MODIFIED ACTIVATED CARBONS AS MATERIALS FOR A DECONTAMINATION OF TI POISONED WATER

МОДИФИЦИРАНИ АКТИВНИ ВЪГЛЕНИ КАТО МАТЕРИАЛИ ЗА ОЧИСТВАНЕ НА ВОДИ ЗАРАЗЕНИ С TI

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ABSTRACT: Removal of large monovalent cations, as highly toxic thallium (Tl), from the waters is a subject of significant interest due to the hazards its pose. Active materials on the basis of activated carbons intended for removal of Tl ions from drinking water was synthesized and characterized in two stages. During the first, deposition and stabilization of the Fe (3+) phase in the internal surface of activated carbon samples (AC/Fe (3+)) was carry out. During the second, deposition on the AC/Fe (3+) of $K_4[Fe(CN)_6]$ phase and subsequent chemical reaction were realized. The removal performance of the samples prepared for Tl ions in aqueous solution was investigated by adsorption process. Increased sorption possibilities were observed toward Tl ions as compare to initial carbons.
KEY WORDS:Tl COMPOUNDS AS TERRORISTIC POISONOUS AGENTS, Tl COMPOUNDS AS SOURCE OF WATER CONTAMINATION, ACTIVE MATERIALS INTENDED FOR REMOVAL OF Tl IONS FROM DRINKING WATER, COMPLEX COMPOUND $Fe_4^{3+}[Fe^{2+}(CN)_6]_3$ ("PRUSSIAN BLUE")

1. Introduction

It is known that the thalium compounds appear to be extremely strong poisons [1,2] to man and animals.

The main source of thalium compounds in water, including underground waters are various mines, mostly for gold yielding but also coal mining, enriching factories and facilities of the color metallurgy. Another source of thalium in waters is the cement factories, the manufacturers of electronic elements, of art glass articles[2,3,4].

A likely source of water contamination (above all potable) with thalium could be the domestic crimes and terroristic actions.

The first ones are made possible by deratization agents (rodenticides) available in the population of a series of countries on a thalium base.

In terms of the use of thalium compounds by terrorists in the quality of poisonous agents for contamination of potable waters, precedents exist which provide for a ground for the priority inclusion of the thalium in the group of terroristic – diversion means [5,6,7,10], etc.

The decontamination of the industrial (the mines in particular) waters from the thalium compounds represents a subject of a series of studies.

For this purpose, various methods have been studied such as reverse osmosis, biological treatment, sulfide sedimentation, etc. [3].

Trials proved that the only generally effective method for decontamination of the industrial and potable waters is the adsorption method.

Due to the nature of the antiterrorist problematic, the literature is lacking data for the decontamination of potable waters contaminated with thalium compounds, but it is absolutely sure that the sorbents used for this purpose are different for the industrial and potable waters.

In this sense, the natural and most of the synthetic zeoliths used (NaY, NaA), incl. modified, cannot provide for decontamination to the required minimal contents of thalium in potable waters, which is 5-7 times lower than the admissible for the decontaminated industrial waters.

A very important reason for this can be the fact that the sorption of thalium ions of industrial waters is realized under controlled pH, whereas in the case of potable water, the pH of water cannot vary but an optimal ratio must be sought: physisorption / chemisorptions, whereas the chemisorbing phases are characterized with high efficiency.

In this sense, the best variant is the use as a chemisorbent, of the complex compound $Fe_4^{3+}[Fe^{2+}(CN)_6]_3$ ("Prussian blue") [8].

The "Prussian blue" according to the American specialists is the active substance of the only antidote used as of the moment against intoxications with thalium compounds[9].

The selection of suitable sorbents for purification of thallium compounds of potable waters is based on the presence in them of suitable texture parameters which are advantageous for the introduction of the chemisorptions phase in the porous texture of the sorbents. Only in this case, the processes of physical adsorption (physisorption) and chemisorptions can be realized optimally and simultaneously in the process of water decontamination from the thallium compounds.

