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Modified Carbon Sorbents for Extraction of Sodium and Calcium Admixtures from the Solutions of Lithium Chloride

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Abstract

Methods of obtaining carbon sorbents modified with the compounds of antimony (V) were developed for the extraction of sodium and calcium admixtures from the solution of lithium chloride. The sorption capacity of the obtained modified carbon materials under static and dynamic conditions was estimated. It was shown that the most efficient sorbent NUMS-K-1 was obtained by the saturation with SbCl_5 followed by its hydrolysis. With antimony content in the carbon sorbent up to 8 %, total dynamic capacity with respect to sodium is 2.2, with respect to calcium 4 mg/g. In the course of dynamic experiments, it was established that the residual concentration of sodium at the outlet of the sorption column reaches 0.25, calcium 2 mg/L. The obtained results meet the requirements to the purity of lithium products. The promising character of the use of carbon sorbents modified with antimony (V) compounds in the processes of lithium chloride purification from sodium and calcium admixtures was demonstrated.

Key words: carbon sorbents modified with antimony (V) compounds, sorption of sodium and calcium, lithium chloride solution

INTRODUCTION

Porous carbon materials (CM) are widely used as adsorbents in the processes involved in chemical, food, pharmaceutical industry. Because the initial components for obtaining them are various carbon-containing wastes, black and brown coal, peat, wood, nut shells, polymers, oil and coke pitch, CM obtained from those waste materials differ in texture characteristics and adsorption properties [1–3]. Among porous CM, special attention is attracted to mechanically strong synthetic nanoporous composite CM manufactured by the Institute of Hydrocarbons Processing (IHP) of the SB RAS (Omsk) [4, 5].

Selectivity with respect to a given component is an essential parameter of a sorbent. Selectivity is achieved due to surface modification (oxidation, saturation with complex-forming substances). The selectivity and effi-

ciency of these sorbents can easily be governed because these properties are determined first of all by the chemical properties of the deposited reagent. In order to make sorbents based on CM with large sorption capacity with respect to a given component, efficient methods of the activation of carbon surface were developed [6, 7]. It was shown that chemical modification of the carbon matrix allows one to obtain new carbon-containing sorbents, in particular those intended for the recovery of mercury from technological lithium-containing solutions [8]. The development of new modified carbon sorbents selective with respect to sodium and calcium has been dictated by the requirements to the ready products of lithium production. One of these requirements is the purification of the technological solution of lithium chloride from Na^+ and Ca^{2+} admixtures that enter the solution with initial lithium carbonate. The data on the residual admixture content in lithium and

lithium chloride, and other characteristics of lithium products manufactured at the Novosibirsk Chemical Concentrates Plant (NCCP) are placed on the official web site of the manufacturer [9].

It is known that oxidized activated coal is suitable to recover calcium from solutions [10–13] and provides rather deep purification from calcium admixture till the preparations of the os. ch. grade are obtained. At the same time, the extraction of sodium ions from solution is a complicated problem. To obtain a carbon sorbent selective to sodium ions, hydrolysed antimony (V) compounds were used as the modifying additive. The choice of these compounds as modifying additives is explained by the ion exchange properties of antimonious acid that were studied in detail in many works [14–17]. It was demonstrated that antimonious acid forms difficultly soluble compounds with alkaline metals. The formed complexes are so strong that the supports, including CM, modified with antimonious acid, can be used to purify the solutions of lithium salts from the admixtures of alkaline metals. Investigation of the sorption of sodium ions from model solutions on CM modified with antimonious acid allowed revealing the dependence of sorption capacity on the method of obtaining antimonious acid and on the texture characteristics of CM [18–22]. So, nanoporous CM is a promising support for making sorbents. In this connection, the goal of the present work was the development of new carbon modified sorbents based on nanoporous CM of Tekhnosorb mark to extract the admixtures of sodium and calcium from the technological solutions of lithium chloride.

