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CHEMICAL COMPOSITION AND PHYSICO-CHEMICAL PROPERTIES OF LITHIUM-CONTAINING WATER RESOURCES

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The aim of the study is determination of chemical composition, physicochemical and biological properties of the Aral Sea water for further selection of the most economical and environmentally friendly method of lithium extraction. It is shown that the content of lithium in water is 0,11 g/l, which is 3-4 times higher than in those used in industry at Chinese enterprises. The chemical oxygen demand is 677,76 mg O_2/l, the biological oxygen demand is 120,50 mg O_2/l.

Keywords: water of the Aral Sea, lithium, chemical composition, physicochemical and biological properties, adsorption

ХИМИЧЕСКИЙ СОСТАВ И ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА ЛИТИЙСОДЕРЖАЩИХ ВОДНЫХ РЕСУРСОВ

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Целью исследования было изучение химического состава, физико-химических и биологических свойств воды Аральского моря для дальнейшего выбора наиболее экономичного и безопасного для окружающей среды способа выделения лития. Показано, что содержание лития в воде составляет 0,11 г/л, что в 3-4 раза выше, чем в используемых в промышленности на предприятиях КНР. Химическая потребность кислорода составляет 677,76 мг O_2/л, биологическая потребность кислорода 120,50 мг O_2/л.

Ключевые слова: вода Аральского моря, литий, химический состав, физико-химические и биологические свойства, адсорбция

LITIY BO'LGAN SUV MANBALARINING KIMYOVIY TARKIBI VA FIZIKKIMYOVIY XUSUSIYATLARI

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Tadqiqotning maqsadi Orol dengizi suvining kimyoviy tarkibi, fizik-kimyoviy va biologik xossalarini o'rganish, keyinchalik litiy qazib olishning eng tejamli va ekologik toza usulini tanlashdan iborat edi. Suvdagi litiyning miqdori 0,11 g/l ni tashkil etishi ko'rsatilgan, bu Xitoy korxonalarida sanoatda qo'llaniladiganidan 3-4 baravar yuqori. Kimyoviy kislorodga bo'lgan talab 677,76 mg O_2/l, biologik kislorodga bo'lgan talab 120,50 mg O_2/l.

Kalit so'zlar: Orol dengizi suvi, litiy, kimyoviy tarkib, fizik-kimyoviy va biologik xossalari, adsorbsiyasi

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Introduction

Lithium and its compounds are widely used in the production of glass, ceramics, lubricants, batteries, refrigerants, chemicals and other industries. World reserves of lithium are about 14 million tons, mainly 70-80% of the reserves are in salt lakes, geothermal waters and solid form contained in lithium ore. Currently, many researchers pay attention to 2600 billion tons of lithium contained in sea waters, which is about 15,000 times more than in solid lithium ores [1].

Figures for lithium resources and reserves vary significantly depending on the source, although there is a consensus that lithium resources in brines are much greater than in solid rocks [2-6]. The most recent USGS data show a total lithium resource (brine + hard rock) of 54,1 Mt. Approximate minimum and maximum lithium resources in hard rock are 12,8 Mt and 30,7 Mt, respectively, while brine data are 21,3 Mt and 65,3 Mt, respectively, for the minimum and maximum scores.

The prevalence of lithium in nature is only 0,0018%. Lithium is considered as a rare element and is an indispensable element for various lithium -ion batteries due to its low density (0,534 g/cm^3) and high electrochemical potential (-3,04 V) [7-9].

Lithium demand is expected to rise steadily and dramatically in the coming years as various types of lithium batteries which are the most promising candidates for powering electric or hybrid vehicles [10-11]. Lithium batteries include both current technologies such as lithium-ion and emerging technologies such as lithium-sulfur or lithium-air [12-15].

Lithium demand is projected to grow by about 60% from 102,000 tons to 162,000 tons lithium carbonate equivalent over the next 5 years, with a huge percentage of this growth coming from battery applications [16-17]. Current lithium resources in continental and salar brines were reported to be approximately 52,3 Mt lithium equivalent, mainly in Argentina, Chile and Bolivia, of which 23,2 Mt could be recovered. [18]. On the other hand, the content of lithium in minerals is 8,8 million tons, huge deposits of which are located in the USA, Russia and China. Evans estimated the reserves and recoverable resources of lithium at 29,79 million tons [19].

Many methods have been reported for extracting lithium from seawater, brines, and geothermal water [20] by solvent extraction, including precipitation, liquid–liquid extraction, selective membrane separation, electrodialysis, ion exchange adsorption, and others [21–24]. Of these methods, the most attention has been paid to ion-exchange adsorption methods using lithium-ion sieves due to their good selectivity for lithium ions and high adsorption properties [25-27]. From the point of view of cost and efficiency, the extraction of lithium ions from solutions by ion exchange adsorption is the most promising method [28].