The synthesis of complex compounds in the porous texture of the sorbents however is complicated by the fact that the active phase which provides the chemisorptions of thallium ions should not impede the physical adsorption, respectively to reduce the specific surface and volume of sorbing pores.

As per the literature data, for the synthesis if the metal ferrocyanides in single pore systems, the Kurim method is most suitable [11]. It is a serious problem that this method has not been applied for micro-mesoporous materials such as for instance the activated carbons, sorbents, suitable for sorption of various water compounds.

The activated carbons are characterized with high specific surface and strongly developed porous structure which makes them suitable both with their adsorption function and as carriers of active phases in various processes for water decontamination.

A problem in the case of the activated carbons would be the synthesis in their porous texture of the relatively large molecules of $Fe_4^{3+}[Fe^{2+}(CN)_6]_3$, without significantly reducing the volumes of the sorbing pores and of the admissionporesto the chemisorbing phase.

The last necessitates some variation (modification) by the Kurim method for synthesis in the pores as per the specificities of the compound (micro-mesoporous textures) such as the activated carbons'.

Besides, considering the dependence of the sorption of metal ions in water media of pH of the latter, it is very important to establish the interval of pH, in which the activated carbons with iron hexaferratic complex в sorbe effectively Tl^{1+}ions and its conformity to pH specific to the most frequent potable waters.

As a result of all stated above, the objective of the study is to obtain activated materials based on activated carbon through a synthesis in their porous texture by the modified method of Kurim of iron (3+) hexacyanoferratic (2+) complex, which active materials should be studied in their quality of sorbents for purification of potable waters contaminated with thallium compounds, as per pH of these waters.

2. Experimental part
2.1. Samples

Since no requirements have been formulated for the basic activated carbons intended for the synthesis of the active materials in the conditions of technological difficulties for the performance of the Kurim synthesis in micro-mesoporous systems, we have adopted the empirical approach for selection. For the purpose, the selected activated carbons were predetermined using the low-temperature (77 K) adsorption of nitrogen some of their texture parameters. On the other hand, the chemical nature of the carbon surface was characterized through the determination of the IEPof these.

For the purposes of study, three types of activated carbons were selected (commercial products) on wooden basis (signified BAC), based on apricot shells (signified AAC) and based on coconut shells (signified CNAC), differing by the values of the specific surfaces and of the rest of the texture parameters. The three activated carbons have been obtained through gas-vapor activation. Their main adsorption – texture parameters and values of the IEP are given in Table 1.

Table 1 Main parameters of the porous texture and values of IEP of the studied activated carbons

Samples	A_{BET}, m^2/g	V_t, cm^3/g	V_{MI}, cm^3/g	V_{MES}, cm^3/g	R_P, Å	IEP
BAC	658	0.38	0.20	0.18	11.6	6.1
AAC	895	0.50	0.29	0.21	11.2	7.6
CNAC	1019	0.61	0.33	0.28	12.0	6.8

A_{BET} – specific surface; V_t – total pore volume; V_{MI} – volume of the micropores; V_{MES} – volume of the mesopores, R_P – average radius of the pores; **IEP** – isoelectric point.

2.2. Synthesis of $Fe_4^{3+}[Fe^{2+}(CN)_6]_3$ in the porous texture of the activated carbons

The synthesis by the Kurim method, in the porous texture of the activated carbons of $Fe_4^{3+}[Fe^{2+}(CN)_6]_3$ represents a practical problem.

The main reason is reduced to the need of preparative provision of uniform distribution on the internal surface of the samples of $FeCl_3.3H_2O$, maximally preserving the contact surface considering the follow up interaction with $K_4[Fe(CN)_6].H_2O$, as well as to the iron (3+) hexacyanoferratic (2+) complex of the thalium ions of the water solutions.