EXPERIMENTAL

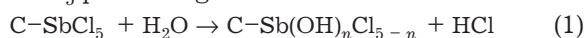
We chose the Tekhnosorb CM for investigation. Its characteristics are: particle size 0.5–0.7 mm, specific surface area 300–400 m²/g, packed density 0.5 g/cm³, total pore volume 0.7–1.1 cm³/g, the volume of mesopores 0.5 cm³/g. This CM was obtained at the IHP (Omsk, Russia) by means of the deposition of pyrolysis products from the butane-propane mixture at 800–900 °C on granulated carbon black in the boiling bed reactor, followed by activation in the presence of CO₂ or water vapour [5]. This technology of the synthesis of CM allows directed variation of texture characteristics, size and

total pore volume. For these reasons, CM is very promising as a matrix for obtaining new sorbents.

CM modification was carried out with the help of the following compounds: SbCl₅, Sb₂O₅ · 3.5H₂O and [SbCl_{5-n}(OH)_n]. The synthesis of these compounds was described in detail in [23].

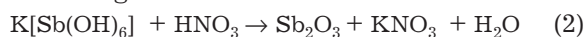
Depending on the method of modification with antimony compounds, sorbents NUMS-K-1 and NUMS-K-2 were obtained. Antimony content in them varies within 2 to 8 %. To obtain modified carbon sorbent, we used the CM purified preliminarily from metal admixtures by treatment in HCl under slow heating for 6 h at a temperature of 70 °C, followed by fourfold washing with distilled water until washing water reached pH 5.5. The solid to liquid ratio during acid treatment was about 1 : 3 by mass. After decanting and separation by filtering, the resulting CM was dried at 80–100 °C for 3 h to reach the constant mass. The data on the concentrations of admixture elements in the samples of initial and purified CM are presented in Table 1.

Carbon modified sorbent NUMS-K-1 was obtained as following. A weighed portion of 22 g CM purified preliminarily from metal admixtures was saturated with 30 g SbCl₅ (SbCl₅ was obtained by chlorination of metal antimony at a temperature of 70–100 °C for 3–5 h) and kept in a closed vessel for 24 h. Then the resulting solution was transferred into a column; 5 L of distilled water was passed through it at a rate of 50 mL/min. Elution process was accompanied by the hydrolysis of SbCl₅ proceeding on carbon surface:



Thus obtained carbon modified sorbent NUMS-K-1 was dried to the constant mass; the amount of NUMS-K-1 was 28 g. Antimony content of this sample was 8 %. Total exchange capacity was determined by means of potentiometric titration with respect to 0.1 M NaOH solution; it was equal to 0.7 mg-eq./g.

Unlike for NUMS-K-1, in order to obtain NUMS-K-2, Sb₂O₅ · 3.5H₂O was precipitated from the solution of K[Sb(OH)]₆ by nitric acid, then the precipitate was washed and dried in the air at 25 °C for 5 days to the constant mass according to reaction was



K[Sb(OH)]₆ was obtained through the interaction of Sb₂O₃ with KOH in the solution of H₂O₂ according to reaction

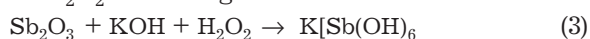


TABLE 1

Concentrations of admixture elements in the samples of initial and purified CM

Element, wavelength of the analytical spectral line, nm	Found, ppm	
	Initial CM	Purified CM
Al I 308.2151	54.7±8.5	12.1±2.1
As I 234.984	1.24±0.19	1.2±0.2
B I 249.7723	1.05±0.14	0.73±0.10
Ba I 223.061	1.33±0.12	0.42±0.06
Ca II 318.1275	369±53	6.7±3.9
Cd I 346.62	0.12±0.04	0.12±0.04
Co 339.537	6.74±0.75	0.363±0.039
Cr II 267.717	11.5±1.5	4.6±0.2
Cu I 327.3954	1.48±0.15	0.92±0.11
K 344.6371	23.6±5.5	0.394±0.037
Fe I 248.8143	124±14	1.5±0.6
Mg I 285.2126	10.9±0.9	4.04±0.53
Mn I 324.8512	3.62±0.42	2.81±0.47
Mo I 313.2594	2.88±0.56	2.87±0.52
Na 312.5208	27.6±4.2	1.21±0.21
Ni I 313.4106	13.8±1.4	6.3±1.8
Pb I 283.3053	4.3±0.29	3.17±0.3
Si I 288.1579	23.1±2.4	11.6±1.1
Sn I 277.982	9.97±0.79	4.95±1.30
Ti 289.1075	5.40±0.75	5.06±0.82
V 280.1058	2.91±0.29	2.07±0.40
Zn 213.8573	2.17±0.32	1.41±0.19
Total impurities, ppm	701.4±90	74.5±17

