

REMOVAL OF COPPER IONS FROM AQUEOUS SOLUTIONS

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Introduction. Increasing the amount of polluted water and lack of clean water is already one of the urgent problems today. One of the most important environmental tasks is the treatment of wastewater from enterprises in various industries. Heavy metals (Me) are among the most biologically dangerous pollutants. The main sources of heavy metal pollution are metallurgical, metalworking and chemical plants. The toxicity of the metal is due to its effect on the metabolism of living organisms and human health. Most heavy metal ions have carcinogenic, mutagenic properties and have a cumulative effect [1].

Given the modern methods of removing heavy metal ions from wastewater, it is advisable to develop innovative technologies for wastewater treatment from heavy metal ions. The quality of treated wastewater must meet the needs until its return for industrial and technical needs of the enterprise, or before discharge into the city sewer system. Solvent sublation is such a perspective method. This method is based on a combination of flotation and extraction methods, based on the passage of gas bubbles through the aqueous phase and the removal of the pollutant substance (sublate) in the organic phase. The organic phase should be lighter than the aqueous, and not dissolve in it. In the process of solvent sublation, surfactants are used, which play the role of collectors, binding to heavy metal ions in water-insoluble hydrophobic sublates, which due to their hydrophobic properties, adhesion forces bind to the bubbles and are removed from the aqueous phase in organic.

The purpose of this work is to develop a technology of solvent sublation of wastewater from heavy metals on the example of copper (II) ions.

To achieve this goal it is necessary to: theoretically justify the choice of method of effective wastewater treatment from heavy metal ions; to study the physico-chemical laws of the process of solvent sublation as a method of removal of copper ions, to propose a method of recovery of the extractant and the basic scheme of purification.

Solvent sublation technology was first proposed as a type of ion flotation in cases where the formation of foam having the required properties for ion flotation is impossible or it is necessary to quantitatively separate the foam for further analysis [2]. A characteristic feature of this flotation process is the method of separating the floated substance (sublate) by concentrating it in a layer of organic liquid on the surface of the aqueous phase.

Advantages and disadvantages of solvent sublation:

- no foam; - the ability to work with large volumes of water bodies, the concentration of which may exceed a ratio of 100: 1, this gives the solvent sublation a great potential in the analysis of elements that are in the water in micro- and nano-quantities;

- the active substance is carried out by gas bubbles and enters the upper layer of the hydrophobic liquid without mixing the phases; - the degree of removal in the process of solvent sublation does not depend on the ratio of the volumes of aqueous and organic phases; - in many cases, the substance to be recovered is concentrated in the organic phase, which greatly facilitates its further processing.

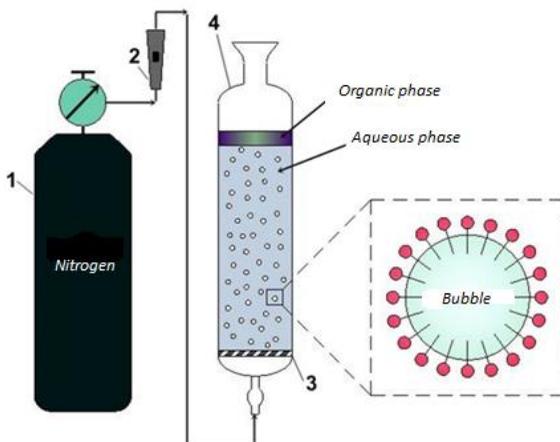
Traditionally, the main disadvantages include low, compared to flotation, productivity due to low gas consumption, which does not destroy the upper layer of organic liquid in the distribution apparatus [3-4].

All solvent sublation systems consist of the following elements [5-6]:

- gas source (it can be both a conventional compressor and a gas cylinder, the most common gases are air, argon and nitrogen);
- gas flow rate and pressure control systems; - rotameter (used to measure gas flow);
- column (usually used glass or plastic columns, at the bottom of which is a partition with the required porosity).

Experimental. 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/dm^3 . The volume of the solution is 200 cm^3 , the volume of the extractant (isoamyl alcohol) is 10 cm^3 . The experimental installation is shown in Fig. 1. The solvent sublation process was carried out to establish a constant residual concentration of copper ions, which was determined by the photometric method on a Portlab 501 single beam scanning spectrophotometer (United Kingdom). 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 copper ions.

A model solution of Cu^{2+} was prepared with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. Standard solution: 1 g / dm^3 . Working concentration: 20 mg / dm^3 . The following collectors were used: sodium caprylate $\text{C}_7\text{H}_{15}\text{COONa}$ and sodium laurate $\text{C}_{11}\text{H}_{23}\text{COONa}$.



1 - cylinder, 2 - rotameter, 3 - solvent sublation column, 4 - Schott filter.

Fig. 1. Experimental installation.

The model solution in the required amount was transferred to a volumetric flask, made the calculated amount of surfactant to achieve the desired ratio of Me: surfactant.

The solution was quantitatively transferred to a solvent sublation column and 10 cm³ of organic phase (isoamyl alcohol) were added. Turned on the gas supply, which was controlled by a flow meter and bubbled the gas through the solution to a constant residual concentration of copper, which determined by standard photometric methods [7].

