processes

MDPI

Article

Simultaneous Removal of Al, Cu and Zn Ions from Aqueous Solutions Using Ion and Precipitate Flotation Methods

Piotr Rybarczyk [1,*] and Bożenna Kawalec-Pietrenko [2*]

[1] Department of Process Engineering and Chemical Technology, Faculty of Chemistry, Gdańsk University of Technology, Narutowicza 11/12 Street, 80-233 Gdańsk, Poland
[2] Polish Federation of Engineering Associations (NOT) Gdańsk, Rajska 6 Street, 80-850 Gdańsk, Poland; kawalecb@gmail.com
* Correspondence: piotr.rybarczyk@pg.edu.pl; Tel.: +48-58-347-12-29

Abstract: This paper presents the results of investigations concerning the simultaneous removal of Al(III), Cu(II), and Zn(II) from dilute aqueous solutions using ion and precipitate flotation methods. The effects of initial solution pH, surface active substance concentration, and the gas velocity on the flotations' efficiency and course are studied. Experimental results are discussed in terms of physicochemical aspects related to aqueous solutions of metal salts. The results indicate that satisfying simultaneous flotations of aluminum, copper and zinc species are observed if the pH value ranges between 7.0 and 9.0. It was found that an increase in collector concentration results in a decrease in the flotation rate constants. An increase in the gas velocity results in an increase in the ion and precipitate flotation rates.

Keywords: ion flotation; precipitate flotation; metal ions; zinc; copper; aluminum; collector

Citation: Rybarczyk, P.; Kawalec-Pietrenko, B. Simultaneous Removal of Al, Cu and Zn Ions from Aqueous Solutions Using Ion and Precipitate Flotation Methods. *Processes* **2021**, *9*, 301. https://doi.org/10.3390/pr9020301

Academic Editor: Monika Wawrzkiewicz
Received: 31 December 2020
Accepted: 2 February 2021
Published: 5 February 2021

1. Introduction

Discharge of waste streams containing metal ions into aquatic systems, mainly due to industrial operations, is still posing a threat to human health and the environment [1,2]. Strict legal standards regarding the permissible concentrations of metals in wastewater require the use of efficient methods of treatment of this type of streams, especially those from the metal and metallurgical industries [3].

The most common method of removing of the metal ions from wastewater is chemical precipitation [4]. It is a simple method, efficient for highly concentrated streams and relatively inexpensive, but has significant disadvantages, i.e., a large volume of sludge with a high water content as a result of precipitation and the chemicals present in the wastewater can hinder the complete precipitation of metals [1]. Therefore, in recent years, for the treatment of industrial wastewater from metal ions, various methods were proposed. These include ion exchange, membrane and adsorption processes [5–7] including the application of low-cost adsorbents [8], bioremediation processes [9], remediation using metallic iron [10], electrokinetic remediation [11], or photochemical remediation [12]. Among others, flotation techniques may be applied for the treatment of wastewaters containing metals [13,14]. Ion and precipitate flotation belong to the adsorptive bubble separation methods, which are of interest due to their high efficiency in the treatment of large volumes of dilute solutions and low operating costs of the process. A brief comparison of selected physicochemical methods of the removal of metal ions from wastewaters is given in Table 1.

Ion flotation allows for the removal of surface inactive ions from the solution. These ions react with the oppositely charged ions of the surfactant acting as a collector and create compounds can be adsorbed and transported on the surface of gas bubbles rising in the bubble layer to the foam formed above the liquid layer [15–17]. The concentration of flotated ions in the product i.e., in the foam condensate, may be many times higher than in the feed solution.

Ion flotation is said to be a highly efficient method for purification of aqueous streams from metal ions when their concentration in the range between 10^{-5} to 10^{-3} mol dm^{-3} [18].

The precipitate flotation differs from ion flotation by means of a different process mechanism. In the precipitate flotation, the feed solution is a suspension containing hydroxides or insoluble metal salts. By adding a surfactant as a collector, the surface-active ions are adsorbed onto the hydroxide-charged micelles, neutralizing the electric charge and making the particle surface hydrophobic. The aggregates formed in this way and adsorbed on the surface of gas bubbles can be flotated [19,20].

Table 1. Physicochemical methods for removal of various metal ions from wastewaters.

Method	Example	Conditions or Metal Concentration Range (mg dm^{-3})	Metal Removal Efficiency, %	Advantages	Disadvantages	References
Precipitation	Hydroxide precipitation	10–10^3 and >10^3	>90	Low cost, ease of operation	High volumes of sludge, cost of sludge processing	[4]
Coagulation and flocculation	Coagulation using aluminum sulfate	pH ranges: 5.5–7.5 and 10.5–11.5; removal of suspended solids	>95	Short sedimentation time, stability of agglomerates	High consumption of chemicals, cost of sludge processing	[21]
Ion exchange	Ion exchange zeolites	<10^3	>90	Selective removal of metal ions	High investment costs, need of solution pre-treatment	[5]
Membrane separation	Reverse osmosis	Removal of organic and inorganic compounds	>97	High process efficiency, durability of equipment	Relatively high cost	[22]
Adsorption	Activated carbon	<10^3	>70	Possibility of adsorbent regeneration	High cost	[1]
Electrochemical processes	Electrochemical precipitation	10–10^3	>95	Low consumption of chemicals, short process time	High costs	[23]
Flotation techniques	Ion flotation	10–10^3	>95	Low costs, process selectivity	Consumption of surface-active substance	[3]

In this work, zinc, aluminum and copper were selected as the research objects. The mentioned metals and their alloys are widely used in different industries, including metallurgy, the aviation, and the chemical industry [24]. Ion and precipitate flotation of aluminum was studied by Shakir and co-workers [25], while investigations on copper were performed by Rubin and co-workers [26]. Ion flotation of copper with calcium or lead was studied by Liu and Doyle [27]. Ion and precipitate flotation of zinc was studied by Jurkiewicz [28]. Ion and precipitate flotation of Al(III) and Cu(II) was investigated by Kawalec-Pietrenko and Rybarczyk as well as by Ghazy and El-Morsy [29,30]. However, to the best knowledge of the authors, a mixture of Al(III), Cu(II) and Zn(II) has not been previously investigated as a research object for ion and precipitate flotation.

A mixture of zinc, aluminum, and copper ions gets into industrial wastewaters, e.g., during the processing of the aluminum brass and the production of brass elements. The operations require the use of large volumes of the process water, which is associated with the formation of significant amounts of wastewater containing low concentrations of metals. Therefore, the use of flotation techniques to treat this type of stream is particularly justified.

Recent research in the field of wastewater treatment using ion and precipitate flotation was related to the use of biosurfactants [17,31–34], more in-depth description of the process mechanisms, e.g., taking into account the physicochemical aspects of the precipitate formation [35,36] or the selective separation of target ions [37]. Kinetic aspects of the ion flotation were also investigated [38].

It seems that an interesting aspect of the research regarding ion and precipitate flotation is related to the analysis of the conditions enabling either the simultaneous removal of several ions from a solution or the selective flotation of a target ion. However, the literature on the subject is dominated by articles describing the foam separation of single metal ions, while there are a few publications on the simultaneous ion and precipitation flotation of two or more metals [29,31,34,39]. The use of flotation techniques in wastewater treatment requires not only information about the course of the ongoing processes, but also about the

possibility of its controlling. Therefore, the aim of this study is to evaluate the influence of the most important process parameters, e.g., pH value of the feed solution, collector concentration (c_{SDS} and c_{CTAB}, for concentration of sodium dodecyl sulphate and cationic cetyltrimethylammonium bromide, respectively), and superficial gas velocity (u_G, on the simultaneous removal of Al(III), Cu(II), and Zn(II) from aqueous solutions using ion and precipitate flotation methods.

2. Materials and Methods

Investigations were performed in a semi-batch bubble column (1) presented in Figure 1. The height of the column was 510 mm and its internal diameter was 50 mm. The G-4 porous frit (4) was mounted at the bottom of the column. A solution sampling port (5) was placed 250 mm above the porous frit. A valve (6) mounted below the porous frit enabled draining the liquid from the column. Waste solution via a pipe (11) was directed to the measuring cylinder.

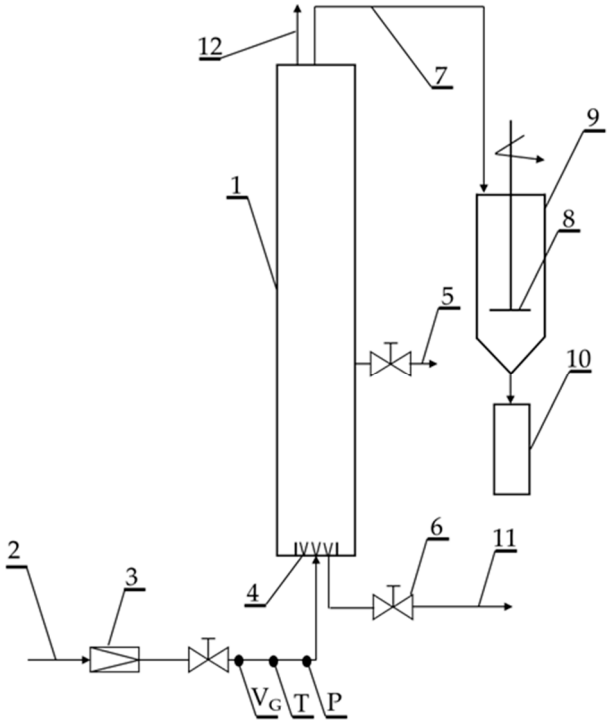

Figure 1. Scheme of a laboratory set-up: 1—bubble flotation column; 2—compressed air line; 3—pressure reduction valve for compressed air; 4—ceramic porous sinter; 5—sampling port for liquid; 6—drainage valve; 7—foam line; 8—rotating horizontal plate; 9—foam container; 10—foam condensate container; 11—waste solution line; 12—air outflow.

Compressed air (2) was supplied to the system through a pressure reduction valve (3). Pressure (P), temperature (T), and volumetric flowrate (V_G) of the air were measured prior to its entering the bubble column. Upon passing through the porous frit, the air stream was dispersed and raised as the bubble swarm through the gas–liquid bubble layer in the flotation column. The foam formed during the process was condensed with a rotating horizontal Teflon plate (8) in a foam container (9). The volume of the foam condensate was measured (10). During the experiments, superficial air velocity (u_G) was equal to 1.51 mm s^{-1} unless stated otherwise.

