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# Application of Flotation for the Separation of Metal-Loaded Resins

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**Abstract:** The separation of two typical Lewatit-type ion exchange resins (TP208 and TP260) was studied by the application of flotation, following their preliminary use for ion exchange of zinc, a common heavy metal found in many wastewater streams. The major examined parameters were the specific type of resin and the respective ion exchange capacity, the required resin concentration for the efficient removal of metal, the influence of wetting on both processes (i.e., ion exchange and flotation), the effect of pH value on the removal of metal and on the regeneration of resin, the type and concentration of used surfactant (primary amine or quaternary ammonium were examined), as well as the effect of frother (ethanol) on flotation efficiency. The regeneration of resins was studied, with respect to the desorption of metal and to the elution of surfactant. The efficiency of combined process, which includes the removal of Zn(II) by ion exchange and the application of flotation for the subsequent solid/liquid separation of metal-loaded resin, showed that almost 100% of zinc was removed and more than 95% of used resin was recovered by flotation in a single stage. The operation was also examined during multiple cycles, i.e., following regeneration of resin; the high efficiency of both processes remained rather constant.

**Keywords:** Ion exchange resin, flotation, separation, zinc

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## INTRODUCTION

Heavy metals can cause significant environmental and human health damage as a result of their toxicity. Zinc was selected in this study as a typical example of common toxic metal, existing in many wastewater streams. The usual treatment methods for the removal of heavy metals from wastewaters include precipitation, adsorption, and ion exchange (1). Although there are certain differences between adsorption, and ion exchange (2), both processes commonly use fixed or fluidized beds (3). As a result of their application these methods produce a solid residue or sludge, loaded with the removed metals. The specific nature of the generated solids will be dependent mainly on the applied adsorbent or ion exchange medium, which could be a variety of resins, minerals, or even different types of biomass.

Bayer manufactures several ion exchange resins belonging to "Lewatit" series dedicated for removal of heavy metals. For example: (i) the OC-1026, a chelating resin with iminodiacetic functional group, is used to treat the zinc-rich industrial waste liquors (4); (ii) the MP62, a weakly basic macroporous anion-exchange resin was applied to zinc cyanide treatment (5); (iii) the TP-214 resin, containing the functional thiourea group was used for the selective separation of silver(I) from copper, zinc, and iron salts (6); and (iv) the TP207, an iminodiacetic resin, was used for the thermo-stripping of copper and zinc ions (7). According to the company (Bayer, 2002) these resins are suitable for the chloro-alkali-electrolysis/brine purification, purification of phosphoric acid baths, zinc galvanizing electrolytes, removal of alkaline earths, and miscellaneous elements from brine, as well as for the removal of heavy metal cations from neutralized effluents. The Lewatit TP208 resin can remove the heavy metals according to the following affinity series:

$$\begin{aligned}&copper > vanadium > uranium > lead > nickel > zinc > cadmium\\&> iron\ (divalent) > beryllium > manganese > calcium\\&> magnesium > strontium > barium > sodium\end{aligned}$$

The removal of heavy metals by the Lewatit TP260 resin from aqueous solutions is in accordance with the following selectivity sequence:

$$\begin{aligned}&uranium > lead > copper > nickel > cadmium > cobalt > calcium\\&> magnesium > strontium > barium > alkalimetals\end{aligned}$$

The processes of sorption and of ion exchange usually take place in appropriate (packed-bed) columns, in order to avoid the subsequent solid/liquid separation of sorbents/resins by the application of time-consuming settling or easily clogging filtration. During the column operation the sorption capacity of used sorbents/resins very seldom can approach the respective maximum (laboratory-determined) values, whereas the relevant kinetics (contact time) are usually not sufficient enough in order to achieve equilibrium. Also, the respective packing materials should be of granulated type aiming to avoid high-pressure losses. Other problems may include the quite complex design equations, as well as common fouling, when the influent contains fine particles, combined with excessive head loss, air binding, and fouling with particulate matter (8). Alternatively, the application of sorbents as finely dispersed powder has been proposed to increase the overall process kinetics due to large surface (contact area); although in this case it is necessary for the subsequent application of an appropriate solid/liquid separation method for the overall removal of metal-laden sorbents/resins.

