Sewage Clearing from Mercury by NCMS Nanocomposite Carbon Sorbent

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Abstract

Pilot trials of a new nanocomposite mesopore sorbent of the NCMS type have been conducted in a purification technology for slightly acidic sewage from mercury. According to the trials, the dynamic capacity with respect to mercury of the NCMS sorbent was equal to 25.6 mg/g. Atomic emission spectroscopy method with the application of a two-jet plasmatron and a registration scheme was used to receive data on the nature of quantitative distribution of mercury and associated impurity-metals (lithium, sodium, potassium, and calcium) across the layers of a sorbent load. It has been demonstrated that the NCMS sorbent concentrates preferentially mercury and potassium, and their mutual ratio is close to the formulation of K_2HgI_4 compound, while impurities of other metals practically do not accumulate in the sorbent.

INTRODUCTION

Environment protection issues take on paramount importance in the context of further development of industry and the use of mercury in great amounts during electrochemical obtaining caustic alkalis and chlorine. It is common knowledge that metallic mercury is highly toxic regarding any forms of life (mercury MPC comprises 0.01 mg/m^3 in the air of the work zone, 0.0003 mg/m^3 in outer air, 0.0005 mg/l in water of water basins, 2.1 mg/kg in soil, the 1st hazard class) [1]. Therefore, a complex of measures in all productions that are based on mercury application in technological processes is developed as regards gas purifying, decontamination of sewage and processing media from mercury. Sorption methods [2], the decisive factor in which is picking a sorbent, are used most widely in the processes.

Previously [3-5], we have developed a mercury-selective modified nanocomposite mesopore carbon sorbent (NCMS), whose static capacity that has been determined with model solutions of mercury (II) nitrate, was equal to 152 mg/g. However, the NCMS dynamic capacity that has been obtained in laboratory conditions appeared to be substantially lower (1.4 mg/g) during the extraction of mercury by this sorbent from processing media [6].

The purpose of this work is to find performance dynamic capacity of NCMS sorbent with respect to mercury in a commercial sorption unit and to determine the nature of distribution of mercury and associated impurity metals across the layer of a sorbent.

EXPERIMENTAL

NCMS sorbent in an amount of 500 kg has been produced under workshop conditions directly in an adsorbtion column according to the technological instruction that has been

TABLE 1

Characteristics of various fractions of NCMS carbon sorbent

Fraction No.	Granular size, mm	A_{BET}, m^2/g	ρ_{sat}, g/cm^3	ΣV of pores with respect to water, cm^3/g	Iodine number, mg/g
1	0.7−1.0	492 ± 13	0.46 ± 0.01	0.82 ± 0.01	220 ± 10
2	1.0−1.5	490 ± 13	0.47 ± 0.01	0.83 ± 0.01	220 ± 10
3	1.5−3.0	362 ± 13	0.50 ± 0.01	0.85 ± 0.01	220 ± 10

worked out in the Institute of Inorganic Chemistry, SB RAS, and Novosibirsk Chemical Concentrates Plant JSC [7]. Table 1 lists the basic characteristics of various fractions of the initial NCMS sorbent. The fractions 2 (400 kg) and 3 (100 kg) were used for the research.

Sewage water (pH 3−4) of the following composition was used for decontamination from mercury (g/l): Cl^- 0.15, Li^+ 0.53, Ca^{2+} 0.002, Mg^{2+} 0.0005, Na^+ 0.043, and K^+ 0.008. The sorption workshop experiment was conducted as follows. Upon a prior settling and filtration, the sewage with input mercury content of 1.5−2.8 mg/l was fed at a rate of 15 m^3/h from top to down to an adsorbtion column (the column height was 3 m, the diameter of 1.5 m) of a standard performance [8] that was filled with NCMS sorbent. The experiment was conducted around the clock. Mercury content was controlled at the outlet from the column during the sorption process. Sampling was made every 24 h.

A residual content of mercury in the solution samples was determined by atomic absorption spectroscopy method (AAS) (a "cold steam" method). Mercury content of sewage at the inlet and outlet from the column was determined as an average over three independent determinations. Sorption process was stopped after the breakthrough content of mercury has been attained in the residual solution (more than 0.13 mg/l). After carrying out of the experiment, mercury-saturated NCMS sorbent was discharged from the column and divided into 20 layers along the height of the sorbent. A sample was taken in each layer, and mercury content and the content of associated metals (sodium, lithium, potassium, and calcium) was determined in the sample by the direct atomic emission spectral analysis method (AES) with the use of a two-jet arc plasmatron and a registration technique [9].