Aqueous solutions containing $Al_2(SO_4)_3 \times 16H_2O$ (Sigma-Aldrich, Steinheim, Germany), $CuSO_4 \times 5H_2O$, and $ZnSO_4 \times 7H_2O$ (POCH, Gliwice, Poland) were prepared using distilled water. Initial concentrations of each of above given metals were either 0.15 or 2 mmol dm^{-3}. These concentrations are typically found in the research on ion and precipitate flotation [27,40] as well as corresponding to concentrations of investigated metals in real industrial

effluents [1,41–43]. Selection of two concentrations, differing by the order of magnitude, enable verification of the effects of important process parameters in the perspective of possible practical applications. The pH value was adjusted by means of H_2SO_4 or NaOH (CHEMPUR, Piekary Śląskie, Poland). Depending on the distributions of ionic species of Al(III), Cu(II), and Zn(II) (Figures A1–A6), freshly prepared aqueous solutions of either anionic sodium dodecyl sulphate (molecular formula: $C_{12}H_{25}NaSO_4$; POCH, Gliwice, Poland) or cationic cetyltrimethylammonium bromide (molecular formula: $C_{19}H_{42}BrN$; International Enzymes Limited, Windsor, United Kingdom) were added as a collector (specified volume was taken from the stock solution containing 1 g dm^{-3} of a given surfactant). These surfactants were selected due to their low price as well as their documented application in similar research [27,41,44], which allows for comparison of the obtained results. In this process, 1 dm^3 of the initial solution was poured into the column. The flotation time (τ) was 60 min, unless otherwise stated.

Concentrations of aluminum, copper, and zinc in solution samples were determined spectrophotometrically (HACH LANGE DR 5000, HACH LANGE, Düsseldorf, Germany). Al(III) and Zn(II) were determined using the xylenol orange method at specified pH values [45–47]. Cu(II) was determined using a method with cuprizone [47].

Zeta potential measurements were performed using a Malvern ZetaSizer Nano ZS apparatus (Malvern Instruments, Malvern, UK). A DTS1060 u-shaped capillary cell was used during the measurements. Zeta potential was calculated using the Smoluchowski approximation.

The effectiveness of the ion and precipitate flotation was calculated using values of the final removal ratio (R):

$$R = \frac{c_0 - c_\infty}{c_0}, \quad (1)$$

where c_0 and c_∞ are concentrations of Al(III), Cu(II), or Zn(II) in the initial solution and in the solution when the flotation is finished (concentration does not change any further), respectively.

The courses of ion and precipitate flotations were recorded as changes in temporary removal ratio (R_τ) during the flotation time (τ) [20,29,48]:

$$R_\tau = \frac{c_0 - c}{c_0}, \quad (2)$$

where c is the temporary concentration of Al(III), Cu(II) or Zn(II) in the solution during flotation.

Based on our own as well as published experimental results [20,29,44,48–52], it is known that the kinetics of ion and precipitate flotations of metal ions can be described by Equation (4), which is analogous to the first-order reaction rate equation:

$$-\frac{dc}{d\tau} = k(c - c_\infty), \quad (3)$$

where k is a flotation rate constant.

After separation of the variable and integration, the following equation was used for the analysis of experimental data:

$$\ln\left|1 - \frac{R_\tau}{R}\right| = -k\tau \quad (4)$$

Dependencies of the Al(III), Cu(II), and Zn(II) forms on the pH value of the aqueous solutions (Figures A1–A6) were prepared using MEDUSA computer software [53].

3. Results and Discussion

3.1. Effect of pH on the Flotation Efficiency

The pH value of the flotation solution is an important parameter affecting both the efficiency as well as the course of the flotation process. The influence of pH value on the efficiency of simultaneous flotation of Al(III), Cu(II) and Zn(II) is presented in Figure 2a

(for initial concentration of each of investigated metals equal to 0.15 mmol dm^{-3}) and Figure 2b (for initial concentration of each of investigated metals equal to 2 mmol dm^{-3}). According to Figure 2a, for pH values lower than 4, the abovementioned metals exist in the solution in a form of cations, mainly Al^{3+}, Cu^{2+}, and Zn^{2+} (Figures A1–A3). Values of the final removal ratio are below 0.1 and the flotation follows the mechanism of ion flotation. This mechanism is related to the stoichiometric proportion between the concentration of the collector i.e., sodium dodecyl sulphate and metal ions, known as colligend ions [15]. For pH values higher than 4.1, values of the aluminum removal efficiency increase because an insoluble aluminum hydroxide is formed. Thus, precipitate flotation of aluminum takes place. For pH values above 5.0, the flotation solution contains micelles of $Al(OH)_3$ as well as soluble ionic forms of copper and zinc. At such conditions, adsorption of these ions on the surface of $Al(OH)_3$ precipitate is possible [54]. This may be a reason for increases in the final removal ratio values ranging between 6.0 and 7.0 and 6.2 and 7.5, respectively, for Cu(II) and Zn(II). According to data presented in Figures A3 and A5, insoluble hydroxides of copper and zinc start to precipitate for pH values higher than 6.1 and 7.5, respectively. At pH = 8.0, micelles containing hydroxides of aluminum, copper, and zinc are present in the flotation solution. Thus, precipitate flotation using anionic sodium dodecyl sulphate is possible, and the values of final removal ratio exceed 0.95 for all investigated metals.

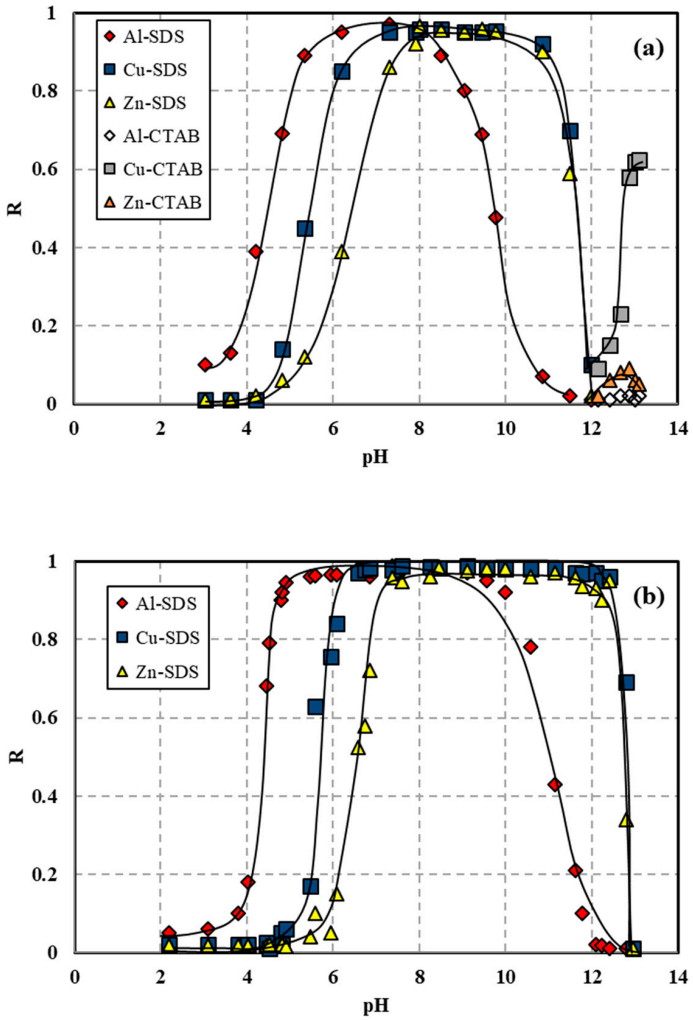

Figure 2. Influence of the pH of initial solution on the final removal efficiency of Al(III), Cu(II) and Zn(II) flotation: (**a**) $c_{0(Al)} = c_{0(Cu)} = c_{0(Zn)} = 0.15$ mmol dm^{-3}, $c_{SDS} = 0.125$ mmol dm^{-3}, $c_{CTAB} = 0.165$ mmol dm^{-3}; (**b**) $c_{0(Al)} = c_{0(Cu)} = c_{0(Zn)} = 2$ mmol dm^{-3}, $c_{SDS} = 0.187$ mmol dm^{-3}.

For pH > 8.5, a decrease in flotation efficiency with respect to Al(III) is observed (Figure 2a). This is because of an increase in solubility of $Al(OH)_3$ which undergoes complete dissolution at pH = 10.4 (Figure A1). In the same time, for a pH range between 8 and 11, values of the final removal ratio for Cu(II) and Zn(II) are still high, i.e., above 0.9. This is due to the lowest solubility of both $Cu(OH)_2$ and $Zn(OH)_2$ at the given pH range (Figures A3 and A5). For pH > 11.5, the values of the final removal ratio of Cu(II) and Zn(II) sharply decrease. Such a phenomenon results from the presence of OH^- ions as well as negatively charged hydrolysis products of Al(III), Cu(II), and Zn(II) in the suspension undergoing the flotation. Adsorption of these anions results in the negative surface charge of agglomerates, mainly containing hydroxides of copper and zinc. This is in accordance with the experimental pH of the isoelectric point for investigated system (Table 2). Thus, flotation with anionic SDS is hindered and a cationic collector must be applied. However, efficient precipitate flotation with cationic CTAB is possible only for $Cu(OH)_2$, since $Zn(OH)_2$ dissolves at pH > 12.0. The solubility of $Cu(OH)_2$ increases for pH > 12.6. At pH 13.0, the final removal ratio for Cu(II) is lower than 0.7 because about 70% of copper exists in a form of insoluble hydroxide (Figure A2).

Table 2. Literature and experimental values of isoelectric points (IEPs) for investigated system.

System	Species	Literature IEP	Experimental IEP
Metal hydroxides	$Al(OH)_3$	8.1–8.9 [55]	8.2 ± 0.2
	$Cu(OH)_2$	9.4–10.0 [55,56]	9.8 ± 0.2
	$Zn(OH)_2$	9–9.5 [55,56]	9.5 ± 0.2
Aggregates containing mixture of metals	Al(III) + Cu(II) + Zn(II)	-	9.8 ± 0.2

The influence of the solution pH on the efficiency of simultaneous ion and precipitate flotation of Al(III), Cu(II), and Zn(II) when the each metal initial concentration is equal to 2 mmol dm^{-3} is shown in Figure 2b. Aluminum, copper, and zinc exist in the form of soluble cations for pH < 3.9, pH < 5.5 and pH < 6.8, respectively. For pH > 3.9, insoluble $Al(OH)_3$ starts to precipitate, while the precipitation of $Cu(OH)_2$ and $Zn(OH)_2$ occurs for higher pH values (Figures A2, A4 and A6). Therefore, for pH values higher than those given above, the flotation efficiency increases with respect to the investigated metal ions. This results from the shift of the process mechanism from ion to precipitate flotation. It can be observed (Figure 2b) that the highest values of the final removal ratio for all investigated metals are noted for pH range between 7.0 and 10.0 when anionic sodium dodecyl sulphate is used. In the given pH range, insoluble hydroxides of Al(III), Cu(II), and Zn(II) predominate in the flotation suspension.

