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## Article

# Removal of chromium (VI) ions from aqueous solutions

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## REMOVAL OF CHROMIUM (VI) IONS FROM AQUEOUS SOLUTIONS

The object of the research is the flotoextraction of chromium (VI) ions from model and real waste waters. Hexavalent chromium compounds pose a serious hazard to surface and ground waters and can have mutagenic and carcinogenic effects on living organisms. The study of the process of flotoextraction as a method of purifying waste water from heavy metals using the example of chromium (VI) ions is an important task. The paper considers flotoextraction of chromium (VI) ions using a cationic surfactant – hexadecylpyridinium chloride and butyl alcohol as the organic phase. The dependences of the process efficiency on the presence of a cationic surfactant, the flotoextraction time, the type of organic extractant, the nature of the collector and the surfactant: Cr molar ratio, the initial concentration of pollutants, and the pH of the initial solution were obtained. Certain rational conditions for flotation allow removing 98–99.6 % of pollutants. The method was tested on real wastewater.

The importance of this study is emphasized by the fact that flotoextraction has a number of features and advantages. In particular, the possibility of multiple concentration of pollutant ions in small volumes of an organic solvent and the possibility of its further regeneration. In this case, a much smaller amount of an organic solvent is used and the process is not limited by the distribution constant (compared to the extraction method). Flotoextraction is also characterized by the absence of foam (compared to the flotation method) and the absence of large amounts of wet sludge (compared to the reagent method). The proposed method provides a sufficient level of chromium ions removal from wastewater, and can also be used in systems for local wastewater treatment with the subsequent return of water to the technological process. This will ensure a reduction in costs for the consumption of water resources, discharge of wastewater into water bodies, and also limit the ingress of harmful substances into the environment.

**Keywords:** chromium (VI) ions, flotoextraction wastewater treatment, hexadecylpyridinium chloride, butyl alcohol.

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## 1. Introduction

The number and variability of compounds of anthropogenic origin that pollute water and are toxic to humans is constantly growing. Hexavalent chromium is one of such compounds because it has a highly toxic, in particular carcinogenic, mutagenic and teratogenic effect on mammals, including humans [1].

The need to extract chromium from spent electrolytes, flushing and waste water from galvanic production is due to both environmental and economic aspects. First, chromium is a toxic metal that is transmitted through food chains and adversely affects human health and the environment, and secondly, it is an expensive non-ferrous metal, the return of part of which in the production process will bring significant profits to the company.

Among the existing numerous methods of chromium-containing wastewater treatment of galvanic production – reagent, ion exchange, sorption, membrane, biochemical, electrochemical [2–4] – the most common, for example, at Ukrainian enterprises is reagent. The technological scheme of chromium-containing wastewater purging from Cr (VI), as a rule, includes the stage of reduction of Cr (VI) to Cr (III).

The effluents are treated with chemical reagents (for example, sodium salts of sulfuric acid) in an acidic medium pH 2–2.8. When using the method of galvanocoagulation (electrocoagulation), Cr (III) is precipitated (with lime milk or caustic soda) in the form of hydroxide and removed by settling. When alkalinizing wastewater, Cr (III) interacts with other (associated) metals present in wastewater and is co-removed.

However, this method has a number of significant disadvantages, namely the formation of a significant amount of wet sludge, a relatively low degree of purification, the loss of valuable components together with water treatment sludge. Therefore, from a technological point of view, it is advisable to remove chromium in one stage and separately from associated elements.

A promising solution to the problem is the method of flotation extraction, which is a combination of ion flotation and liquid extraction, and combines the advantages of both methods. During flotoextraction, the floated substance (sublate) is concentrated in a thin layer of organic liquid on the surface of the aqueous phase [5, 6]. In contrast to conventional liquid extraction, in this process the mass transfer from the aqueous to the organic phase occurs

with the participation of gas bubbles. The process is implemented at low gas consumption, to prevent the destruction of the upper layer of organic liquid [7, 8].

Thus, *the object of the study* was the floatoextraction of chromium (VI) ions from model and real wastewater. *The purpose of this work* was to study the patterns of extraction in the process of flotation extraction of hexavalent chromium ions. This is necessary to determine the optimal conditions for the process and to identify the stages of the process and the factors that increase the degree of extraction and concentration of chromium ions.

## 2. Methods of research

A description of the experimental setup and research methods is provided in previous publications [9, 10]. The studies were performed on model aqueous solutions of chromium (VI) in the range of initial concentrations of 50–250 mg/dm<sup>3</sup> and at different Cr:surfactant molar ratios. Hexadecylpyridinium chloride with a concentration of 0.05 mol/dm<sup>3</sup> served as a surfactant. The volume of the test solution was 200 cm<sup>3</sup>, the volume of the extractant was 10 cm<sup>3</sup>, and the duration of the floatoextraction was up to a constant residual concentration of chromium (VI), which was determined photometrically [11].