Research methods

The water of the Aral Sea was used for the experiments. Administratively, more than half of the Aral Sea is located in the southwestern part of Uzbekistan (Karakalpakstan) and in the northeastern part of Kazakhstan. Until the 1960s, the area of the Aral Sea averaged 68,000 km^2. It was the fourth largest sea in the world (after the Caspian Sea, Lake Superior in America and Lake Victoria in Africa) and the second largest in the Eurasian continent (after the Caspian Sea).

The salt composition of the dry deposits of the Aral can be characterized as chloride-sulfate (more than 80% sodium chloride, the rest sodium sulfate and 2-6% magnesium sulfate). The western basin contains chloride-sulfate-magnesium salts (40-60% sodium chloride, 20-40% sodium sulfate, the rest is magnesium salts).

Chemical analysis of initial solutions, intermediate and final products was carried out by known methods, as well as using atomic emission spectrometry, using inductively coupled plasma (ICP) as a source of excitation of atoms. Which is a highly ionized inert gas (argon) with the same number of electrons and ions supported by an RF (radio frequency) field. The temperature obtained in the plasma desolvates, converts into vapor and ionizes the atoms of the sample under study by mass spectrometry (MS) and atomic emission spectrometry (AES). Typically, detection limits range from less than - namogram (ICP-MS) to less than - microgram (ICP -AES) per liter [31].

The density of solutions and pulps was determined using a PZh-2 pycnometer with a measurement accuracy of 0,05 rel.%. The kinematic viscosity of solutions and pulps was measured with glass capillary viscometers VPZh-1 and VPZh-2 with an error of 0,2% [29-30].

The density value was calculated by the formula

$$\rho = \frac{m}{v};$$

where m is the mass of the pulp, g; ν is the capacity of the pycnometer, cm^3.

Viscosity was determined according to the following formula

$$\eta = \kappa \cdot \rho \cdot \tau;$$

where κ is the viscometer constant and is equal to 0,3262 and 3,404, respectively, for VPZH-1 and VPZH-2 with a capillary diameter of 1,31 mm. is the pulp density in g/cm^3. τ is the time of passage of the pulp through the capillary of the viscometer, s.

Plasma Atomic Emission Spectrometer ICPE-9000. The method of atomic emission spectrometry using inductively coupled plasma (ICP) as a source of excitation of atoms. Which is a highly ionized inert gas (argon) with the same number of electrons and ions supported by an RF (radio frequency) field. The temperature obtained in the plasma desolvates, converts into vapor and ionizes the atoms of the sample under study by mass spectrometry (MS) and atomic emission spectrometry (AES). Typically, detection limits range from less than - namogram (ICP-MS) to less than - microgram (ICP-AES) per liter [31].

Results and its discussion

For research, to find the conditions for the release of lithium, water samples were taken in an amount of 30 kg from various places in the Aral Sea. The average composition of the salty waters of the Aral Sea contains (g/l): Li^+ – 0,11, Na^+ – 54,92, K^+ – 3,67, Ca^{2+} – 0,80, Mg^{2+} – 10,25, B_2O_3 – 0,03, Cl^- – 70,90.

Table 1 shows the data of atomic emission spectrometry of the Aral Sea water analysis in comparison with the brines used in production in China, Chile, and Tibet.

The Aral Sea (Table 1) is lithium-rich brine with lithium reserves of 19,82 million tons

Table 1

Comparative composition of the water of the Aral Sea with the industrial solutions used

Solution	Total salts, g/l	pH	Content of components, g/l							
			Li^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	B_2O_3	Cl^-	SO_4^{2-}
Aral Sea	130,9	8,0	0,11	54,92	3,67	0,80	10,25	0,03	70,90	-
Atacama, Chile	289,2	10	1,22	76,52	18,56	0,31	7,83	0,64	130,83	20,07
Salt Lake, Zabuye Tibet	439,8	9,3	0,63	122,5	48,10	-	-	10,30	181,30	33,60
Salt Lake, Qinghai Chaerhan	266,4	6,9	0,030	59,36	10,11	0,84	23,72	0,25	166,67	-
Tibetan Geothermal Water Yangbajing	10,4	8,6	0,025	0,68	0,14	0,21	-	0,36	0,97	0,12

in terms of lithium chloride, which is of great strategic importance. Therefore, it is very important to develop an acceptable technology for a direct, green and efficient way to extract lithium from the original brine with neutral and low salinity in order to ensure the security of lithium energy in Uzbekistan and international competition in the field of green energy. The development of an acceptable technology will make it possible to involve mineral water resources of lithium in industrial production.

The physical and chemical properties of the water of the Aral Sea have been determined. The results obtained are shown in Table 2.

Chemical oxygen demand (COD) is an indicator of the content of organic substances in water, expressed in milligrams of oxygen (or other oxidizing agent in terms of oxygen) used to oxidize organic substances contained in one liter (1 dm³) of water. It is one of the main indicators of the degree of contamination of drinking, natural and wastewater with organic compounds (mainly anthropogenic or technogenic). Determined by various laboratory methods.

