periodica polytechnica

Chemical Engineering
55/2 (2011) 45–48
doi: 10.3311/pp.ch.2011-2.01
web: http://www.pp.bme.hu/ch

RESEARCH ARTICLE

Extraction of cadmium from phosphoric acid by trioctylphosphine oxide/kerosene solvent using factorial design

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Received 2011-01-11, accepted 2011-10-10

Abstract

Cadmium is present in all types of phosphates in concentrations ranging from 1 - 90 ppm. During digestion of phosphates by concentrated sulfuric acid to produce phosphoric acid by the wet method 70-80% wt of cadmium is transferred to the phosphoric acid while 20-30% wt remains in solid phosphogypsum. Cadmium is then transferred from the phosphoric acid to the fertilizers. Most environmental regulations try to reduce the percentage of cadmium in the fertilizers. Several studies were carried out to reduce the concentration of cadmium in phosphoric acid. Some used ion-exchange techniques. Others used liquid-liquid extraction by alkaline solvents such as trioctylamine (TOA). Several investigators used commercial phosphoorganic solvents such as Cyanex 302 and Cyanex 93. This paper studies the extraction of cadmium from phosphoric acid by trioctylphosphine oxide (TOPO) solvent in kerosene. The extraction was enhanced by the presence of Cl^- in the solution. The temperature had a negative effect on the extraction. Increasing the concentration of cadmium while keeping chloride ion concentration constant decreased the extraction. The extraction was increased by increasing the concentration of the phosphoric acid.

Keywords

Phosphoric acid · cadmium · extraction · factorial design ·

Acknowledgement

The author wishes to express his thanks to the General Director of the Atomic Energy Commission of Syria Dr Ibrahim Othman for approving and financing this project.

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1 Introduction

Cadmium is present in all kinds of phosphates in concentrations from 1 to 90 ppm. Cadmium is responsible for the disease called itai-itai which was caused by the presence of 1 mgL^{-1} cadmium in water in Japan. The effect is enhanced several times by the presence of copper and zinc. During the manufacture of phosphoric acid by the wet method most of the cadmium in the phosphate is transferred to the phosphoric acid and then to the fertilizers while 20-30% wt remains in the phosphogypsum. The distribution of cadmium between the acid and the solid phosphogypsum phase varies according to the operating conditions of the reactor, the process used for digestion and the properties of the crude phosphates used. It was found that increasing chloride ion concentration leads to increasing its transfer into the acid. In a sludge of phosphoric acid with a concentration of 30% wt P_2O_5 there were high concentrations of cadmium. Most environmental regulations state that cadmium should not exceed 20 ppm in the fertilizer. Cadmium in the fertilizer dissolves in water and is then transferred to the food chain [1]. Skorovarov stated that there is no relation between cadmium and uranium in the phosphates [2]. He pointed out that the best method to remove cadmium from phosphoric acid was by liquid-liquid extraction with trioctylamine (TOA) in kerosene. He extracted cadmium from a laboratory prepared phosphoric acid solution containing chloride ion. He deduced that cadmium in phosphoric acid was present in its chloride salt form. Almela [3] extracted cadmium II from a chloride medium with a concentration of 1 $molL^{-1}$ using the commercial Cyanex 302 in kerosene. He deduced that substituting 1 atom of oxygen by 1 atom of sulfur in the solvent enhances the extraction. Almela [4] in another work tested the distribution of Cd , Cr, Ti between phosphoric acid and the solvent p(1,1,3,3 tetra methyl butyl) phenyl phosphoric acid in kerosene at 20 ^{0}C. He found that at a concentration of $H_3PO_4 >$ 7 M the extraction increases in the following order:

$$Ti > Cr > Cd$$

While at a concentration of $H_3PO_4 < 5$ M the extraction increases in the order :

$$Cr > Cd > Ti$$

He also found that extraction increases by increasing Cd and solvent concentrations. Rickelton [5] examined the feasibility of removing cadmium from phosphoric and hydrochloric acids so as to produce an acid containing 0.5 mgL^{-1} of Cd. It is also known that trioctylphosphine oxide (TOPO) extracts cadmium from hydrochloric acid and not from phosphoric acid media. So the presence of Cl^- in phosphoric acid enhances the extraction of cadmium. He used Cyanex 93 which contains 93% wt TOPO. Elyayaoui [6] used ^{109}Cd in laboratory phosphoric acid media with concentrations less than 4 $molL^{-1}$ and at pH < 2.7 which are close to the real commercial phosphoric acid. He used di (2-ethyl hexyl) phosphoric acid (DEHPA) solvent in benzene with 2 $molL^{-1}$ concentration. He found that the distribution ratio of Cd (II) was very small compared with $Th^{4+}$and UO_2^{2+}. He deduced that Cd was present in its Cd^{2+} form at concentrations less than 4 $molL^{-1}$ while at higher concentrations 25% of the Cd was in the form of the complex $Cd(H_3PO_4)^+$. Reddy [7] extracted Zn^{2+} and $Cd^{2+}$from thiocynate solution with bis-2ethylhexyl sulphoxide (B2EHSO) in benzene using tracer studies. For comparison he extracted both ions by tri butyl phosphate (TBP). He pointed out that the extraction by B2EHSO was stronger than by TBP because of the increased alkalinity due to the S – O bond in the first solvent. Magda et al [8] used n-octanol solvent to purify wet commercial phosphoric acid. It was possible to remove all copper, cadmium and zinc by this method. Abdalbake et al [9] studied the precipitation of Cd, As and sulfate ions from phosphoric acid. Cd was precipitated by addition of sodium sulfide. They found that precipitation of Cd is increased by increasing the concentration of sodium sulfide. The precipitation of Cd decreased by increasing the temperature from 20 to 60 ^{0}C.

