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**THE CHARACTERISTICS OF THE FLOTATION-BASED
EXTRACTION OF HEAVY METALS FROM WASTE WATERS BY
THE TREATMENT WITH CARBOXYLATE SURFACTANTS**

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The principal technological parameters of the flotation-based removal of nickel and copper by means of carboxylate surfactants have been established. The effects of pH, collector concentration, the order of the introduction of carboxylate surfactants and pH regulator solutions, and waste treatment time on the flotation efficiency have been determined.

Key words: ion flotation, collectors, carboxylate surfactants, galvanic flow.

Introduction. The rapid industrial development is associated with the increased demand for energy, growth of transport communications and active use of chemicals, particularly in agriculture, leading to significantly higher levels of chemical pollution of the soils and plants.

Among the most dangerous environmental pollutants are heavy metals. The accumulation of heavy metals in the soil decreases the yield and worsens the quality of agricultural plant crops and livestock products. Furthermore, the exposure to heavy metals increases the morbidity of the population and lowers its life expectancy [1].

Galvanic industrial waste waters are a significant source of environmental pollution as they contain heavy metal salts, acids, and bases [2]. Therefore, purification of galvanic waste waters from heavy metal ions and overall reduction in the exposure of the environment to galvanic waste are important tasks of the industrial factories. Nonetheless, despite steady technological improvements of galvanic processes and existing environmental protection measures, the purity of water resources and environmental pollution by galvanic industrial waste waters remain significant problems.

Analysis of relevant research. Flotation is one of the most promising methods of phase separation and concentration of waste water pollutants with different dispersion levels [3,4]. The principal technological parameters that affect flotation-based removal of heavy metal ions from industrial waste waters are pH, the length of the hydrocarbon moiety of the fatty acid collector, collector concentration, temperature and treatment time.

The aim of the study. In this study, the effects of pH, the length of the hydrocarbon chain of fatty acid collectors and their concentration on the efficiency of flotation-based extraction of Ni^{2+} and Cu^{2+} cations have been examined.

Study results. Actual galvanic industrial waste waters (table 1) that

contained Ni²⁺ and Cu²⁺ ions at a concentration range of 25–50 mg/L have been studied.

Table 1. The composition of metallisation electrolytes and the chemical state of copper and nickel in experimental samples

Experimental process	Electrolyte composition		Chemical state
	Component	Concentration g/dm ³	
Copper coating	CuSO ₄ · 5H ₂ O	15–2500	Cu ²⁺
	H ₂ SO ₄	50–70	
	CuSO ₄ · 5H ₂ O	70–90	Cu(P ₂ O ₇) ²⁻
	K ₄ P ₂ O ₇	330–380	
	H ₃ BO ₃	15–25	
	(NH ₄) ₂ SO ₄	75–85	Cu(NH ₃) ₄ ²⁺
	CuSO ₄	10–20	
	Na ₂ SO ₄	30–40	
NH ₄ OH	80–90		
Nickel coating	NiSO ₄	230–320	Ni ²⁺
	H ₃ BO ₃	25–40	
	NiCl ₂ · 6H ₂ O	40–60	

Waste water pH level ranged from 5 to 6. In some experiments, solutions that imitated galvanic industrial waste waters were utilised (table 2). Water solutions of potassium soaps of saturated fatty acids with hydrocarbon moieties that comprised 11 (lauric acid) or 13 (myristic acid) carbons were used as collectors.

Table 2. Composition of the solutions that imitated galvanic industrial waste waters

Substances contained in waste waters	Concentration of substances, mg/ dm ³
Nickel	25–50
Copper	25–50
Ammonium chloride	3
Trisodium phosphate	46
Sulfuric acid	46
Hydrochloric acid	45–65
Orthophosphoric acid	45–65
Sodium nitrate	18
Sodium sulphate	40
Dextrin	0,01
Suspended substances	41–90
Chemical oxygen demand	10–96 (mg O ₂ /dm ³)

The collectors were introduced into the waste waters at a concentration

range of 0.01–0.07%. The solutions were alkalisied to pH 11.6 to prevent the hydrolysis. The amount of collectors introduced was stoichiometrically sufficient for the formation of $\text{Me}(\text{RCOO})_2$ compounds (where R is a hydrocarbon moiety and Me is a Ni or a Cu atom). The concentrations of the collectors in the solutions was below the critical micelle concentration. The reaction of the collectors with Cu^{2+} and Ni^{2+} ions rapidly led to the formation of Cu^{2+} and Ni^{2+} soaps (sublates) that had limited solubility [6]. Solution pH level before the flotation was 8.5–9.5.

