

## **Ion flotation and its applications on concentration, recovery, and removal of metal ions from solutions**

**Fatma Arslan, Gülay Bulut**

Istanbul Technical University, Mining Faculty, Mineral Processing Engineering Department, 34469 Maslak, Istanbul, Turkey

Corresponding author: [arslanf@itu.edu.tr](mailto:arslanf@itu.edu.tr) (Fatma Arslan)

**Abstract:** Many industries, especially mining and metallurgy, deal with solutions containing ions. In some cases, these metal ions need to be concentrated and recovered from solutions and sometimes removed from wastewater. The ion flotation method has been applied for wastewater and water treatment, recovery of precious and platinum group metals, preconcentrating of rare earth elements, selective separation of multicomponent ions from dilute solutions, and analytical chemistry. It has been employed to separate heavy metals from a liquid phase using bubble attachment, originated in mineral processing. In these cases, ion flotation has an important place among other methods because it is a cheap and practical method. In this study, many ion flotation studies, especially applied at laboratory scale, were reviewed. This method gives very successful and promising results in removing heavy metals with toxic effects from wastewater and selective separation of metal ions from very low concentrated solutions. Ion flotation may take place in industrial scale operations with the new developments in flotation machines and collectors with better selectivity, high efficiency, lower cost, and environmental friendliness.

**Keywords:** ion flotation, heavy metals, rare earth metals, waste water, preconcentration

### **1. Introduction**

Flotation, a process originating from the minerals industry, has nowadays found extensive use in wastewater treatment and has been employed to separate heavy metals from a liquid phase using bubble attachment, originated in mineral processing. It is also finding its way in hydrometallurgical applications and especially ion flotation is used as a separation technology for concentrating, recovering, and removing metal ions from dilute aqueous solutions. Today, the recovery or removal of metal ions from solutions is an important issue that concerns many scientific fields. Most industries encounter, especially in low-concentration solutions. The removal or recovery of metal ions from these solutions provides significant gains both economically and environmentally.

The rapid development of industry and the increasing productivity of many industrial branches such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc., have resulted in the pollution of ground water sources by discharging heavy metal containing wastewaters directly or indirectly into the environment, especially in developing countries; thus, people worldwide face the problems of lack of fresh water together with the spread of various diseases due to organic and inorganic contaminants (Doyle, 2003; Fu and Wang, 2011). Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic (Fu and Wang, 2011). Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium. Most of the waste sludge also contains various acids (e.g. HCl, HNO<sub>3</sub>), organics (e.g. EDTA), and inorganic substances (Ksenofontov et al, 2019). Heavy metals ions can be removed by biological treatments. Metal ions can enter water bodies and soil, accumulate in animals and plants through the food chain, and eventually accumulate in the human body, seriously endangering human health and life due to their non-degradability, mobility and persistence, therefore

they need to be removed from wastewaters before discharging (Doyle, 2003). Heavy metal wastewater treatment techniques are chemical precipitation (hydroxide precipitation, sulfide precipitation, chemical precipitation combined with other methods, heavy metal chelating precipitation), ion exchange, adsorption (activated carbon adsorbents, carbon nanotubes adsorbents, low-cost adsorbents, bioadsorbents), membrane filtration (ultrafiltration, reverse osmosis, nanofiltration, electrodialysis), flotation (dissolved air flotation, precipitate flotation, ion flotation), coagulation-flocculation, evaporation, and electrochemical treatment (electrocoagulation, electroflotation, electrodeposition) (Fu and Wang, 2011) and the methods for sludge dewatering is alkaline and acid hydrolysis for neutralization and biological treatment (Ksenofontov et al, 2019). However, these removal methods have many disadvantages such as high cost, generation of large amounts of sludge, high reagent or energy requirements, time consumption, incomplete removal of target ions, production of secondary wastes and difficulty of treatment of large volumes of wastewater (Doyle, 2003).

In hydrometallurgy and in nuclear industry several methods are commonly used for the concentrating, recovery, and removal of metal ions from dilute solutions. These methods include solvent extraction, precipitation, ion-exchange resins, evaporation, extraction in microheterogeneous systems, supported liquid membrane and they offer a number of advantages such as high decontamination and extraction rates, but have inherent limitations such as the use of an organic solvent, operating costs, environmental impact and production of secondary wastes (Micheau et al., 2018).

Flotation was first and widely used in the mining industry that can go for many years and is a process for separating finely divided solids from each other. Flotation is also one of the methods used for both the recovery and removal of metal ions from solutions. It can be generally defined as the selective separation of solid particles, liquid droplets, chemicals, ions, or biological things from a bulk liquid based on their surface properties (Gaudin, 1957; Rubio et al., 2001; Petrov et al., 2015; Kyzas and Matis, 2018). In the process collision between going up bubbles and matter suspended in the liquid, followed by possible adhesion of the particle to the bubble surface and separation of the resulting bubble-particle aggregate from that liquid.

Flotation, a process originating from the minerals industry, has nowadays found extensive use in wastewater treatment (Fu and Wang, 2011) and is also finding its way in hydrometallurgical applications and especially ion flotation is used as a separation technology for concentrating, recovering, and removing metal ions from dilute aqueous solutions has been employed to separate heavy metals from a liquid phase using bubble attachment, originated in mineral processing (Matis and Mavros, 1991). It has been employed to separate heavy metals from a liquid phase using bubble attachment, originated in mineral processing and Fig. 1 shows the difference between froth flotation and ion flotation (e.g. ion flotation) in general (Jain et.al. 2020).

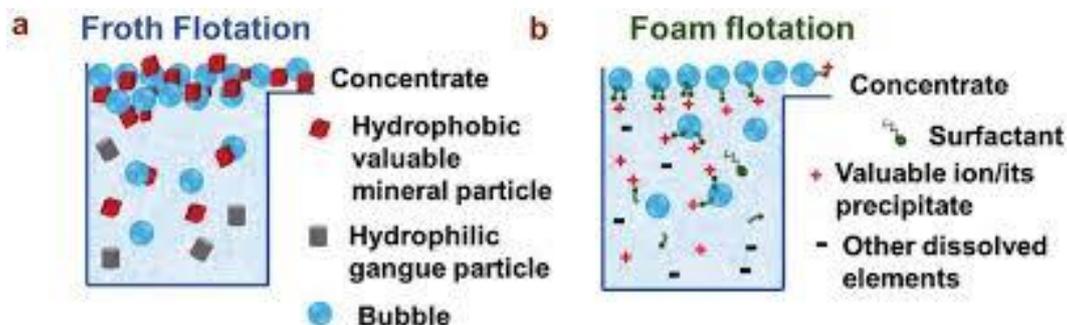


Fig. 1. Comparison of (a) Froth and (b) Foam Flotation (Jain et.al. 2020)

Flotation offers several advantages over the more conventional methods, such as high metal selectivity, high removal efficiency, high overflow rates, low detention periods, low operating cost and production of more concentrated sludge (Rubio et al., 2002). But the disadvantages involve high initial capital cost, high maintenance and operation costs. Dissolved air flotation (DAF), ion flotation, and precipitation flotation are the main flotation processes for especially in wastewater treatment (removal

of heavy metal ions & organics), sludge dewatering, cleaning drinking water, and recovery of metals from dilute solutions (e.g. rare earth metals, precious metals).

Dissolved air flotation (DAF), is to allow micro-bubbles of air to attach to the suspended particles in the water, developing agglomerates with lower density than water, causing the flocs to rise through the water and accumulating at the surface where they can be removed as sludge (Lundh et al., 2000). Precipitate flotation process is another alternative of flotation method, based on the formation of precipitate and subsequent removal by attachment to air bubbles. Depending on the concentration of the metal solution, the precipitation may proceed via metal hydroxide formation or as a salt with a specific anion (sulfide, carbonate, etc.) (Capponi et al., 2006).

Environmental and hydrometallurgical applications of this technology include the selective separation of specific solids or liquids from solid suspensions, liquids from liquid emulsions or certain dissolved species from solutions (Petrov et al., 2015). In Fig. 2, the similarities in flotation of ions and molecules with the flotation of minerals are given (Petrov et al., 2015).

