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INVESTIGATION OF SOLVENT SUBLATION OF COBALT IONS FROM WATER SOLUTIONS

Об'єктом дослідження є флотоекстракція в системі кобальт-додецилсульфат натрію. Дослідження флотоекстракційного очищення стічних вод від іонів важких металів малочисельні і носять розрізнений та несистематичний характер. Тому дослідження процесу флотоекстракції як методу очищення стічних вод від важких металів на прикладі іонів кобальту (II) є перспективним. У роботі досліджено модельні водні розчини кобальту концентрації 20 мг/дм³ з використанням аніонної поверхнево-активної речовини (ПАР) – додецилсульфату натрію та ізоамілового спирту в якості органічної фази. Отримано раціональні умови процесу: рН 10, молярне співвідношення Co²⁺:ПАР=1:2, витрата повітря 45 см³/хв, температура 20 °C, об'єм екстрагенту (ізоаміловий спирт) – 10 см³, тривалість процесу – 20 хв. За цих умов ступінь видалення іонів кобальту в ізоаміловий спирт склала 85 %. Процес описується кінетичним рівнянням першого порядку. Розраховано константи швидкості процесу. Важливість проведеного дослідження підкреслюється тим, що флотоекстракція має ряд особливостей та переваг. Зокрема, можливість багатократного концентрування іонів забруднника у невеликих об'ємах органічного розчинника та можливість його подальшої регенерації. При цьому використовується значно менша кількість органічного розчинника та процес не лімітується констан- тою розподілу (у порівнянні з методом екстракції). Флотоекстракція також характеризується відсутністю піни (у порівнянні з методом флотації) та відсутністю великих кількостей вологого осаду (у порівнянні з реагентним методом). Запропонований у роботі метод забезпечує достатній рівень очищення стічних вод від іонів металів, а також може бути застосований в системах локального очищення стоків з наступним поверненням води у технологічний процес. Це забезпечить зниження витрат на споживання водних ресурсів, скидання стічних вод у водні об'єкти, а також обмежить потрапляння шкідливих речовин у навколишнє середовище. Крім того, особливості флотоекстракції дозволяють регенерувати екстрагент та ПАР.

Ключові слова: *видалення іонів кобальту, флотоекстракційне очищення стічних вод, додецилсульфат натрію, ізоаміловий спирт.*

1. Introduction

Existing technologies for the purification of waste water from heavy metal ions are imperfect. This necessitates the search and implementation of alternative methods aimed at the complete purification of wastewater from pollutants of various nature. To achieve a more complete purification of wastewater from heavy metal ions, it is proposed to apply the solvent sublation method, which has several advantages compared with other known flotation methods [1, 2]. The uniqueness of this process is the method of extracting sub-late substances (sublate) by concentrating it in the layer of organic liquid – extractant – on the surface of the aqueous phase [3–5]. Sublate is capable of either forming a suspen-sion, is retained due to wetting, or dissolved in the organic phase [6, 7]. Equilibrium in this process is established at the interface of the aqueous-organic phase. The amount of collected sublate in the organic layer does not depend on its volume, since equilibrium is not established in the entire system. The passage of sublate into the organic layer from the phase boundary is a process due to the movement of a stream of gas bubbles. This is not a spontaneous distribu-tion process, which is associated with the relative solubi-lity of sublate in two phases. Despite all the advantages of solvent sublation, to date, this method of purification has not yet received wide industrial application. However, there are numerous experimental results of studies of the regularities and optimal parameters of this process, which

substantiate the expediency of the expanded use of solvent sublation [8, 9]. Therefore, an experimental study of the nature of the effect on the extraction efficiency of the fol-lowing parameters *is relevant*: the nature of the extractant, the pH of the medium, the duration of solvent sublation, the value of the molar ratio of surfactants (surface-active substances): Metal, gas consumption, temperature of the aqueous phase. Thus, *the object of research* is solvent subla-tion in the cobalt- sodium dodecyl sulphate system. And *the aim of research* is studying the solvent sublation, as a method of purifying waste water from heavy metals by the example of cobalt (II) ions.

2. Methods of research

To study the solvent sublation process, a cylindrical glass column with a diameter of 35 mm was used. Air was supplied by a compressor to the bottom of the column, flow was controlled by a rotameter. Air dispersion was carried out through a Schott filter. The concentration of cobalt ions in model solutions was 20 mg/dm³. The volume of the solution is 200 cm³, the volume of the extractant (isoamyl alcohol) is 10 cm³. The solvent sublation process was carried out to establish a constant residual concentration of cobalt ions, which was determined by the photometric method on a Portlab 501 single beam scanning spectrophotometer (United Kingdom) [10]. The pH adjustment was carried out with solutions of NaOH and HCl with a concentration

of 0.1 mol/dm^3 (pH of aqueous solutions was measured using a pH-meter pH-150MI (Russia)). The efficiency of the solvent sublation process was evaluated by the extraction degree of cobalt ions.