The main characteristic of the system is the degree of removal X - the ratio of the difference between the initial and residual concentrations to its initial concentration, expressed as a percentage:

$$X_M = \frac{(C_{M,0} - C_{M,res})}{C_{M,0}} \cdot 100\%,$$

where X_M - the degree of removal of the test ion, $C_{M,res}$ - the residual concentration of the ion in the test solution, $C_{M,0}$ - the initial concentration of the ion.

Research results and discussion. The efficiency of the solvent sublation is influenced by number of factors. Process parameters such as the acidity of the medium, the duration of the process, the choice of extractant, the number of reagents are determined by the properties of the complexing agent and the metal and should be studied on a case-by-case basis. The determining factor in choosing the pH of the solution is the stability of the complex compound. Collectors are added to the system in order to increase the hydrophobicity of the formed complexes.

Selection of extractant. Of great importance in solvent sublation is the selection of the extractant. The removal process with butanol, isobutanol, pentanol, isopentanol, undecyl alcohol, octanol, hexanol, isoctanol was investigated. It has been investigated that the best extractant is isoamyl alcohol, which has a branched structure and, as a consequence, a better ability to retain sublates. Comparative characteristics of the extractants by the degree of removal are shown in Fig. 2. The volume of the organic phase is 10 cm³.

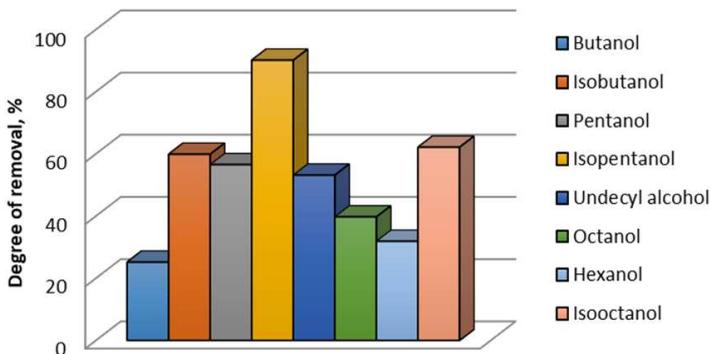


Fig. 2. Comparative characteristics of extractants by the degree of removal of Cu²⁺ ions.

Dependence of the degree of removal of Cu²⁺ ions on the ratio of Cu²⁺: surfactant (Surf). The graph (Fig. 3) shows the results of experiments with the following ratios of Cu²⁺: Surf = 1: 0.5; 1: 1; 1: 1.5; 1: 2; 1: 2.5. It was investigated that the ratio of Cu²⁺:

Surf=1: 1,5 is the most optimal and the degree of removal is 99.9% for $C_{11}H_{23}COONa$ and 99% for $C_7H_{15}COONa$.

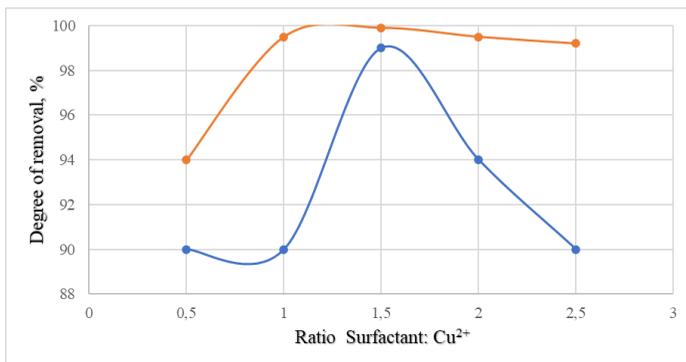


Fig. 3. Dependence of the degree of removal of copper (II) ions on the molar ratio of Cu: Surf (red $C_{11}H_{23}COONa$, blue $C_7H_{15}COONa$).

The decrease in the degree with a further increase in the ratio can be explained by the appearance of excess surfactants in the aqueous phase. As a result, it is difficult to transfer the substance from the aqueous to the organic phase and its accumulation on the interface of the water-organic layer.

Dependence of the degree of removal of Cu^{2+} on the pH of the solution. The pH of the test solution was varied in the range of 2-9. The effect of pH on the degree of removal, the duration of the process - 20 min, the molar ratio of Cu^{2+} : Surf= 1: 1,5, the volume of the aqueous and organic phases (isoamyl alcohol) - 200 cm³ and 10 cm³ respectively. According to the obtained data (Fig. 4), the best removal of copper (II) takes place at pH 5-6. Therefore, the obtained data indicate that the molar ratio is an important factor in the process of solvent sublation. However, only the right pH will achieve the maximum degree of removal.