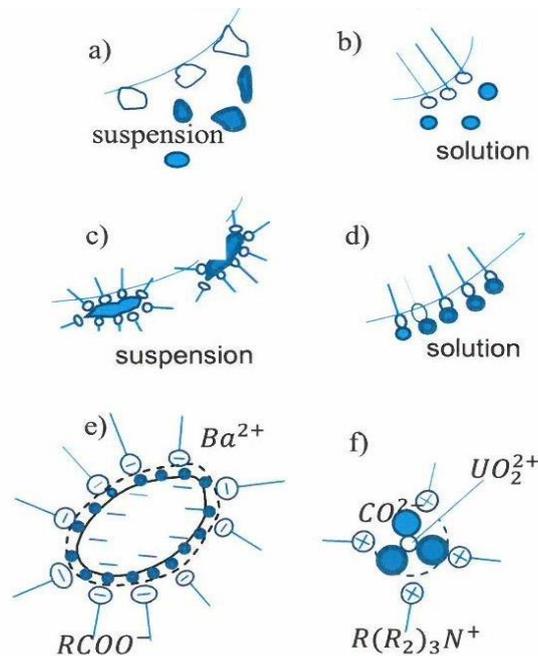


Fig. 2. Illustration of the similarities in flotation of ions and molecules with the flotation of minerals (a) Flotation active mineral particles are adsorbed on surface of bubbles while inactive mineral particles remain in the bulk; (b) Surface active components of solution are adsorbed on surface of bubbles, while other ones, eg. surface inactive, remain in the bulk; (c) Onto surface of bubbles are adsorbed mineral particles covered with collector; (d) On surface of bubbles is adsorbed sublat (individual chemical compound), which consists of colligend (indicates the ion to be removed) and the collector; (e) ions are attracted by fatty acid anion collector adsorbed on surface of quartz particles (f) ion is a binder between ion and four ions of alkyl ammonium collector (Petrov et.al., 2015).

Ion flotation is a practical method that can be used to remove various metal ions from solutions. This review focuses on the applications of ion flotation in wastewater treatment, and in hydrometallurgy, such as rare precious metal recovery, pre-concentrating of rare earth elements, and selective separation of multicomponent ions from dilute solutions.

## 2. Ion flotation and removal of metals from waste waters

Pollutants generated in the effluent are classified as organic and inorganic pollutants, which have a different range of toxic levels in it. Biological, physical and chemical methods are widely used in the treatment of organic pollutants. But these methods are not suitable for the inorganic pollutants like heavy metals. Because of their qualities like solubility, oxidation-reduction characteristics, and complex formation, the heavy metal decomposition plays a major concern (Lee and Dhar, 2012; Carolin, et al., 2017; Taseidifar et al., 2017; Wu et al., 2019) and heavy metal pollution has become one of the most

serious environmental problems today. Heavy metals are generally considered to be those whose density exceeds 5 g per cubic centimeter. A large number of elements fall into this category; some of them are more important relevance in the environmental context. Arsenic is usually regarded as a hazardous heavy metal even though it is actually a semi-metal (Carolin, et al., 2017; Barakat, 2018). Due to the discharge of large amounts of metal-contaminated wastewaters, industries bearing heavy metals, such as Cd, Cr, Cu, Ni, As, Pb, and Zn, are the most hazardous among the chemical-intensive industries. Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body (Barakat; 2018). In recent years, various methods for heavy metal removal from wastewater have been extensively studied (Rubio et al., 2002; Pooja et al., 2022).

Ion flotation is one of them and is an assuring method for heavy metal elimination from wastewater. Langmuir and Schaefer (1937) revealed the phenomenon where insoluble stearic acid on the surface of a solution can adsorb metal ions dissolved in the solution. Ion flotation is based on this phenomenon, was first applied by Felix and Sebba (1959) for heavy metal removal from waste waters. By using surfactants into the wastewater, the ion metal species transmitted into hydrophobic. These hydrophobic ions interact with pumped air bubbles to form flocs and removal of flocs takes place consequently. This process can be influenced by many physical and chemical factors such as type and concentration of collector and frother, time of flotation, pH, ionic strength and ion metal. Since these factors are interrelated, ion flotation control is quite difficult to find the optimum conditions (Yuan et al., 2008; Salmani et al. 2013). Ion flotation process is schematically show in Fig. 3, and is based on imparting the ionic metal species in wastewaters hydrophobic by use of surfactants and subsequent removal of these hydrophobic species by air bubbles (Polat and Erdoğan, 2007). The amount of surfactant needed in ion flotation is directly related to the amount of the metal to be removed (surface-inactive ion) and generally is not influenced by the amount of solution. At least, a stoichiometric amount is required theoretically (Matis and Mavros, 1991). Furthermore, the collectors must be present at least at stoichiometric equivalence with respect to the targeted metal ions concentration, which in combination with their high price makes the technique economically less attractive. Nevertheless, such constrains can be addressed by developing methods to strip and recover the metals from the loaded foam as well as to regenerate and re-use the surfactant (Xanthopoulos and Binnemans, 2021).

The mechanisms for the removal of metal ions are mainly attributed to electrostatic attraction, ion exchange and surface complexation between the surfactant and target ions; these ions are then separated from the solution by attachment to gas bubbles passing through the solutions (Chang et al., 2019). More investigations on metal ion removal via ion fotation were undertaken by many researchers and main parameters such as collectors or surfactant and frother type, ionic strength, pH were examined. The surfactant (collector) is usually an ion having a charge opposite to that of the surface inactive ion (sometimes termed colligend); thus, cations and anions are floated with anionic and cationic surfactants, respectively (Matis and Mavros, 1991). Since ion flotation depends on surfactants as collectors, efficient and non-toxic surfactants are required. Chemical synthetic surfactants have been introduced to have strong collection ability, good selectivity, and easy construction. However, the cost

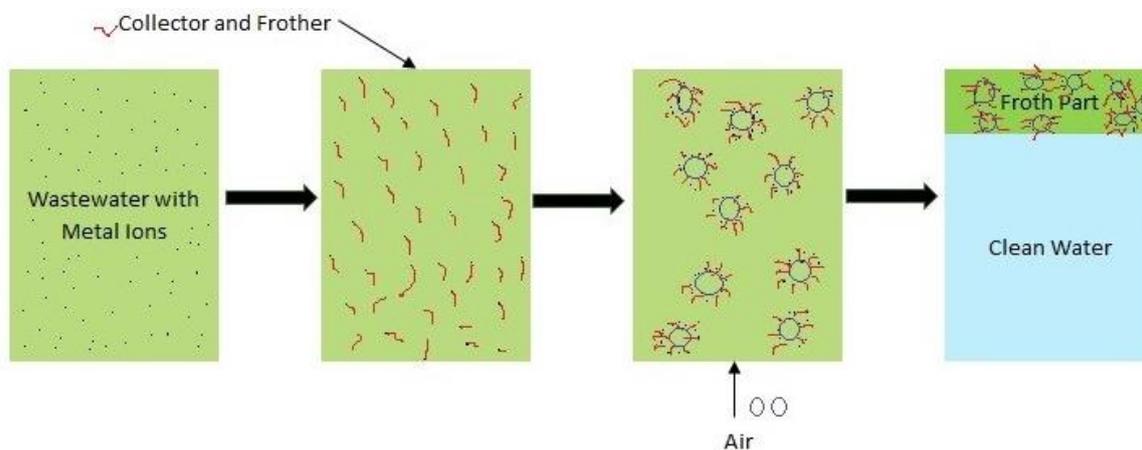


Fig. 3. Schematic of the process of ion flotation

and toxicity issues limit them. On the other side, biosurfactants sound more environmentally friendly, but they exhibited low removal rates, large dosage quantity, and longtime process (Peng et al., 2019). In this regard, nanoparticles have been proposed as new collectors that showed both benefits of synthetic- and biosurfactants (Peng et al., 2019; Taseidifar et al., 2019; Hoseinian et al., 2020; Qasem et al., 2021; Jia et al., 2022).