It is worth noting that relative little information was so far published, regarding the post-treatment of metal-laden sorbents. A rather simple method could be the burning of (organic) sorbents and the recovery of contained heavy metals from the produced ash, but often this approach would not be environmentally acceptable, due to subsidiary pollution problems. It may be also uneconomical to treat the costly organic resins in this manner, because they usually require careful regeneration, recycling, and simultaneous recovery of metals for reuse. Flotation can provide a viable alternative method for the separation and recycling of metal-laden sorbent materials.

Flotation is one of the techniques proposed and evaluated for the remediation of metal-contaminated soil and water, both surface and groundwater (9). It is a common separation technique in mineral processing fields (10). It is also used for the treatment of water or wastewater, and as a solid/liquid separation technique, when there is a need to remove metal hydroxides, or sulfide sludge, following the precipitation of toxic metals (11). The dispersed-air flotation technique is usually preferred, especially for laboratory-scale experiment, for the generation of necessary bubbles over the dissolved-air (12).

In several cases, zeolites (13) or double-layered hydroxides, such as hydrotalcite (14), were used as efficient sorbent materials for the removal of metals. Attention was also focused on the binding abilities of different biological materials for metals (15), and in a recent investigation three types of biomass were examined for the extraction of copper, zinc, and nickel ions from aqueous solutions (16). In the aforementioned papers the sorption process was combined with the subsequent application of flotation for the separation of metal-laden sorbent materials.

In the present investigation, the combined metal removal by common ion exchange resins and their efficient separation by application of flotation during multicycle operation mode were examined. This research is part of a larger project with the acronym *Metasep* (2004), which also involves the use of membranes for downstream separation in order to obtain clean (recyclable) effluent; in this case, flotation can be considered as the pretreatment stage of microfiltration, which could follow.

## MATERIALS AND METHODS

Two common ion exchange resins were examined in this study, supplied by Bayer (Germany); Lewatit TP208 is a weakly acidic macroporous cation exchanger with chelating iminodiacetate groups, whereas Lewatit TP260 is also a weakly acidic, macroporous cation exchanger, but with chelating aminomethyl-phosphonic acid functional groups. Table 1 presents certain characteristic properties of these resins. The particle size of resins during the experiments was reduced in size, as compared with the original; they were used in the size range 70–100 μm. The natural pH of resins suspension was around 9.

This paper has not been focused on the selective separation of metal cations; zinc was selected as the investigated metal, considered rather as a mere example of typical toxic pollutant to be removed from metal-laden wastewaters. The initial concentration of Zn(II) was 50 mg/L in most cases, which is a typical concentration of this metal in several waste streams (1). The preliminary ion exchange stage of zinc removal, using these Lewatit resins, was performed applying an agitated system (magnetic stirring at 700 rpm). The contact time of resin with the aqueous solution of metal was 15 min, found as satisfactory during preliminary experiments. The concentration of used resin was mostly 1 g/L, although higher concentrations were also examined.

The electrokinetic measurements of resin particles were carried out by micro-electrophoresis in a Rank Brothers Mark II apparatus. The chemical determination of the remaining metal concentration in the collected effluent samples was conducted by atomic absorption spectrometry (AAS), applying the respective standard procedure.

The batch dispersed-air flotation cell was used for the subsequent separation experiments of metal-laden resin by flotation; it consisted of a cylindrical column, with an inner diameter of $4 \times 10^{-2}$ m, made from Plexiglas, with a cylindrical ceramic porous gas sparger (with diameter $10^{-2}$ m, height $2 \times 10^{-2}$ m and average porosity 10–16 μm), located close to the cell

***Table 1.*** Characteristic properties of examined resins (supplied by Bayer)

| Property | Lewatit TP208 | Lewatit TP260 |
|---|---|---|
| Stability in pH range | 0–14 | 0–14 |
| Stability at temperature (°C) | −20 to 80 | −20 to 85 |
| Bulk weight (kg/m$^3$) | 240.19 | 234.34 |
| Density (kg/m$^3$) | 1167.73 | 961.08 |
| Water retention (%) | 55–60 | 60 |
| Original size (μm) | 390–1410 | 390–1410 |

More information can be found in reference 27.

bottom. The air superficial velocity was constant ($2 \times 10^{-3}$ m/s). The conditioning time of resin particles with the added surfactant (flotation collector) was 5 min, in order to induce hydrophobicity of them and to enhance the efficiency of flotation, whereas the flotation retention time was 10 min. Most of the experiments were conducted at pH 6, in order to avoid zinc precipitation as hydroxide, which would complicate the ion exchange process. The results of flotation experiments were expressed in the usual way, i.e., as percentage recoveries R(%), analyzed gravimetrically, collection by suction of the concentrate (foamate) from the surface.