For pH > 10.0, the solubility of $Al(OH)_3$ increases, resulting in a decrease in the removal efficiency of aluminum (Figure 2b). Aluminum hydroxide dissolves at pH = 11.6. On the other hand, values of the removal ratio for copper and zinc are still very high (about 0.99) up to a pH value about 12.0. For pH > 12.0, the flotation efficiency of Cu(II) and Zn(II) decreases. For pH > 13.0, beside insoluble hydroxides of copper and zinc, negatively charged products of hydrolysis of aluminum, copper and zinc prevail in the flotation solution. Due to the adsorption of these anions, the surface charge of agglomerates is negative, thus the flotation with anionic collector is hindered and values of the removal efficiency drop to zero for pH > 13.0. Due to the broad range of pH values in which anionic SDS is an effective collector in the investigated system (from about pH = 7 to pH = 10, for all metals), the authors decided not to investigate the system behavior with cationic CTAB. This is because of the high ionic strength at high pH values (pH > 12), as well as due to presence of soluble anionic species in these conditions, which suggests that ion flotation may prevail, and thus stoichiometric, i.e., very high concentrations of CTAB must be used.

Analysis of results presented in Figure 2a,b reveals that an increase in the initial concentration of metals in the flotation solution corresponds to an increase in the pH range of efficient flotation with anionic collector. This results from two phenomena. Firstly, the pH range of the lowest solubility of Al(III), Cu(II) and Zn(II) is higher when the

metal concentrations are higher (Figures A1–A6). Secondly, with an increase in the metal concentration, both the size and the number of metal hydroxide micelles increase. Thus, the concentrations of OH^- ions as well as negatively charged products of metals hydrolysis required to give the negative charge to agglomerates also increase.

It can be noted that the regulation of the initial solution pH allows for selective flotation of the metal mixture components. For example, it is possible to separate Al(III) from its mixture with Cu(II) and Zn(II) when the solution pH is about 5.0 (Figure 2b).

3.2. Effect of pH on the Flotation Rate Constant

The pH value of the initial solution affects not only the flotation efficiency but also the rate of the process. This effect results mainly from the form of metal existence in the solution as well as from the prevailing mechanism of flotation. Experimental values of flotation rate constants for Al(III), Cu(II), and Zn(II) are given in Table 3. Curves presenting changes in the temporary removal ratio with flotation time are presented in Figures A7–A12. Values of the rate constants were found as the slope of the straight line, represented by Equation (4). The values of correlation coefficient (R^2) exceeding 0.95 justify that the course of both ion and precipitate flotation may be correctly described by the first-order chemical reaction rate [29].

Table 3. Effect of pH on the flotation rate constants during flotation of Al(III), Cu(II), and Zn(II) mixture.

Metal	$c_{0(Al)} = c_{0(Cu)} = c_{0(Zn)} = 0.15$ mmol dm^{-3}, $c_{SDS} = 0.125$ mmol dm^{-3}			$c_{0(Al)} = c_{0(Cu)} = c_{0(Zn)} = 2$ mmol dm^{-3}, $c_{SDS} = 0.187$ mmol dm^{-3}		
	pH	k, min^{-1}	R^2	pH	k, min^{-1}	R^2
Al(III)	4.8	0.523	0.973	4.5	0.380	0.977
	6.1	0.829	0.971	5.5	0.621	0.986
	7.2	1.208	0.980	6.9	0.802	0.985
	8.0	1.580	0.968	8.7	1.176	0.980
	9.6	0.904	0.960	10.5	0.510	0.983
Cu(II)	6.1	0.617	0.975	5.5	0.468	0.992
	7.2	1.340	0.965	6.9	0.663	0.986
	8.0	1.527	0.983	7.8	0.889	0.975
	9.0	1.467	0.977	8.7	1.123	0.990
	11.0	0.825	0.993	10.5	0.549	0.995
Zn(II)	6.1	0.475	0.986	6.9	0.592	0.990
	7.2	1.154	0.994	7.3	0.689	0.996
	8.0	1.389	0.996	7.8	0.839	0.984
	10.2	1.043	0.993	8.7	1.161	0.980
	11.0	0.783	0.989	10.5	0.521	0.997

The data presented in Table 3 show that the flotation rate constants for given metallic species are the highest for pH ranges corresponding to the highest removal efficiency. At the same time, these pH ranges reflect the lowest solubility of hydroxides of investigated metals [4]. For example, values of the flotation rate constant for Al(III) increase for the pH range between 4.8 and 8.0 (when initial concentration of each of investigated metals is 0.15 mmol dm^{-3}). For the pH < 5, soluble species of Al^{3+} and $AlOH^{2+}$ are present in the flotation solution, and thus ion flotation can occur and the value of the flotation rate constant is relatively low (0.523 min^{-1}). For pH > 4.8, the aluminum hydroxide $Al(OH)_3$ predominates as the aluminum compound in the solution, and thus $Al(OH)_3$ precipitate flotation occurs. For pH > 8.0, the aluminum flotation rate constant decreases, both due to dissolution of aluminum hydroxide as well as to increase in the share of negatively charged species of Al(III). Similar discussion of results, based on the electrochemical equilibria for investigated systems (Figures A1–A6), is valid in terms of Cu(II) and Zn(II).

Analysis of data presented in Table 3 provides an interesting conclusion on the flotation mechanism of Al(III), Cu(II), and Zn(II). Flotation rate constants, specific for each investigated metal, attain similar values. For example, values of the flotation rate constants are 1.176, 1.123, and 1.161 min^{-1}, respectively, for aluminum, copper, and zinc, when the

solution pH is 8.7. Such values of flotation rate constants indicate that a simultaneous flotation of all investigated metals is more probable than flotations of hydroxides of single, different metals. This is probably due to formation of a mixed precipitate which undergoes flotation. It is known [4] that precipitation of given metal hydroxides from polymetallic solutions is accompanied by co-precipitation or adsorption of other metals, which undergo precipitation at higher pH values when they singly occur in the aqueous solution.

The results presented in Table 3 as well as in Figure 2 indicate that the most optimal pH values, i.e., enabling the highest process efficiency are pH = 8.0 when c_0 = 0.15 mmol dm^{-3} and pH = 8.7 when c_0 = 2 mmol dm^{-3}. These pH values correspond to the course of the process with respect to the mechanism of precipitate flotation. Thus, the effects of collector concentration and air velocity were studied for precipitate flotation at given pH values. This is in accordance with some literature data for single metals. For example, Shakir et al. [25] obtained removal ratio of Al(III) equal to about 0.97 for pH = 6.0 when c_{SDS} = 0.4 mmol dm^{-3} and $c_{0(Al)}$ = 20 mmol dm^{-3}. Jurkiewicz [28] obtained a removal ratio of Zn(II) equal to about 0.92 for pH = 9.0 when c_{SDS} = 0.2 mmol dm^{-3} and $c_{0(Zn)}$ = 1 mmol dm^{-3}.

3.3. Effect of Collector Concentration on the Flotation Efficiency

Ion flotation is based on the separation of surface-inactive (colligend) ions from aqueous solutions by means of surface-active substance. The colligend ions interact with oppositely charged functional groups of surfactants at the gas–liquid interface [20]. Thus, successful realization of ion flotation results from stoichiometry of the above described reaction, which ensures the electrical neutrality of the formed compound. Therefore, at least stochiometric concentration of the collector to colligend ion is necessary to ensure complete removal of the target ion from the solution. For anionic sodium dodecyl sulphate as well as investigated metal ions, the following stoichiometric proportions are valid: c_{SDS}:c_{Al3+} = 3:1; c_{SDS}:c_{Cu2+} = c_{SDS}:c_{Zn2+} = 2:1. The influence of the collector concentration on the values of Al(III), Cu(II), and Zn(II) removal ratio is given in Figure 3.

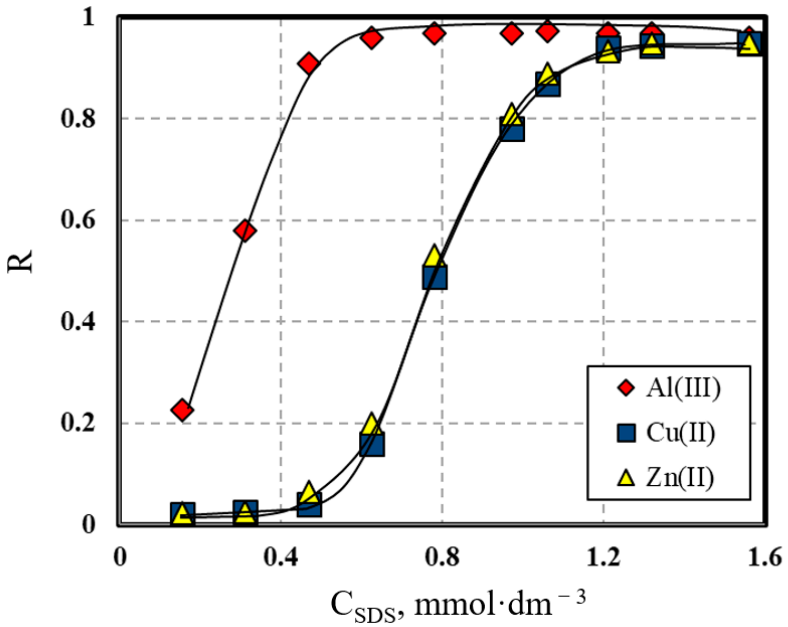

Figure 3. Influence of the SDS concentration on the efficiency of simultaneous ion flotation of Al(III), Cu(II), and Zn(II): c_0 = 0.15 mmol dm^{-3}, pH = 3.0.