Ion flotation studies were conducted to investigate the selective removing several metals from waste waters by Polat and Erdoğan (2007). Various parameters such as airflow rate, surfactant and frother concentrations and water chemistry were examined to determine the optimum flotation conditions. Anionic sodium dodecyl sulfate (SDS) and cationic hexadecyltrimethyl ammonium bromide (HTAB) were used as collectors in this study. They found that it was possible to find conditions to concentrate these metals with recoveries as high as 90% in a froth phase. Their tests demonstrated that it was also possible under suitable conditions to remove the metals from each other. In the selected cases of copper-silver and copper-zinc systems, copper could be selectively concentrated in the froth phase, leaving the other metal in solution.

Doyle and Liu (2003) observed that when ion flotation with dodecylsulfate is done on a mixture of copper and calcium ions in the presence of Trien, the copper is removed preferentially, whereas in the absence of Trien, the calcium is removed preferentially. This behavior could find useful applications in effluent and water treatment. Trien was shown to markedly increase the removal rates of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  during ion flotation with dodecylsulfate and lower the steady-state concentration reached.

Ion flotation is a separation process involving the adsorption of a surfactant and counterions at an air/aqueous solution interface (Liu and Doyle, 2009). It shows great promise for removing toxic heavy metal ions from dilute aqueous solutions. It was found that a chelating surfactant, dodecyldiethylenetriamine (Ddien), could selectively remove one metal ion over others at different pH values. Selectivity was attributed to the formation of surface-active chelated species at specific pH. Surface tension data show that  $[\text{M}-(\text{Ddien})_2]^{2+}$  is more surface-active than  $[\text{M}-(\text{Ddien})]^{2+}$  and other Ddien species, thus the relative fraction of  $[\text{M}-(\text{Ddien})_2]^{2+}$  in the solution determined the metal ion flotation efficiency. The effect of Ddien on the ion flotation of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  was investigated because these ions have very similar crystal ionic radii. Ni is selectively removed from copper by ion flotation with Ddien. Cobalt behaved similarly.

Hoseinian et al. (2015) applied Ethylhexadecyldimethylammonium bromide (EHDABr) and sodium dodecyl sulfate (SDS) as a collector in the ion flotation process for the removal of Ni(II) and Zn(II) ions. The results revealed that the recovery of these metal ions was obtained at 88% and 92%. Removal of cadmium, lead and copper by ion flotation with a plant-derived bio-surfactant tea saponin was also studied. In this regard, the maximum removal of ions was 81.81% with a ratio of tea saponin to metal of 3:1 (Yuan et al., 2008).

The ionic strength is an important factor that affects ion flotation, and the content of impurity salts in the solution is one of the main factors that affect the ionic strength of the aqueous solution. There are other soluble salt ions in wastewater, and the amount of these ions determines the ionic strength of the solution. Soluble ions in water can participate in the reaction between anions and cations in the form of ion exchange, so that the ionic strength will affect the reaction process between anionic surfactants and heavy metal ions. According to the research by Salmani et al. (2013), it was found that an increase in ionic strength adversely affected removal efficiency. They also found that the removal of cadmium ions by ion flotation process is very sensitive to the ionic strength. Therefore, the ionic strength of wastewaters must be decreased by an acid (such as  $\text{H}_2\text{SO}_4$ ) before ion flotation. Subsequently, the application of ion flotation for cadmium ions removal from aqueous dilute solutions seems to be efficient. Jia et al. (2022) shows that with increasing ionic strength, the removal rate for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions remain basically unchanged, while the flotation removal rate for  $\text{Cr}^{3+}$  ions decreased rapidly.

Actual wastewater is often not composed of one type of heavy metal ion but a variety of heavy metal ions. Ion flotation could not only work on single metal ions but also on multicomponent metal ions. The removal of heavy metals, single and together by ion flotation has been investigated by some researchers. Jia et al. (2022) shows the flotation removal rates for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cr}^{3+}$  in mixed and single ion solutions. For the mixed ions, the removal of metal ions is lower than that of single ions. Mahmoud et al. (2015) carried out an investigation of the simultaneous removal of cationic ion nickel(II) and anion

ion chromium(VI) from simulated wastewaters and aqueous solutions. The results indicated that removals of more than 99.5% were obtained for both nickel(II) and chromium(VI) in a single step via flotation. In the removal of heavy metals from wastewater, if there is not much difference between the removal recoveries, it is more appropriate to float the heavy metals together.

Ion flotation is particularly sensitive to the pH because the pH determines the nature and the charge of the collector (the degree of ionization) and the colligend (hydrolysis), and causes variations in the ion collecting mode. The acidity (pH) of the wastewater is an important controlling variable in the ion flotation process and thus the effect of pH has been studied by different researchers (Rashed and Nath, 2013; Polat and Erdoğan, 2007; Mahmoud et al. 2015). It is also noted that the following phenomena can take place when the pH changes: (a) colligend hydroxides may form, and precipitate flotation may take place instead of ion flotation; (b) extreme values of pH block flotation because the ionic strength is higher. The importance of pH in ion flotation was expressed by Micheau et al (2018) in case of neodymium as in the Fig. 4.

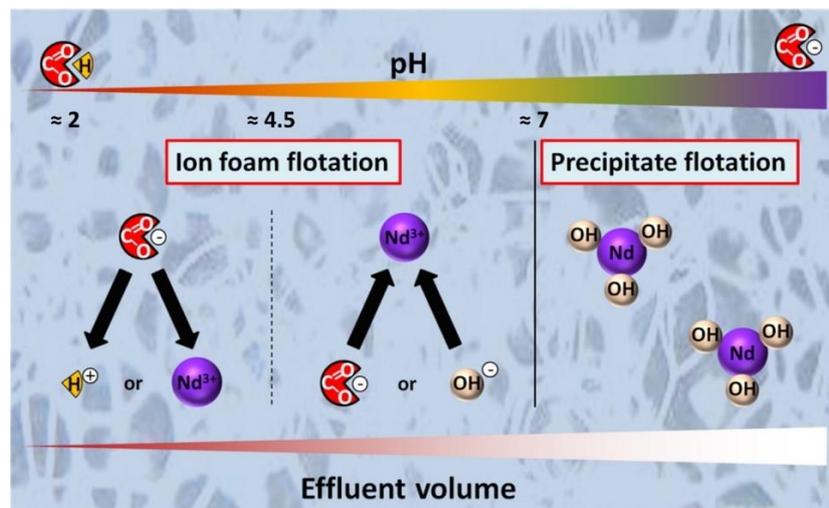


Fig. 4. Effect of pH on ion foam flotation of neodymium (Micheau et al., 2018)

Process waters exiting from mining, petroleum and metallurgical operations are widespread throughout the world and can become contaminated by various pollutants. These substances include powders, chemicals, metal ions, oils, organic and others, sometimes rendering the water useless for recycling as process water, often dangerous for the environment, and sometimes causing losses of valuable materials (Galvin et al., 1994). The ion flotation technique is proposed to clean process waters which are produced in flotation plants that contain low concentrations of metals such as Cu, Pb, Cd, Zn and Ni, just by adding another flotation unit cell in the end of the process as the process flowchart shown in Fig. 5 proposed in by Yenial and Bulut (2017).