3. Research results and discussion

Fig. 1 shows the dependence of the extraction degree of Co^{2+} ions on the molar ratio of Co^{2+}:surfactant.

According to the results (Fig. 1), in the range of molar ratios of Co^{2+}:surfactant from 1:0.5 to 1:1.5, the degree of cobalt extraction is not enough. This is due to the fact that this amount of surfactant is not enough to fully bind cobalt to sublate. When using sodium dodecyl sulfate, the highest extraction degree of cobalt ions is 84.46 % with a ratio of Co^{2+}:surfactant = 1:2. Further, there is a decrease in the efficiency of solvent sublation, because with an increase in the amount of surfactant in solution (Co^{2+}:surfactant = 1:2.5 and so on) in the aqueous phase, an excess amount of surfactant anions appears.

The dependence of the Co^{2+} extraction degree on the pH of the solution. Hydrogen index is corrected in the range of 3–11 (Fig. 2).
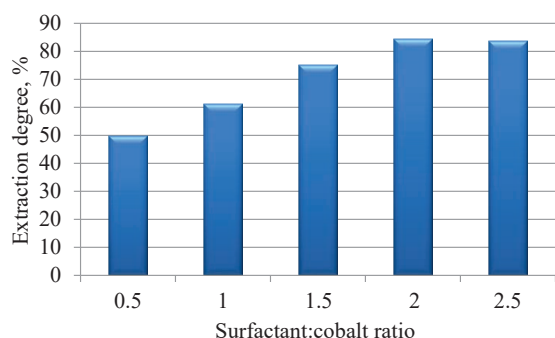

Fig. 1. Dependence of cobalt (II) ions extraction degree on the surfactant:cobalt molar ratio
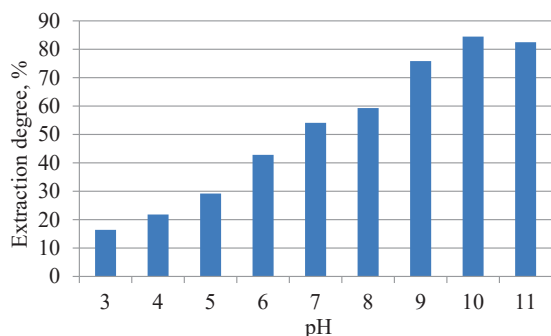

Fig. 2. Dependence of cobalt (II) ions extraction degree on pH

It is better to extract Co^{2+} at pH 10. At this pH cobalt sublate is in the form of a neutral hydroxide molecule, which is hydrophobized by surfactant.

Fig. 3 shows the dependence of the Co^{2+} extraction degree on the duration of the solvent sublation process with a different Co^{2+}:surfactant molar ratio. The process was carried out for 25 minutes. Sampling for analysis was performed every 5 minutes.

The rational process duration was 20 minutes. The increase in the solvent sublation duration is almost no effect on the Co^{2+} extraction degree.

Air consumption is an important factor during the solvent sublation process (Fig. 4).
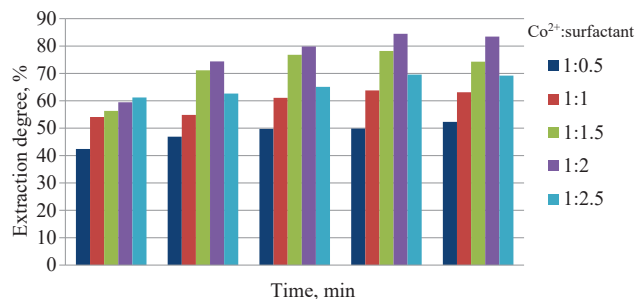

Fig. 3. Dependence of cobalt (II) ions extraction degree on the duration of the process at a different molar ratio
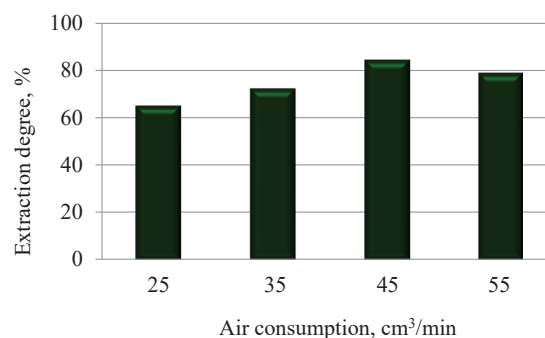

