PURIFICATION OF WATERS FROM BORON BY FATTY ACIDS SOLID-PHASE EXTRACTION

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ABSTRACT

Boron compounds are applied in different industries due to their fire retardancy, heat resistance, nonlinear optics and antiwear properties. The extraction of boron from natural waters in the form of boric acid can relieve the increasing consumption of this element. The optimal conditions of solid extraction of boron from natural waters by caprylic and stearic acid with different carriers (mannitol and paraffin) are investigated. The effect of the temperature and the phase contacts number is presented. The optimal temperature is found equal to 60°C. The best results are obtained at the 3rd phase contact: up to 74.12 % in case of the "fatty acids-paraffin" system.

Keywords: boron, purification, solid-phase extraction, fatty acids, mannitol, paraffin.

INTRODUCTION

Boron has to be recovered as it is an essential element in various industries ranging from atomic energy to pharmaceutical one [1 - 5] due to its fire retardancy, heat resistance, nonlinear optics and antiwear properties [6]. Though boron exists at low concentrations in the environment, a concentration in the range of 10 mg dm^{-3} - 100 mg dm^{-3} or even higher is frequently found in water resources including sewage, industrial wastewater, and agricultural effluents affected by anthropogenic discharges [7 - 10]. High concentrations of boron are recorded in the rice fields of Kazakhstan leading even to "boron toxicosis" [11]. The removal of boron from aqueous solutions is of high importance because it is poisonous to the environment [12].

Several methods can be used to extract boron including acid precipitation, solvent extraction, adsorption, and crystallization [13 - 18].

Most boron treatment technologies are based on boron complexation, which requires further separation or filtration of the boron containing complexes obtained. But these additional treatment steps affect the boron removal efficiency and the corresponding costs [19].

Fusible solid extractants (fatty acids, paraffin) are currently the most commonly used and promising extractants for purification of industrial wastewater from heavy metals, uranium compounds and a number of organic substances (phenols, paints, aldehydes, etc.). They are of practical interest in terms of reducing the solubility of the extractant in the aqueous phase without reducing its extraction characteristics. The choice of diluents is determined by the fact that the extractability of borates is significantly influenced by the content in the extract of complex-forming functional groups capable of forming stable complexes with borate anions.

The fatty acids, FA, used for the extraction of boron from aqueous solutions are characterized by the simplicity of their preparation, easy regeneration, and fast establishment of equilibrium.

The natural water of the Aktyubinsk region of the Republic of Kazakhstan is rich in boron-containing

compounds. The closed joint stock company (CJSC) "Fosfokhim" is the source of the environmental pollution of Alga city in Aktyubinsk region. Its emissions to the atmospheric air contain sodium tetraborate salts, fluoride compounds, boron-containing dust, sulfuric acid vapors, and sulfurous anhydride. During the observation period in the air basin, the excess of MPC for sulfur dioxide (up to 7 - 8 times), boron-containing dust (up to 4.0 times) and hydrogen fluoride (up to 2 - 4 times) are repeatedly noted. The anthropogenic pollution of the surface and the groundwater is caused by the presence of more than 20 thousand tons of boron compounds in a sludge accumulator. This resulted to their penetration to the system of domestic and drinking water supply.

The present investigation is aimed at the determination of the optimal conditions of solid extraction of boron from natural waters by caprylic and stearic acid using different carriers (mannitol and paraffin).

EXPERIMENTAL

Extractants

Individual technical fractions of fatty acids (FA), caprylic and stearic acids, were used as fusible solid extractants under solid-phase extraction conditions. They were provided as "ultra pure". An inert diluent of FA paraffin of a carbon atoms number $n_C > 15$ was introduced. The amount of the extractants used varied between 200 g and 300 g.

The most important characteristics of the extractants used in the present study are given in Table 1.

Water samples description

Mineralized boron-containing water was used in the study of the solid-phase extraction process. Its characteristics are presented in Table 2. The data given in Table 2 shows that the natural-drinking water taken for the analysis refers is highly mineralized. Boron-containing mineral waters of a boron content of 1.43 mg dm^{-3} were prepared on the ground of this water.