### 3. Recovery of metals from dilute aqueous solutions

Ion flotation is also used in hydrometallurgical applications as a separation technology for concentrating, recovering, and removing metal ions from dilute aqueous solutions. The technique of ion flotation provides a simple physical method for concentrating the ions present in very dilute liquors. The ions in the liquor, with the aid of a suitable surfactant, adsorb at the surface of rising air bubbles, and report to a froth product (Nicol et al., 1992). The ion concentrations are usually low ( $10^{-5}$  to  $10^{-3}$  mol/L) and flotation occurs from a true ionic solution, the higher colligend concentrations require significant collector consumption with increasing operation costs. The ion flotation examples that will be given here are recovery of precious metals, preconcentrating of rare earth elements, and selective separation of multicomponent ions. Ion flotation is studied on recovering metals such as Ag, Au, rare earth elements, platinum group metals, radioactive and base metals (Matis and Lavros, 1991). Selective separation of metals from aqueous solutions is always very important in hydrometallurgy and most of the solutions produced in hydrometallurgical processes contain more than one metal ion. As a result, it is often necessary to separate one metal of interest from other ions. The selective separation of metals

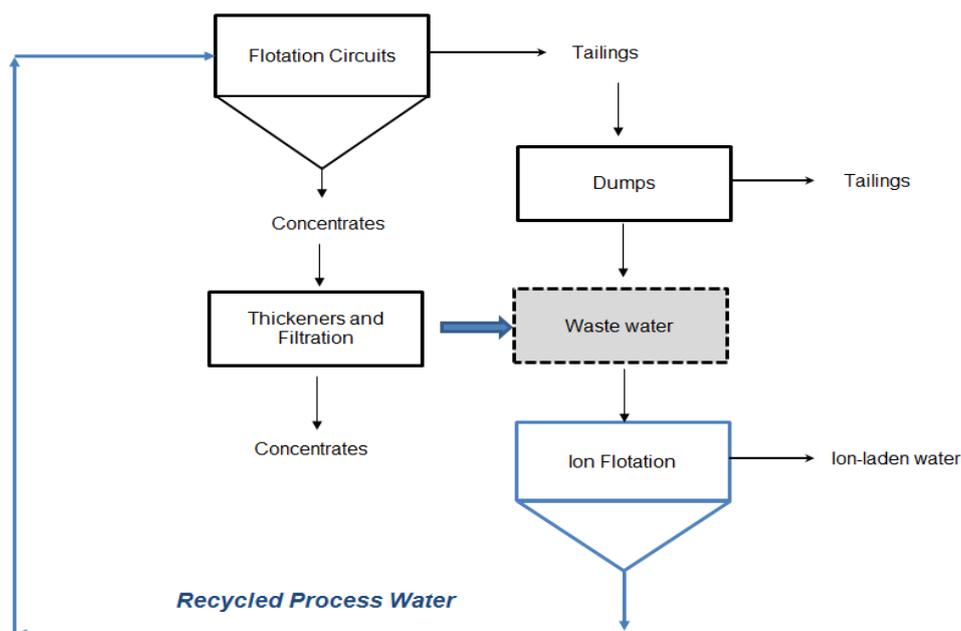


Fig. 5. Water cleaning in flotation plant by ion flotation (Yenial and Bulut, 2017)

by flotation is an important part of the overall process for recovering metals from dilute solutions and contributes to the recycling of metals (Zambolis et al., 2011). Flotation is a less conventional separation process for metal ions in aqueous solution, but may be effective in many cases with satisfactory and sometimes surprising results. Although ion flotation has not yet been adopted in commercial hydrometallurgical operations, the process has many attractive features that are promising for treating dilute solutions and effluents (Matis and Lavros, 1991).

### 3.1. Separation of multicomponent ions

In selective separation of multicomponent ions, ion flotation is a promising separation technology for recovering or removing target ions from the solutions usually contain more than one ion (Chang et al., 2019). Separation of one colligend of interest from other ions is quite necessary for economic reasons and environmental restrictions. Therefore, information on the selectivity between different ions is important for designing an ion flotation process for recovering valuable components from solutions (Chang et al., 2019).

There are numerous studies on ion flotation of metal ions from dilute solutions, carried out for many years. Hoseinan et al. (2021) investigated the most suitable conditions for the combined separation of nickel and zinc ions from aqueous solution using triethylenetetramine (Trien) as a neutral organic chelating ligand and sodium dodecyl sulfate (SDS) as an anionic collector for ion flotation. The most suitable conditions for ion flotation were found as a pH of 9.7, a Trien/Ni(II) mole ratio of 2 and an SDS/Ni(II) mole ratio of 2 and the nickel ion removal is higher than that for zinc ions. At a pH of 9, the removal of nickel and zinc ions reaches a maximum of 88.4% and 79.9% respectively, corresponding to a 9% higher removal of nickel ions compared to zinc ions. The effect of impeller speed on Ni(II) removal by ion flotation is also investigated and SDS from Merck and Dowfroth 250 from Dow chemical were used as collector and frother (Hoseinian et al., 2019). The results showed that the Ni(II) removal increases with increasing impeller speed from 600 to 800 rpm from less than 41% to 88%, respectively, and after that, it decreases to 79% with increasing impeller speed to 900 rpm in the first 4 min of flotation. Competitive ion flotation of Zn(II) and Cd(II) ions from dilute aqueous solutions by a series of lipophilic protonionizable lariat ethers of varying ring sizes, in the presence of nonylphenol ether as the foaming agent, has also been reported (Ulewicz et al., 2006).

Barium ion flotation with sodium laurylsulfate is studied in aqueous solution at pH=6 and in nitric acid solution at pH=1 (Bernasconi et al., 1987a). The mechanisms controlling this extracting process are described by determination of the solubility curves, and by electrokinetic, conductimetric, surface

tension and turbidity measurements. The ion flotation process arises from the combination of a chemical process corresponding to the interactions between the collector and the ion to be removed. Surface properties of barium laurylsulfate are controlled by the adsorption of the collector and barium laurylsulfate was found to float easily. In the continuing study by Bernasconi et al. (1987b), barium ion flotation with sodium laurylsulfate, a model was built in order to estimate the recovery curves and particularly the optimal metal ion recovery conditions as a function of nitric acid content and initial barium concentration. The computed results were in very good accordance with the shape of the flotation curves obtained in aqueous solution with several values of initial barium concentration and in various nitric acid concentrations. The barium recovery curves as a function of the laurylsulfate concentration are typically curves to one maximum and the flotation behavior of the barium ions is different when sodium octylbenzenesulfonate is used as collector, presenting double flotation phenomena, which has never been observed before (Rivera et al., 1996).

The removal of zirconium from uranyl nitrate solutions by ion flotation was studied and alkylsulfate of various chain length (C10, C12, C14) were used as collectors (Bernasconi et al., 1988). The chemical reactions between Zr and the surfactants are found out by the determination of the solubility curves. Zr can be removed from high concentrated acid uranyl nitrate solutions, but the recovery rate decreases when the ionic strength increases.

An investigation of the ion flotation of the transition metal cations In(III), Cr(III), Fe(III), Cd(II), Mn(II), Co(II), Zn(II) and Ag(I) with sodium dodecylbenzene sulfonate and sodium dodecyl sulfonate as the collectors was conducted (Walkowiak, 1991). The selectivity sequence of  $\text{Ag(I)} < \text{Mn(II)} < \text{Zn(II)} < \text{Co(II)} < \text{Fe(III)} < \text{Cr(III)} < \text{In(III)}$  was established and it was found that the preferential removal of certain metal ions is closely related to the ratio of ionic charge to ionic radius and the solubility products of the metal-collector compounds.

Liu and Doyle (2009) removed Cd(II), Zn(II) and Cu(II) from solution via ion flotation with rhamnolipid as a surfactant; they found that ions with larger crystalline radii preferentially reacted with the surfactant. The ratios of the ionic radii for the competitive systems were 1.03, 1.28 and 1.32 for Zn/Cu, Cd/Zn and Cd/Cu, respectively. The obtained selectivity coefficient values were in accordance with the ratios of the ionic radii, which suggests that the selectivity sequence of these metals in ion flotation with rhamnolipid as the collector is  $\text{Cd(II)} > \text{Zn(II)} > \text{Cu(II)}$ .

The selective flotation of copper, zinc, and arsenic ions from dilute aqueous solutions were investigated (Stalidis et al., 1988). Phase separation was accomplished effectively by the dissolved-air technique for the production of fine gas bubbles, and a short-chain xanthate was applied as the collector for copper ions, dialkyldithiocarbamate for zinc, and ferric sulfate for the pentavalent arsenic. The procedures followed were ion flotation for copper and zinc, and adsorbing colloid flotation for arsenic (without a surfactant). Ionic flotation of cadmium and arsenic III by sodium diethyldithiophosphate  $(\text{CH}_3\text{CH}_2\text{O})_2\text{PS}_2\text{Na}$  is also examined in phosphoric acid solutions from 1 to 7 M/L (Jdid et al., 1986). The flotation recovery rate of Cd and As increases with the colligend concentration, the excess of the collector and the increasing level of  $\text{H}^+$  concentration.