## 3. Research results and discussion

Organic substances that are poorly soluble in water and differ significantly in density ( $\rho < 1 \text{ g/cm}^3$ ) were studied as an extractant. In addition, no less important factor, influencing the success of the process, is the interaction of the formed sublimate and extractant. The latter should solvate the sublimate, should not destroy it, should not have foaming properties and form stable emulsions with water in the organic phase, have low interfacial tension to prevent coalescence of bubbles at the entrance to the organic solvent and be non-volatile [6].

Experimental studies of a number of organic substances – ethylenebenzene, butyl and amyl esters of acetic acid, butanol, isobutanol, amyl, isoamyl alcohols have shown that the organic substance butanol, with which the extraction process is most complete, shows itself best as an extractant.

The determining factor in choosing the pH of the initial solution is the stability of the complex compound, formed by the interaction of surfactants with the chromium ion. In the vast majority of cases, an acidic and neutral environment is used to avoid the formation of metal hydroxides.

The experiment was performed under the following conditions:

- initial concentration of Cr (VI) ions – 100 mg/cm<sup>3</sup>;
- molar ratio of Cr:hexadecylpyridinium chloride=1:2;
- duration of flotation extraction 20 minutes;
- volume of alcohol 10 cm<sup>3</sup>.

Studies have shown (Fig. 1) that the optimal pH values are in the range of 1–4 and 6–6.5, but the most effective extraction is observed at pH 4. It is at this value there is the most stable and complete interaction between chromate ions and surfactant ions, which allows you to intensify the extraction process.

The concentration of surfactants is one of the important factors in the process of flotation extraction. As mentioned earlier, the surfactant reduces the surface tension of the aqueous phase, which reduces the size of the bubbles, as

well as on the water-organic solvent interface, which helps the bubbles to cross the border without coalescence.

The process was carried out for 20 minutes, adjusting the pH to 4 (Fig. 2).

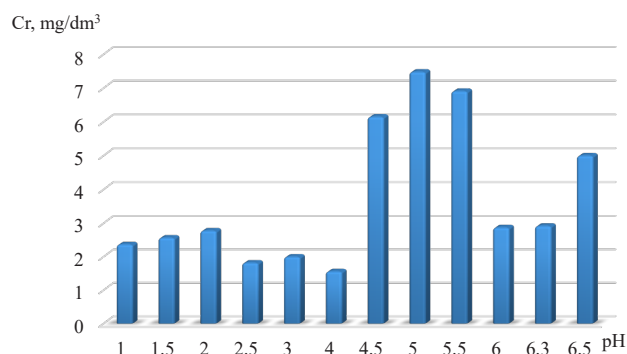


Fig. 1. Dependence of the residual concentration of chromium ions on pH

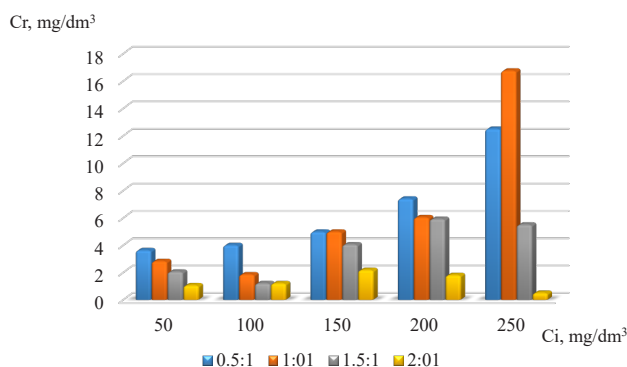


Fig. 2. Dependence of the residual concentration of chromium ions for different initial concentrations on surfactants:Cr ratio

When the surfactant is added to the model solution with increasing amount, the degree of extraction increases and reaches maximum values, regardless of the initial concentration, at the molar ratio of surfactant:Cr=2:1.

To determine the influence of the thermal factor, the studies were conducted in the temperature range of 25–65 °C (Fig. 3). The solution with the molar ratio of Cr:hexadecylpyridinium chloride=1:2, pH 4 and the organic phase volume=10 cm<sup>3</sup>, was heated in a water thermostat and floatoextracted for 5 minutes.