The opportunities for introduction of the ferric chloride from aqueous and non-aqueous (methanol) solutions were studied. Based on a comparison of the adsorption-texture parameters (determined via low-temperature adsorption of nitrogen) of samples of activated carbons with introduced $FeCl_3.3H_2O$ from water and methanol media, it was found that in the case of use of the aqueous solution, probably as a result of blocking parts of the porous texture, the specific surfaces, total and mesoporous volumes decrease with the average of about 20-23% for the three carbons.

On the opposite, in the case of the methanol solutions, such effect was not observed. This determined the use of methanol solutions of $FeCl_3.3H_2O$ for the introduction in the porous texture of the activated carbons.

The introduction of $K_4[Fe(CN)_6].H_2O$ was carried out from aqueous solutions, after vacuum drying of the samples with ferric chloride at room temperature.

The samples with introduced ferric chloride and $K_4[Fe(CN)_6].H_2O$ phases were left in a desiccant, at room temperature for 24 hours, during which it was assumed that the forming of the complex $Fe_4[Fe(CN)_6]_3$ is complete.

The main adsorbtion – texture parameters of the synthesized activated materials (signified accordingly as Fe/BAC, Fe/AAC and Fe/CNAC), calculated based on their adsorption isotherms (77 K), are given in table 2.

Table 2 The summary assay of iron and main texture parameters of active materials

Active material samples	Summary content of Fe (mass %)	A_{BET}, m^2/g	V_t, cm^3/g	V_{MI}, cm^3/g	V_{MES}, cm^3/g	R_P, Å
Fe/BAC	12.6	547	0.31	0.18	0.15	11.3
Fe/AAC	12.3	743	0.39	0.23	0.16	10.5
Fe/CNAC	13.0	825	0.50	0.27	0.22	12.1

2.3. Methods of study

The activated carbons and synthesized activated materials on their base are characterized via the low temperature nitrogen adsorption (77.4 K) with Quantachrome Instruments NOVA 1200e (USA) apparatus.

Based on the adsorption-desorption nitrogen isotherms, via the specialized software set in the equipment, the following texture parameters were calculated:

- specific surface area (A_{BET}) by the equation of *Brunauer–Emmett–Teller*, for the interval P/P_O = 0.05 - 0.35 (adsorptive N_2, 77.4 K);

- total volume of the pores (V_t) as per the Gurvich rule for P/P_O = 0.95 (adsorptive N_2, 77.4 K);

- volume of the micropores (V_{MI}) using the Density functional theory (DFT) (adsorptive N_2, 77.4 K);

- volume of the mesopores (V_{MES}) as a difference between the total volume and the volume of the micropores (adsorptive N_2, 77.4 K);

- average radius of the pores (R_P) as a relation of the double V_t and A_{BET}(adsorptive N_2, 77.4 K);

The texture parameters of the samples calculated by the methods referred are presented in Table 1 and 2.

The isoelectric points (IEP) of the carbons were determined by the method of NohSchwarc [12]. For the purpose, for each of the carbons, three different initial solutions were prepared with different pH (accordingly 3, 6 and 11), using HNO_3 (0.1 M) andNaOH (0.1 M). Six flasks were filled each with 20 mlof the solutions and with different quantities of activated carbon (0.05, 0.50, 0.75, 1.00, 5.00 and 10.00g). The balance pH was determined after 24 hours. The curves of the dependences of pH on the carbon masses demonstrate plateau and the isoelectric point is defined as the value which turns the change of pH to zero.

The summary content of iron (Fe^{3+} and Fe^{2+}) in the activated materials was determine via atomic absorption using a spectrometer type Pye Unicam SP 90B.

The study of the sorption of the thalium ions (Tl^{1+}) in potable water of the initial activated carbons and the activated materials Fe/BAC, Fe/AAC and Fe/CNAC, obtained on their ground, was carried out by the method of the periodic adsorption (concentration 0,91 mg/land pHin the interval 3-7.5, 293 K), as a difference of the concentrations before and after adsorption determined through atomic absorption analysis (spectrometer type Pye Unicam SP 90B).