Extraction of boric acid from water

A thermostated cell was used for the extraction. The scheme of the laboratory installation is shown in Fig. 1. The prepared mixture was stirred until equilibrium was established. Then the aqueous phase was transferred to a beaker and the boric acid content was determined.

Determination of the boric acid concentration

The portion of the test solution was acidified by hydrochloric acid until a weakly acidic reaction determined by methyl red and boiled for 1min - 2 min for carbon

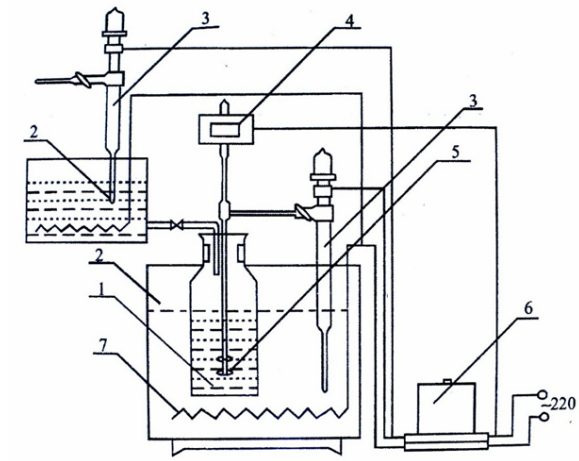

Fig. 1. A scheme of the laboratory installation: 1 – a reactor; 2 - a thermostat; 3 - a contact thermometer; 4 - a temperature relay; 5 - a mixer; 6 – an electric motor; 7 - a hotplate.

Table 1. Physico-chemical characteristics of extractants.

System	C_{CMC}, kmole·m^{-3}	σ_{CMC}, mN·m^{-1}	$G_{CMC}\times10^{-4}$, mN·m^2·kmole^{-1}	$G\times10^{9}$, kmole·m^{-2}	$S_{CMC}\times10^{20}$, м^2	$-\Delta G^0_M$,	$-\Delta G^0_a$,
						kJ·mole^{-1}	
SDS–PVA	$2\cdot10^{-4}$	30	20	3	56	21	35
CTAB–PVA	$3\cdot10^{-5}$	42	98	2	84	26	41

Table 2. Analysis of natural-drinking water for the content of the main components, mg dm^{-3}

Ca^{2+}	Mg^{2+}	Cd^{2+}	Cu^{2+}	Cl^-	NO_3^-	F^-	SO_4^{2-}	HCO_3^-
75.00	30.20	0.014	0.004	63.9	30.8	0.48	249.0	630.2

Table 3. Effect of temperature on recovery of boron extraction.

Extractants	Temperature, °C	Residual boron content in solution, mg dm^{-3}	Recovery, %
FA	40	0.92	35.66
	50	0.85	40.56
	60	0.83	42.66
	70	0.83	42.66
FA – mannitol	40	0.93	34.97
	50	0.79	44.76
	60	0.76	46.85
	70	0.75	47.55
FA – paraffin	40	0.97	32.17
	50	0.88	38.46
	60	0.86	39.86
	70	0.85	40.56

dioxide removal. It was cooled to room temperature and neutralized by standard 0.1 N NaOH solution. Methyl red was used to determine the neutralization point.

Phenolphthalein (10 drops - 15 drops) and 1 g of mannitol were added to the neutralized sample. Then it was titrated with 0.1 N NaOH until the appearance of a pink color. Mannitol was added at the end of the titration to ensure that the sample solution was not acidic. Otherwise, the titration was continued while the color of the indicator changed with the addition of mannitol.