TABLE 2

Results of commercial-grade tests for sewage decontamination from mercury by NCMS sorbent

Time, h	C_{Hg}, mg/l at the inlet	at the outlet	V, m^3	Mercury amount on the sorbent, g/kg
24	1.5 ± 0.3	0.0005 ± 0.0001	360	1.1 ± 0.2
48	1.5 ± 0.3	0.0005 ± 0.0001	720	2.2 ± 0.4
72	1.5 ± 0.3	0.0005 ± 0.0001	1080	3.2 ± 0.6
96	1.5 ± 0.3	0.0005 ± 0.0001	1440	4.32 ± 0.8
120	1.5 ± 0.3	0.0005 ± 0.0001	1800	5.4 ± 1.0
144	1.5 ± 0.3	0.0005 ± 0.0001	2160	6.5 ± 1.2
168	1.5 ± 0.3	0.0005 ± 0.0001	2520	7.6 ± 1.4
192	2.8 ± 0.6	0.009 ± 0.002	2880	9.6 ± 1.9
216	2.0 ± 0.4	0.009 ± 0.002	3240	11.0 ± 2.2
240	2.0 ± 0.4	0.009 ± 0.002	3600	11.1 ± 2.2
456	2.0 ± 0.4	0.009 ± 0.002	6840	24.1 ± 4.8
504	0.8 ± 0.2	0.13 ± 0.03	7560	25.6 ± 5.1
528	1.6 ± 0.3	1.4 ± 0.3	7920	26.8 ± 5.4

Mercury sorption degree (α) from a solution was calculated with the formula

$$\alpha = 100(C_{Hg}^{i} - C_{Hg}^{f})/C_{Hg}^{i} \qquad (1)$$

where C_{Hg}^{i} is mercury content in the initial solution at the column inlet, mg/l; C_{Hg}^{f} is an average mercury content in a fixed volume of the solution after sorption, mg/l.

Performance dynamic capacity (PDC, mg/g) of NCMS sorbent with respect to mercury was calculated by the equation

$$PDC = 1000(C_{Hg}^{i} - C_{Hg}^{f})V/m \qquad (2)$$

where V is the fixed volume of the passed solution, m^3; m is the sorbent mass in the adsorbtion column, kg.

RESULTS AND DISCUSSION

Table 2 presents the results of commercial tests of NCMS sorbent for sewage decontamination from mercury. One can see that 2520 m^3 of sewage were cleared from mercury to a level of MPC of 0.0005 mg/l within one week during the course of the experiment. The overall duration of the experiment was equal to 21 days; the volume of the sewage that has been cleared from mercury, to 7920 m^3. The performance dynamic capacity of the sorbent with respect to mercury until a breakthrough amounted to 25.6 mg/g, which is comparable with a PDC for a VP-1AP anion exchanger that was used earlier in a technology of wastewater decontamination from mercury [10].

Figures 1, 2 display mercury sorption degree from a solution *versus* the sorption time and an output dependence curve for mercury content after sorption on the passed volume. The height of the working layer of the sorbent has been determined from the output curves by the Michaels−Trable equation [8], and the height have appeared to be equal to the height of the fixed sorbent bed (0.9 m). Thus, the sorbent has shown high PDC and 100 % efficiency of the sorbent use.

Figure 3 presents distribution curves for mercury and associated metals (lithium, sodium, potassium, and calcium). The mass fraction of mercury in the NCMS sorbent comprises 0.3−1.1 %, its maximum quantity (550−728 g) falls on high layers of the sorbent, and it decreases across the layer to 179 g. Lithium content varies within the range of 0.05−1.2 mass %, that of sodium − 0.026−0.089 mass %, calcium − 0.013−0.12 mass %, and potassium − 0.030−0.90 mass %. According to AES data, the waste sorbent contain 8 kg of mercury, 1.7 kg of lithium, 0.8 kg of calcium, 2.3 kg of potassium, and 0.4 kg of sodium. The content of sodium, calcium, lithium in the NCMS sorbent is virtually identical throughout the sorbent layers and it bears witness to their weak sorption. A sharp difference in the behaviour of impurities is observed for potassium.

It is evident from data of Fig. 3 that the variation in the potassium content across the layers repeats the character of changing mercury content, and in so doing, the mass ratio of the content of mercury to potassium, according to the analysis, is 3.5 : 1. By virtue of the fact that the mass ratio Hg : K = 2.6 : 1 for $K_2[HgI_4]$ compound, and it is equal to 5.2 : 1 for $K[HgI_3] \cdot H_2O$ compound, we can rather con-
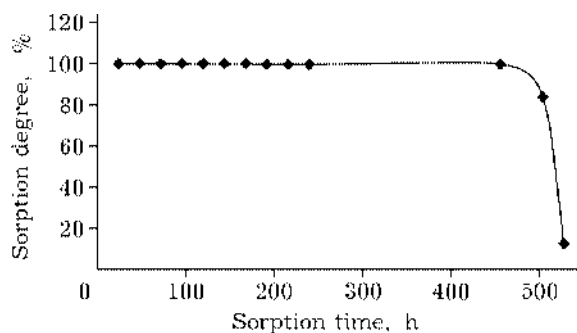