As flotation collectors three common cationic surfactants were applied: the (primary) dodecylamine (denoted here after as DA), the hydrochloric salt of dodecylamine (DA-Cl), and a quaternary, hexadecyl trimethylammonium bromide (HDTMA-Br). In the case of DA-Cl and of HDTMA-Br, the respective aqueous solutions were used, in contrast to DA, where an ethanolic solution was used, because DA is almost insoluble in water. Residual concentrations of HDTMA-Br and DA were determined colorimetrically with a UV-visible spectrophotometric method (17). Ethanol (0.1% v/v) was used as a convenient frother, when aquatic solutions of surfactants were used, in order to decrease the bubbles size and to increase the foam stabilization.

Nitric acid solutions were mainly applied for the regeneration of used resins. Following the desorption of metal, resin particles were washed with 1 M NaOH (for neutralization reasons) and then with deionized water, before their subsequent reuse.

The experimental procedure for the multicycles operation experiments, including combined ion exchange and flotation processes, was the following:

i. The resin (1 g/L) was initially conditioned (activated) with 1 M $HNO_3$ (80 mL/g) solution.
ii. During the First treatment cycle, zinc (50 mg/L) was ion exchanged at pH 6 and separated by flotation (using 100 mg/L HDTMA-Br, in presence of 0.1% ethanol).
iii. The metal-laden resin was regenerated for 1 h with 1 M $HNO_3$ (80 mL/g resin).
iv. During the Second to the Fifth cycles, the only differentiation from the aforementioned conditions was the use of a lower concentration of surfactant (50 mg/L) for the separation by flotation.

## RESULTS AND DISCUSSION

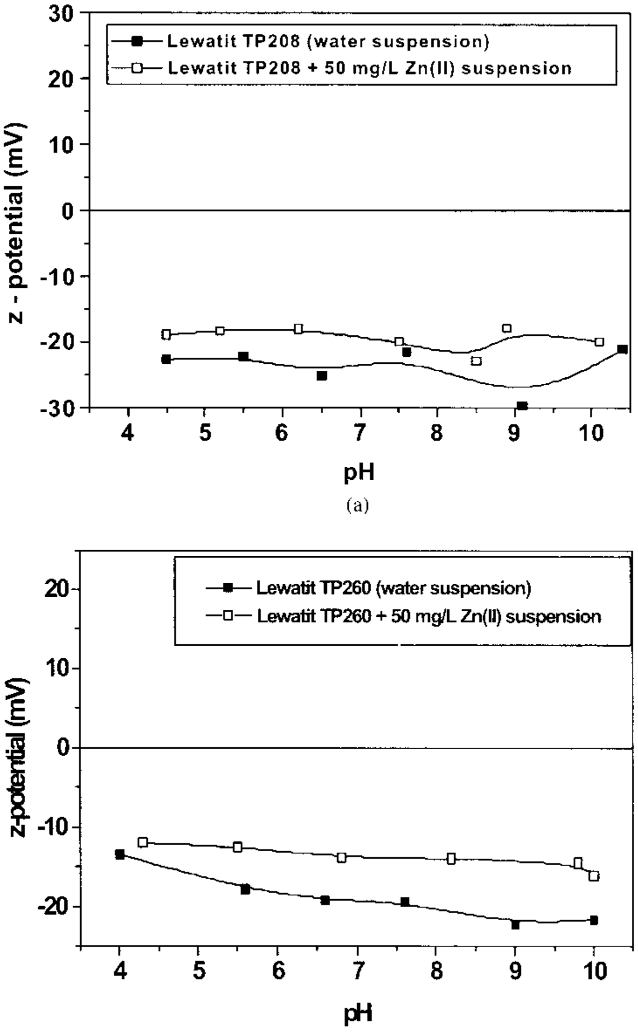
Several examples of emerging flotation devices and techniques, including some rather unconventional, have been recently reported by Rubio et al. (18). The use of flotation may offer a great potential, as for example in the minerals beneficiation industry, due to high suspension loading and the efficiency of established separation schemes, already available. The method of *sorptive flotation*, as termed by the suggesting researchers (19), includes the metals removal though sorption, followed by the separation of the usually finally suspended metal-laden particles (sorbents) by flotation. This combined process was investigated in-depth during laboratory or pilot-scale experiments, showing promising capabilities.