The results presented in Figure 3 indicate that for a collector concentration lower than 0.45 mmol dm^{-3}, only Al^{3+} ions undergo ion flotation, while copper and zinc ions remain in the solution. Such a phenomenon suggests both the competition effects between colligend ions and ions of collector during the formation of floatable surface-active species

as well as the possibility of the separation of the mixture components depending on the collector concentration. The results show that the flotation of Cu^{2+} and Zn^{2+} is possible for the SDS concentration higher than 0.45 mmol dm^{-3}. The values of the final removal ratio for Cu(II) and Zn(II) increase for collector concentration between 0.45 and 1.20 mmol dm^{-3}. The SDS concentration equal to 1.20 mmol dm^{-3} is close to the stoichiometric one, which is 1.15 mmol dm^{-3} for the investigated system. Thus, within the studied collector concentration range, the values of the removal ratio for copper and zinc ions do not change when c_{SDS} > 1.20 mmol dm^{-3}.

The abovementioned competition between colligend ions and ions of collector results from varied affinity of metal cations towards anions of surface active substances. It is known that the higher the mentioned affinity is, the higher the ionic potential of a given cation is [57,58]. Ionic potentials for Al^{3+}, Cu^{2+}, and Zn^{2+} are 5.77, 2.74, and 2.25 (elementary charge A^{-1}), respectively [57,59,60]. This is why aluminum ions are selectively flotated from its mixture with copper and zinc ions when the collector concentration is sub-stoichiometric.

Influence of the collector concentration on the precipitate flotation of Al(III), Cu(II), and Zn(II) is shown in Table 4. Comparison of the results obtained for ion and precipitate flotation reveals that the collector concentration needed to reach high values of final removal ratio (i.e., R > 0.9) is several times lower for precipitate flotation than in ion flotation. Such a discrepancy in the collector concentration may be explained by the stoichiometry of the formation of a metal ion–collector product in ion flotation as well as micelles formation during precipitate flotation. In precipitate flotation, metal hydroxides present in the flotation suspension form micelles. The surface charge of a micelle is many times lower than the net charge of ions included in the hydroxides. Thus, the amount of the collector required for the charge neutralization is many times lower that it would be in the case of ion flotation of the same number of metal ions.

Table 4. Effect of the collector concentration on the efficiency of simultaneous precipitate flotation of Al(III), Cu(II), and Zn(II) mixture.

c_0, mmol dm^{-3}	pH	C_{SDS}, mmol dm^{-3}	R_{Al}	R_{Cu}	R_{Zn}
0.15	8.0	0.022	0.441	0.638	0.421
		0.044	0.810	0.730	0.653
		0.075	0.950	0.920	0.897
		0.094	0.957	0.940	0.920
		0.125	0.965	0.970	0.980
		0.250	0.966	0.971	0.975
		0.484	0.963	0.960	0.956
		0.625	0.956	0.950	0.953
2	8.5	0.014	0.231	0.199	0.214
		0.035	0.498	0.456	0.477
		0.070	0.832	0.812	0.833
		0.125	0.929	0.932	0.922
		0.187	0.978	0.980	0.979
		0.250	0.979	0.980	0.978
		0.347	0.971	0.977	0.978
		0.693	0.960	0.960	0.959

The results presented in Table 4 show that an increase in collector concentration results in the increase in the values of final removal ratio of investigated metals. However, the increase in the values of the final removal ratio is observed to a certain value of SDS concentration, above which a further increase in collector concentration does not affect the removal efficiency.

The ratio of the collector concentration to the concentration of metals in the solution decreases with the increase in metal concentration (Table 4). This effect is probably associated with a decrease in the density of surface electric charge when the sizes of metal hydroxide micelles increase due to an increase in metal concentration. In such a case,

the concentration of the collector required for the charge neutralization is lower when the metal concentration is higher.

3.4. Effect of Collector Concentration on the Flotation Rate Constant

An influence of the collector concentration on the values of flotation rate constants for Al(III), Cu(II), and Zn(II) is presented in Table 5, while the curves presenting changes in the temporary removal ration with flotation time are given in Figures A13–A18. The results indicate that an increase in the collector concentration results in a decrease in the flotation rate constants for investigated metals. This effect is clearly visible in the case of the precipitate flotation process. The authors decided not to present data on ion flotation since only stoichiometric proportion of collector to colligend ions is reasonable in this case. Sub-stoichiomteric concentrations of collector result in low process efficiency, while excess collector concentrations lead to competition between colligend ions and collector ions for adsorption at the gas–liquid interface as well as excessive foaming occurs.

Table 5. Effect of collector concentration on the values of the flotation rate constants during flotation of Al(III), Cu(II), and Zn(II) mixture.

Metal	$c_{0(Al)} = c_{0(Cu)} = c_{0(Zn)} = 0.15$ **mmol dm^{-3} pH = 8.0**			$c_{0(Al)} = c_{0(Cu)} = c_{0(Zn)} = 2$ **mmol dm^{-3} pH = 8.7**		
	c_{SDS}, **mmol dm^{-3}**	**k, min^{-1}**	**R^2**	c_{SDS}, **mmol dm^{-3}**	**k, min^{-1}**	**R^2**
Al(III)	0.125	1.580	0.968	0.187	1.176	0.980
	0.220	0.867	0.990	0.347	0.589	0.991
	0.355	0.216	0.969	0.485	0.505	0.996
	0.625	0.045	0.984	0.625	0.345	0.973
	0.815	0.030	0.988	0.874	0.244	0.976
Cu(II)	0.125	1.527	0.983	0.187	1.123	0.990
	0.220	0.964	0.992	0.347	0.607	0.991
	0.355	0.217	0.981	0.485	0.490	0.996
	0.625	0.057	0.994	0.625	0.307	0.987
	0.815	0.035	0.989	0.874	0.252	0.997
Zn(II)	0.125	1.389	0.996	0.187	1.161	0.980
	0.220	0.952	0.993	0.347	0.597	0.992
	0.355	0.242	0.984	0.485	0.513	0.997
	0.625	0.060	0.994	0.625	0.320	0.995
	0.815	0.037	0.987	0.874	0.254	0.998

A decrease in the flotation rate constants with an increase in the collector concentration may be explained as follows. When the collector concentrations are higher than the minimum concentration required for the occurrence of flotation, in the flotation suspension micelles containing metal hydroxides and ions of collector co-exist with free i.e., not adsorbed ions of collector. With an increase in the collector concentration, the share of free collector ions in the suspension increases. Therefore, a competition for the gas–liquid interface area between the floatable aggregates and the free collector ions is observed in the system. Free collector ions are smaller than micelle–collector aggregates and thus these free collector ions are preferentially adsorbed at the gas–liquid interface [20]. This results in a decrease in the values of Al(III), Cu(II), and Zn(II) flotation rate constants with the increase in the collector concentration. What is more, a delay effect [20,29] for flotation of metal-collector compounds in comparison to the flotation of free collector is clearly visible in Figures A13–A15.

Analysis of data given in Table 5 reveals that the flotation rate constants for each of the investigated metals are similar. This is in accordance with previously formulated statement (p. 3.2.) that investigated metals undergo simultaneous flotation in the form of agglomerates containing micelles of metal hydroxides and adsorbed ions of collector.

3.5. Effect of Air Velocity on Flotation Efficiency

Air velocity is an important parameter affecting both the course as well as the efficiency of ion and precipitate flotation. This is because the volume of foam generated during flotation us much dependent on the gas velocity [61]. Furthermore, resulting volume of the foam condensate decides about the enrichment of the colligend. From this perspective, low volumes of foam containing possibly high concentrations of removed ions are favored. The effects of the air velocity on the efficiency of ion and precipitate flotation as well as on the volume of foam condensate are presented in Table 6.

Table 6. Effect of the air velocity on the efficiency of simultaneous ion or precipitate flotation of Al(III), Cu(II) and Zn(II) mixture.

c_0, mmol dm^{-3}	c_{SDS}, mmol dm^{-3}	pH	u_G, mm s^{-1}	R_{Al}	R_{Cu}	R_{Zn}	V_c, cm^3
0.15	1.186	3.0	0.56	0.84	0.71	0.71	70
			0.79	0.95	0.89	0.90	105
			1.51	0.96	0.95	0.96	240
			2.40	0.97	0.96	0.98	315
0.15	0.125	8.0	0.13	0.94	0.93	0.92	7
			0.72	0.97	0.97	0.95	13
			1.51	0.98	0.98	0.97	20
			3.24	0.96	0.96	0.93	45
2	0.187	8.7	0.23	0.96	0.99	0.99	10
			1.12	0.97	0.99	0.99	15
			1.51	0.97	0.98	0.97	27
			2.86	0.97	0.99	0.99	40

V_c–volume of foam condensate, cm^3.

Analysis of the data given in Table 6 reveals that the gas flow rate does not greatly affect the values of the final removal ratio. The only exception is for low air velocities for ion flotation. This phenomenon may be explained as follows: the selected time of flotation (120 min) may be too little for complete ion flotation at low air velocity. This statement is supported by the shape of curves in Appendix A (Figures A19–A21). What is more, for ion flotation when u_G = 0.56 mm s^{-1}, the values of the final removal ratio for Cu(II) and Zn(II) are much lower than for Al(III). Additionally, curves presenting the course of the processes (Figures A19–A21) reveal that Al^{3+} is preferentially flotated from its mixture with Cu^{2+} and Zn^{2+}. This is in accordance with previous discussion on the effect of collector concentration and a competition effect between investigated metal cations for both preferential interactions with anionic collector as well as for adsorption at the available gas–liquid interfacial area.

3.6. Effect of Air Velocity on the Flotation Rate Constant

The flotating air velocity, for fixed process conditions with respect to solution pH and collector concentration, influences the values of the flotation rate constants. This is because of the fact that the flotation rate constant depends on the rate of formation of the gas–liquid interface [20,61–63]. As shown in Table 7 (results presenting original experimental recordings, i.e., changes in temporary removal ratio with flotation time, Figures A19–A27), an increase in the air velocity results in an increase in the flotation rate constants for Al(III), Cu(II), and Zn(II). Values of the flotation rate constants for ion flotation conditions (pH = 3.0) are an order of magnitude lower than for precipitate flotation conditions. The results show that the flotation rate constant is proportional to the gas velocity with the exponent value of about 0.78 [64]. This is in accordance with other similar results published in the literature [20,29]. It is known that the generated gas-phase interfacial area is proportional to the gas flow rate with the exponent value of about 0.44 [20]. The discrepancy between the above given values of the exponents indicates that the observed increase in the flotation rate together with an increase in the gas flow rate results also from the turbulence in

the liquid and not only from the available gas-liquid interfacial area. An increase in the turbulence in the liquid increases the probability of a collision between the solid particle aggregates and air bubble in the bubble layer, thus increasing the flotation rate.

