

Solvent Extraction of Cadmium (II) from Sulfate Medium by Bis(2-ethylhexyl) Phosphoric Acid in Toluene

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Abstract

The solvent extraction of cadmium (II) from sulfate medium by bis (2-ethylhexyl) phosphoric acid (D2EHPA) diluted in toluene was investigated. Optimum pH range for extraction of Cd (II) is 5 to 6, by use of 0.1 M of organic reagent in toluene. Then, Cd (II) was stripped with 4.0 M HCl from Organic phase. The effect of temperature on the extraction was carried out by temperature variation from 278 to 318 K and has led to that the temperature variation has negligible effect on extraction process. Extraction and stripping equilibrium times were studied to determine the optimum time of cadmium extraction reaction rate. The stoichiometry of the probable extracted species was determined on the basis of slope analysis by plotting log D versus log [(HR)₂] curve (D is the ratio of distribution of cadmium in organic/aqueous phase and (HR)₂ is dimeric form of extractant). Cadmium is extracted by a cation-exchange mechanism as CdR₂.2HR.

Keywords: Liquid- liquid extraction, D2EHPA, organic phase, stripping, stoichiometry, cation-exchange mechanism.

Introduction

Cadmium (II) is often present in industrial wastewaters such as mining, metallurgy and surface treatments, in the concentrations of down to hundred milligrams per cubic decimeter.

These effluents cause serious environmental problems because cadmium compounds are potentially harmful and toxic and are listed by the Environmental Protection Agency as one of 129 priority pollutants¹. Thus, numerous investigations have been carried out for removing heavy metals from industrial wastewaters using several methods such as chemical precipitation, liquid – liquid extraction (solvent extraction), solid – liquid extraction (adsorption and resin ion exchange) and In fact, every metal ion needs its own selective extractant, which makes this selection very important but very difficult^{19,20}, because solvent extraction is based on the difference of the ability to form a chemical complex between selective extractant and the metal ion. Thus, the obtained extraction and separation ability are highly dependent on the chemical structure of the extractants having effective ligands. In present work, the cationic extractant D2EHPA has been used for the extraction of Cd(II) because it has been extensively studied for solvent extraction of numerous metal ions such as Zinc, Beryllium, Copper, Vanadium, Indium, Gallium and rare earth elements²¹.

reverse osmosis²⁻⁵. Some of these methods are expensive and have limitations. The general advantage of solvent extraction is its efficacy for recovering the metal ions at high concentration with high selectivity and is suitable for continuous operations. In this field, the commercial organophosphorous extractants such as (EHPNA, D2EHPA, OPAP, TOPS 99, TOPO, TBP, Cyanex 923, cyanex 272, cyanex 921, cyanex 302, PC88A, LIX 860, LIX 622, LIX 973N and LIX84-I) are currently the subjects of several studies dealing with the separation of various metal ions such as Cu (II), Ni (II), Zn (II), Cd (II), Co (II), Fe (III), Pb (II) in different media, with different selective extractions⁶⁻¹⁸.

Materials and Methods

Reagents. The stock solution of cadmium (II) sulfate (1000 mg.L⁻¹(ppm)) was prepared by dissolving analytical grade chemical (Merck Germany) in deionized water. A small amount of H₂SO₄ was added to the solution to prevent hydrolysis of metal ions. The standard solutions of cadmium used in extraction studies (5 mg.L⁻¹) were prepared by dilution of the stock solution. The commercial extractant D2HEPA was obtained from BDH and was used without further purification. Toluene (Merck, Germany), was used as the diluents. All other

inorganic reagents used, namely, sulfuric acid, sodium acetate, and acetic acid were analytical grade (Merck, Germany) and were employed for adjusting the aqueous phase to the desired value.

Apparatuses. For determining Cd (II) concentrations, an inductively coupled plasma atomic emission spectrometer (ICP – AES, VHSTA –PRO Varian) was used. Determining and adjusting pH of solution was performed by a Denver Instrument UB -10 pH- meter.