The preliminary electrokinetic study, presented as Fig. 1 for the case of Lewatit TP208 and of TP260, provided certain preliminary information, regarding the type of necessary addition of surfactant for the induced separation of fine particles by flotation. The observed negative surface charge throughout the examined pH range (4–10) proved the application of a cationic surfactant to render hydrophobic, and hence floatable, the resin particles. The latter was also apparent in Fig. 2a, where the removal of zinc was around 100%, for both resin types. The floatability of resins by the addition of primary amine (DA) was also apparent. In a single stage, around 98% separation recovery was found, which decreased slightly, following the addition of higher surfactant concentrations (Fig. 2b).

The effect of frother concentration on flotation recovery (ethanol was conveniently used) was also examined. The addition of a frother in dispersed-air flotation can simultaneously decrease the surface tension and form a stable foam layer, decreasing the respective bubble size. Consequently, the rate of bubbles rise was decreased, whereas the available number of bubbles for flotation was increased resulting in the overall improved process efficiency. The results showed that 0.1% v/v ethanol concentration was proved to be sufficient for the case of DA-Cl, regarding the efficient separation of Lewatit (Fig. 3a). The flotation of the other resin, Lewatit TP208, becomes effective with the addition of higher frother concentration (around of 2% v/v) (Fig. 3b).

A common quaternary cationic surfactant, HDTMA-Br was also examined as flotation collector; the addition of 15 mg/L HDTMA-Br led to satisfactory separation (recovery) of resin (about 92%), in case of Lewatit TP260 (Fig. 4a). The separation results were equally efficient also for the case of Lewatit TP208, although a higher concentration of HDTMA-Br (about 50 mg/L) was demanded in this case. The relative comparison of the aforementioned surfactants, for both resins (Fig. 4), showed that HDTMA-Br would be the most efficient flotation collector under the examined conditions.

Zinc hydroxide usually precipitates above the pH value of about 7.5, depending also on the other physicochemical conditions (20). Therefore, the eventual bulk or surface precipitation was not expected to interfere with the ion exchange process, because these experiments were taken mostly at pH 6. It has to be mentioned that the pH of solution affects also the speciation of added surfactants, i.e., primary amine can be appeared as $RNH_{2(aq)}$ or $RNH_3^+$ forms (21).

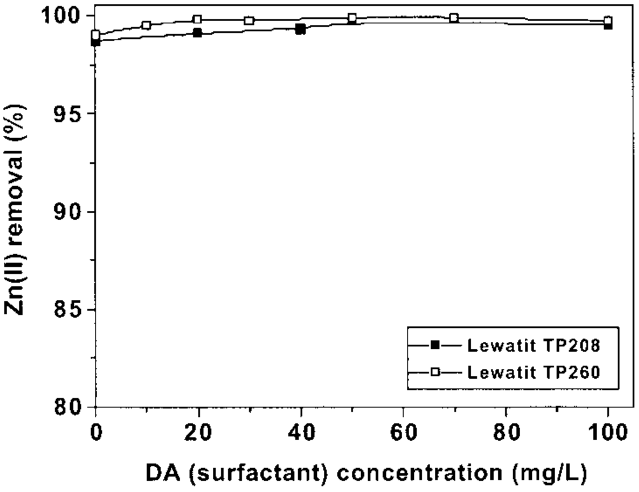


(a)

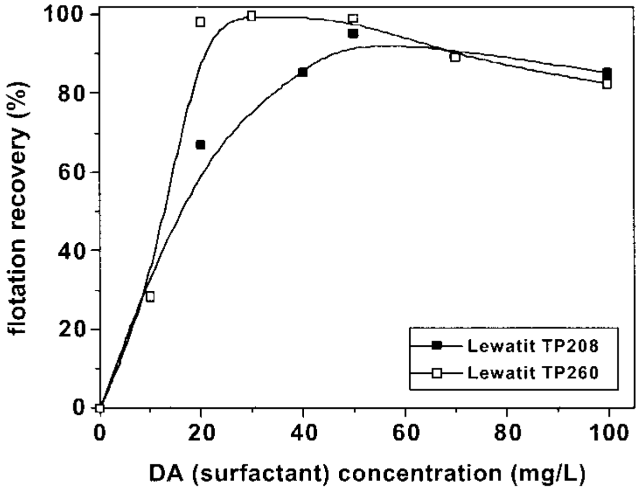
(b)

*Figure 1.* Electrokinetic measurements of (a) of Lewatit TP208, and (b) Lewatit TP260, as a function of solution pH, in presence (50 mg/L, corresponding to 0.0008 M ionic strength) and absence of zinc cations.