The uranium concentration within the oceans is about 3.3 mg/kg, the average amount of uranium in river waters is approximately 1.3 nmol/kg and uranium content of land waters (fresh water flowing over the land; flood water; the water of lakes, rivers, springs, etc., as opposed to sea-water) more than 1 ppb is considered abnormal (Akl and Mahmoud, 2018). This extreme dilution in the existence of relatively high concentration of other ions makes difficult to determine trace heavy metals directly. Flotation techniques are extensively used for that purpose (analytical chemistry) and the quantity of organic solvent is far small compared to that is used in the traditional liquid-liquid extraction (Akl and Mahmoud, 2018). A new process for uranium recovery from industrial phosphoric acid at 30% of  $\text{P}_2\text{O}_5$  is applied by the ionic flotation process with an anionic organophosphorous collector (Jdid et al., 1983). The results were obtained in laboratory-scale experiments on industrial wet-process acid. Recoveries greater than 90% were obtained even at temperatures of about 60°C, collector consumption without recycling of the surface-active reagent was about 12 kg/kg U. Much of the reagent, however, can be recovered for recycling by attack with sodium hydroxide on the floated phase after filtration. This enables a precipitate containing about 30% U to be produced and decreases collector consumption to about 3 kg/kg U.

Recovery of soluble uranium compounds can be considered for mine water and industrial solutions (Jude and Fratila, 1973). Results are presented of an investigation of the ion-flotation method, the selection of suitable reagents for the extraction of uranium compounds from solutions and the applicability of the method to uranium mine water being reviewed. Various reagents were studied in acid, neutral and alkaline media, best results being obtained following treatment with amine and Aerofloat group reagents.

An experimental investigation is presented of the flotation of dichromate ion using a cationic surfactant, ethylhexadecyldimethylammonium (EHDA) bromide (Grieves and Schwartz, 1966). Dichromate ion forms a colloidal complex with EHDA ion in a molar ratio of 1:2, which may be efficiently floated from solution and concentrated in stable foam produced by excess surfactant. Experiments indicated the reduction of dichromate from 50 to 15 mg/l, producing a foam stream containing 450 mg/l of dichromate.

The germanium together with other metals and metalloids contained in the fly ash generated in a gasification plant is extracted by aqueous leaching and the selective recovery of germanium from aqueous leachates by ion flotation, using a complexing agent and a surfactant has been studied (Hernandez-Exposito et al., 2006). The use of different ligands with dodecylamine as collector and the effect of the pH were evaluated and the optimum conditions for germanium recovery found as: catechol as complexing agent, triple stoichiometric ratio of the reagents, and pH 4-7 with 100% germanium recovery.

Removal of aluminium (contaminated with up to 7% beryllium) from a 2:1 molar aluminium/beryllium mixture was possible by ion flotation of the oxalate complexes at pH 4 with long-chain fatty amines (especially tetradecylamine) with good recovery (90%) (Lusher and Seba, 1965). In another study targeted on the process of eliminating the major cationic species co-existed with natural processed Be solution such as Be, Fe, and Al by ion flotation with the aid of sodium lauryl sulfate (SLS) (Abdeldaim et al., 2014).

Ion flotation has been successfully applied to recover W and Mo from the solution of tailing pond in a dressing plant of Russia, and 30–40 t of  $WO_3$  and 3–3.5 t of Mo per year were additionally recovered (Zhang, 1990). Obvious advantages have been demonstrated in the actual application of ion flotation, which drives it more widely industrial utilization.

In most of the studies; it was generalized that the selectivity of multicomponent ions is closely related to the valence, crystalline radii, and hydrated radii of the metal ions, the ratio of ionic charge to ionic radius, pH, and hydrolysis together with the solubility products of the metal-collector compounds (Chirkst et al., 2009). Therefore, the selective separation of multicomponent ions can be easily accomplished with proper collectors and accurate models should also be developed and established to predict the selectivity of different ions. Collectors used in ionic flotation of multicomponent ions listed above are summarized in Table 1.

### 3.2. Separation of rare and alkaline earth metals

Rare-earth metals (REMs) and their compounds become increasingly important for modern technology and individual REMs are in the highest demand in the world market (Chirkst et al., 2011). Large amounts of REMs are used in the form of a mixture of oxides in metallurgical, glass-making, and ceramic industries. Cerium, neodymium, samarium, europium, and gadolinium are most widely used as compounds of individual REMs. Therefore, it is necessary to develop a technology for production of a wide assortment of individual rare-earth elements. A promising way is to use the flotation technique, which can produce a concentrate with 60–70% REM oxides. Rare earth industries face the difficulty of separating certain elements from their sum and ion flotation is a promising technology. The ion flotation is a process in which ions present in dilute solutions are recovered with ionogenic surfactants serving as collecting agents. Numerous studies carried on the recoveries of rare earth elements from dilute leach solutions. Ion flotation of rare-earth metals with sodium dodecyl sulfate and the effect of chloride ions on this process were studied (Christ et al., 2011a). Values of the distribution coefficients were obtained and it was found that the addition of chloride ions had a tendency toward a decrease in the distribution coefficients and a shift of the maximum recovery to the range of higher pH values. The distribution coefficients reach the maximum value at a chloride concentration of 0.01 M.

Table 1. Collectors used in ionic flotation of multicomponent ions.

Metal Ions	Collector type	Reference
Ni, Zn	Triethylenetetramine (Trien) and sodium dodecyl sulfate (SDS)	Hoseinian et al., 2021
Zn, Cd	Lipophilic protonionizable lariat ethers	Ulewicz et al., 2006
Ni	SDS from Merck and Dowfroth 250	Hoseinian et al., 2018
Cu, Ni, Co	Dodecyl diethylenetriamine (Ddien)	Liu and Doyle, 2009
Cu, Zn, As	Short-chain xanthate for Cu, dialkyldithiocarbamate for Zn, ferric sulfate for As	Stalidis et al., 1988
In(III), Cr(III), Fe(III), Cd(II), Mn(II), Co(II), Zn(II) and Ag(I)	Sodium dodecylbenzene sulfonate and Sodium dodecyl sulfonate	(Walkowiak, 1991).
Ba	Sodium laurylsulfate	Bernasconi et al., 1987(a,b) Rivera et al., 1996
Zirconium	Alkylsulfate of various chain length (C10, C12, C14)	Bernasconi et al., 1988
Cd, As	Sodium diethyldithiophosphate (CH <sub>3</sub> CH <sub>2</sub> O) <sub>2</sub> PS <sub>2</sub> Na	Jdid et al., 1986
Uranium Uranium compounds	Anionic organophosphorous collector Amine and Aerofloat group reagents	Jdid et al., 1985 Jude and Fratila, 1973
Chromium (Dichromate ions)	Cationic surfactant, ethylhexadecyldimethylammonium (EHDA) bromide	Grieves and Schwartz, 1966
Ge	Different ligands with dodecylamine	Hernandez-Exposito, et al., 2006
Al (with Be) Coexisted metals of Be, Fe, Al	The oxalate complexes with long-chain fatty amines (especially tetradecylamine) Sodium lauryl sulfate (SLS)	Lusher and Seba, 1965 Abdeldaim et al., 2014

Ion flotation of cerium, samarium, and europium from nitrate solutions with sodium dodecyl sulfate, as flotation reagent, were reported (Chirkst et al., 2009; Lobacheva et al., 2013). The dependences of the distribution coefficients of rare earth ions in the ion flotation on pH of an equilibrium aqueous phase were obtained. Flotation lanthanide ions (Ce, Sm, Eu) are recovered by sodium dodecyl sulfate in the form of basic dodecyl sulfates  $\text{Ln}(\text{OH})(\text{C}_{12}\text{H}_{25}\text{OSO}_3)_2$  and the selective extraction of  $\text{Sm}^{3+}$ ,  $\text{Ce}^{3+}$ , and  $\text{Eu}^{3+}$  is possible at pH 4, 6, and > 6.5, respectively, from solutions of their salts by using sodium dodecyl sulfate as surfactant.

