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Synergistic Effect of MEHPA on Co-Extraction of Zinc and Cadmium with DEHPA

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□ ABSTRACT □

Simultaneous extraction of zinc and cadmium by mix of Di-2-Ethyl Hexyl Phosphoric Acid (DEHPA) and Mono-2-Ethyl Hexyl Phosphoric Acid (MEHPA) and synergistic effect of (MEHPA) on co Extraction of Zinc and cadmium with DEHPA was investigated. It was shown that extraction of zinc and an increase of PH would increase cadmium by DEHPA and/ or MEHPA. The results also illustrate that $pH_{0.5}$ of zinc by an increase in (MEHPA) from 0.1 to 8 vol% did not vary significantly while that of cadmium differs from 0,63 to 2,4. In other words, MEHPA prevents selective extraction of zinc from aqueous media including both zinc and cadmium. Studies on selective separation parameter $ß_{Zn/Cd}$ show that it was reduced 50 to 13 times through an increase in MEHPA from 0.1 to 8.0 vol%.

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الفعل التآزري لحمض أحادي أتيل هكسيل الفوسفور على استخلاص التوتياء والكادميوم بواسطة حمض دي أتيل هيكسل الفوسفور

الدكتور أحمد رجب *
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(قبل للنشر في 2005/3/3)

□ الملخّص □

تمت دراسة استخلاص التوتياء والكادميوم في آن واحد بواسطة مزيج من ثنائي أتيل هكسيل حمض الفوسفور **(DEHPA)** وآحادي **2**- أتيل هكسيل حمض الفوسفور **(MEHPA)** والفعل التآزري للحمض **(MEHPA)** على استخلاص عنصر التوتياء بواسطة الحمض **(DEHPA)**.

لقد تبين أن استخلاص التوتياء والكادميوم بواسطة **(DEHPA)** مع/ أو بواسطة **MEHPA** سيزداد بزيادة الـ **PH**.

كما أوضحت النتائج أن استخلاص التوتياء عند **PH =0,1** بازدياد **MEHPA من 0.1 إلى 8** بالمئة حجماً يكون غير فعال بينما يختلف عند عنصر الكادميوم من **0.63** إلى **2.4** وبتعبير آخر فإن حمض **MEHPA** يحول دون استخلاص التوتياء من وسطه المائي بوجوده مع عنصر الكادميوم.

إن دراسة عامل الفصل $\beta_{zn/cd}$ بينت أن قيمته تتناقص من **50** إلى **13** مرة خلال زيادة تركيز الحمض من **0.1** إلى **0.8** بالمئة حجماً.

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INTRODUCTION:

Nowadays, efforts to extract zinc from low-grade mines have been developed by extraction of high grade zinc ore. Considering the concentration of dissolved zinc during leaching of low grade ore, presence of impurities such as Cd, Ni. Co in electrolyte and also the need for ultra high pure (UHP) zinc through electrowining process, the purification process is very attractive one.

Solvent extraction is one of the most economical and practical purification processes [1]. This method is used for extraction and purification of zinc from leach liquors. Approximately, all zinc producing with solvent extraction units utilizes DEHPA as an organic solvent [2]. Therefor, study of zinc solvent extraction has been investigated by different researches (Thorsen, 1983, Glutler, 2000)[3-4].

Investigations of solvent extraction of zinc have further been carried out by pure DEHPA (Owusu, 1998, Zielinski, 1998, Salimi et al 2000). Based on Researches (Darvishi 2001 and Karimianpoor 2001) it has been shown that in strong acidic conditions a part of CYANEX 301, CYANEX 302 or DEHPA decomposed and the new organic compound would replace them[5]. It seems that, one of alkyl organic group completely breaks and is substituted by hydrogen. However in case of DEHPA, this compound can be decomposed to MEHPA. Consequently, during stripping of zinc complexes from DEHPA, some MEHPA is formed, so that the concentration of MEHPA increases gradually during the process.

EXPERIMENTAL METHODS:

Batch experiments were carried out in flask containing equal volumes (20ml) of both aqueous and organic phases. The mixture was agitated at a constant temperature with a mechanical shaker[6].The experiments were allowed to run for one hour in order to reach equilibrium. The samples were retained for three hours and the two phases were separated by passing through a separation funnel. Experiments were carried out at room temperature. The initial concentration of zinc or cadmium in the aqueous phase in all experiments was 5 g/L. Zinc or cadmium content of the aqueous phase was analyzed with titration method with EDTA at presence of Eirochromnblack T as indicator. Zinc or cadmium contents of the organic phase were determined through mass balance calculations[7].