The sorption effectiveness (S, %) of the initial activated carbons and the synthesized active materials on their ground in terms of the thalium ions (Tl^{1+}) in potable water, depending on pH of water has been expressed in percentage against the initial concentration (100 %)

3. Discussion of the experimental results

The comparison of the adsorption texture parameters of the initial activated carbons (Table 1) and of the activated materials (Table 2) demonstrate that as a result of the synthesis in the pores of the activated carbons of the iron (3+) hexacyanoferric (2+) complex, all adsorption texture parameters practically change, however preserving the high values of the specific surfaces and the average radiuses of the pores, to levels facilitating the free access of the thalium ions to the phase introduced.

The data for the summary assay of iron (Fe^{3+} and Fe^{2+}) in the activated materials (Table 2) demonstrates close values for the three samples. This provides us a ground to consider that the effectiveness of the iron hexacyanoferric phase in the samples is also close.

The results for the sorption effectiveness (S, %) of the initial active carbons and the synthesized active materials on their base in terms of the thalium ions (Tl^{1+}) in potable water, depending on the pH of water, under the conditions of the experiments are presented in Table 3.

Table 3 Sorption effectiveness of the initial activated carbons and the synthesized active materials in terms of the thalium ions, depending on the pH of water

pH	sorption effectiveness, %					
	BAC	AAC	CNAC	Fe/BAC	Fe/AAC	Fe/CNAC
3	15	19	16	57	54	50
4	23	27	20	71	63	59
5	25	28	22	58	66	74
6	28	20	21	84	73	90
7	21	18	21	77	72	92
7.5	20	17	19	75	70	86

The analysis of the results from Table 3 demonstrates the determining role of pH of water medium on the sorption activeness of the samples both for the initial activated carbons and the activated materials synthesized on their base.

Impression is made by the strongly dominating sorption capability of the activated materials compared to the initial activated carbons on the base of which these are obtained, and also that the maximal sorption of Tl^{1+} ions in the activated carbons was displaced compared to the activated materials in the field of the lower pH (pH about 4 - 5), and also that, regardless of the difference in the adsorption texture parameters, the sorption effectiveness in the studied activated carbons is very close. Most likely, a limiting factor in the sorption of the Tl^{1+} ions by the activated carbons happen to be their IEP.

Except that, the sorption activity of the activated materials in terms of the Tl^{1+} ions is significantly higher compared to the initial activated carbons, it is determined also by the pH of water. The three studied samples sorb best within the interval pH: 6 - 7, which is a very important interval since it corresponds to the pH of most of the potable water in our country.

In the field of the low values of pH (pH = 3 - 4), the sample Fe/BAC sorbs best the Tl^{1+} ions.

Based on the results of Table 2 and 3, it can be concluded that a direct dependence between the specific surfaces, total and mesoporous volumes of the pores of the activated materials (for practically identical amounts of $Fe_4[Fe(CN)_6]_3$ phase) on one hand, and their sorption capacities in terms of Tl^{1+} ions in the potable water, is lacking.

For the interval of values of pH (pH=5-7), characterizing with the highest sorption in the studied process, by its sorption activity against the thalium ions, the activated materials can be presented in the following downward row: Fe/CNAC > Fe/BAC > Fe/AAC.

4. Conclusion

Activated materials have been synthesized through modified method of Kurim based on activated carbon and the iron (3+) hexacyanoferric (2+) complex, intended for the decontamination of potable water poisoned with Tl^{1+} iones.

The active materials obtained possess significantly higher sorption activeness against the thalium (Tl^{1+}) ions compared to the initial activated carbons.

Dependence has been established between pH of the water media and the sorption effectiveness in terms of the Tl^{1+} ions on behalf of the activated materials. The maximal sorption effectiveness is observed for the interval of pH (pH about 6-7) specific to most of the potable water in our country.

The results obtained provide us a ground to continue our studies on the synthesis of activated materials with introduced iron hexacyanoferric phase and other micro-porous carriers other than the activated carbons.

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