Chirkst et al. (2009) found that as the pH increased, the distribution coefficients of yttrium(III), cerium(III) and europium(III) sharply increased to almost 100%. The pH values of initial extraction (4.5 for yttrium(III), 5.5 for cerium(III), 6.2 for europium(III)) indicate that these ions can be recovered and separated from each other by adjusting the pH value via ion flotation with sodium dodecyl sulfate serving as the collector. In another study of the same researchers, it was also found that cerium(III) and yttrium(III) could be concentrated individually from solutions of their salts at pH 4.5 to 6 when sodium dodecyl sulfate was used as the surfactant (Chirkst, et al., 2009). Cerium(III) extraction with oleic acid in *o*-xylene from nitrate solutions was also studied (Chirkst, et al., 2011b) and the extraction mechanism and the dependence of the distribution ratio on pH and composition of the organic and aqueous phases were examined. Chirkst et al. (2009) discovered that the distribution coefficients of yttrium(III) and cerium(III) sharply increased to almost 100% at pH 4.5 and 6, respectively. Therefore, recovery of yttrium(III) began at pH 4.5 and recovery of cerium(III) began at pH 6. Thus, a general conclusion can be drawn that selective recovery of REMs can be obtained by varying the pH value.

Additionally, they used sodium dodecyl sulfate as a collector to concentrate lanthanides; upon addition of chloride ions in concentrations of 0.01 to 0.1 M, the maximum recovery to the region of higher pH values were noted (Chirkst, et al., 2011c). The same phenomenon was also found when

floating and concentrating La(III) from nitrate and nitrate-chloride solutions with dodecyl sulfate as the collector. (Chirkst et al., 2012).

Yttrium (III) and ytterbium (III) cations ion flotation from diluted aqueous solutions in the presence of chloride ions using sodium dodecyl sulfate as collector agent were studied by Lobacheva et al. (2016). The maximum yttrium recovery (as  $Y(OH)_3$ ) and separation coefficient could be obtained at a chloride concentration of 0.01 M and pH 7.8.86, the maximum recoveries of yttrium and cerium ions could be obtained at pH 5.5 and 7.0, respectively, by ion flotation according to their other research. This allows recovery and separation of cerium and yttrium cations from their salts in the course of processing of lean technogenic raw materials at properly chosen pH values. Conditions for the concentration of yttrium from aqueous solution by ion flotation using  $\alpha$ -sulphonated fatty acids were also studied (Rose and Seba, 1969). The effects of change of collector and colligend concentration and pH, as well as the effect of interfering ions, were investigated and maximum recovery was 99.5% under the optimum conditions within 30 minutes; increasing the pH to 8 resulted in the extraction rate of 3 times faster compared to that of pH 2.75. The study of ytterbium ions removal from aqueous standard test solutions by ion flotation with sodium dodecyl sulphate was also conducted (Lobacheva, 2021). The maximum removal of ytterbium (III) was achieved at pH = 8.30. and ytterbium floated as basic dihydroxyytterbium dodecyl sulphate  $Yb(OH)_2(C_{12}H_{25}OSO_3)$ .

The effect of various ions with different radius and charge such as aluminum, calcium, and iron on the selective ion flotation of neodymium using sodium dodecyl sulfate as a collector was investigated (Khatir et al., 2021). The optimum conditions for ion flotation of neodymium are found as collector dosage of  $21 \times 10^{-4}$  M, air flow rate of 100 mL/min, and pH of 3 with 85.4% and 26.5% recovery for neodymium and water, respectively. The effect of other ions on the ion flotation of neodymium was also evaluated. In selective separation of neodymium ion from aluminum ion by ion flotation, fluorine ion was applied as a chelating agent (Khatir et al, 2022) and the results showed that the presence of fluorine ions increased the selective separation of neodymium ion, enhancing the selectivity coefficient during the process, and neodymium ion recovery was higher than that of aluminum ions, indicating the ion recovery order based on the enhancing order of crystal ionic radius.

Selective ion flotation of neodymium ions from aluminum, iron, and calcium ions using sodium dodecyl sulfate (SDS) as a surfactant and di-(2-ethylhexyl) phosphoric acid (D2EHPA) as an extractant was performed to selectively recover neodymium ions from solutions in a binary system of ions (Khatir et al., 2022). The results indicated that the D2EHPA caused an increase in the neodymium ion recovery in the presence of all competing ions. Using D2EHPA, the calcium ion removal decreased and the removal of iron and aluminum ions increased. The Gibbs free energy of neodymium-D2EHPA complex formation was more than that of other ions, which led to an increase in the selective recovery of neodymium ions. The aluminum ions had a greater effect on decreasing the neodymium recovery than iron or calcium ions. Similar Gibbs free energy and complex structures of the neodymium and aluminum ions with D2EHPA led to the less selective separation of neodymium from aluminum.

Ion foam flotation of neodymium ( $Nd^{3+}$ ) was studied using a pH-sensitive surfactant, the nonaoxyethylene oleylether carboxylic acid, which has the peculiarity of remaining water soluble in the presence of multivalent cations (Micheau et al., 2018). In their study the flotation efficiency factors were determined as a function of pH and for two different (surfactant/Nd) molar ratios, equimolar (1/1) or stoichiometric (3/1). An opposite trend was observed, showing low (b30%) and high (N95%) ion extraction yields respectively for equimolar and stoichiometric conditions. It was shown that; i) the determination of the surfactant/Nd speciation solutions is essential to understand the very different behaviors between equimolar and stoichiometric experiments and ii) the ion extraction process is mainly driven by interfacial mechanisms. In terms of applications they show that once the ion extraction is efficiently performed for pH values between 5 and 7, the recovery of the surfactant is possible by performing a second flotation process at lower pH 2.5. In conclusion ion foam flotation using this pH sensitive surfactant was shown to be highly efficient for the removal of traces and ultra-traces of metal ions.

A flotation circuit operating on a continuous basis has been designed and constructed for removal of Sr ions from simple aqueous solutions with a highly concentrated solutions of  $\alpha$ -sulphopalmitic acid ( $\alpha$ -SPA) (Davis and Seba, 1966). The effects of changing the gas rate and flow rates of both the Sr and

collector solutions were examined and under steady-state conditions, a continuous Sr extraction rate of 97.3% was achieved.

An experimental investigation is presented on flotation of Co(II), Sr(II), and Cs(I) cations from very dilute aqueous solutions with protonionizable crown ethers: monoethyl *sym*-(butyl)dibenzo-16-crown-5-oxymethylphosphonic acid, sodium 3-[*sym*-(decyl) dibenzo-16-crown-5-oxy]propanesulfonate, and *sym*-(decyl) dibenzo-16-crown-5-oxyacetic acid, used separately or together with a nonionic foaming agent (Triton X-100) (Charewicz et al., 2001). According to results, the separation of Sr and/or both Sr with Cs from extremely dilute aqueous solutions with these collectors was efficient and fast, which might have a practical meaning for the decontamination of aqueous solutions containing radioactive isotopes. Thus, protonionizable crown ether derivatives of sufficient surface activity and water solubility could make a new generation of specific collectors for flotation of aqueous ions.

Collectors used in ionic flotation of rare and alkaline earth metal ions explained above are summarized in Table 2.