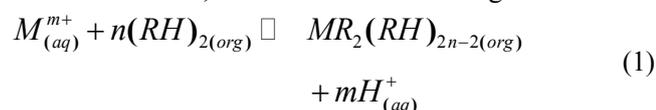
Procedure. The organic and aqueous solutions were equilibrated in 50-ml separator funnel with an organic/aqueous ratio (O/A) of 1:1 (10 ml organic solution and 10 ml aqueous solution) which was shaken vigorously for 20 minutes. The pH values in the aqueous phases were measured by pH-meter. In the extraction tests, the initial pH of the aqueous phase was kept constant by adding sodium acetate buffer, before equilibration was carried out (20 minutes). After equilibration, the separator funnel was left standing for at least 10 min for completing phase separation by allowing the small organic droplets in the aqueous phase, to enter into the organic phase.

The phases were then disengaged very carefully. The metal-loaded organic phase was stripped with 4.0 M HCl with an O/A ratio of 2:1 for a period of 10 minutes.

The resulted aqueous phase was then analyzed for its cadmium content by an ICP-AES. All studies were carried out in duplicate. The standard deviation observed was always less than 2 %. The cadmium (II) concentration in the organic phase was obtained by mass balance. The distribution ratio, D, was calculated from the ratio of the equilibrium concentration of cadmium in the organic phase to that one in the aqueous phase. All the extraction and stripping experiments were carried out at ambient temperature ($25 \pm 1^\circ\text{C}$).

Results and discussion

Effect of equilibrium pH. The overall reaction in the extraction of metal cations by cationic extractants, as the case of D2EHPA, can be show as following:



Where M represents metal, for example the cadmium, RH is the molecule of D2EHPA, m metal valence, n the stoichiometric coefficient and subscripts (aq) and (org) refer to aqueous and organic phases, respectively.

The equilibrium constant is given by the following equation:

$$K_{eq} = \frac{[MR_2(RH)_{2n-2}]_{(org)} [H^+]_{(aq)}^m}{[M^{m+}]_{(aq)} [(RH)_2]_{(org)}^n} \quad (2)$$

This shows the influence of pH of aqueous phase on the reversible reaction of the complexation – decomplexation

process in solvent extraction system. Thus, distribution ratio of the metal ion depends on a number of variables such as equilibrium pH, solution composition, type of diluent, etc.

The effect of equilibrium pH on the cadmium extraction percentage in the initial pH range 1.0-6.0 is shown in Figure 1, where the D2EHPA concentration in the organic phase was 0.1 M. The data show that, the extraction of Cd (II) in the pH range of 5.0 to 6.0 is quantitative (because of hydrolysis of Cd (II) ion, the extraction in the higher pHs may not be precise). The highest value of the cadmium extraction percentage was attained at equilibrium pH 5.0 – 6.0. The optimum pH 5 was chosen for further studies.

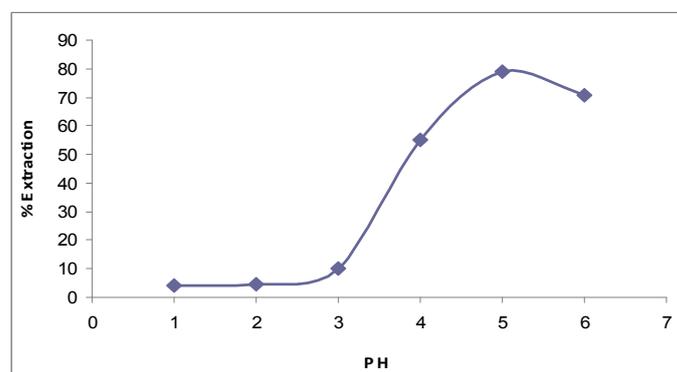


Fig.1- Extraction percentage of Cd(II) vs. pH in solvent extraction test ([Cd (II)]_{aq, in}=5 mg.L⁻¹; [D2EHPA]=0.1 M in toluene; T=25°C)

Effect of extractant concentration. The cadmium extraction with various concentration of D2EHPA in toluene was studied in the concentration range of 0.001 – 0.1 M. The other parameters such as, temperature, pH, contact time and type of the diluent were not changed. As shown in Table 1, for organic solution containing D2EHPA, it was observed that the percentages of cadmium extraction increase as the extractant concentration increases. The maximum cadmium extraction yield was obtained with 0.1 M D2EHPA in toluene.

