Zinc, Cooper and Cadmium Solvent Extraction at Equilibrium in Liquid-liquid Systems

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The generation of liquid effluents containing heavy metal residues from industrial activities presents a potential hazardousness for environment and human health. The extraction of Zn (II), Cu (II) and Cd (II) from aqueous solutions was performed using solvents corresponding from both efficient and economic point of view. After the preliminary studies and taking into account the literature indications, the following solvents have been experimented: DEHPA (di 2 ethylhexyl phosphoric acid) with TOPO (tri-n-octylphosphine oxide) and Cyanex 272 (di 2,4,4trimetylpentyl phosphinic acid).

Keywords: heavy metal residues, DEHPA, TOPO, Cyanex 272

In order to achieve this goal, several techniques are being used. Among them, supported liquid membranes technologies are showing their potential for application in the removal of metals contained in liquid effluents. Supported liquid membranes are a combination between conventional polymeric membranes and solvent extraction. Several configurations are used: flat-sheet supported liquid membranes, and hollow fiber modules. In order to improve their effectiveness, smart operations have been developed: non-dispersive solvent extraction, non-dispersive solvent extraction with strip phase dispersion and hollow fiber renewal liquid membrane [1-4].

A hydrometallurgical route based on the liquid–liquid extraction technique using Cyanex 272 as solvent is investigated for the selective separation of metal values, in particular, zinc and manganese from spent alkaline batteries. The recycling route consists of following steps: [2] cryogenic dismantling of the spent batteries, [3] pre-treatment of the internal material consisting of drying, grinding and screening in order to produce a dry homogeneous powder, [4] sulphuric acid powder leaching and [5] metal separation by liquid–liquid extraction. Bench scale experiments have shown that zinc and manganese are easily separated using 20% (v/v) Cyanex 272. Therefore, the proposed route can treat residues from both zinc–carbon and alkaline batteries because the metal composition of these batteries is quite similar. The metal content of other batteries such as Ni–Cd and nickel-metal hydride (NiMH) has been also determined in order to include them in future investigations [6-9, 25].

Three major types of pre-concentration methods were evaluated and optimised for the extraction and determination of Cd, Cu, Ni, Pb and Zn from seawater samples. The traditional APDC/DDDC-Freon liquid–liquid extraction method showed excellent results for a multi-elemental analysis. In the solid phase extraction method, the performances of a traditional Amberlite XAD-4 and a novel Dowex Optipore V-493 were evaluated. Application of Dowex Optipore V-493 resin provided better results at low concentrations than the generally used Amberlite XAD-4 resin using low sample volumes. However, the presence of natural organic compounds may decrease extraction efficiency of both resins for Cu. Thus, a pre-treatment with UV irradiation is advantageous for samples with high organic content. Cobalt co-precipitation methods showed good Cu and Ni recoveries, but gave poor results for Cd at low concentrations. In addition, high sample volumes are required. Both solid phase and co-precipitation methods showed unsatisfactory results in determination of Pb. Finally, a summary of methods advantages are given for choosing the most suitable method [10-18, 24].

The selective liquid-liquid extraction of various alkali and transition metal cations from the aqueous phase to the organic phase was carried out by using p-tert-butylcalix[4]arene (L1), p-tert-butylcalix[6]arene (L2), tetra-ethyl p-tert-butylcalix[4]arene-tetra-acetate (L3), tetra-methyl-p-tert-butyl-calix[4]arene-tetra-ketone (L4), calix[n]arenes (n=4 and 6) bearing oxime groups and a polymeric calix[4]arene. It was found that compounds L5 and L6, showed selectivity towards Ag^+, Hg^+, Hg^{2+}, Cu^{2+}, and $Cr3^{3+}$ and the order of the extractability was $Hg^+ > Hg^{2+} > Ag^+ > Cu^{2+} > Cr^{3+}$. The polymeric calix[4]arene (L8) was selective for Ag^+, Hg^+ and Hg^{2+}.

The extraction of Zn(II), Cu(II) and Cd(II) from aqueous solutions was performed using solvents corresponding from both efficient and economic point of view. After the same preliminary studies and literature indications, the following extractants have been experimented: di (2 ethylhexyl) phosphoric acid (DEHPA) with tri-n-octylphosphine oxide (TOPO) and di (2,4,4trimetylpentyl) phosphinic acid (Cyanex 272).

The di(2 – ethylhexyl) phosphoric acid (DEHPA) represent an acid esther having the formula $[(C_2H_5)C_6H_{12}O]_2PO(OH)$ symbolized as HR, H representing the inter exchangeable ion according to the reaction:

$$M^{3+}_{(aq)} + 6\overline{HR} \rightleftharpoons \overline{MR_2(HR)_4} + 2H^+_{(aq)}$$

where M^{2+} represent a divalent cation (Zn^{2+}, Cu^{2+}, Cd^{2+}).