Table 2. Collectors used in ionic flotation of rare and alkaline earth metal ions

Metal Ions	Collector type	Reference
Cerium, neodymium, samarium, europium, gadolinium	A-sulphonated fatty acids	Christ et al., 2011b
Rare Earth Metals	Sodium dodecyl sulfate	Christ et al., 2011a
Neodymium	Sodium dodecyl sulfate Nonaoxyethylene oleyether carboxylic acid	Khatira et al., 2021 Khatir et al., 2022 Micheau et al., 2018
Cerium, samarium, europium	Sodium dodecyl sulfate	Chirkst et al., 2009; Lobacheva et al., 2013
Yttrium(III), cerium(III), europium(III)	Sodium dodecyl sulfate	Chirkst et al., 2009
Cerium(III)	Oleic acid in <i>o</i> -xylene	Chirkst, et al., 20011b
Lanthanides	Sodium dodecyl sulfate as a collector with addition of chloride ions	Chirkst, et al., 2011c
La(III)	Dodecyl sulfate	Chirkst et al., 2012
yttrium(III), ytterbium (III)	Sodium dodecyl sulfate as a collector with addition of chloride ions	Lobaceheva et al., 2016
ytterbium	Sodium dodecyl sulfate	Lobaceheva, 2021
yttrium	$\alpha$ -Sulphonated fatty acids	Rose and Seba, 1969
neodymium	Sodium dodecyl sulfate (SDS) as a surfactant and di-(2-ethylhexyl) phosphoric acid (D2EHPA) as an extractant	Khatir et al., 2021; Khatir et al., 2022
Sr	$\alpha$ -Sulphopalmitic acid (a-SPA)	Davis and Seba, 1966
Co(II), Sr(II), Cs(I)	Protonionizable crown ethers	Charewicz et al., 2001

### 3.3. Separation of precious and platinum group metals

In the original studies, ion flotation was mostly used for preconcentrating precious metals from dilute solutions. Ion flotation can be used to recover multiple precious metal ions or their cyanide complexes (Doyle, 2003). A pilot scale study on recovering gold cyanide anions from heap leaching liquor via ion flotation was with the cetyltrimethyl ammonium bromide (CTAB) as the collector resulted in almost 100% of the gold recovery which can be recycled (Galvin et al., 1994). The results indicated that the recyclability of the reagent is about 80% and the trial involved a total of 13 reagent recycle stages.

Reyes et al. investigated the recovery of silver in spent diluted solutions through ion flotation using a column. A recovery of 97% could be obtained using 0.06 g/L of sodium isopropyl xanthate (SIX) and 0.04 g/L of frother (Reyes, et al., 2012).

In the study on silver recovery from dilute aqueous solutions containing thiosulphates by ion flotation, it is found that a high recovery of silver (almost 100%) could be obtained using dodecylamine as the collector together with ethanol (0.5%) as the frother (Zouboulis, 1995).

Ion flotation experiments on an aqueous solution of gold and silver cyanide anions with cetyltrimethylammonium bromide as the collector resulted in almost 100% gold recovery, and cetyltrimethylammonium bromide exhibited significant selectivity for gold over silver (Galvin, et al., 1992).

The recovery of cationic complexes of rhodium and palladium in dilute hydrochloric acid solutions with ion flotation using sodium dodecyl benzenesulfonate (SDBS) as the surfactant showed that the cationic complexes of rhodium(III) and palladium(II) can be effectively floated with SDBS (He, 1991).

The anionic chlorocomplexes of Au(III), Ir(III), Pd(II) and Pt(IV) could also be recovered from aqueous solutions by ion flotation with cationic collectors such as pentadecyl trimethyl ammonium bromide (PTMAB) and hexadecyl tripropyl ammonium bromide (HTPAB) with the recoveries of each metal as 99.9%, 99.8%, 99.45 and 99.7%, respectively (Berg and Downey, 1980a).

The anionic chlorocomplexes of Au(III), Pt(IV), Pd(II), Ir(IV), Ir(III) and Rh(III) can be floated from aqueous solutions with cationic surfactants of the type  $\text{RNR}'_3\text{Br}$  (Berg and Downey, 1980b). The flotation behavior of each metal is reported with respect to variations of hydrochloric acid and sodium chloride concentrations, the R and R' chain lengths, initial surfactant concentrations and initial metal ion concentrations. The flotation behavior of the metals is compared to the anion-exchange selectivity coefficients and a flotation selectivity sequence of  $\text{Au(III)} > \text{Pt(IV)}, \text{Ir(IV)}, \text{Pd(II)} > \text{Ir(III)} > \text{Rh(III)}$  is generally observed. Nearly 100% of Au(III), Pt(IV), Ir(IV) and Pd(II) can be recovered from dilute solutions using the ion flotation procedures.

The anionic chlorocomplexes of platinum(IV) and iridium(III) are separated by ion flotation from acidic aqueous solutions with cationic surfactants of the type  $\text{C}_{16}\text{H}_{33}\text{NR}'_3\text{Br}$ , where R' is methyl, ethyl, n-propyl, or n-butyl. The  $\text{PtCl}_6^{2-}$ , which forms readily floatable salts with each of the surfactants, is selectively floated from the  $\text{IrCl}_6^{3-}$  and recovered after flotation in n-butyl acetate (Berg and Downey, 1981). The efficiency of the separation increases as the R' chain length increases and a quantitative separation is obtained with hexadecyltributyl-ammonium bromide (HTBAB) in 0.1 M HCl solutions.

Mixtures of iridium(IV) and rhodium(III) as  $\text{IrCl}_2^-$  and  $\text{RhCl}_3^-$  are separated by ion flotation (Berg and Downey, 1980c). The iridium(IV) is selectively floated from aqueous solutions of pH 2 and 0.05% Ce(IV) with either hexadecyltripropylammonium bromide (HTPAB) or hexadecyltributylammonium bromide (HTBAB). The rhodium(III) does not float under the same conditions and the floated iridium sublimate is collected in n-butyl acetate without contamination by the unfloted rhodium. The separation of iridium and rhodium by ion flotation offers advantages over previous methods.

Mixtures of iridium(IV) and ruthenium(III) as  $\text{IrCl}_2^-$  and  $\text{RuCl}_4^-$  are separated by ion flotation (Downey and Clipper, 1985). Iridium (IV) is selectively floated from mixtures of the metal complexes in aqueous 1.0 M hydrochloric acid with hexadecylpyridinium bromide (HPB) and nitrogen. Ruthenium(III) does not float under the same conditions. In order to assess the usefulness of this procedure, the separation was also investigated with hexadecyltrimethylammonium bromide and hexadecyltripropylammonium bromide, from solutions of varying concentrations of sodium chloride, sodium nitrite and hydrochloric acid. Under optimum conditions at the  $5 \times 10^{-5}$  M level, 78% of the iridium is recovered free of ruthenium, provided that excess of HPB and  $> 1$  M chloride are present.

A simple, rapid method for the separation of hafnium from aqueous solutions has been investigated using Hf tracer (Downey et al., 1985). Cationic hafnium complex ions were floated from dilute acid solutions with sodium lauryl sulfate (SLS) and anionic hafnium complexes were floated from basic and oxalic acid solutions with hexadecyltrimethyl ammonium bromide (HTMAB). The conditions necessary for quantitative recovery of the metal and mechanisms of flotation are described.

A laboratory investigation was undertaken on the gold-thiourea system over the whole pH range, aiming at the separation of gold by flotation from dilute solutions with cetyl-trimethylammonium bromide (Zouboulis et al, 1993). The further addition of ethyl alcohol, acting mainly as a frother, was

found to improve gold recoveries remarkably reaching over 95%. Similarly, a laboratory investigation was also carried out on the silver-thiourea system for the recovery of silver by ion flotation with sodium dodecylbenzenesulfonate and the silver recovery rate reached 96% under the optimum conditions (He, 1998).

Ion flotation was examined as an alternative method for the recovery of silver from dilute aqueous solutions containing complexing agents (thiosulphates) with the cationic surfactant dodecylamine, (ethanol or water solutions) (Zouboulis, 1995). The main physicochemical parameters influencing the process were found as pH of the solution, concentrations of surfactant, of thiosulphate, and of silver, with the kinetic parameters, such as flotation time and gas flowrate. High recovery of silver (approaching 100%) was obtained at the optimum defined conditions. Additionally, The application of the proposed method for the treatment of spent solutions, generated after the development of X-rayed films, was also studied.

Collectors used in ionic flotation of precious and platinum group metal ions listed above are summarized in Table 3. General flowsheet for recovering metals from dilute solutions is given in Fig. 6.