Effect of various stripping phases. The cadmium doped D2EHPA, was stripped with HCl, HNO₃ and H₂SO₄ with equal concentration 4.0 M at O/A ratio of 2:1 for a period of 10 min. The obtained results are summarized in Table 2. About 83% of cadmium was transferred in to the aqueous receiving phase with using 4.0 M HCl. Thus, to attain quantitative stripping, 4.0 M HCl was used for this study.

Effect of contact time. The obtained results, reported on Figure 2 and Table 3, respectively, show that cadmium extraction.

With 0.1 M D2EHPA in Toluene the equilibrium obtained (maximum extraction in operating conditions) in

about 10 min, which means very fast complexation. The extraction percentage reached to a constant amount within 20 minutes, so all laboratory scale tests were

carried out within 20 minutes, in order to ensure the liquid equilibrium was reached.

Table 1- Results of solvent extraction tests at different D2EHPA concentrations in toluene.

Concentration of the extractant (M)	Extraction (%) of Cadmium
0.001	20.0
0.01	67.6
0.1	82.2

$[Cd(II)]_{aq, in} = 5 \text{ mg.L}^{-1}$; pH = 5, T=25°C

Table 2 - Results of cadmium stripping from the organic phase.

Acid	Concentration of the stripping solution (M)	Stripping ratio (%)
HCl	4.0	83.1
HNO ₃	4.0	33.4
H ₂ SO ₄	4.0	30.1

$[Cd(II)]_{aq, in} = 5 \text{ mg.L}^{-1}$; [D2EHPA]=0.1 M in toluene; T=25°C

Table 3. Cadmium extraction as a function of time.

30	25	20	15	10	5	(min)	time
76.8	76.9	76.7	76.9	76.5	74.2	Extraction (%)	Cd ²⁺

$[Cd(II)]_{aq, in} = 5 \text{ ppm}$; [D2EHPA]=0.1 M in toluene; pH=5, T=25°C

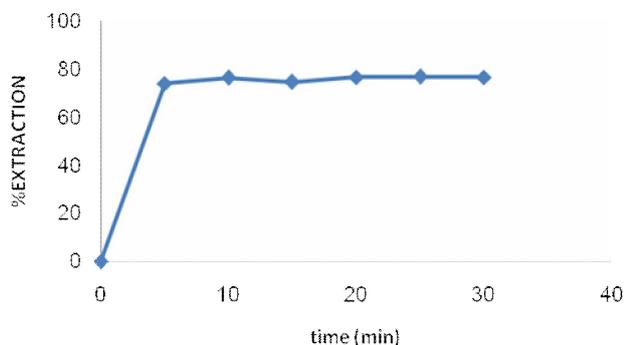


Fig.2- kinetics of cadmium extraction measured as extraction percentage. $[Cd(II)]_{aq, in} = 5 \text{ mg.L}^{-1}$; [D2EHPA] =0.1 M in toluene; pH = 5, T=25°C

Effect of temperature. The extraction of Cd (II) with fixed concentration of D2EHPA in toluene was studied in the temperature range of 278-318K. The experimental data show that the extraction percentages do not change significantly in the temperature range studied. It is also evident that the better extraction yield was achieved at

room temperature as shown in Table 4.

This unusual extraction behavior can be correlated with the strong complex formation between the metal ions and extractant that was stable in the organic phase. Consequently, all the experiments were carried out at room temperature (298 K).

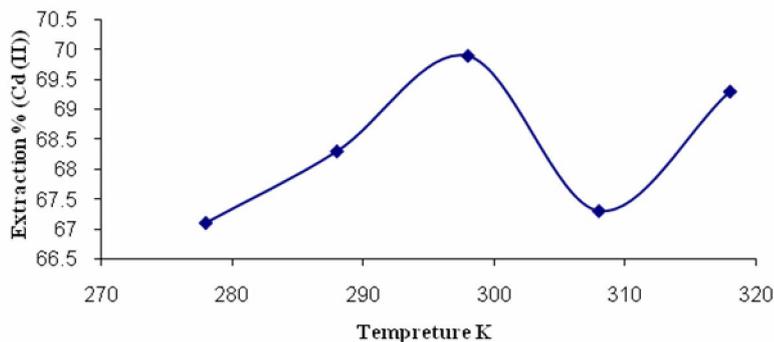


Fig. 3 – effect of temperature on Extraction of Cd (II)

Table 4. Effect of temperature on the extraction of Cd(II) with 0.1M D2EHPA in toluene.