Fig. 4. Dependence of cobalt (II) ions extraction degree from the air consumption

The extraction of cobalt ions is only 72.4 % with air consumption in the range of 25–35 cm^3/min, since this number of air bubbles is not enough to completely transfer pollutants into the organic phase. The highest degree of extraction of cobalt ions is observed at an air consumption of 45 cm^3/min. At large values, there is a slight decrease in the extraction degree. This is due to the fact that with an increase in the rate of movement of air bubbles, a partial violation of the integrity of the organic layer occurs and, as a result, part of the sublate returns to the aqueous phase.

Fig. 5 shows the dependences of the Co^{2+} ions extraction degree on the temperature of the aqueous phase. Studies were conducted in the range of 10–40 °C. Solvent sublation parameters: process duration – 20 min, molar ratio of Co^{2+}:surfactant – 1:2, pH 10.
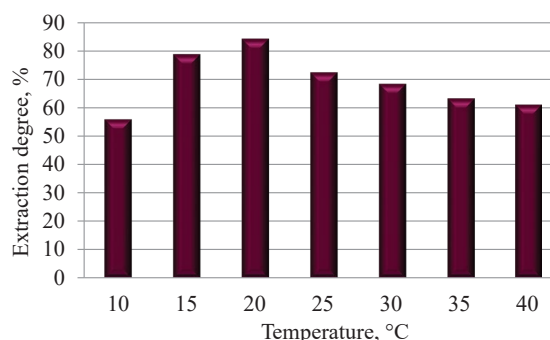

Fig. 5. Dependence of cobalt (II) ions extraction degree on the temperature of the aqueous phase

The process takes place in the adsorption mechanism and, accordingly, with increasing temperature there is

a decrease in the efficiency of the process, explains the decrease in the extraction degree of cobalt. Fig. 6 shows the graphical dependences of the natural logarithm of the cobalt ion concentration on the solvent sublation duration. This is the first order of reaction, because the graphical dependence is straightforward.
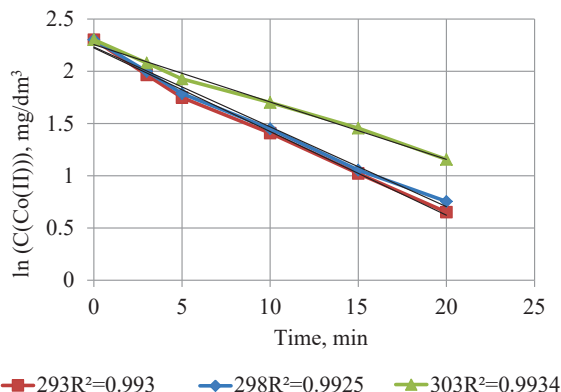
Fig. 6. Dependence of the natural logarithm of the concentration of cobalt ions on the solvent sublation duration at various temperatures

To calculate the reaction rate constant, the formula (for the first order reaction) is used:

$$k = \frac{1}{\tau} \cdot \ln \frac{C_0}{C_\tau},$$

where τ – solvent sublation duration; C_0 and C_τ – the initial and current concentrations of cobalt ions.

The results of the calculations of the constant are given in Table 1.

Table 1

Reaction rate constants of the solvent sublation

Temperature, K	293	298	303
k, min^{-1}	0.096	0.090	0.065

The first order of the process and the value of the process rate constant indicate the course of solvent sublation in the stationary diffusion mode, when the limiting stage is the diffusion of particles extracted from the surface of gas bubbles [11].

4. Conclusions

The extraction of cobalt ions with a concentration of 20 mg/dm^3 from aqueous solutions in the cobalt – sodium dodecyl sulphate system by solvent sublation is studied. Based on experimental studies, the optimal process conditions are obtained: the volume of extractant (isoamyl alcohol) – 10 cm^3, the ratio of cobalt ions in the surfactant – 1:2, pH 10, air consumption – 45 cm^3/min, the process duration – 20 min, phase temperature – 20 °C. Under these conditions, the extraction degree of cobalt ions is about 85 %. The solvent sublation process of cobalt ions is described by a kinetic equation of the first order, the velocity constants are calculated. The proposed method of solvent sublation purification can be an alternative and innovative method of wastewater purification before discharge into reservoirs or in the case of their return to the circulating water supply.

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