3.7. Cost Estimation of Selected Methods for Removal of Metal Ions from Aqueous Solutions

Selection of a treatment method for the purification of wastewater streams from metal ions requires careful analysis of the properties of both treated and purified streams. Such analysis should cover several parameters, including solution pH, concentration of target pollutants as well as the expected purification efficiency. In several papers on ion and precipitate flotation, it was said that these processes are economically attractive comparing to other methods, especially when high volumes of containing low metal concentrations are considered [29,41,62]. Such a statement is true; however, few data are available on the evaluation of the costs of these processes. The low costs of ion and precipitate flotation result from the relatively low requirements for specific equipment and energy input for the operation. Apart from the apparatus for flotation, these processes require a surface-active substance as collector, acid or base solutions for pH regulation and, in general, a supply of compressed air. Grieves in 1970 estimated the cost of treatment of wastewaters containing Cr(III) to be about USD 0.12 to 0.15 per 1 m^3, respectively, for dispersed and dissolved air flotation [65]. A brief comparison of costs associated with selected methods of wastewater treatment is proposed in Table 8 [66].

Table 7. Effect of the air velocity on the values of the ion and precipitate flotation rate constants for Al(III), Cu(II), and Zn(II).

Metal	$c_{0(Al)} = c_{0(Cu)} = c_{0(Zn)} = 0.15$ mmol dm^{-3}						$c_{0(Al)} = c_{0(Cu)} = c_{0(Zn)} = 2$ mmol dm^{-3}		
	pH = 3.0 $c_{SDS} = 1.186$ mmol dm^{-3}			pH = 8.0 $c_{SDS} = 0.125$ mmol dm^{-3}			pH = 8.7 $c_{SDS} = 0.187$ mmol dm^{-3}		
	u_G, mm s^{-1}	k, min^{-1}	R^2	u_G, mm s^{-1}	k, min^{-1}	R^2	u_G, mm s^{-1}	k, min^{-1}	R^2
Al(III)	0.56	0.029	0.981	0.13	0.214	0.995	0.23	0.276	0.981
	0.79	0.033	0.996	0.72	0.554	0.992	1.12	0.880	0.980
	1.51	0.069	0.976	1.51	1.580	0.968	1.51	1.176	0.985
	2.40	0.087	0.964	3.24	2.621	0.995	2.86	1.903	0.988
Cu(II)	0.56	0.030	0.976	0.13	0.205	0.981	0.23	0.262	0.984
	0.79	0.034	0.991	0.72	0.600	0.987	1.12	0.855	0.981
	1.51	0.069	0.978	1.51	1.527	0.983	1.51	1.123	0.990
	2.40	0.088	0.986	3.24	2.547	0.977	2.86	1.994	0.958
Zn(II)	0.56	0.030	0.975	0.13	0.227	0.985	0.23	0.257	0.996
	0.79	0.041	0.977	0.72	0.636	0.974	1.12	0.861	0.985
	1.51	0.070	0.951	1.51	1.389	0.996	1.51	1.161	0.980
	2.40	0.091	0.971	3.24	2.614	0.984	2.86	2.207	0.970

Table 8. Estimated costs of selected methods for wastewater treatment.

Method	Average Cost, € m^{-3}	Average Energy Consumption, kWh m^{-3}
Reverse osmosis	0.22	2.1
Nanofiltration	0.18	0.5
Adsorption	0.07	0.1
Ion exchange	0.10	0.1
Electrodialysis	0.20	0.6

Analysis of data given in Table 7 reveals that adsorption- and ion exchange-based techniques provide the most cost-effective conditions for wastewater treatment [66]. Thus, ion and precipitate flotation as adsorptive bubble separation techniques, are economically attractive solutions to be considered for application during wastewater purification, especially when dilute streams are taken into account [62].

4. Conclusions

The results presented in this paper reveal that the pH of the initial solution is an important parameter governing the flotation mechanism and efficiency. The highest values of the final removal ratio for Al(III), Cu(II), and Zn(II) were noted for a pH range between

7.0 and 9.0. This pH range corresponds to the precipitate flotation carried out using the anionic collector. Moreover, the regulation of pH value enables the selective flotation of Al(III) for pH values lower than 5.0 using anionic SDS and the selective flotation of Cu(II) for pH higher than 12, using cationic CTAB.

During ion flotation at pH = 3.0, Al^{3+} ions are preferentially removed from the solution prior to Cu^{2+} and Zn^{2+}.

The course of the ion and precipitate flotation processes may be described by the first-order reaction rate equation.

An increase in the collector concentration results in a decrease in the flotation rate constants for investigated metals.

An increase in the flotating air velocity results in an increase in the ion and precipitation flotation rates. Flotation rate constants for Al(III), Zn(II), and Cu(II) are proportional to the gas flow rate in the exponent of 0.78.

For specified process conditions of precipitate flotation, i.e., pH value, collector and metal concentration, air velocity, flotation rate constants for Al(III), Zn(II), and Cu(II) are similar, indicating that these metals are simultaneously removed from aqueous solutions in the form of mixed precipitate, containing hydroxides of above named metals.

It is proposed that further research on the application of ion and precipitate flotation to remove metals should include pilot-scale investigations on real wastewater samples. It is expected that such investigations define the areas of possible utilization of these processes in the wastewater treatment technologies together with deep economic and environmental analyses of benefits from using ion and precipitate flotation techniques.

Author Contributions: Conceptualization, P.R. and B.K.-P.; methodology, P.R. and B.K.-P.; software, P.R.; formal analysis, B.K.-P.; investigation, P.R.; writing—original draft preparation, P.R.; writing—review and editing, B.K.-P. and P.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data available in a publicly accessible repository as well as in a publicly accessible repository that does not issue DOIs. All data referred to in this paper are accessible according to the list of references. All experimental data created by Authors are presented in this paper.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

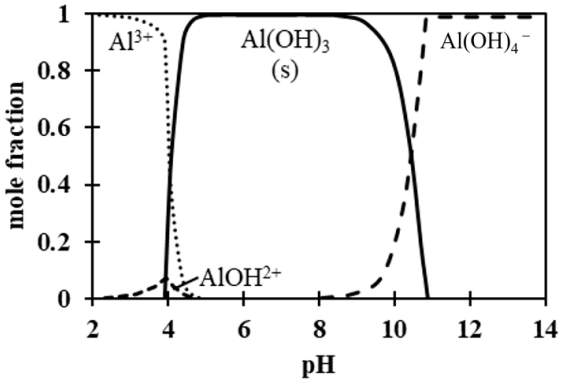

Figure A1. Dependences of Al(III) forms on the pH value of the aqueous solutions (c_0 = 0.15 mmol dm^{-3}).

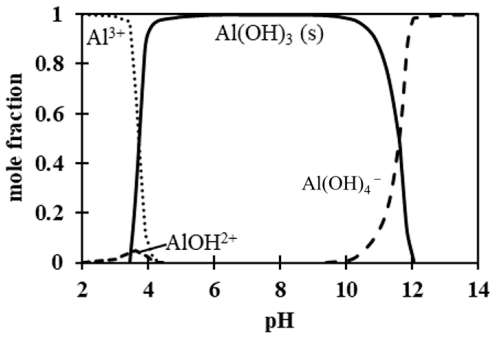

Figure A2. Dependences of Al(III) forms on the pH value of the aqueous solutions (c_0 = 2 mmol dm^{-3}).

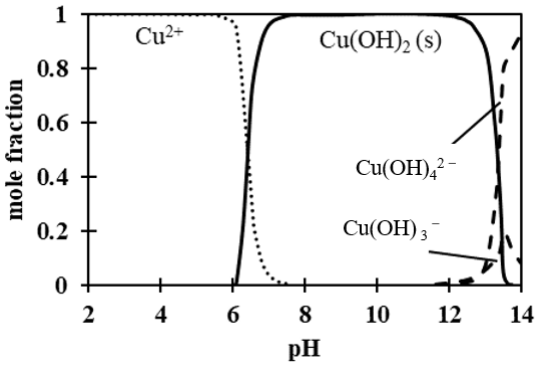

Figure A3. Dependences of Cu(II) forms on the pH value of the aqueous solutions (c_0 = 0.15 mmol dm^{-3}).

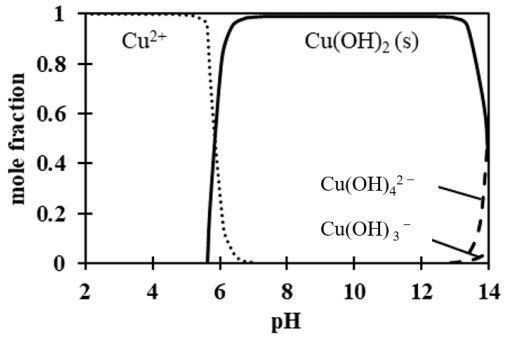

Figure A4. Dependences of Cu(II) forms on the pH value of the aqueous solutions (c_0 = 2 mmol dm^{-3}).

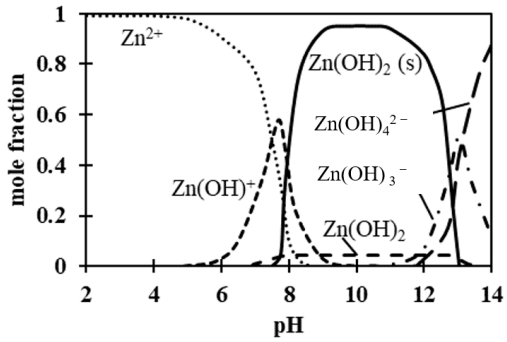

Figure A5. Dependences of Zn(II) forms on the pH value of the aqueous solutions (c_0 = 0.15 mmol dm^{-3}).

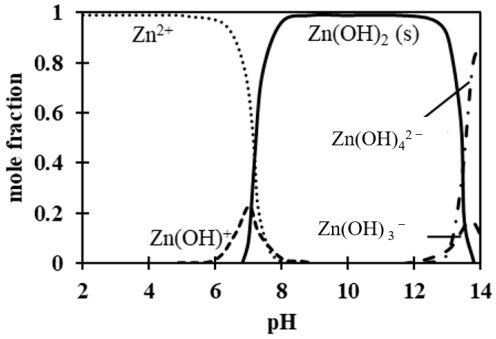

Figure A6. Dependences of Zn(II) forms on the pH value of the aqueous solutions (c_0 = 2 mmol dm^{-3}).