Note. . $P = 0.95$, $n = 8-20$.

The NUMS-K-2 sorbent was obtained by keeping a weighed portion of 20 g CM, preliminarily purified from metal admixtures, in the solution of 1.5 M $K[Sb(OH)_6]$ for 24 h. Then the CM was separated by filtering, washed and dried. The amount of thus obtained sorbent was 28 g, with antimony content 8 %. Total exchange capacity of NUMS-K-2 according to the data of potentiometric titration was 1 mg-eq./g. It should be noted that the static capacity of the sorbent with respect to sodium and calcium ions depends on antimony content of the sorbent.

RESULTS AND DISCUSSION

The following dependence of the static capacity with respect to sodium ions on antimony content was established for NUMS-K-1: for

antimony content 2, 3, 5, 8 % the static capacity of the sorbent was 9.4 ± 1.5 (0.40 ± 0.06), 8.6 ± 1.4 (0.40 ± 0.06), 11.1 ± 1.8 (0.48 ± 0.08) and 17.3 ± 2.8 (0.75 ± 0.12) mg/g (mg-eq./g), respectively. So, the static capacity increases with an increase in antimony content. Sorption of sodium and calcium on NUMS-K-1 and NUMS-K-2 sorbents were studied with model and technological solutions under static and dynamic conditions. It was shown that the sorption of sodium ions from model solutions under static conditions on the NUMS-K-1 sorbent is very rapid. The equilibrium is achieved within 15 min (Fig. 1). Experiments on the extraction of sodium and calcium admixtures from the technological solution of lithium chloride was carried out with NUMS-K-1 and NUMS-K-2 under dynamic conditions. The technological solution

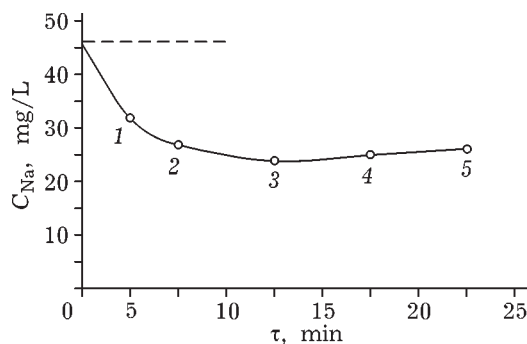


Fig. 1. Kinetic curves of sodium sorption on NUMS-K-1: 1 – average of four values (33, 32, 34, 27); 2 – average of 3 values (26, 29, 27); 3 – average of 3 values (24, 27, 23); 4 – average of 2 values (24, 26); 5 – average of 2 values (23, 29).

of lithium chloride was prepared as follows: 2 kg of lithium carbonate was placed in a vessel 10 L in volume, then chlorination was carried out for 4 h. The solution of lithium chloride having the following composition was obtained, g/L: LiCl 142, LiClO 5.2, LiClO₃ 35, Ca 0.075, Na 0.05. For dynamic measurements, we used glass columns with the diameter 9–11 mm,