Mannitoboric acid was formed as a result of the interaction of mannitol with boric acid. It was titrated with sodium hydroxide in accordance with:

$2(C_6H_8)(OH)_6 + H_3BO_3 \leftrightarrow H[BO_2(C_6H_8)_2(OH)_{12}] + H_2O$

$H[BO_2(C_6H_8)_2(OH)_{12}] + NaOH \leftrightarrow NaBO_2 + C_6H_8(OH)_6 + H_2O$

RESULTS AND DISCUSSION

It is well known that a room temperature is considered optimal for carrying out extraction studies. This is due to the fact that organic solvents react quite ambiguously to temperature changes (an emulsion appears, a phase separation is observed, etc.). FA are liquefied in this study at higher temperatures: 40°C and above. The optimal temperature is determined in a series of experiments whose results are presented in Table 3.

The boron recovery rate increases with temperature increase from 40°C to 60°C. The further increase to 70°C does not lead to significant extraction. For example, the recovery at 60°C is 46.85 % in FA-mannitol system, while it amounts to 47.55 % at 70°C. Therefore, in order to save time and energy, the further studies of boric

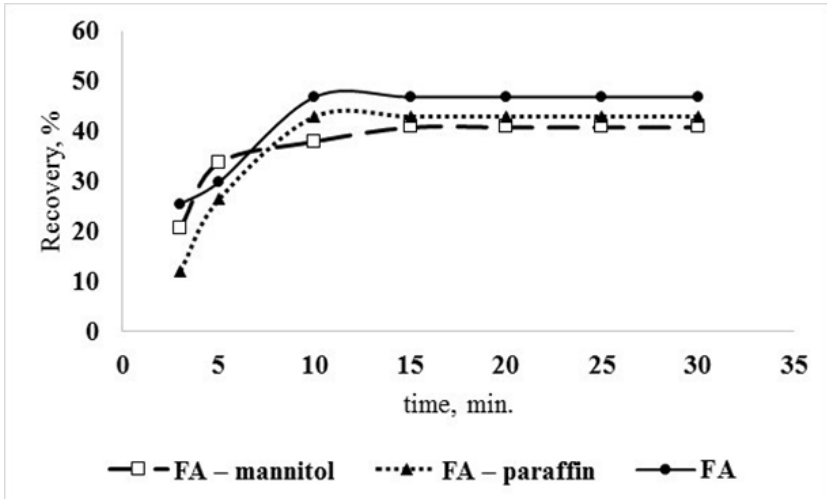

Fig. 2. Dependence of boric acid recovery on the phase contact time.

Table 4. Effect of number of phase contacts on recovery of boron extraction.

Extractants	Residual boron content in solution, mg dm^{-3}	Number of phase contacts	Recovery, %
FA	0.85	I	40.56
	0.64	II	55.24
	0.51	III	64.33
FA – paraffin	0.85	I	40.56
	0.71	II	50.35
	0.47	III	67.13
FA – mannitol	0.77	I	46.15
	0.61	II	57.34
	0.37	III	74.12

acid extraction from boron-containing mineral waters are carried out at the temperature of 60°C, accepted as the optimum one.

Fig. 2 shows the dependence of the recovery of boric acid on the phase contact time. The extraction equilibrium in the investigated systems is established within 10 min - 15 min.

It is known that the final result of the extraction process is significantly influenced by the number of the phase contacts. The results referring to the phase contacts number are presented in Table 4. It is evident that the recovery (R) increases with increase of the phase contacts. The best results are obtained in case of FA - paraffin after the 3rd phase contact. The recovery value equals to 74,12 %.

The high molecular alcohol mannitol is used as an electron donor additive to FA. The ratio of the main extractant and the additive is 100:1. As seen from the Table 4 mannitol contributes to an increase of the recovery of the analyzed component by almost 18 % when compared to that in pure FA. The degree of extraction of boric acid in the system H_3BO_3 –H_2O – FA – mannitol is 74.12 %.

The separation of the phases using solid extractants is not complicated by such factors as the appearance of emulsions, the prolongation of the phase-settling process, and other negative processes characteristic for liquid extraction.

CONCLUSIONS

The optimal temperature of boric acid extraction from boron-containing mineral waters refers to 60°C. The further temperature increase leads to insignificant increase of the recovery in view of energy consumption and time. The recovery increases with increase of the phase contact number. The best results (74.12 % of recovery) are obtained after the 3rd phase contact in FA – paraffin system.

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