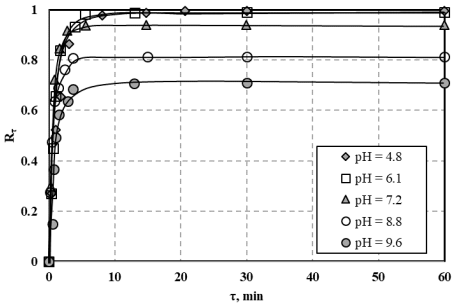

Figure A7. Changes in Al(III) temporary removal ratio during ion and precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of pH (c_0 = 0.15 mmol dm^{-3}, c_{SDS} = 0.125, u_G = 1.51 mm s^{-1}).

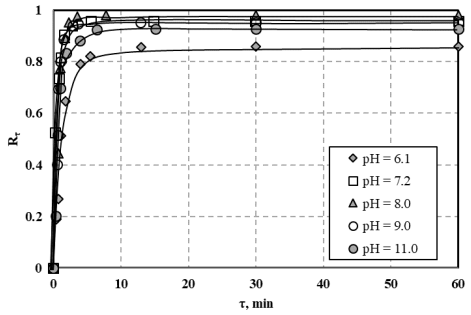

Figure A8. Changes in Cu(II) temporary removal ratio during ion and precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of pH (c_0 = 0.15 mmol dm^{-3}, c_{SDS} = 0.125, u_G = 1.51 mm s^{-1}).

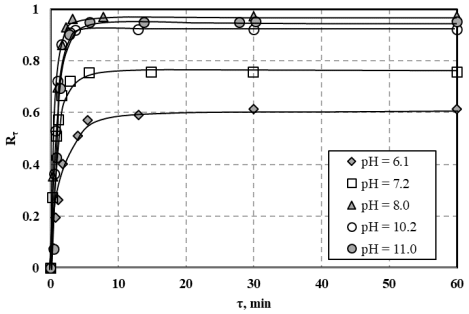

Figure A9. Changes in Zn(II) temporary removal ratio during ion and precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of pH (c_0 = 0.15 mmol dm^{-3}, c_{SDS} = 0.125, u_G = 1.51 mm s^{-1}).

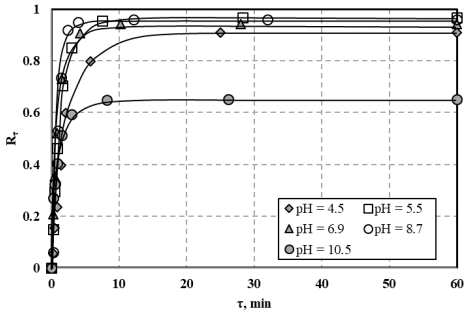

Figure A10. Changes in Al(III) temporary removal ratio during ion and precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of pH (c_0 = 2 mmol dm^{-3}, c_{SDS} = 0.187, u_G = 1.51 mm s^{-1}).

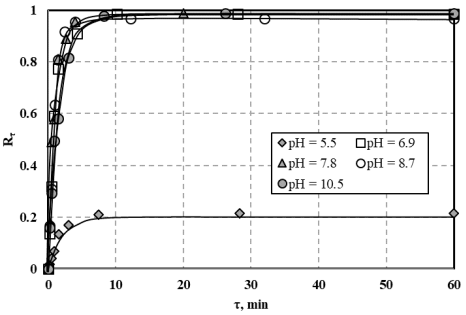

Figure A11. Changes in Cu(II) temporary removal ratio during ion and precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of pH (c_0 = 2 mmol dm^{-3}, c_{SDS} = 0.187, u_G = 1.51 mm s^{-1}).

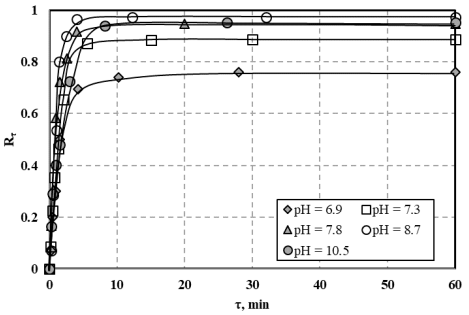

Figure A12. Changes in Zn(II) temporary removal ratio during ion and precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of pH (c_0 = 2 mmol dm^{-3}, c_{SDS} = 0.187, u_G = 1.51 mm s^{-1}).

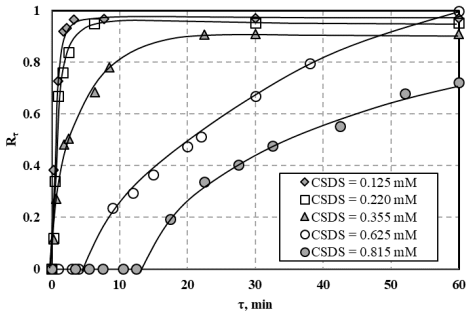

Figure A13. Changes in Al(III) temporary removal ratio during precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of collector concentration (c_0 = 0.15 mmol dm^{-3}, pH = 8.0, u_G = 1.51 mm s^{-1}).

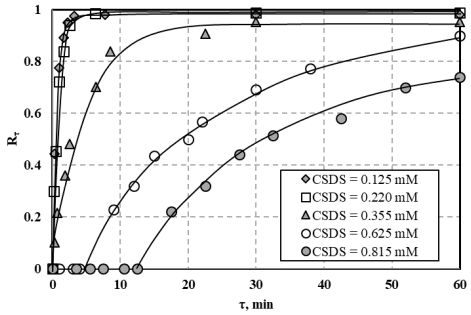

Figure A14. Changes in Cu(II) temporary removal ratio during precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of collector concentration (c_0 = 0.15 mmol dm^{-3}, pH = 8.0, u_G = 1.51 mm s^{-1}).

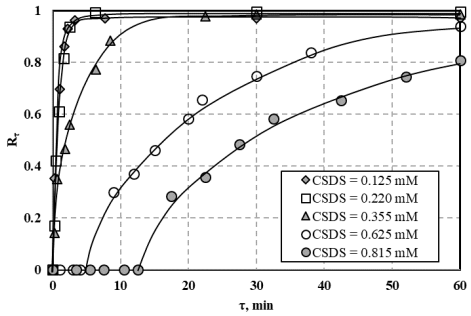

Figure A15. Changes in Zn(II) temporary removal ratio during precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of collector concentration (c_0 = 0.15 mmol dm^{-3}, pH = 8.0, u_G = 1.51 mm s^{-1}).

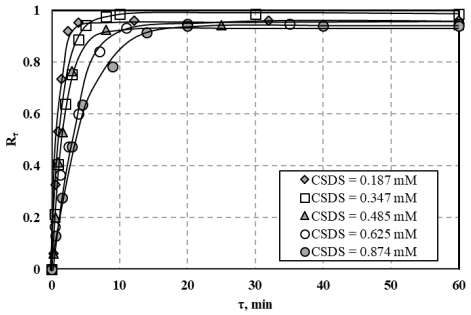

Figure A16. Changes in Al(III) temporary removal ratio during precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of collector concentration (c_0 = 2 mmol dm^{-3}, pH = 8.7, u_G = 1.51 mm s^{-1}).

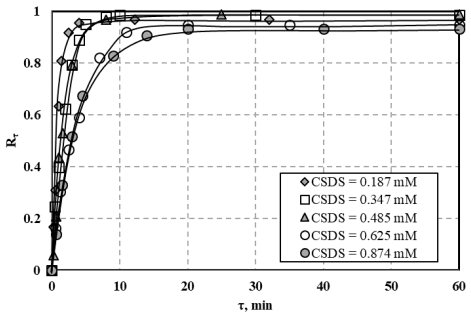

Figure A17. Changes in Cu(II) temporary removal ratio during precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of collector concentration (c_0 = 2 mmol dm^{-3}, pH = 8.7, u_G = 1.51 mm s^{-1}).

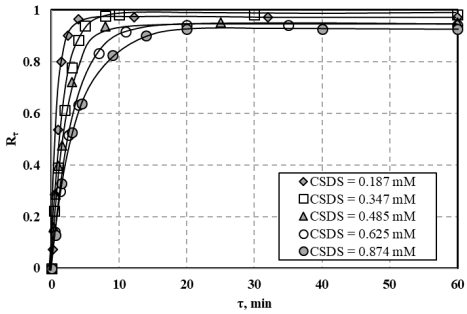

Figure A18. Changes in Zn(II) temporary removal ratio during precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of collector concentration (c_0 = 2 mmol dm^{-3}, pH = 8.7, u_G = 1.51 mm s^{-1}).

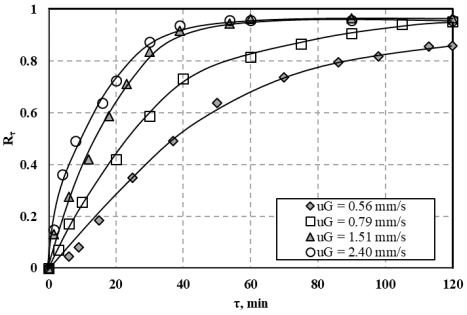

Figure A19. Changes in Al(III) temporary removal ratio during ion flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of air velocity (c_0 = 0.15 mmol dm^{-3}, pH = 3.0, c_{SDS} = 1.186 mmol dm^{-3}).

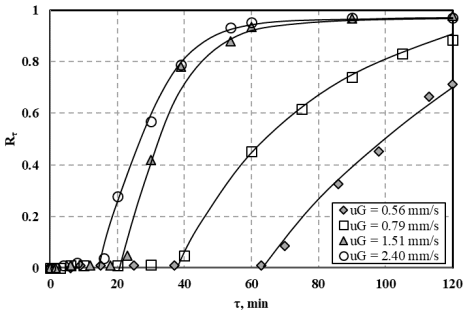

Figure A20. Changes in Cu(II) temporary removal ratio during ion flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of air velocity (c_0 = 0.15 mmol dm^{-3}, pH = 3.0, c_{SDS} = 1.186 mmol dm^{-3}).

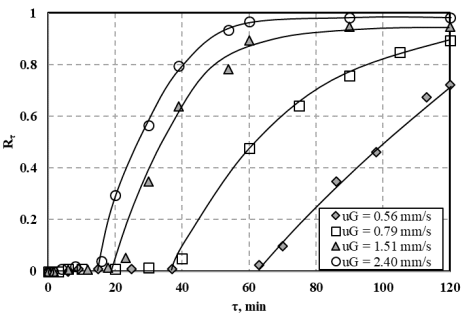

Figure A21. Changes in Zn(II) temporary removal ratio during ion flotation from solution containing Al(III), Cu(II) and Zn(II) mixture—effect of air velocity (c_0 = 0.15 mmol dm^{-3}, pH = 3.0, c_{SDS} = 1.186 mmol dm^{-3}).