The possibility to float the metal-loaded resin particles at natural pH (around 9) was also investigated. In this case, the separation (recovery) by flotation for both resin types was almost equal to that previously found (i.e., for pH = 6). Using DA as flotation collector (20 mg/L) the flotation recovery was in the range of 98–99%, whereas using DA-Cl (even at higher



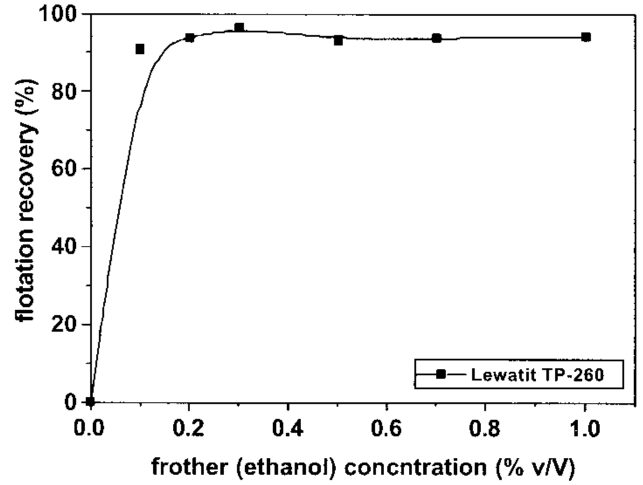
(a)



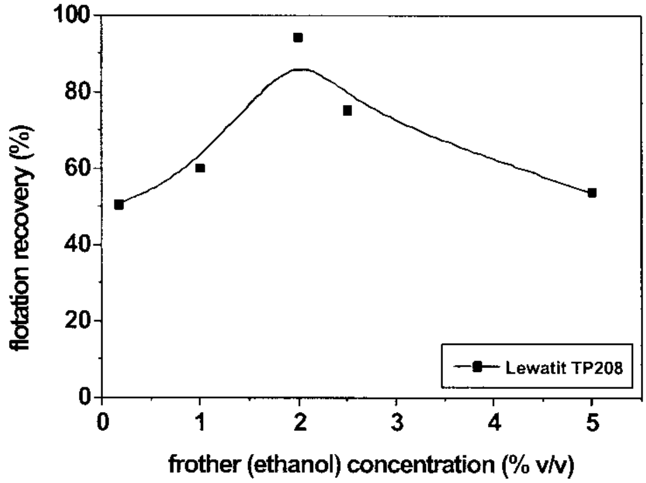
(b)

***Figure 2.*** (a) Zn(II) removal by ion exchange, and (b) flotation recovery (separation) of metal-laden resin, using Lewatit TP208 and Lewatit TP260 respectively, applying DA as surfactant; conditions: resin concentration 1 g/L, $[C_{Zn(II)}]_{initial}$ 50 mg/L, pH 6, ion exchange time 15 min, conditioning time 5 min, flotation time 10 min.

concentration 50 mg/L) the recovery by flotation was in the range of 90–95%. Nevertheless, it is worth mentioning that at this higher pH value (9) most of metals cations are being hydrolyzed to form insoluble precipitates, therefore the ion exchange process is expected to be highly influenced (interfered).



(a)



(b)

*Figure 3.* Effect of frother concentration on flotation recovery of resins: (a) Lewatit TP260, and (b) Lewatit TP208; conditions: resin concentration 1 g/L, pH 6, surfactant DA-Cl, surfactant concentration 50 mg/L, conditioning time 5 min, frother ethanol, flotation time 10 min.