the height of sorbent layer was varied from 30 to 76 cm, filtration rate was 30 to 100 mL/h, pH was 3–5. Calcium and sodium concentrations in the initial lithium chloride solution and at the outlet of adsorption columns were determined by means of atomic absorption spectrometry. The results of the experiments on the purification of lithium chloride solution from sodium and calcium ion admixtures are shown in Tables 2, 3. The necessary residual concentration of calcium admixture was 10 mg/L, sodium 5 mg/L. The dynamic capacity of the sorbent before skip (the concentration of 5 mg/L was taken as the skip) for sodium was equal to 1.8 mg/g; the total dynamic capacity with respect to sodium was 2.2 mg/g. The dynamic capacity of the sorbent before skip for calcium (the concentration of 10 mg/L was taken as the skip) was 2.6 mg/g. The total dynamic capacity was 4 mg/g. The total dynamic exchange capacity for NUMS-K-2 for the given concentration conditions for sodium was equal to 0.09 mg/g, for calcium 0.47 mg/g.

TABLE 2

Outlet concentrations of sodium and calcium in the sorption of lithium chloride on NUMS-K-1 (column diameter: 0.9 cm, height of layer: 50 cm, filtration rate: 30 mL/h, sorbent mass: 28 g, concentrations of calcium and sodium in the initial solution: 100 and 50 mg/L, respectively)

Experiment No.	V_{skip} , mL	Concentration, mg/L	
		Na	Ca
1	30	0.25±0.01	2.0±0.1
2	90	0.25±0.01	2.0±0.1
7	240	0.25±0.01	2.0±0.1
8	270	0.25±0.01	6.0±0.3
9	300	0.25±0.01	6.0±0.3
10	330	0.25±0.01	2.0±0.1
11	360	0.25±0.01	5.0±0.3
14	480	0.25±0.01	2.0±0.1
15	510	0.25±0.01	2.0±0.1
16	540	0.25±0.01	3.0±0.1
17	590	0.25±0.01	2.0±0.1
18	690	0.25±0.01	2.0±0.1
19	710	0.25±0.01	2.0±0.1
20	740	1.0±0.1	2.5±0.1
21	990	5.0±0.3	50.0±2.5
25	1040	23.0±0.1	70.0±3.5

TABLE 3

Outlet concentrations of sodium and calcium in the sorption of lithium chloride on NUMS-K-2 (height of layer: 50 cm, filtration rate: 30 mL/h, sorbent mass: 28 g, concentrations of calcium and sodium in the initial solution: 0.005 and 0.019 g/L, respectively)

Experiment No.	V_{skip} , mL	Concentration, mg/L	
		Na	Ca
1	30	0.25±0.01	2.0±0.1
2	60	0.25±0.01	2.0±0.1
3	90	0.25±0.01	2.0±0.1
4	120	0.25±0.01	2.0±0.1
5	150	0.25±0.01	2.0±0.1
6	180	0.25±0.01	2.0±0.1
15	450	0.25±0.01	2.0±0.1
16	480	0.3±0.01	2.0±0.1
17	510	2.5±0.1	2.0±0.1
18	540	5.0±0.3	2.0±0.1
19	570	5.0±0.3	2.0±0.1
20	600		2.0±0.1
21	630		2.0±0.1
22	660		2.0±0.1
23	690		2.0±0.1
24	720		12±0.6
25	750		20.0±1.0

CONCLUSIONS

1. Methods of obtaining sorbents based on carbon material of Tekhnosorb mark modified with the compounds of antimony (V) were developed for the extraction of sodium and calcium admixtures from lithium chloride solutions.

2. It was shown that the most efficient sorbent NUMS-K-1 is obtained by the saturation of CM with the solution of SbCl_5 followed by the hydrolysis of antimony chloride. For antimony content 8 % in the carbon sorbent, the total dynamic capacity with respect to sodium is equal to 2.2 mg/g, with respect to calcium 4 mg/g.

3. It was shown in dynamic experiments that the residual concentration of sodium in lithium chloride solution at the outlet of the sorption column reaches 0.25 mg/L, calcium 2 mg/L, which meets the requirements to the purity of lithium products.

Thus, the promising character of the use of carbon sorbents modified with antimony (V) compounds in the processes of lithium chloride purification from sodium and calcium admixtures was demonstrated.

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