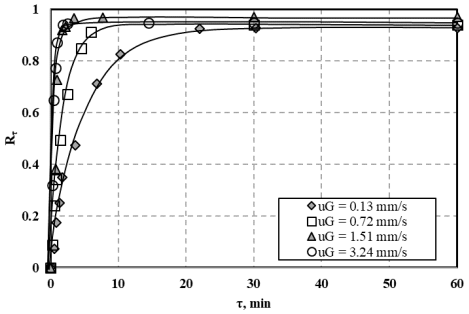

Figure A22. Changes in Al(III) temporary removal ratio during precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of air velocity (c_0 = 0.15 mmol dm^{-3}, pH = 8.0, c_{SDS} = 0.125 mmol dm^{-3}).

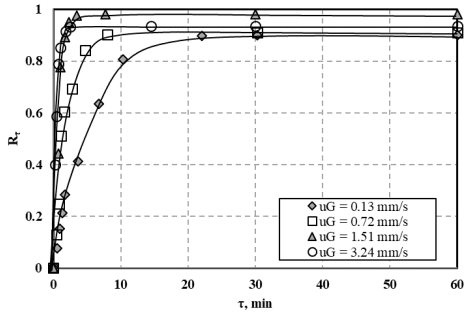

Figure A23. Changes in Cu(II) temporary removal ratio during precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of air velocity (c_0 = 0.15 mmol dm^{-3}, pH = 8.0, c_{SDS} = 0.125 mmol dm^{-3}).

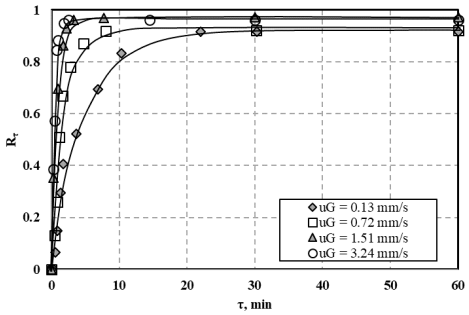

Figure A24. Changes in Zn(II) temporary removal ratio during precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of air velocity (c_0 = 0.15 mmol dm^{-3}, pH = 8.0, c_{SDS} = 0.125 mmol dm^{-3}).

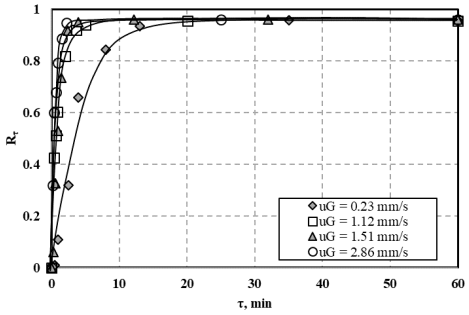

Figure A25. Changes in Al(III) temporary removal ratio during precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of air velocity (c_0 = 2 mmol dm^{-3}, pH = 8.7, c_{SDS} = 0.187 mmol dm^{-3}).

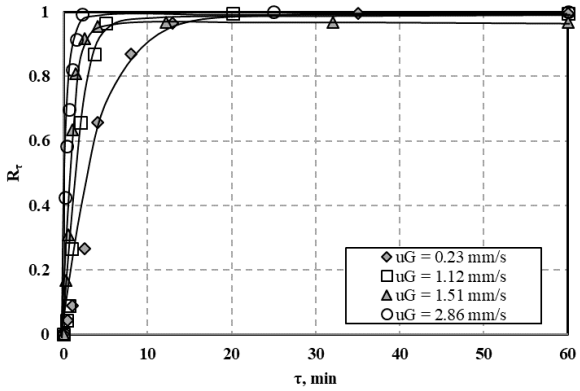

Figure A26. Changes in Cu(II) temporary removal ratio during precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of air velocity (c_0 = 2 mmol dm^{-3}, pH = 8.7, c_{SDS} = 0.187 mmol dm^{-3}).

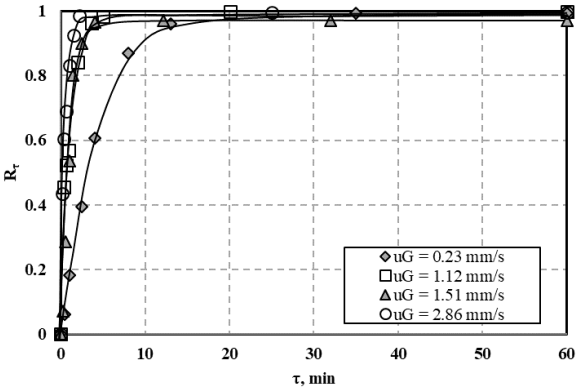

Figure A27. Changes in Zn(II) temporary removal ratio during precipitate flotation from solution containing Al(III), Cu(II), and Zn(II) mixture—effect of air velocity (c_0 = 2 mmol dm^{-3}, pH = 8.7, c_{SDS} = 0.187 mmol dm^{-3}).

References

1. Fu, F.; Wang, Q. Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manag.* **2011**, *92*, 407–418. [CrossRef]
2. Wang, M.; Wang, Z.; Zhou, X.; Li, S. Efficient Removal of Heavy Metal Ions in Wastewater by Using a Novel Alginate-EDTA Hybrid Aerogel. *Appl. Sci.* **2019**, *9*, 547. [CrossRef]
3. Santander, M.; Valderrama, L.; Guevara, M.; Rubio, J. Adsorbing colloidal flotation removing metals ions in a modified jet cell. *Miner. Eng.* **2011**, *24*, 1010–1015. [CrossRef]
4. Blais, J.F.; Djedidi, Z.; Cheikh, R.B.; Tyagi, R.D.; Mercier, G. Metals Precipitation from Effluents: Review. *Pract. Period. Hazard. Toxic Radioact. Waste Manag.* **2008**, *12*, 135–149. [CrossRef]
5. Kurniawan, T.A.; Chan, G.Y.S.; Lo, W.H.; Babel, S. Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chem. Eng. J.* **2006**, *118*, 83–98. [CrossRef]
6. Al-Senani, G.M.; Al-Fawzan, F.F. Adsorption study of heavy metal ions from aqueous solution by nanoparticle of wild herbs. *Egypt. J. Aquat. Res.* **2018**, *44*, 187–194. [CrossRef]
7. Wołowiec, M.; Komorowska-Kaufman, M.; Pruss, A.; Rzepa, G.; Bajda, T. Removal of Heavy Metals and Metalloids from Water Using Drinking Water Treatment Residuals as Adsorbents: A Review. *Minerals* **2019**, *9*, 487. [CrossRef]
8. Joseph, L.; Jun, B.M.; Flora, J.R.V.; Park, C.M.; Yoon, Y. Removal of heavy metals from water sources in the developing world using low-cost materials: A review. *Chemosphere* **2019**, *229*, 142–159. [CrossRef]
9. Kulshreshtha, A.; Agrawal, R.; Barar, M.; Saxena, S. A Review on Bioremediation of Heavy Metals in Contaminated Water. *IOSR J. Environ. Sci. Toxicol. Food Technol.* **2014**, *8*, 44–50. [CrossRef]
10. Gheju, M. Decontamination of hexavalent chromium-polluted waters: Significance of metallic iron technology. In *Enhancing Cleanup of Environmental Pollutants*; Springer International Publishing: Berlin/Heidelberg, Germany, 2017; Volume 2, pp. 209–253. ISBN 9783319554235.
11. Shiba, S.; Hirata, Y.; Seno, T. In-Situ Electrokinetic Remediation of Soil and Water in Aquifer Contaminated by Heavy Metal. In *Groundwater Updates*; Springer: Tokyo, Japan, 2000; pp. 135–140.