Occasionally, higher resin concentration may be applied, due to imposed removal of higher concentration of pollutants. Fig. 5 shows the respective flotation tests using 4 g/L initial concentration of Lewatit TP260 and TP208 resins. In this case, higher amount of surfactant was required (200 mg/L

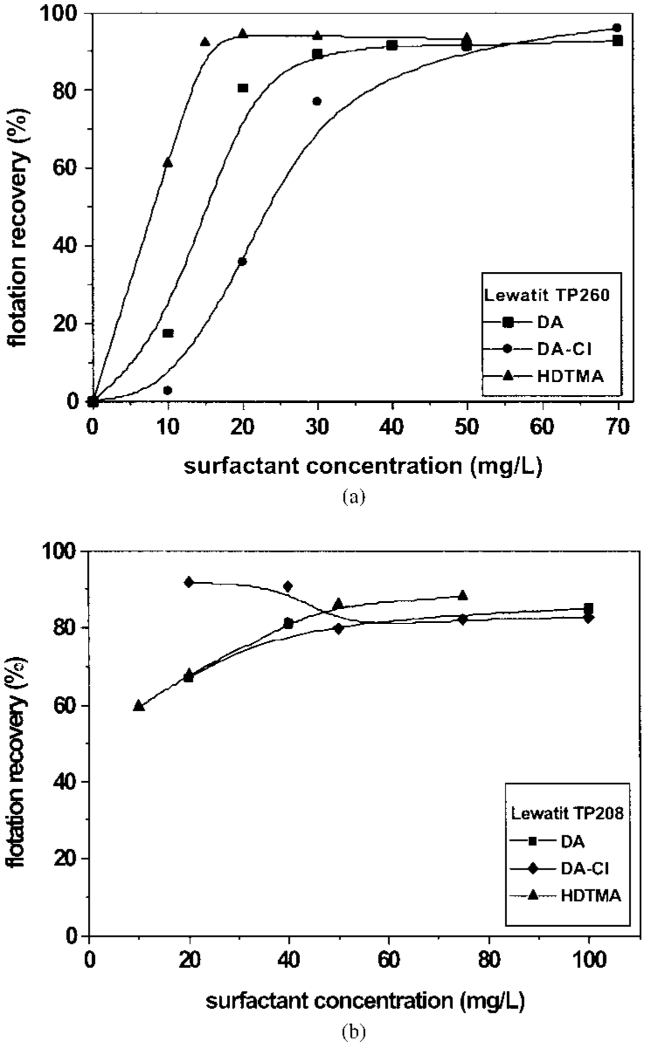


*Figure 4.* Flotation recovery of resins as influenced by initial surfactant concentration, for the three examined surfactants (DA, DA-Cl and HDTMA-BR), in case of (a) Lewatit TP208, and (b) Lewatit TP260; conditions: resin concentration 1 g/L, pH 6, conditioning time 5 min, frother ethanol (concentration 0.1% v/v in case of DA-Cl and HDTMA-Br), flotation time 10 min.

DA-Cl) than that with 1 g/L initial resin concentration (50 mg/L DA-Cl), noting that the flotation recovery for both cases was around 91%. Also, using 200 mg/L DA as surfactant, the flotation results of 4 g/L Lewatit TP260 were similar to those obtained with 1 g/L resin (i.e., around 92%).

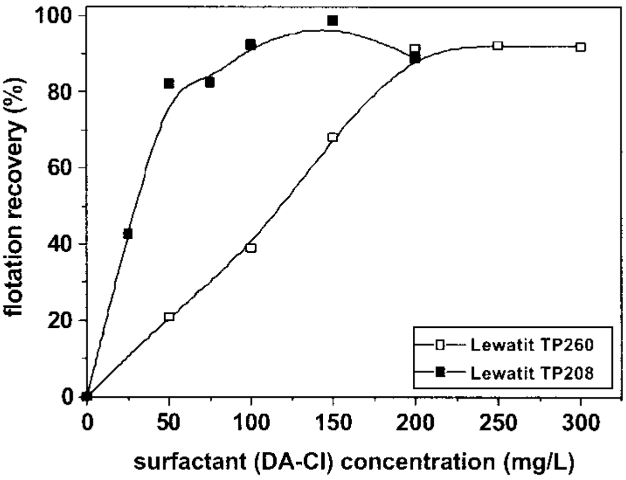


*Figure 5.* Flotation recovery of resins as influenced by initial surfactant (DA-Cl) concentration, for Lewatit TP260 or Lewatit TP208; conditions: resin concentration 4 g/L, pH 6, conditioning time 5 min, frother concentration 1% v/v, flotation time 10 min.

The flotation behavior of Lewatit TP208 at concentration 4 g/L was proportional to that of Lewatit TP260, i.e., the flotation recovery with 150 mg/L DA-Cl and 2% v/v ethanol was almost 100%. For comparison reasons, it is worth noting that in mineral processing an average consumption of amines, used as flotation collectors, was reported to be 0.05–0.25 kg per tone of mineral ore (22).