RESULTS AND DISCUSSION:

Effect of PH:

Experiments were carried out to study the effect of pH on the extraction of zinc and cadmium with different organic solvents. This parameter was investigated at constant ([MEHPA] : [DEHPA]) ratio and isotherm conditions. Extraction curves for different values of MEHPA (0.1 and 6vol%) are illustrated in Figure 1. It was seen that cadmium extraction for MEHPA concentration equal to 0.1 and 6 occurs at $0.27< pH< 0.94$ and $0.85<pH<3.2$, respectively. For the same MEHPA concentration, zinc extraction occurs at $0.3<pH<2.03$ and $0.48< pH<1.89$, respectively.

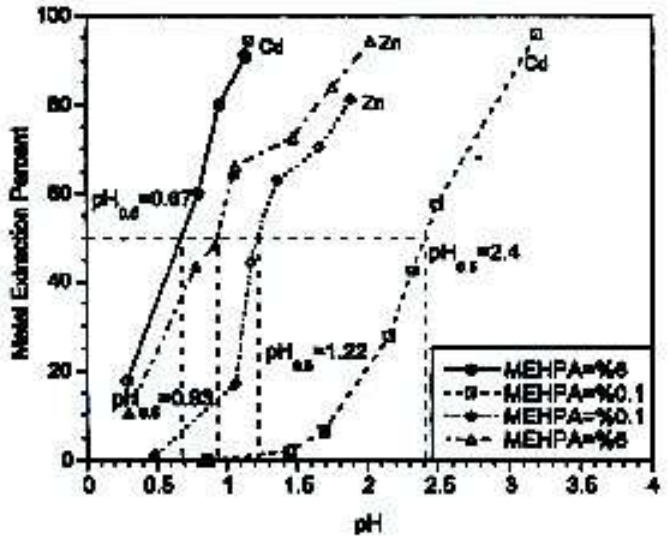


Fig. 1- Extraction percent of Zinc and cadmium at 25°C for MEHPA={6%,0.1}

The extraction curves showed a synergistic shift to the right by decreasing the relative amount of MEHPA with respect to the constant extractant concentration (20vol %) of organic phase. The figure 1 also shows that the equilibrium pH values of which 50% extraction of metals ($pH_{0.5}$). For cadmium extraction, When MEHPA concentration at organic solution increases from 0.1 to 6 $pH_{0.5}$ value decreases from 2.4 to 0.67, respectively, while for zinc extraction it decreases from 1.22 to 0.93. The selectively of the mixture can be expressed by the difference between the pH0.5 values of the two metals. The data obtained for pH0.5 and ΔpH0.5 of the metals are illustrated in Table 1.

Variation of log DM (M = zinc or cadmium) vs. pH for different values of MEHPA (0.1 and 6vol%) is shown in Figure 2. This figure shows that log DM varies linearly with pH at different concentration values of MEHPA with a constant slope around 2 for cadmium while that for zinc varies from 1.7 to 0.98 respectively at MEHPA 0.1 and 6vol%. Slope value difference for zinc and cadmium is probably related to different extraction mechanisms at presence or absence of MEHPA. Therefore, MEHPA causes more extraction tendency for cadmium than for zinc at higher concentrations.

The effect of MEHPA: DEHPA Ratio:

The effect of MEHPA on extraction at different acid media conditions was investigated. Variation of logs D versus MEHPA/DEHPA ratio is illustrated in figure 3. It is seen that variation of log D versus MEHPA/DEHPA ratio for cadmium is faster than that of zinc. These results virtually show that tendency of MEHPA to extract cadmium is more than its tendency to extract zinc. At higher MEHPA concentration extraction of cadmium has a more tendency to the extraction of zinc. During the purification process of metals, desired metal is only extracted in organic phase and impurities are rejected to rafinate.

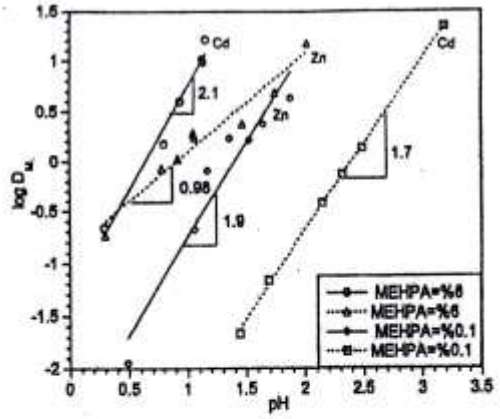
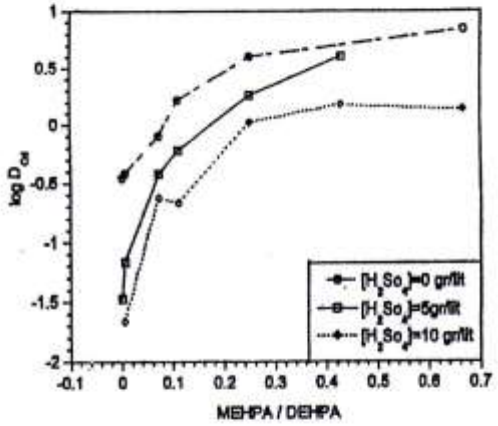


