and procedures for modification of surface chemistry have been used (Maroto-Valer et al., 2004; Nastas et al., 2008; Nastas, 2006; Tcaci et al., 2011).

2.1. Characterization of carbonaceous adsorbents

Structural parameters (obtained from sorption isotherms of nitrogen at 77 K) of carbonaceous adsorbents and surface chemistry are presented in tables 1 and 2.

Total surface groups of the initial activated carbon (**CAi**, obtained from nut shells by physical-chemical method of activation) and of the samples obtained by modification with urea at different temperatures (Tcaci et al., 2011) (**CAN-200**, **CAN-300**, **CAN-400**, **CAN-500**, **CAN-600**, **CAN-700** and **CAN-800**) are presented in Fig. 1.

Testing of carbonaceous adsorbents for the elimination of hydrogen sulfide and nitrite ions from model solutions was performed in static conditions (Rusu et al., 2010). Elemental sulfur, thiosulfate, sulfite, sulphate and nitrite ions were determined by standard methods (***, 1995).

Table 1. Structural parameters of activated carbons (Maroto-Valer et al., 2004; Maroto-Valer et al., 2006)

Sample	Characteristics	S_{BET} , m ² /g	S_{me} , m ² /g	V_s , cm ³ /g	V_{micro} , cm ³ /g	D, Å
CAP23	<i>Obtained from peach stones by physical-chemical method</i>	957	110	0,57	0,42	23,8
CAPO23	<i>Obtained from peach stones, modified by oxidation</i>	869	130	0,52	0,35	23,9
CAPO23Cu	<i>Obtained from peach stones, modified by oxidation,</i>	839	120	0,50	0,34	23,8
CAPO23Fe	<i>following impregnation with Cu and Fe ions</i>	811	110	0,48	0,37	23,7
CAPr36	<i>Obtained from plum stones by physical-chemical method</i>	1199	128	0,68	0,51	22,7
CAPrO36	<i>Obtained from plum stones, modified by oxidation</i>	1099	130	0,61	0,50	23,4
CAPrO36Fe	<i>following impregnation with Fe ions</i>	1028	120	0,59	0,48	23,0

S_{BET} – BET surface area;

S_{me} – mesopore surface area;

V_s – total pore volume;

V_{micro} – micropore volume;

D – average pore diameter.

Table 2. Surface chemistry of activated carbons (Nastas et al., 2008; Rusu et al., 2007)

Sample	Characteristics	Character of the functional groups. Amount, meq/g				
		Total acidic	Carboxylic		Phenolic	Total basic
			Strong	Weak		
CAP23	<i>Obtained from peach stones</i>	0,58	0,10	0,19	0,29	0,59
CAPO23	<i>modified by oxidation</i>	2,71	1,34	0,31	1,06	0,35
CAPr36	<i>Obtained from plum stones</i>	0,73	0,22	0,10	0,41	0,69
CAPrO36	<i>modified by oxidation</i>	2,48	0,99	0,48	1,01	0,43
CAN-7	<i>Obtained from nut shells by chemical method with H₃PO₄</i>	1,79	0,74	0,31	0,74	0,10
CAPr-1	<i>Obtained from plum stones by chemical method with H₃PO₄</i>	1,98	0,48	1,10	0,40	0,10
CAP-7	<i>Obtained from peach stones by physical chemical method with NH₃/H₂O</i>	0,37	-			1,07
CAP-8	<i>Obtained from peach stones by physical chemical method with SO₂/H₂O</i>	0,28	-			0,67

Efficiency of carbonaceous adsorbents for removal of hydrogen sulfide and nitrite ions from solutions in the presence of carbonaceous adsorbents (particle size 0,63 - 1,00 mm) were performed by using lab installation provided with an air bubbler and recovery flask for aerated hydrogen sulphide (Rusu et al., 2010). All sulfur species were recalculated as H₂S, and removal of hydrogen sulfide from solutions was expressed as R, %.

3. RESULTS AND DISCUSSION

3.1. Removal of hydrogen sulfide

3.1.1. Removal of hydrogen sulfide from model solutions

Testing of adsorbents for the elimination of hydrogen sulfide from model solutions in static conditions (Fig. 1) emphasize high capacity for carbonaceous adsorbent obtained from peach stones modified with copper ions (CAPO23Cu).