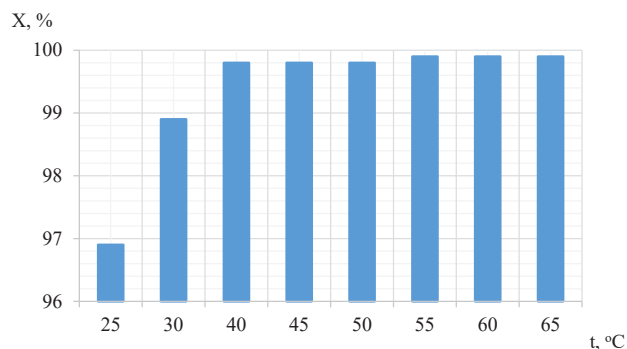


Fig. 3. Dependence of the degree of extraction of chromium ions on temperature

Fig. 3 shows that with increasing temperature, the degree of extraction increases and the process time decreases significantly. This is due to the fact that with increasing temperature, the speed of Brownian motion of molecules

increases, and hence the probability of the reaction increases. But with increasing temperature, the extractant evaporates and its amount decreases.

At room temperature with a relatively short duration of the flotation extraction process, the degree of purification is negligible. It has been established, that the optimal time, required to achieve the maximum value of the purification degree, is 35 minutes. This time can indicate the full course of the exchange reaction between surfactants and dichromate ions (Fig. 4).

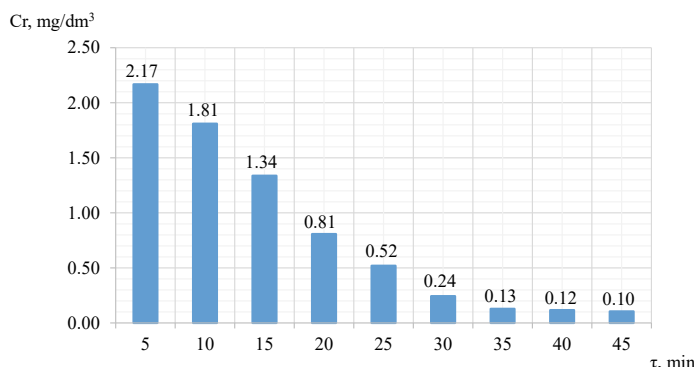


Fig. 4. Dependence of the residual concentration of chromium (VI) ions on duration of flotation extraction

The determined rational conditions of flotation extraction were tested on real sewage of the galvanic shop of one of the enterprises of Kyiv (Ukraine) with the content of chromium (VI) ions as 19.3 mg/dm<sup>3</sup>. The degree of removal was 97.8 %, the residual concentration of pollutant 0.43 mg/dm<sup>3</sup>.

Limitations of the studies can be considered the small volume of the working solution (200 cm<sup>3</sup>), the lack of control over the residual concentration of cationic surfactants and the size and number of gas bubbles.

Thus, the proposed method allows to remove chromium (VI) from wastewater ions without its prior conversion to chromium (III). The method provides a sufficient level of wastewater treatment, and can be used in local wastewater treatment systems with the subsequent return of water to the process. This will reduce the cost of water consumption, discharge of wastewater into water bodies, as well as limit the ingress of harmful substances into the environment. In addition, the features of flotation extraction allow to regenerate the extractant and surfactant. For further study of the method it is necessary to pay attention to the residual content of cationic surfactants – hexadecylpyridinium chloride, which is a very toxic substance. But the literature suggests that this content will not be high, because it is known, that the surfactants themselves, including cationic, are well removed by floatoextraction.

#### 4. Conclusions

Floatoextraction removal of chromium (VI) ions from aqueous solutions was studied. The dependences of the process efficiency on the presence of cationic surfactant, flotation extraction time, type of organic extractant, nature of the collector and molar ratio of surfactant:Cr, initial pollutant concentration, pH of the initial solution were obtained. A decrease in the degree of removal of chromium ions above pH 4 is associated with a change in the degree

of dissociation of the collector (surfactant) and the shape of the chromium anion. The number of chromate ions increases and the degree of extraction of dichromate ions decreases. The amount of surfactants significantly affects the efficiency of the process. A high degree of removal (low residual concentrations of dichromate ions) for higher concentrations of Cr (VI) can be achieved by increasing the amount of surfactants. Temperature has a weak effect on the efficiency of the process, but a slight heating (30–35 °C) reduces the duration of the purification process, for example, at a temperature of 30 °C 98.9 % purification is achieved in 5 minutes. At room temperature, the same high degree of removal of Cr (VI) ions is achieved by increasing the flotation extraction time to 30–35 minutes. Therefore, the obtained dependences can be used to select the parameters of the process depending on the requirements for the quality of purified water.

The determined rational conditions of flotation extraction allow to remove 98–99.6 % of the pollutant. It has been established, that the process, in the presence of cationic surfactants, should be carried out under the following conditions: collector – hexadecylpyridinium chloride in the molar ratio of Cr (VI) – 2:1; extractant – butanol; pH 4; process duration not less than 20 minutes at insignificant heating.

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