The tr-n-octyl phosphine (TOPO) represents a phosphine oxide having the formula $(C_8H_{17})_3PO$ with complexing

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properties because of the electron giving oxygen joined to phosphorus:

$$M^{2+}_{(aq)} + SO_4^{2-} + \overline{4TOPO} \rightleftharpoons \overline{MSO_4(TOPO)_4}$$

The di(2,4,4 – trimetyl pentyl) phosphinic acid represents a phosphine acid having the formula $[(C_5H_8(CH_3)_3]_2PO(OH)$. The ion extraction process occurs similar to the case of DEHPA, according to ion exchange and complex formation mechanism [19-23].

Experimental part

Materials and methods

$ZnSO_4$, $CuSO_4$, $CdSO_4$ were prepared by dissolving the corresponding salts in deionized water. Sodium hydroxide and sulphuric acid were used in order to adjust the *p*H and also for the re extraction processes.

The solvents and thinners used for the extraction processes were commercially available products based on heptane. After contact between the organic phase and aqueous salt solution the experiences were performed under a sufficient stirring time (about 20 min) in order to attain equilibrium. The metal concentration in aqueous phase was determined by Atomic Absorption Spectrometry using a Savantaa AAS Spectrometer.

The zinc, copper and cadmium extraction isotherms have been determined using the above mentioned experimental method. Because the distribution ratio of Zn, Cu and Cd cations in organic and aqueous phases essentially depends on *p*H previous experiments have been made in order to put in evidence the relative dependence of metal extraction as a function of *p*H.

Results and discussions

The results are presented in the table 1 and the figures 1 and 2.

The figures show that the removal of all three metals is essentially achieved at a *p*H value of about 4.5 in DEHPA and about 6.5 in Cyanex 212. Both Zn and Cd are strongly extracted while Cu is less extracted. These results show that there is no possibility of complete extraction from acid effluents, a controlled neutralization being necessary to achieve full extraction of all metals, because of the significantly high *p*H required for metal removal.

The experimental data concerning the equilibrium extraction of Zn, Cd and Cu in the organic phase containing 0.2 M DEHPA +0.01 M TOPO in heptane are presented in the table 2 and in the figures 4, 5 and 6. The extraction isotherms confirm the extraction series Zn>Cd>Cu in the domain of *p*H 3.0 – 5.5.

Table 1
Zn, Cu AND Cd DISTRIBUTION RATIO ON CYANEX 22 AND DEHPA AS A FUNCTION OF *p*H, IN HYDROCHLORIC MEDIA

pH		2.5	4.5	6.5
Cyanex 22	Zn	70.3	97.1	98.1
	Cd	63	91	96.9
	Cu	2.4	30.9	89.8
DEHPA	Zn	90.1	98.2	99.1
	Cd	89.1	96.3	97.7
	Cu	29.9	93.7	96.1

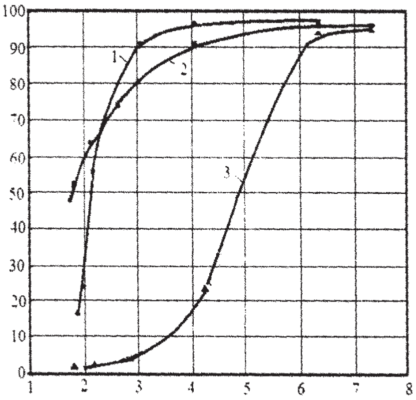

Fig. 1. Dependence of equilibrium extraction ratio on *p*H from solutios containing: 1 –Zn, 2 – Cd, 3 – Cu. Organic phase: 0.2 M Cyanex 22 in heptan. Initial cation concentration: 0.5 – 1.5 g/L.

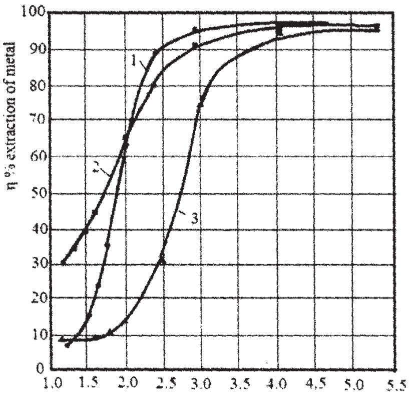

Fig. 2. Dependence of equilibrium extraction ratio on *p*H from solutions containing: 1 –Zn, 2 – Cd, 3 – Cu. Organic phase: 0.2 M DEHPA +0.01 M TOPO in heptane. Initial cation concentration: 0.5 – 1.5 g/L

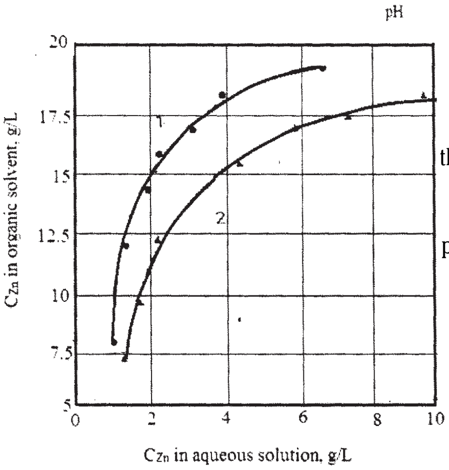

Fig. 3. Dependence of zinc concentration in the organic phase on the concentration in the aqueous phase at equilibrium. Organic phase =0.2 M DEPHA in heptane; 1 – *p*H = 2.5; 2 – *p*H = 4.5