Table 3. Collectors used in ionic flotation of precious and platinum group metal ions

Metal Ions	Collector type	Reference
Precious metal ions (gold cyanide anions)	The cetyltrimethyl ammonium bromide (CTAB) as the collector	Galvin et al., 1994
Silver	Sodium isopropyl xanthate (SIX) Dodecylamine as the collector together with ethanol (0.5%) as the frother	Reyes, et al., 2012 Zouboulis, 1995
Gold and silver cyanide anions	Cetyltrimethylammonium bromide as the collector	Galvin et al., 1992
Gold (thiourea complex)	Cetyl-trimethylammonium bromide	Zouboulis et al, 1993
Silver (thiourea complex)	Sodium dodecylbenzenesulfonate	He, 1998
Silver (thiosulphate complex)	Cationic surfactant dodecylamine	Zouboulis, 1995
Rhodium and palladium	Sodium dodecyl benzenesulfonate (SDBS)	He, 1991
Anionic chlorocomplexes of Au(III), Ir(III), Pd(II) and Pt(IV)	Cationic collectors such as pentadecyl trimethyl ammonium bromide (PTMAB) and hexadecyl tripropyl ammonium bromide (HTPAB)	Berg and Downey, 1980a
Anionic chlorocomplexes of Au(III), Pt(IV), Pd(II), Ir(IV), Ir(III) and Rh(III)	Cationic surfactants of the type RNR' <sub>3</sub> Br	Berg and Downey, 1980b
The anionic chlorocomplexes of platinum(IV) and iridium(III)	Cationic surfactants of the type C <sub>16</sub> H <sub>33</sub> NR' <sub>3</sub> Br, where R' is methyl, ethyl, n-propyl, or n-butyl.	Berg and Downey, 1981
Mixtures of iridium(IV) and rhodium(III) as IrCl <sub>2</sub> <sup>-6</sup> and RhCl <sub>3</sub> <sup>-6</sup>	Hexadecyltripropylammonium bromide (HTPAB) or Hexadecyltributylammonium bromide (HTBAB)	Berg and Downey, 1980c
Mixtures of iridium(IV) and ruthenium(III) as IrCl <sub>2</sub> <sup>-6</sup> and RuCl <sub>3</sub> <sup>-6</sup>	Hexadecylpyridinium bromide (HPB) and nitrogen	Downey and Clipper, 1985
Hafnium	Cationic hafnium complex ions with sodium lauryl sulfate (SLS) Anionic hafnium complexes with hexadecyltrimethyl ammonium bromide (HTMAB).	Downey et al., 1985

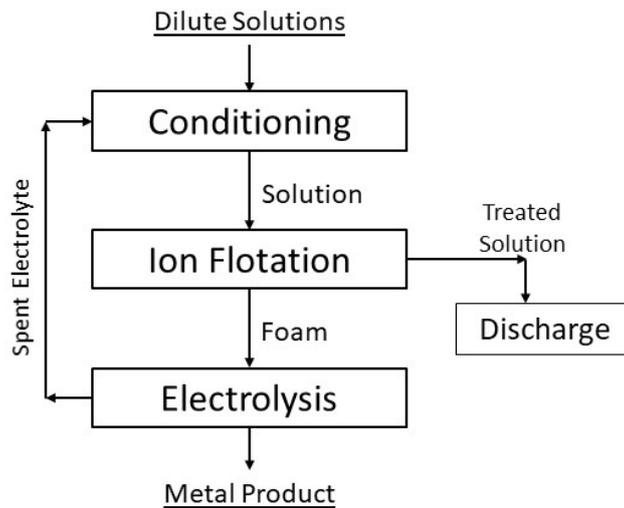


Fig. 6. General flowsheet for recovering metals from dilute solutions

#### 4. Conclusions

In more than last two decades, environmental concerns of industrialization became more important resulting in more restricted environmental regulations. Thus, an improved quality in treatment of effluents, more effective and efficient wastewater treatment techniques are needed. Process waters exiting from mining, petroleum and metallurgical operations are widespread throughout the world and can become contaminated by various pollutants. Flotation is ever increasingly used in waste treatment, particularly in the mining and metallurgical industry. Especially ion flotation process appears to be an effectively promising one for the removal of heavy metal ions from a large volume of wastewaters with low metal concentrations to reduce pollution and recycle resources. Additionally, acid mine drainage waters, which contain significant heavy metals and are highly acidic, can also be treated with this method.

Nowadays, decreasing in the mineral raw material reserves resulted in processing more complex and low grade ores as well as their conversion products such as slags, cakes, dust, muds, containing heavy and rare metals. Selective separation of metals in aqueous solutions presents a valid reason for the future application of flotation in hydrometallurgy. Ion flotation was originally used for pre-concentrating precious metals from dilute solutions and should also ensure the more effective rare-earth metals recovery and the separation of the similar, in terms of chemical and physical properties, components at the expense of using the surfactants. Therefore, ion flotation may become an alternative to liquid-liquid extraction such as ion exchange and solvent extraction processes. Ion flotation has been used for laboratory separations for about half a century. Modern environmental constraints are driving the search for new separation processes suitable for the commercial treatment of dilute solutions.

It can be concluded that ion flotation is a promising separation technology in the fields of wastewater treatment, mineral beneficiation, such as rare precious metal recovery, and hydrometallurgy, such as pre-concentrating of rare earth elements, selective separation of multicomponent metal ions, and analytical chemistry. As a result of researches summarized above, chronological developments according to the publication years of ion flotation studies are illustrated in Fig. 7. Ion flotation has been widely recognized by the public due to its simplicity, rapidity, economy, good separation yields, and suitability for a variety of target ions at various levels. Although ion flotation has a long history for laboratory-scale metal separations, it has been tested at the pilot scale for recovering gold from leach solutions and only during the last few years application of this method in full industrial scale (Mo and W) has been reported. With the new developments in flotation machines and collectors (e.g. biosurfactants, nano particle surfactants), better selectivity, high efficiency, lower cost, and environmental friendliness, application of ion flotation in industrial scale operations will be seen more. It has many attractive features that are promising for treating dilute solutions and effluents, therefore there should be more studies in a pilot scale applications and hybrid technologies may also be used.

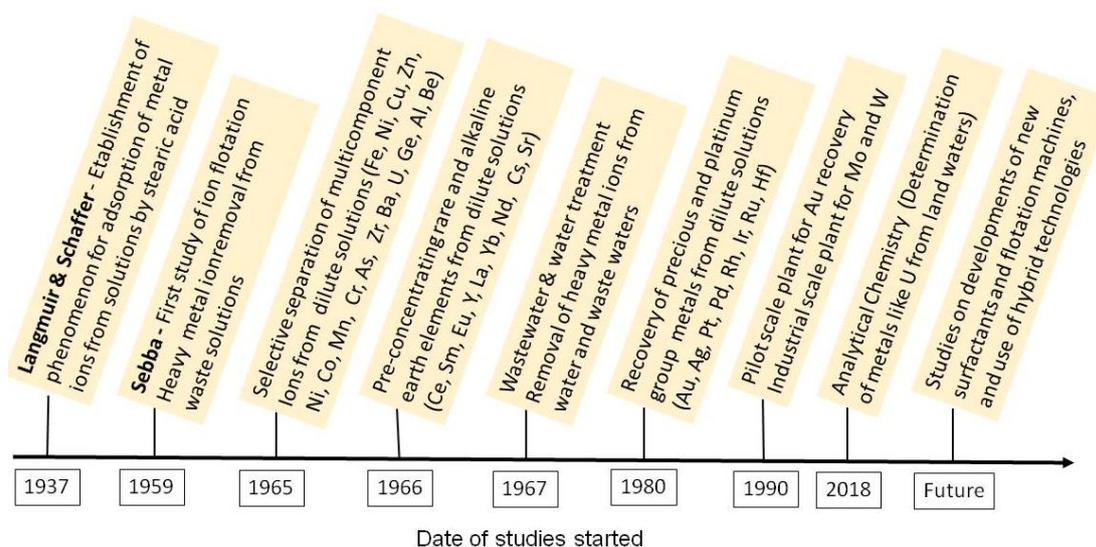


Fig. 7. Chronological developments of ion flotation studies according to the starting year

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