The adjustment of pH values of waste waters carried out in order to change the chemical composition of Cu^{2+} - and Ni^{2+} -compounds has been performed either before or after the addition of the collector.

Flotation-based extraction of the sublates was performed in a glass thermostated column ($d = 0.03$ m, $h = 0.1$ m). A porous glass plate (Schott filter № 4) in the bottom of the column was used to disperse air with the speed of 2×10^{-5} m³/min. The efficiency of the flotation process was calculated based on the rate of extraction of heavy metal ions from waste waters according to the following formula:

$$\alpha = \frac{C_0 - C}{C_0} \times 100\% \quad (1),$$

where α is the rate of extraction, C_0 is the concentration of heavy metals at the start of the experiment, and C is the concentration after the flotation-based treatment.

Concentrations of heavy metal ions before and after flotation were determined according to standard methods [7].

Electrokinetic potential (ζ) of sublate particles was measured by using microelectrophoresis [8].

Our experiments showed that potassium myristate was a more efficient collector of Ni^{2+} and Cu^{2+} ions than potassium laurate at all pH values tested (Fig. 1). This observation is likely explained by the relatively lower solubilities of Ni^{2+} and Cu^{2+} myristate salts compared to those of respective laurates.

Furthermore, hydrophobicity and foam-forming propensity of potassium myristate were significantly higher than those of potassium laurate. Almost complete flotation-based extraction of Ni^{2+} and Cu^{2+} ions (80–100%) with either laurate or myristate being used as collectors was observed at pH levels that were significantly higher than those at which the respective hydroxides start to precipitate.

Collector efficiency during flotation-based extraction of Ni^{2+} and Cu^{2+} ions critically depended on whether the collector was introduced into waste waters before or after pH adjustment. If the collector was introduced before pH adjustment, the rate of flotation-based extraction was 5–10% higher than in the case of the introduction of the collector occurred after pH adjustment.

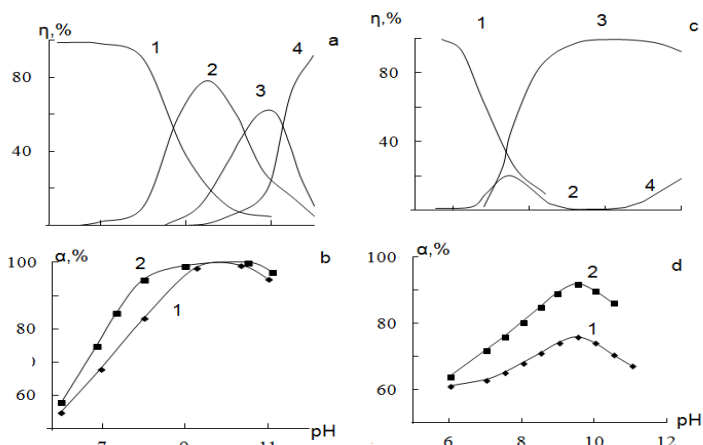


Fig. 1. The effect of pH of waste waters on the a) fraction (η) of nickel as Ni^{2+} (1), NiOH^+ (2), Ni(OH)_2 (3), Ni(OH)_3^- (4); b) rate of flotation-based extraction of nickel by using potassium laurate (1) and potassium myristate (2); c) fraction (η) of copper as Cu^{2+} (1), CuOH^+ (2), Cu(OH)_2 (3), Cu(OH)_3^- (4); d) rate of flotation-based extraction of copper by using potassium laurate (1) and potassium myristate (2). The collectors were introduced into waste waters before pH adjustment.

When the collector was introduced into waste water before pH adjustment to 9.0, the concentration of the collector sufficient for practically complete extraction of Ni^{2+} ions did not exceed 50–70% of the concentration stoichiometrically necessary for the formation of the intermediate (neutral) soap. In contrast, the flotation-based extraction of Cu^{2+} ions required significantly higher collector levels (>100% of the stoichiometric concentration necessary for the formation of the intermediate soap) (table 3).

When the concentration of the collector was stoichiometric, and it was added before pH adjustment, the flotation-based extraction of Ni^{2+} and Cu^{2+} ions proceeded more efficiently (96–100% of the theoretically possible value) and rapidly (10–15 min) at those pH values when nickel and copper are in the forms of hydroxides (pH 9–11) rather than at more acidic pH (6.0), when those metals are in the form of soaps with limited solubility.