Fig. 2- Variation of log D vs. pH at constant MEHPA concentration



(a)

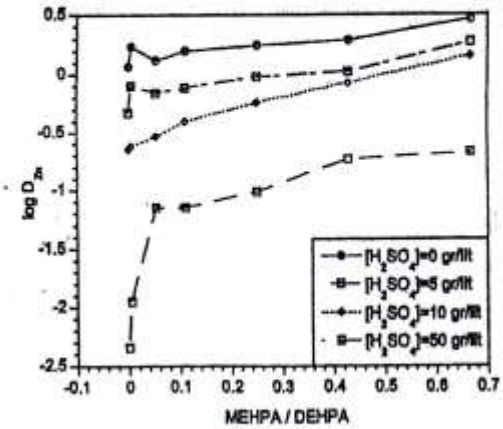


Fig. 3- Variation of log D versus proportion of MEHPA to DEHPA concentration at different acid media a) cadmium b) zinc

Table 1. $pH_{0.5}$ for zinc, cadmium and Δ $pH_{0.5}$

MEHPA	$PH_{0.5}$				
	Cd	Zn	$Cd.Cd_{MEHPA}$	$Zn-Zn_{MEHPA=8\%}$	Cd-Zn
%8	0.63	0.99	0.00	0.00	-0.36.
%6	0.67	0.93	0.04	-0.06	-0.26
%4	0.74	0.92	0.11	-0.07	-0.18
%2	1.28	1.00	0.65	0.01	0.28
%1	1.47	1.14	0.84	0.15	0.33
%0.1	2.40	1.22	1.77	0.23	1.18

The effect of MEHPA: DEHPA Ratio on Metal Extraction Selectivity:

The separation factor (β) is an important parameter to define selectivity of extraction of metals. In case of cadmium and zinc, separation factor is defined as:

$$^{\beta}Zn/Cd = \frac{^{D}Zn}{^{D}Cd}$$

Tendency of cadmium's distribution factor to zero indicates a better separation of zinc and cadmium from each other. In other words, at a higher separation factor it is easier to perform selective extraction.

Variation of $\beta_{Zn/Cd}$ versus MEHPA/DEHPA at several acid media conditions is shown in Figure 4. As it is seen at a low MEHPA concentration the selectivity of Zn over Cd is high. Variation of β is less than one for high MEHPA concentrations and more than 10 for low MEHPA concentration and pH. Based on the results of Figure 4 the β values at less MEHPA concentration proportionate to β values at higher MEHPA concentrations varies from 13 to 50 times.

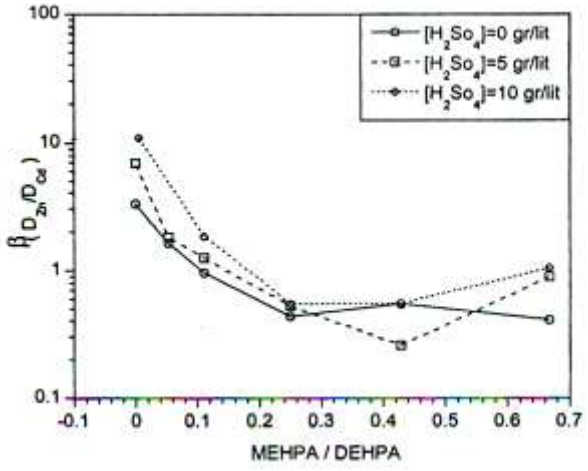


Fig. 4- variation of βzn/Cd versus proportion of (MEHPA); (DEHPA) concentration at different aqueous media

CONCLUSION:

This study was based on decomposition problem of DEHPA in industrial production of zinc. Results obtained for zinc and cadmium were evaluated in terms of β as applicable and useful parameter. The experimental results indicated that MEHPA could influence the extraction mechanism. MEHPA caused the extraction curves to shift to the left of the diagram. The synergistic shift to the left for cadmium was larger than that of zinc, hence at less MEHPA values, zinc is extracted prior to cadmium but at high MEHPA values, this condition is vice versa. On the other hand, MEHPA along with DEHPA changes the extraction mechanism, especially for zinc; therefore, any change in extraction mechanism calls for a very tight control of system parameters or substitution. Some new organic solutions achieve the same production capacity.

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