Quantity of H₂S aerated and oxidized to sulphur species in the presence of catalysts are presented in Table 3. Results highlight the important role of oxygenated functional groups on the surface. It is stated that the ability on oxidation of hydrogen sulphide to sulphur species of higher degree of oxidation (SO₃²⁻ and SO₄²⁻) is more pronounced for higher content of strong carboxylic groups on the surface (CAPO23, Tables 2 and 3). Carbonaceous adsorbent CAP23-N, obtained from peach stones and modified with urea, also presents good capabilities for hydrogen sulfide removal from solutions (Figs. 2, 3 and Table 3).

Catalytic activity of carbons differs, and reaction rate for hydrogen sulfide removal increases as CAPO23Fe <CAPO23Cu <CAP23-NiO≈CAP23-N (Fig. 3). The results (Figs. 1, 3, and Table 3) emphasize high capacity of hydrogen sulfide removal for carbonaceous adsorbent obtained from peach stones modified with copper ions (CAPO23Cu).

Modification of surface chemistry of activated carbons with transition metals changes its catalytic properties (Maroto-Valer et al., 2004; Maroto-Valer et al., 2006). State or form of the impregnated metal greatly influences the selectivity of sulfur species formation in solution (Nastas, 2006). In the presence of NiO (sample CAP23-NiO, Tab. 3) the main sulfide oxidation product is elemental sulphur while in the case of adsorbents modified with copper and iron ions the sulfide oxidation products are thiosulfate, sulfite and sulfate ions, and there is no present elemental sulphur.

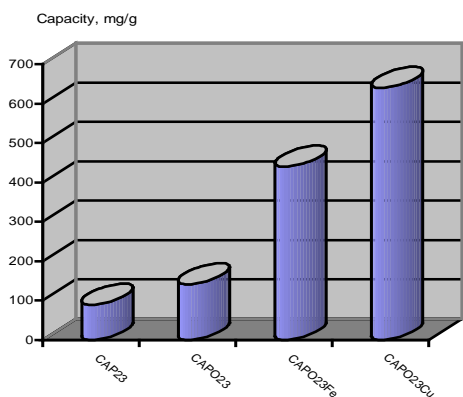


Fig. 1 Capacity of carbonaceous adsorbents to remove hydrogen sulfide from solution.

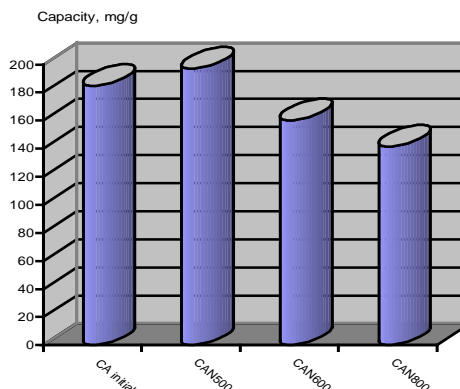


Fig. 2 Capacity of carbonaceous adsorbents (following modification with urea at different temperatures) to remove hydrogen sulfide from solution.

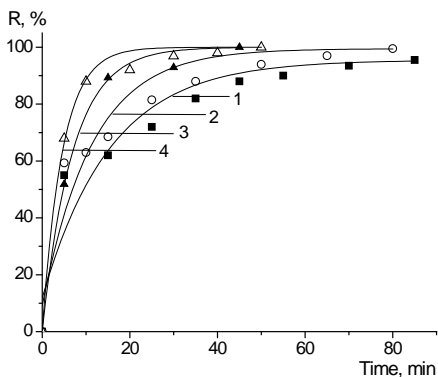


Fig. 3 Kinetics of the removal (R, %) of hydrogen sulfide from model solution in the presence of adsorbents: (1)-CAPO23Fe; (2)-CAPO23Cu; (3)-CAP23-NiO; (4)-CAP23-N. ($C_0 = 10 \text{ mg/L}$, $\text{pH} = 8,5$, $\text{ratio } \text{mgO}_2/\text{mgH}_2\text{S} = 3/4$)