Table 2

Physical and chemical properties of the water of the Aral Sea

Property	Values
General hardness, mg-eq/l	1195,00
Hardness, carbonate, mg-eq/l	13,00
Hardness, non-carbonate, mg-eq/l	1182,00
CO_2 free, mg/l	132,00
Oxidability mg O_2/l	2
Chemical oxygen demand (COD),	677,76
Biological oxygen demand (BOD),	120,50
C_{org}, mg C/l	254,16
F, mg/l	1,61

As can be seen from the research results, the COD index in the samples is 677,76 mg O_2/l. This exceeds the allowable amount, which should be no more than 100 mg O_2/l. The reason for the high rate can be explained by the presence of inorganic and organic substances in water in the form of C_{org}. Due to the fact that the water sample contains organic substances, COD was determined by the bichromate method according to [32].

Biochemical oxygen demand (BOD) is the amount of oxygen consumed for aerobic biochemical oxidation under the action of microorganisms and for the decomposition of unstable organic compounds contained in the test water.

BOD is one of the most important criteria for the level of pollution of the reservoir with organic substances and determines the amount of easily oxidized organic pollutants in the water.

The analysis determines the amount of oxygen that has gone for a set time (usually 5 days - BOD_5) without access to light at 20 °C for the oxidation of pollutants contained in a unit volume of water. The difference between the concentrations of dissolved oxygen in the water sample immediately after sampling and after sample incubation is calculated. As a rule, ~ 70% of easily oxidized organic substances are oxidized within 5 days under normal conditions. Almost complete oxidation (BOD_{total} or BOD_{20}) is achieved within 20 days.

For sources of centralized domestic drinking water supply (GOST 2761-84) and water bodies used for fishery purposes, $BOD_{full.}$ should not exceed 3 mg O_2/l, for reservoirs of cultural and domestic water use - 6 mg/l. The maximum allowable BOD values for the same water bodies are 2 mg/l and 4 mg/l, respectively. BOD should not exceed 150 mg/l, otherwise it may interfere with the vital activity of flora and fauna in the reservoir.

Exceeding the COD and BOD levels can lead to a lack of oxygen in the water, which will lead to irreversible damage to aquatic life [33].

Further, experiments were carried out to determine the density and viscosity of the Aral Sea water depending on temperature.

The viscosity and density of the Aral Sea waters were determined in the temperature range from 20 to 80 °C. The results obtained are shown in Figures 1 and 2.

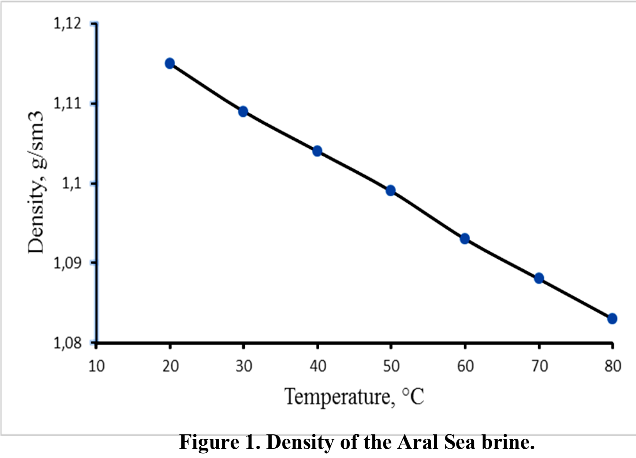

Figure 1. Density of the Aral Sea brine.

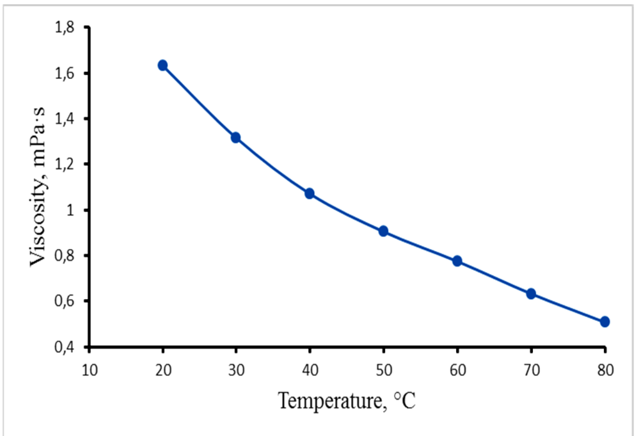

Figure 2. Viscosity of the Aral Sea brine.

As can be seen from the above data, with an increase in temperature from 20 to 80°C, the density and viscosity of water decrease. Thus, the density has a linear dependence and decreases from 1,115 g/cm^3 at 20 °C to 1,083 g/cm^3 at 80 ° C. In this case, the viscosity decreases from 1,633 cps to 0,507 cps, respectively.

Conclusion

It follows from the data obtained that the brines of the Aral Sea can practically be used for the industrial extraction of lithium, which contain 0,11 g/l of lithium and, in contrast to the Qinghai Chaerhan Salt Lake and the Tibetan Yangbajing geothermal water, from which lithium production has been established in the PRChina, contain 3,7-4,4 times less lithium than in the water of the Aral Sea. Adsorption can be considered the most probable method for separating lithium from the waters of the Aral Sea from both economic and environmental points of view.

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