The possible influence of resins wetting on their flotation behavior was also examined at natural pH and is presented in Table 2 for Lewatit TP208 and in Table 3 for Lewatit TP260. Although, the wetting behavior is expected to influence the floatability of resins, i.e., their hydrophobic/hydrophilic character, specific influence was not noticed for both cases. For instance, using DA-Cl as collector and after 2 h of preliminary wetting, the

*Table 2.* Flotation recovery of Lewatit TP208 by three different surfactants (DA, DA-Cl, and HDTMA-Br), following wetting. Conditions: Resin concentration 1 g/L, pH 9, surfactant concentration 40 mg/L, conditioning time 5 min, frother (ethanol) in concentration 2% v/v (in case of DA-Cl and HDTMA-Br), flotation time 10 min

| Wetting time (h) | Flotation recovery (%) DA | Flotation recovery (%) DA-Cl | Flotation recovery (%) HDTMA-Br |
|---|---|---|---|
| 0 | 85.2 | 94.2 | 88.5 |
| 16 | 89.2 | 89.3 | 97.8 |

***Table 3.*** Flotation recovery of Lewatit TP260 by three different surfactants, DA ($C_{DA} = 20$ mg/L, DA-Cl ($C_{DA\text{-}Cl} = 50$ mg/L) and HDTMA-Br ($C_{HDTMA\text{-}Br} = 20$ mg/L) following wetting. Conditions: Resin concentration 1 g/L, pH 9, conditioning time 5 min, frother (ethanol) concentration 0.1% v/v (in case of DA-Cl and HDTMA-Br), flotation time 10 min

| Wetting time (h) | Flotation recovery (%) DA | Flotation recovery (%) DA-Cl | Flotation recovery (%) HDTMA-Br |
|---|---|---|---|
| 0 | 99.8 | 91.0 | 99.4 |
| 2 | 95.0 | 93.0 | 99.4 |
| 24 | 95.7 | 91.5 | 94.0 |

recovery of Lewatit TP260 was 93% approximately, after 24 h of wetting almost the same (91.5%), while the respective immediate value (i.e., without preliminary wetting) was also 91%. Lewatit TP208 behaves also similarly, i.e., the flotation recovery without wetting, using DA-Cl as surfactant, was 94.2% and after 16 h of wetting was 89.3%.

The examined ion exchange resins showed significant advantages, as for example good mechanical, thermal, and chemical stability. Their main disadvantage is the relatively high cost, therefore the regeneration and ability of them to be used during multiple cycles operation is necessary and it has been studied, aiming also to the production of a more concentrated metal solution, from which the recovery and reuse of contained metal values could be subsequently achieved, e.g., by electrolysis (23). Surfactant-modified zeolites (by hexadecyl-trimethyl ammonium) have been recently examined as efficient ion exchangers; the process economics were also related to the respective regeneration ability (24). The flotation was also used, adding as surfactant DA, for the separation of metal-laden biomass sorbent (*Streptomyces rimosus*); the reuse and recycling of biosorbent, following washing with a mixture of sodium sulfate and citrate (eluant), was proved efficient during multiple cycles of operation (25). A two-stage relevant biosorption process (pilot-scale experiments) showed that efficient wastewater treatment could be achieved, whereas the applied biomass will be reused in counter-current mode (26).

Preliminary attempts of resin regeneration and reuse for metal removal purposes were carried out in two subsequent treatment cycles, using 0.1 M hydrochloric acid (2 h mixing/contact time). The zinc desorption was almost 100%, while the surfactant was not eluted. Using the same concentration of surfactant and frother, the recovery (separation) during the second cycle of flotation was equal to the first one, for both resins. Following these preliminary promising results, two aqueous solutions of $HNO_3$ (0.1 and 1 M) were selected as elution media following preliminary comparable evaluation among water, NaOH, HCl, $CH_3COOH$, $H_2SO_4$, and $HNO_3$. The respective results are presented in Table 4 for Lewatit TP208 and in Table 5 for Lewatit TP260; the more concentrated $HNO_3$ solution (1 M) was finally selected. It is believed that $HNO_3$ does not induce any oxidative degeneration of the resins functional groups (resins do not contain any easy oxidized groups and the used $HNO_3$ solution is a relatively weak acid solution). By using around 160 mL of 0.1 M or 80 mL of 1 M $HNO_3$ per gram of metal-loaded ion exchanger, and following 1 h of contact time by mixing, it was possible to achieve complete elution of zinc and regeneration of resin.