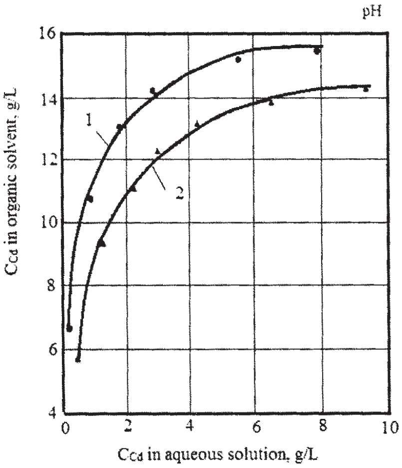

Fig. 4. Dependence of cadmium concentration in the organic phase on the concentration in the aqueous phase at equilibrium. Organic phase =0.2 M DEPHA in heptane; 1 – *p*H = 2.5; 2 – *p*H = 4.5

Table 2
DISTRIBUTION CONCENTRATION (g/L) of Zn, Cd AND Cu IN ORGANIC AND AQUEOUS PHASES AND DISTRIBUTION COEFFICIENTS OF THE SAME ELEMENTS

pH = 2.5								
Zn			Cd			Cu		
Or.	Aq.	D_{Zn}	Or.	Aq.	D_{Cd}	Or.	Aq.	D_{Cu}
7.4	0.82	9.1	5.6	0.68	8.3	3.4	0.8	4.3
11.5	1.9	6.1	10.9	2.1	5.2	5.1	2.1	2.4
16.2	6.1	2.7	14.3	7.8	1.8	6.1	3.9	1.5
17.4	7.9	2.2				6.5	5.9	1.1
pH = 4.5								
Zn			Cd			Cu		
Or.	Aq.	D_{Zn}	Or.	Aq.	D_{Zn}	Or.	Aq.	D_{Zn}
7.6	0.52	14.6	6.5	0.47	13.8	5.1	0.6	8.3
11.7	0.97	12.1	11.2	0.95	11.7	6.5	1.1	6.4
15.3	2.1	7.3	13.2	2.1	6.3	7.8	2.0	3.9
18.6	5.8	3.2	15.5	5.9	2.6	8.8	6.1	1.45

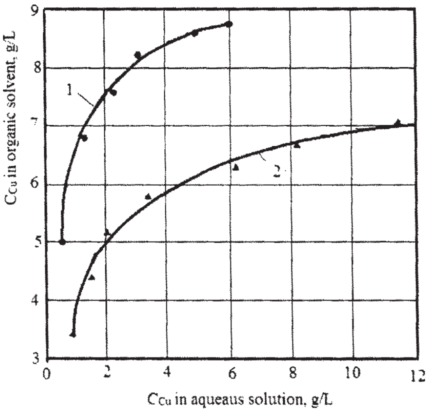

Fig. 5. Dependence of copper concentration in the organic phase on the concentration in the aqueous phase at equilibrium. Organic phase =0.2 M DEPHA in heptan; 1 – *p*H = 2.5; 2 – *p*H = 4.5

Conclusions

It is very important to underline the distribution coefficient variation with the aqueous solution concentration (table 2). For instance, the variation of zinc concentration from about 0.82 to 7.9 g/L determines at *p*H = 2.5, a variation of distribution coefficient from 9.1 to 2.2. At the same *p*H, the variation of cadmium concentration from 0.68 to 7.8 g/L determines the distribution coefficient variation from 8.3 to 1.8. Considering the cadmium ions, the variation from 0.8 to 5.9 g/L is followed by a variation from 4.3 to 1.1 of the distribution coefficient. The same phenomenon could be observed at other *p*H values. Increasing the *p*H (under the precipitation limit) of the solutions containing Cu, Cd and Zn ions leads to an important increase of the distribution coefficient.

A practical conclusion could be retained considering the distribution coefficient variation with Zn, Cd and Cu concentration in aqueous solution. So, an important extraction efficiency could be obtained from solutions containing less than 1g/L Zn, Cd and Cu ions. That's why the extraction of metals is recommended when using diluted solutions. Another practical conclusion refers to the possibility of high elimination of copper contained as impurity in Zn-Cd-Cu solutions. This possibility increases when considering the extraction ratio variation with *p*H (figs. 2 and 3).

There is no real possibility to ensure a selective cadmium extraction from solutions containing both zinc and cadmium when the two cations concentration are of the same order of magnitude.

In the case of small cadmium concentration in comparison with zinc, the separation could be performed considering the big difference between the distribution coefficients in diluted and relative concentrated aqueous solution (see table 2).

Acknowledgements:P The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/134398.

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Manuscript received: 20.01.2015