318	308	298	288	278	(k)	T
69.3	67.3	69.9	68.3	67.1	Extraction (%)	Cd ²⁺

[Cd (II)]_{aq, in}=5 mg.L⁻¹; pH=5; T=25°C

Stoichiometry of extracted species. The results for extraction of cadmium (II) for various concentrations of D2EHPA are shown in Figure 3. The Stoichiometry of the probable extracted species was determined on the basis of slope analysis by plotting Log D versus Log [(HR)₂] graph. Where D is the distribution coefficient of cadmium in organic/aqueous phase and (HR)₂ is dimeric form of extractant. The plot has a slope of approximately 0.5. Consequently, cadmium is extracted from sulfate medium as a 1:2 metal / reagent complex.

Assuming that all D2EHPA molecules are present as dimers in toluene and therefore the extraction of divalent cadmium ion with D2EHPA is described simply as:

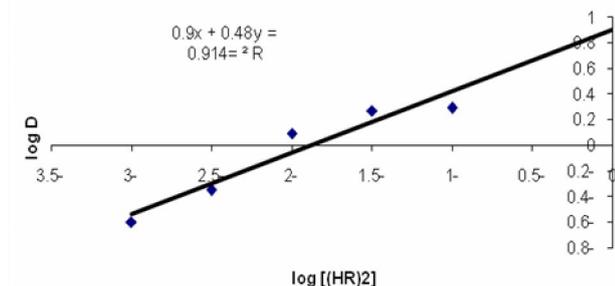


Fig.4- Slope analysis for the extraction of Cd²⁺ from sulfate medium, using different concentrations of D2EHPA in toluene.

Under the present experimental conditions the concentration of metal in the organic phase is negligible compared to the concentration of extractant. Thus, the distribution ratio of cadmium at constant pH with extractant was found to be independent of initial cadmium (II) concentration, indicating a mononuclear species under the experimental conditions. The extracted species is thus concluded to be CdR₂.2HR.

Applications. This method has been applied for determining of Cd (II) concentration in the Tadjan River's water (Sari-Iran) and Talar River's water (Kiakola-Iran).The Procedure has been applied as described above in pH = 4 and at room temperature .The measurements have been carried out by ICP-AES and in duplicate. The obtained results have reported in table 4. Note that the result of Cd (II) concentration in Tadjan River's water is much closed to the result indicated in a recent investigation²² .

Table 5. The amounts of Cd (II) in Tadjan and Talar River's water

Test water zone	Average value of Cd(II), μgL ⁻¹
Tadjan River's water	28.3
Talar River's water	32.2

Conclusion

The obtained results from this study can be summarized as following:

1. D2EHPA is shown to a cheap, good and stable extractant. It is more selective for recovery of cadmium (II) from sulfate media.
2. It should be noted that at pH 5, maximum extraction efficiency is obtained with 0.1 M D2EHPA in toluene.
This concentration of D2EHPA is less than the concentration of the other commercial extractants in the extraction processes.
3. D2EHPA extracts cadmium very rapidly. Equilibrium was reached within 10 min.

4. Cadmium (II) can be selectively stripped from doped organic phase with 4.0 M HCl at the 2:1 Volume ratio.
5. Better extraction of cadmium was achieved at room temperature and it is independent of the temperature variation; contrarily to the behavior of the other commercial extractants.
6. D2EHPA extracts cadmium (II) by a cation-exchange mechanism, and the stoichiometry of the extracted complexes with D2EHPA has been determined by slope analysis as a 1:2 metal/reagent complex, consequently, the species in the organic phase is $CdR_2 \cdot 2HR$.

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