12. Litter, M.I. Mechanisms of removal of heavy metals and arsenic from water by TiO_2-heterogeneous photocatalysis. *Pure Appl. Chem.* **2015**, *87*, 557–567. [CrossRef]
13. Deliyanni, E.A.; Kyzas, G.Z.; Matis, K.A. Various flotation techniques for metal ions removal. *J. Mol. Liq.* **2017**, *225*, 260–264. [CrossRef]
14. Peleka, E.N.; Gallios, G.P.; Matis, K.A. A perspective on flotation: A review. *J. Chem. Technol. Biotechnol.* **2018**, *93*, 615–623. [CrossRef]
15. Sebba, F. *Ion Flotation*; Elsevier Publishing Company: New York, NY, USA, 1962.
16. Zouboulis, I.; Matis, K.A. Separation of Heavy Metals from Effluents by Flotation. In *Pretreatment in Chemical Water and Wastewater Treatment*; Springer: Berlin/Heidelberg, Germany, 1988; pp. 159–166.
17. Chang, L.; Cao, Y.; Fan, G.; Li, C.; Peng, W. A review of the applications of ion floatation: Wastewater treatment, mineral beneficiation and hydrometallurgy. *RSC Adv.* **2019**, *9*, 20226–20239. [CrossRef]
18. Zouboulis, A.I.; Matis, K.A. Ion flotation in environmental technology. *Chemosphere* **1987**, *16*, 623–631. [CrossRef]
19. Selecki, A. *Rozdzielanie Mieszanin. Metody Niekonwencjonalne*; Wydawnictwo Naukowo-Techniczne: Warszawa, Poland, 1972.
20. Kawalec-Pietrenko, B.; Selecki, A. Investigations of Kinetics of Removal of Trivalent Chromium Salts from Aqueous Solutions Using Ion and Precipitate Flotation Methods. *Sep. Sci. Technol.* **1984**, *19*, 1025–1038. [CrossRef]
21. Gawroński, R. *Procesy Oczyszczania Cieczy*; Oficyna Wydawnicza Politechniki Warszawskiej: Warszawa, Poland, 2006.
22. Gryta, M.; Tomczak, W.; Bastrzyk, J. Badania rozdzielania brzeczek z bakteryjnej fermentacji glicerolu w układzie ultrafiltracja—nanofiltracja. *Inżynieria Apar. Chem.* **2013**, *52*, 423–424. (In Polish) [CrossRef]
23. Nouri, J.; Mahvi, A.H.; Bazrafshan, E. Application of electrocoagulation process in removal of zinc and copper from aqueous solutions by aluminum electrodes. *Int. J. Environ. Res.* **2010**, *4*, 201–208. [CrossRef]
24. Zhang, J.; Klasky, M.; Letellier, B.C. The aluminum chemistry and corrosion in alkaline solutions. *J. Nucl. Mater.* **2009**, *384*, 175–189. [CrossRef]
25. Shakir, K.; Aziz, M.; Benyamin, K. Foam separation. Studies on the foam separation of Al(III) and the use of Al(III) hydroxide as a coprecipitant in the adsorbing colloid flotation of trace metal ions; part I: Foam separation of Al(III). *Tenside Surfactants Deterg.* **1990**, *27*, 329–335.
26. Rubin, A.J.; Johnson, J.D. Effect of pH on Ion and Precipitate Flotation Systems. *Anal. Chem.* **1967**, *39*, 298–302. [CrossRef]
27. Liu, Z.; Doyle, F.M. A thermodynamic approach to ion flotation. II. Metal ion selectivity in the SDS-Cu-Ca and SDS-Cu-Pb systems. *Colloids Surfaces A Physicochem. Eng. Asp.* **2001**, *178*, 93–103. [CrossRef]
28. Jurkiewicz, K. The removal of zinc from solutions by foam separation, II. Precipitate flotation of zinc hydroxide. *Int. J. Miner. Process.* **1990**, *29*, 1–15. [CrossRef]
29. Kawalec-Pietrenko, B.; Rybarczyk, P. Al(III) and Cu(II) simultaneous foam separation: Physicochemical problems. *Chem. Pap.* **2014**, *68*, 890–898. [CrossRef]
30. Ghazy, S.; El-Morsy, S. Precipitate Flotation of Aluminum and Copper. *Trends Appl. Sci. Res.* **2008**, *3*, 14–24. [CrossRef]
31. Hogan, D.E.; Curry, J.E.; Maier, R.M. Ion Flotation of La^{3+}, Cd^{2+}, and Cs^{+} using Monorhamnolipid Collector. *Colloids Interfaces* **2018**, *2*, 43. [CrossRef]
32. Peng, W.; Chang, L.; Li, P.; Han, G.; Huang, Y.; Cao, Y. An overview on the surfactants used in ion flotation. *J. Mol. Liq.* **2019**, *286*, 110955. [CrossRef]
33. Salmani Abyaneh, A.; Fazaelipoor, M.H. Evaluation of rhamnolipid (RL) as a biosurfactant for the removal of chromium from aqueous solutions by precipitate flotation. *J. Environ. Manag.* **2016**, *165*, 184–187. [CrossRef]
34. Sobianowska-Turek, A.; Ulewicz, M.; Sobianowska, K. Ion flotation and solvent sublation of zinc(II) and manganese(II) in the presence of proton-ionizable lariat ethers. *Physicochem. Probl. Miner. Process.* **2016**, *52*, 1048–1060. [CrossRef]
35. Wu, H.; Huang, Y.; Liu, B.; Han, G.; Su, S.; Wang, W.; Yang, S.; Xue, Y.; Li, S. An efficient separation for metal-ions from wastewater by ion precipitate flotation: Probing formation and growth evolution of metal-reagent flocs. *Chemosphere* **2021**, *263*, 128363. [CrossRef] [PubMed]
36. Wu, H.; Wang, W.; Huang, Y.; Han, G.; Yang, S.; Su, S.; Sana, H.; Peng, W.; Cao, Y.; Liu, J. Comprehensive evaluation on a prospective precipitation-flotation process for metal-ions removal from wastewater simulants. *J. Hazard. Mater.* **2019**, *371*, 592–602. [CrossRef] [PubMed]
37. Zakeri Khatir, M.; Abdollahy, M.; Khalesi, M.R.; Rezai, B. Selective separation of neodymium from synthetic wastewater by ion flotation. *Sep. Sci. Technol.* **2020**. [CrossRef]
38. Soliman, M.A.; Rashad, G.M.; Mahmoud, M.R. Kinetics of ion flotation of Co(II)-EDTA complexes from aqueous solutions. *Radiochim. Acta* **2015**, *103*, 643–652. [CrossRef]
39. Jurkiewicz, K. Adsorptive bubble separation of zinc and cadmium cations in presence of ferric and aluminum hydroxides. *J. Colloid Interface Sci.* **2005**, *286*, 559–563. [CrossRef] [PubMed]
40. Salmani, M.H.; Davoodi, M.; Ehrampoush, M.H.; Ghaneian, M.T.; Fallahzadah, M.H. Removal of cadmium (II) from simulated wastewater by ion flotation technique. *Iran. J. Environ. Health Sci. Eng.* **2013**, *10*. [CrossRef]
41. Polat, H.; Erdogan, D. Heavy metal removal from waste waters by ion flotation. *J. Hazard. Mater.* **2007**, *148*, 267–273. [CrossRef] [PubMed]
42. Bartkiewicz, B. *Treatment of Industrial Wastewaters (in Polish)*; PWN: Warszawa, Poland, 2007; ISBN 978-83-01-16267-2.
43. Ruffer, H.; Rosenwinkel, K. *Treatment of Industrial Wastewaters (in Polish)*; Oficyna Wydawnicza Projprzem-EKO: Bydgoszcz, Poland, 1998; ISBN 83-906015-2-4.

44. Medina, B.Y.; Torem, M.L.; De Mesquita, L.M.S. On the kinetics of precipitate flotation of Cr III using sodium dodecylsulfate and ethanol. *Miner. Eng.* **2005**, *18*, 225–231. [CrossRef]
45. Študlar, K.; Janoušek, I. The photometric determination of zinc with xylenol orange. *Talanta* **1961**, *8*, 203–208. [CrossRef]
46. Mochizuki, T.; Kuroda, R. Rapid continuous determination of aluminium in copper-base alloys by flow-injection spectrophotometry. *Fresenius' Z. Anal. Chem.* **1982**, *311*, 11–15. [CrossRef]
47. Marczenko, Z.; Balcerzak, M. *Spektrofotometryczne Metody w Analizie Nieorganicznej*; Wydawnictwo Naukowe PWN: Warszawa, Poland, 1998; ISBN 9788301126124.
48. Stoica, L.; Oproiu, G.C.; Cosmeleata, R.; Dinculescu, M. Kinetics of Cu^{2+} separation by flotation. *Sep. Sci. Technol.* **2003**, *38*, 613–632. [CrossRef]
49. Jiao, C.S.; Ding, Y. Foam separation of chromium (VI) from aqueous solution. *J. Shanghai Univ.* **2009**, *13*, 263–266. [CrossRef]
50. Opriou, G.; Lacatusu, I.; Stoica, L. Examination of kinetic flotation process for two experimental Cu(II) and Ni(II)—A-benzoinoxime systems, based on kinetic literature models. *Rev. Chim.* **2009**, *60*, 641–645.
51. Reyes, M.; Patiñeo, F.; Tavera, F.J.; Escudero, R.; Rivera, I.; Pérez, M. Kinetics and recovery of xanthate-copper compounds by ion flotation techniques. *J. Mex. Chem. Soc.* **2009**, *53*, 15–22. [CrossRef]
52. Reyes, M.; Patino, F.; Tavera, F.J.; Escudero, R.; Ribera, I.; Perez, M. Kinetics and Hydrodynamics of Silver Ion Flotation. *J. Mex. Chem. Soc.* **2012**, *53*, 15–22.
53. Puigdomenech, I. *MEDUSA (Make Equilibrium Diagrams Using Sophisticated Algorithms)*; Royal Institute of Technology: Stockholm, Sweden, 2010.
54. Crawford, R.J.; Harding, I.H.; Mainwaring, D.E. Adsorption and Coprecipitation of Single Heavy Metal Ions onto the Hydrated Oxides of Iron and Chromium. *Langmuir* **1993**, *9*, 3050–3056. [CrossRef]
55. Parks, G.A. The Isoelectric Points of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems. *Chem. Rev.* **1965**, *65*, 177–198. [CrossRef]
56. Drzymała, J.; Lekki, J.; Szczypa, J. Zerowy ładunek powierzchniowy tlenków i wodorotlenków metali (in Polish). In *Prace Naukowe Instytutu Chemii Nieorganicznej i Metalurgii Pierwiastków Rzadkich Politechniki Wrocławkiej (40). Studia i Materiały (16)*; Wydawnictwo Politechniki Wrocławskiej: Wrocław, Poland, 1978.
57. Walkowiak, W. Mechanism of Selective Ion Flotation. 1. Selective Flotation of Transition Metal Cations. *Sep. Sci. Technol.* **1991**, *26*, 559–568. [CrossRef]
58. Charewicz, W.A.; Holowiecka, B.A.; Walkowiak, W. Selective flotation of zinc(II) and silver(I) ions from dilute aqueous solutions. *Sep. Sci. Technol.* **1999**, *34*, 2447–2460. [CrossRef]
59. Atkins, P. *Podstawy Chemii Fizycznej*; Wydawnictwo Naukowe PWN: Warszawa, Poland, 2002. (In Polish)
60. Jensen, W.B. The quantification of electronegativity: Some precursors. *J. Chem. Educ.* **2012**, *89*, 94–96. [CrossRef]
61. Rubin, A.J.; Johnson, J.D.; Lamb, J.C. Comparison of variables in ion and precipitate flotation. *Ind. Eng. Chem. Process Des. Dev.* **1966**, *5*, 368–375. [CrossRef]
62. Doyle, F.M. Ion flotation—Its potential for hydrometallurgical operations. *Int. J. Miner. Process.* **2003**, *72*, 387–399. [CrossRef]
63. Hinojosa-Reyes, M.; Rodríguez-González, V.; Arriaga, S. Enhancing ethylbenzene vapors degradation in a hybrid system based on photocatalytic oxidation UV/TiO 2-In and a biofiltration process. *J. Hazard. Mater.* **2012**, *209–210*, 365–371. [CrossRef] [PubMed]
64. Rybarczyk, P. Równolegle Przebiegające Procesy Separacji Pianowej Jonów Al(III), Cu (II) i Zn(II) z Roztworów Ich Mieszanin. Ph.D. Thesis, Gdansk University of Technology, Gdańsk, Poland, 2015.
65. Grieves, R. Foam Separations for Industrial Wastes: Process Selection on JSTOR. *J. Water Pollut. Control Fed.* **1970**, *42*, 336–344.
66. Bolisetty, S.; Peydayesh, M.; Mezzenga, R. Sustainable technologies for water purification from heavy metals: Review and analysis. *Chem. Soc. Rev.* **2019**, *48*, 463–487. [CrossRef] [PubMed]