Table 3. Quantity of H₂S aerated and oxidized to sulfur species in the presence of catalysts (C₀= 10 mg/L, pH=8,5, ratio mgO₂/mgH₂S = 3/4, solid/liquid ratio of 1:800)

Catalysts (characteristics)	Quantity aerated, %	Quantity oxidized %	Quantity (%) of H ₂ S oxidized to sulfur species:		
			S ⁰ coloidal	∑(S ₂ O ₃ ²⁻ +SO ₃ ²⁻)	SO ₄ ²⁻
CAP23 (acidic groups 0,6 meq/g, pH 5,2)	12,0	88,0	20,4	12,5	67,1
CAPO23 (acidic groups 2,7 meq/g, pH 4,6)	4,3	95,6	6,1	27,1	65,9
CAP23-N (modified with urea, 3,7% N)	5,2	94,8	0	30,6	69,4
CAP23-NiO (0,5 meq Ni ²⁺ /g)	5,3	94,7	95,5	4,5	0
CAPO23Fe (0,8 meq Fe ³⁺ /g)	23,3	76,5	0	33,8	66,2
CAPO23Cu (0,4 meq Cu ²⁺ /g)	41,6	58,3	0	41,9	58,1

3.1.2. Removal of hydrogen sulfide from ground water

Figure 4 shows the kinetics of hydrogen sulfide removal from model solution (with concentration and pH appropriate to natural conditions) and from sulfurous ground waters (Hincesti, RM). Generally, the kinetics of these processes is the same in the presence of catalyst CAPO23Cu. To be mentioned that in both cases the colloidal sulfur has not been registered (Table 4). Therefore, this catalyst can be used for a long time, keeping the pores unblocked, and may be recommended for practical usage for hydrogen sulfide removal from groundwater.

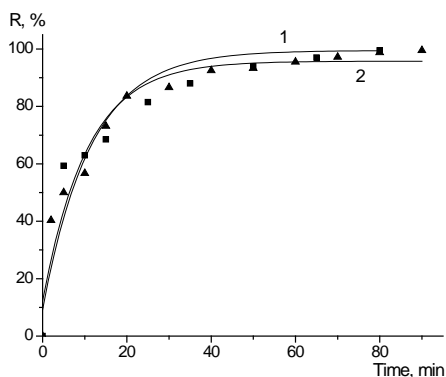


Fig. 4 Kinetics of the hydrogen sulfide removal (R, %) in the presence of CAPO23Cu from: (1)-model solution (C₀=10 mg/L, pH 8,5); (2)-sulfurous ground water (C₀=6,7 mg/L, pH 8,6).

Table 4. Quantity of H₂S aerated and oxidized to sulfur species in the presence of CAPO23Cu (ratio mgO₂/mgH₂S = 3/4, solid/liquid ratio of 1:800)

Catalyst	Quantity aerated, %	Quantity oxidized %	Quantity (%) of H ₂ S oxidized to sulfur species:		
			S ⁰ colloidal	∑(S ₂ O ₃ ²⁻ + SO ₃ ²⁻)	SO ₄ ²⁻
CAPO23Cu (0,4 meq Cu ²⁺ /g)	<i>Model solution. Initial concentration of H₂S C₀=10 mg/L, pH 8,5</i>				
	41,6	58,3	0	41,9	58,1
	<i>Ground water. Initial concentration of H₂S C₀=6,7 mg/L, pH 8,6</i>				
	16,4	83,6	0	52,0	48,0

3.2. Removal of nitrite ions

3.2.1. Removal of nitrite ions from model solutions

Comparative analysis emphasizes high capacity for removal of nitrite ions by carbonaceous adsorbents obtained from plum and peach stones, modified with iron ions (CAPO23Fe, CAPrO36Fe), also obtained from nut shells by chemical method with phosphoric acid (CAN-7) (Fig. 5). Generally, catalytic activity of these adsorbents is comparable and reaction rate is as CAPO23Fe ≈CAPrO36Fe≈CAN-7.