Nickel at pH 9–11 exists as Ni(OH)^+ and Ni(OH)_2 , whereas copper primarily exists as Cu(OH)_2 . These observations are likely explained by the fact that the amount of the collector required for the formation of hydrophobic surface of nickel and copper hydroxides (pH = 9.0) is lower than when intermediate soaps of these metals are formed (pH = 6). The electrokinetic potential ζ of sublate particles at pH 9.0 was negative and did not exceed 30 mV. Therefore, these particles coagulated on the surface of the liquid and accumulated on the boundary that separated liquid and gas phases.

Table 3. The effect of the amount of potassium myristate and potassium laurate (q, % of stoichiometrically required) on the rate of flotation-based extraction (%) of Ni²⁺ (A) and Cu²⁺ (B) from galvanic waste waters at different pH levels

q, %	A, Ni ²⁺		B, Cu ²⁺	
	pH 6	pH 9	pH 6	pH 9
Potassium myristate				
25	19.5	43.7	21.3	41.2
50	35.2	96.1	43.3	75.2
75	46.1	98.0	57.4	88.1
100	54.4	99.0	68.1	96.1
125	58.2	99.9	79.6	97.0
150	62.4	99.9	83.1	97.0
Potassium laurate				
25	17.3	39.2	21.8	24.3
50	39.1	89.1	49.3	54.3
75	47.3	98.4	59.1	70.1
100	53.4	99.9	64.2	77.4
125	58.1	99.9	68.2	82.3
150	60.3	99.9	73.4	84.9

Micelle structure of the sublates can be described by the following micelle formula (taking into account the charge of the metal ion being extracted from the solution): $\{m[\text{Me}(\text{RCOO})_2]_n\text{RCOO}^-(n-x)\text{K}^+\}^- x\text{K}^+$ (for waste waters with pH 6.0) and $\{m[\text{Me}(\text{OH})_2]_n\text{RCOO}^-(n-x)\text{K}^+\}^- x\text{K}^+$ (for waste waters with pH 9.0, where n is the number of potential-determining ions in the micelle granule and x is the number of counter ions in the diffusion layer).

Conclusions and perspectives of further research

1. The principal technological parameters (pH, collector concentration, waste treatment time, and the order of introduction of the collector and pH regulator) of the flotation-based removal of Ni²⁺ and Cu²⁺ from galvanic industrial waste water by using carboxylated surfactants have been determined.

2. It has been demonstrated that the amounts of Ni²⁺ and Cu²⁺ ions extracted by using potassium myristate and of Ni²⁺ ions extracted by using potassium laurate were directly proportional to the collector concentration. The concentration of the collector necessary for the flotation-based extraction of Ni²⁺ and Cu²⁺ ions was dependent on the nature of the metal and on the order of collector introduction into waste water (before or after pH adjustment).

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Бельдй М., Пожарицкий А. ЗАКОНОМЕРНОСТИ ПРОЦЕССА ФЛОТАЦИИ ПРИ ОЧИСТКЕ СТОЧНЫХ ВОД ОТ ИОНОВ ТЯЖЕЛЫХ МЕТАЛЛОВ С ПОМОЩЬЮ КАРБОКСИЛСОДЕРЖАЩИХ ПАВ

Определены основные технологические параметры флотационного выделения никеля и меди с помощью карбоксилсодержащих поверхностно-активных веществ (ПАВ). Установлен характер влияния реакции среды (рН), расхода собирателей, последовательность введения в растворы собирателя и регулятора рН и время обработки растворов на результаты флотации.

Ключевые слова: ионная флотация; собиратели; карбоксилсодержащие ПАВ; гальваностокки.

Бельдй М., Пожарицкий О. ЗАКОНОМІРНОСТІ ПРОЦЕСУ ФЛОТАЦІЇ ПРИ ОЧИСТКІ СТІЧНИХ ВОД ВІД ІОНІВ ТЯЖКИХ МЕТАЛІВ ЗА ДОПОМОГОЮ КАРБОКСИЛВІСНИХ ПАВ

Визначені основні технологічні параметри флотаційного виділення нікелю і міді за допомогою карбоксилвісних поверхнево-активних речовин (ПАР). Встановлений характер впливу реакції середовища (рН), витрати збирачів, послідовність введення у розчини збирача і регулятора рН та час обробки розчинів на результати флотації.

Ключові слова: іонна флотація; збирачі; карбоксилвісні ПАР;