The multicycles combined operation, including ion exchange and flotation and using HDTMA-Br as surfactant (Table 6), was tested for the case of Lewatit TP208 during five successive cycles, assuming that the behavior of Lewatit TP260 was similar and taking into account their previous general comparable attribute. It was found that during the first operating cycle the addition of higher surfactant concentration was required, than during the following four cycles. The initial use of 100 mg/L and subsequently of 50 mg/L HDTMA-Br resulted to separation (recovery) by flotation in the range 87.3–94.8% for all treatment cycles. As far as the surfactant desorption is concerned, HDTMA-Br elution was not observed (the desorption was found to be around 0.01% in every cycle), whereas Zn(II) was efficiently removed by ion exchange and subsequently quantitatively eluted (almost 100%).

## CONCLUSIONS

The ion exchange experiments concluded that 1 g/L of both examined Lewatit resin types could effectively remove 50 mg/L of Zn, within 15 min contact time. The z-potential of resins was found to be negative; therefore the addition of cationic surfactants was examined. It was observed that the three examined cationic surfactants (DA, DA-Cl, and HDTMA-Br) can be used to float the metal-laden particles, and among them the quaternary

***Table 4.*** Regeneration of zinc-loaded Lewatit TP208 by using $HNO_3$ solutions as function of used $HNO_3$ volume; Zn(II) concentration 50 mg/L, contact time of Lewatit TP208 with $HNO_3$ solution 1 h

| Used $HNO_3$ volume (mL $HNO_3$/g Lewatit TP208) | 0.1 M $HNO_3$ Zn(II) recovery (%) | 1 M $HNO_3$ Zn(II) recovery (%) |
|---|---|---|
| 333 | 100.0 | 100.0 |
| 167 | 100.0 | 100.0 |
| 83 | 91.5 | 100.0 |
| 33 | 46.0 | 90.9 |

***Table 5.*** Regeneration of zinc-loaded Lewatit TP260 by using $HNO_3$ solutions, as function of used $HNO_3$ volume; Zn(II) concentration 50 mg/L, contact time of Lewatit TP208 with $HNO_3$ solution 1 h

| Used $HNO_3$ volume (mL $HNO_3$/g Lewatit TP260) | 0.1 M $HNO_3$ Zn(II) recovery (%) | 1 M $HNO_3$ Zn(II) recovery (%) |
|---|---|---|
| 333 | 100.0 | 100.0 |
| 167 | 100.0 | 100.0 |
| 83 | 92.6 | 100.0 |
| 33 | 62.7 | 100.0 |

amine performed better. This application of flotation separation can be useful in cases, where suitable ion exchangers are synthesized and applied in agitated (mixing) mode as fine powder; hence, it would be better to apply them in suspended (finely dispersed) mode, because in packed beds configuration high-pressure losses are expected to be developed.

It was shown that the pH value did not substantially affect the efficiency of flotation separation. It was also observed that the influence of wetting was not important for the ion exchange properties of resins. Among the possible regeneration reagents, the use of 1 M $HNO_3$ was preferred (80 mL/g of resin). Zinc was quantitatively (around 100%) desorpted, while most of the added (initially) surfactant (HDTMA-Br) remained adsorbed in resin particles. During the subsequent treatment cycles the ion exchangers can remove Zn(II) with the same high effectiveness (99.9%). The flotation recovery during all treatment cycles was high, although a supplementary

***Table 6.*** Flotation recovery of Lewatit TP208 following multicycles operation treatment, for two different cases: *Case 1*: The surfactant addition during the first operating cycle was 50 mg/L, while during the following four cycles 20 mg/L. *Case 2*: The surfactant addition during the first operating cycle 100 mg/L and during the following four cycles 50 mg/L. Conditions: Resin concentration 1 g/L, pH 6, surfactant HDTMA-Br, conditioning time 5 min, frother (ethanol) concentration 2% v/v, flotation time 10 min

| Treatment cycle | Case 1 flotation recovery (%) | Case 2 fotation recovery (%) |
|---|---|---|
| 1st | 65.3 | 94.2 |
| 2nd | 87.6 | 93.7 |
| 3rd | 72.2 | 94.8 |
| 4th | 80.0 | 87.3 |
| 5th | 73.4 | 92.0 |

addition of surfactant concentration was found to be necessary, during each successive operation cycle.

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