There are certain differences for active carbons obtained by chemical method of activation (CAN-7, CAPr-1) used for oxidation of nitrite ions. Although, both adsorbents have a good developed surface chemistry, sample CAN-7 posses a higher capacity for nitrite ions oxidation, for about 2 times, in comparison with CAPr-1 (Table 2, Fig. 5). There are certain differences concerning surface chemistry of these samples. Active carbons CAN-7 possess much stronger carboxyl functional groups than CAPr-1. Carboxyl functional groups for CAN-7 are characterized by values of pK_a 4,5-4,7 while for CAPr-1 such values constitute 5,5-6,0 (Nastas et al., 2008; Rusu et al., 2007). The results (Fig. 5) show much smaller capacities for carbonaceous adsorbents obtained from plum stones by physical-chemical method (CAP-7, CAP-8) and for nitrogen enriched samples, obtained from nut shells (CAN-400, CAN-500, CAN-600, CAN-700, CAN-800). These active carbons contain predominantly basic functional groups (Table 2).

3.2.2. Removal of nitrite ions from ground water

Kinetics of the nitrite ions removal in the presence of CAN-7 (carbonaceous adsorbent obtained from nut shells by chemical method of activation) from model solution and ground water correlate well (Fig. 6). The oxidation process of nitrite ions in the absence of active carbons has practically zero effect. Thus, researches demonstrate efficiency of usage of active carbons

obtained by chemical activation for water treatment with purpose for nitrite ions removal from natural waters.

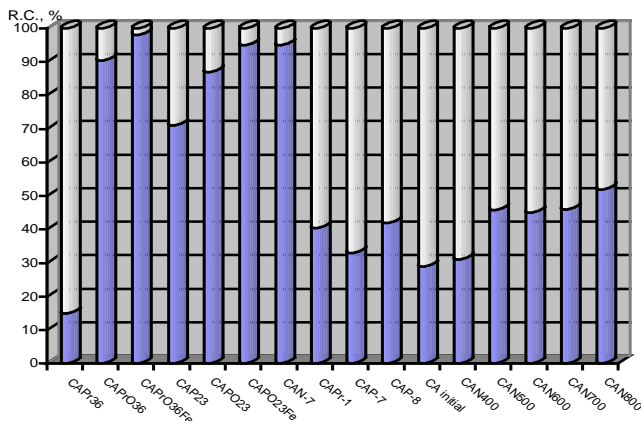


Fig. 5 *Relative capacity (R.C., %) of carbonaceous adsorbents to remove nitrite ions from solutions*

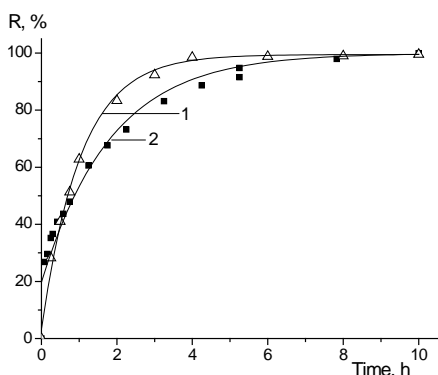


Fig. 6 *Kinetics of the nitrite ions removal (R, %) in the presence of CAN-7 (carbonaceous adsorbent obtained from nut shells by chemical method of activation) from: (1)-model solution ($C_0=10$ mg/L, pH 7,0); (2)- ground water (Chisinau, R.M., $C_0=12,6$ mg/L, pH 5,9).*

4. CONCLUSIONS

The role of the surface functional groups of carbonaceous adsorbents, their acid-basic properties, and the influence of the type of impregnated heteroatoms (N, O,) or metals (Fe, Cu, Ni,) on removal of hydrogen sulfide species and nitrite ions have been researched.

The effects of surface modification of carbonaceous adsorbents towards the catalytic processes of hydrogen sulfide species oxidation were pointed out. The efficiency of the catalyst obtained from peach stones by impregnation with Cu^{2+} ions of oxidized active carbon was established, being recommended for practical purposes to remove the hydrogen sulfide species from the sulfurous underground waters.

Comparative analysis of carbonaceous adsorbents reveals the importance of surface chemistry for oxidation of nitrite ions. Data demonstrate efficiency of the catalyst obtained from nut shells by chemical activation, being recommended for practical purposes to remove nitrite ions from natural waters.

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