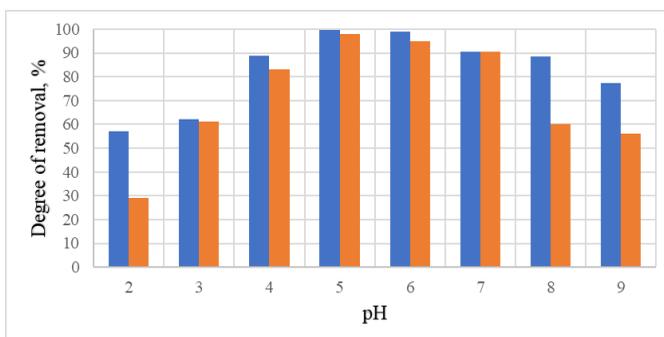


Fig. 4. Dependence of the degree of removal of copper (II) ions on pH (red $C_{11}H_{23}COONa$, blue $C_7H_{15}COONa$).

The dependence of the degree of removal of Cu^{2+} on the duration of the solvent sublation. The solvent sublation was performed for 30 minutes. The sample was taken for analysis every 5 minutes. As can be seen from Fig. 5, the optimal duration of the process was 15 minutes with 98,6 % removal of copper for $C_{11}H_{23}COONa$ and 97,3 % for $C_7H_{15}COONa$ at a ratio of Cu: Surf = 1: 1,5. When the process lasts longer than 15 minutes, there is a decrease in the degree of removal, which can be explained by the partial transition of the substrate from the organic to the aqueous phase.

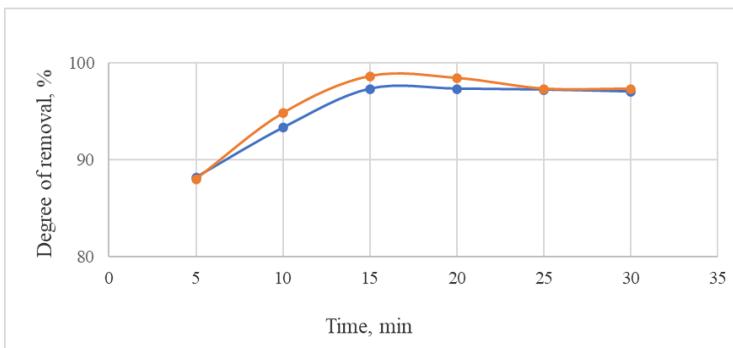


Fig. 5. Dependence of the degree of removal of copper (II) ions on the duration of the process (red $C_{11}H_{23}COONa$, blue $C_7H_{15}COONa$).

Dependence of the degree of removal of copper ions on the initial concentration of the working solution. Initial concentrations of the working solution studied: 20-250 mg/cm^3 . The process time is 20 minutes.

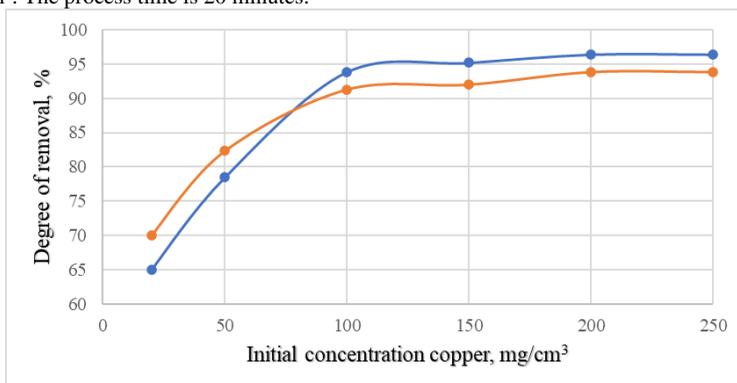


Fig. 6. Dependence of the degree of removal at different initial concentration (red $C_{11}H_{23}COONa$, blue $C_7H_{15}COONa$).

It was obtained that the highest degree of removal – 93,9% for $C_7H_{15}COONa$ and 96,4% for $C_{11}H_{23}COONa$ is achieved at an initial metal concentration of 200 mg / cm³. That is, with increasing concentration of the initial working solution, the degree of removal increases (Fig. 6). This can be explained by the fact that the coagulation process takes place in the system, even the intensive formation of aggregates was visually noticeable. The decrease in the degree of removal with decreasing concentration can be explained by a decrease in the probability of convergence of particles and, accordingly, the ability to coagulate.

Conclusions. An urgent problem today is the protection of the environment from pollution by toxic industrial waste. Paying attention to the ecological situation on the planet, technologies that use closed cycles with minimal waste generation are becoming competitive. The imperfection of the existing technologies of wastewater treatment contaminated with heavy metal ions necessitates the search for such methods that allow to treat wastewater to the maximum allowable concentration and to carry out the regeneration of valuable components. The solvent sublation method satisfies the following requirements. One of the characteristic features of this method is the possibility of repeated concentration of metal ions in small volumes of organic solvent. It is established that the process of sublation is influenced by a number of factors: pH of the solution, molar ratio of Me: surfactant, initial concentration of extracted metal ions, duration of the process. The regularities of solvent sublation of Cu^{2+} ions from aqueous solutions are investigated and the following rational conditions of the purification process are revealed: surfactant – sodium laurate $C_{11}H_{23}COONa$; pH 5-6; the molar ratio of Cu^{2+} : surfactant = 1: 1,5; process duration – 15 min, organic phase – isoamyl alcohol; volume of organic phase – 10 cm³; the volume of the aqueous phase is 200 cm³. For these conditions, the degree of withdrawal is 97-99%.

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