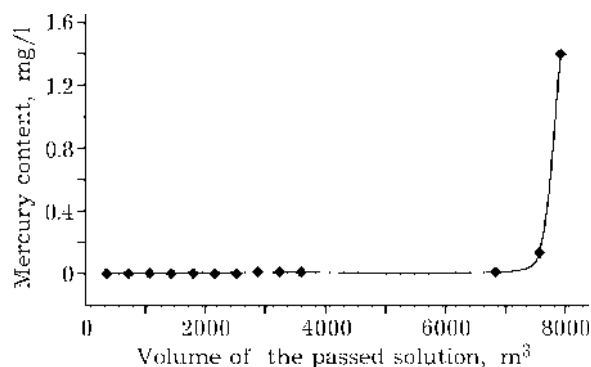Fig. 1. Mercury sorption degree from a solution on NCMS sorbent *versus* time.

Fig. 2. Output curve for mercury content as a function *versus* passed volume.
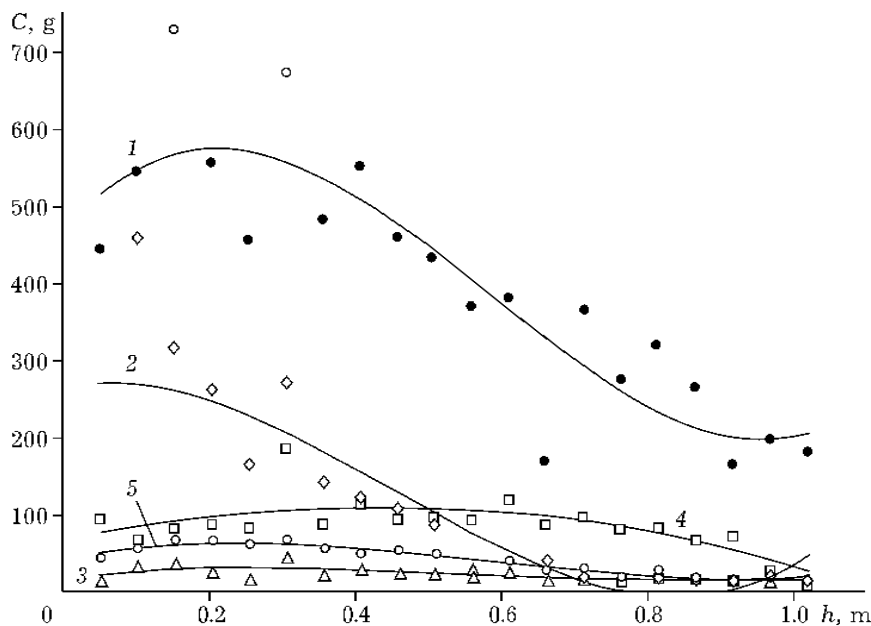
Fig. 3. Curves of changing content of mercury and alkali metals across a layer of the waste NCMS sorbent: Hg (*1*), K (*2*), Na (*3*), Li (*4*), Ca (*5*).

fidently assume that the formation of slightly soluble coordination compounds of mercury with iodine occurs during mercury sorption from acid solutions on the NCMS carbon sorbent that has been modified by iodine, particularly, the formation of the known $K_2[HgI_4]$ compound or its mixture with $K[HgI_3] \cdot H_2O$.

Based on data for the dependence of the distribution of mercury and potassium across sorbent layers, it looks rather understandable that no correlation is observed in the mutual behaviour of sodium, calcium, lithium, and mercury. With tetraiodomercurate anion, these cations form more soluble compounds in water as compared to $K_2[HgI_4]$. The acquired data on the mutual behaviour of potassium and mercury during sorption from water solutions confirm the coordination model of chemisorption of mercury and other metals from liquid media on sorbents akin to NCMS that we have formulated earlier [11].

CONCLUSIONS

1. The performance dynamic capacity with respect to mercury for NCMS sorbent has been determined during decontamination of commercial sewage from mercury, and it was equal to 25.6 kg/t.

2. Dependences of the distribution of the content of mercury and associated metals (lithium, sodium, potassium, and calcium) on the height of the sorbent layer have been obtained. It has been demonstrated that NCMS simultaneously concentrates mercury and potassium (presumably in the form of K_2HgI_4), while the character of distribution of lithium, sodium, and calcium over the height of the sorbent remains practically constant.

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