This paper investigates the extraction of Cd from phosphoric acid by TOPO/ kerosene solvent. The effect of temperature, concentration of phosphoric acid, concentration of cadmium and especially the influence of Cl^- on this extraction is studied.

2 Experimental

2.1 Materials

TOPO solvent from Fluka Co with $>$ 97.0% wt purity was used. A special kerosene from Pemco Chemical Ab with flash point of 76 ^{0}C at least and with aromatic content of 0.5% maximum was used as diluent. A laboratory phosphoric acid from Merck with 85% to 88 % wt H_3PO_4 was used. The acid was diluted with water to obtain a solution containing 28% wt P_2O_5. The cadmium with the required concentration was added in the form of $Cd(NO_3)_2.4H_2O$ from Merck with 99.0% wt purity minimum. KCl laboratory grade from Merck was added to obtain the required concentrations.

2.2 Apparatus and procedures

Extraction was carried out in vessels stirred by magnetic stirrers and placed in a thermostat vessel of 80 L volume to control the temperature. The mixture was stirred for 10 minutes to reach equilibrium and was allowed 30 minutes to separate. A sample of the phosphoric acid was analyzed before and after extraction by a polarograph Model 693(VA) Processor from Metrohm Co. The concentration of cadmium in the organic phase was calculated from material balance. The distribution ratio was calculated from the relationship:

$$D = [\mathrm{Cd}\ ]_{\mathrm{O}}/[\mathrm{Cd}\ ]_{\mathrm{A}} \qquad (1)$$

Where $[Cd]_O$ = Concentration of cadmium in the organic phase (mgL^{-1}) and $[Cd]_A$ = Concentration of cadmium in the aqueous phase (mgL^{-1}).

2.3 Design of experiment by factorial design

Experiments were carried out at 20 ^{0}C. The concentrations of cadmium, potassium chloride and phosphoric acid were chosen according to values shown in Table 1.

3 Results and Discussions

3.1 Extraction isotherm for Cd

The extraction isotherm for cadmium from phosphoric acid was determined using P_2O_5=28% wt , Cd =50 mgL^{-1} , KCl=0 gL^{-1} at 20 ^{0}C and different phase ratios. The solvent was 0.5 mol L^{-1} TOPO in kerosene . The results are presented in Table 2. These results are plotted in Fig. 1. The relation is of the form :

$$\mathrm{Y} = \mathrm{a}\ \mathrm{X}^{\mathrm{b}} \qquad (2)$$

Where X= Concentration of cadmium in the aqueous phase (mg L^{-1}) and Y= Concentration of cadmium in the organic phase (mg L^{-1}).

Tab. 1. Factorial design of extraction of Cd

[Cd] mgL^{-1}	[KCl] gL^{-1}	$[P_2O_5]$ %	D
50	10	14	2.65
10	10	14	19.66
50	50	14	9.32
10	50	14	91.59
50	10	28	12.22
10	10	28	99.00
50	50	28	51.08
10	50	28	332.33

Tab. 2. Isotherm of Cd extraction from phosphoric acid by TOPO solvent KCl=0 g L^{-1}

Phase Ratio A/O	7/3	3/7	1/4
X mgL^{-1}	48.5	47.1	46.2
Y mgL^{-1}	3.5	1.24	0.95

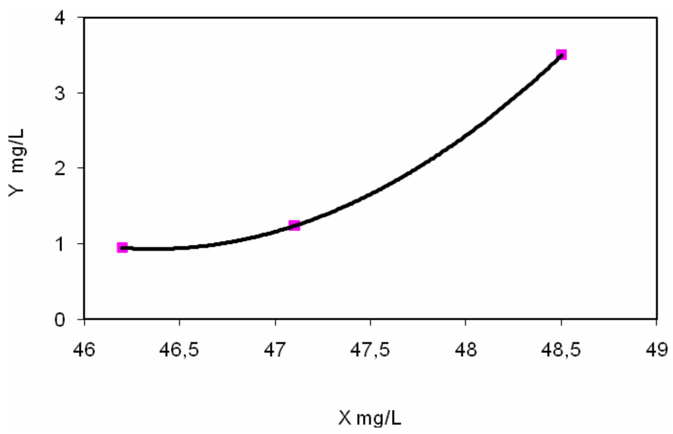

Fig. 1. Extraction isotherm for Cd from phosphoric acid P_2O_5=28% wt, Cd =50 mgL^{-1}, T= 20 ^{0}C, KCl=0 gL^{-1}, TOPO=0.5 $molL^{-1}$

3.2 Effect of temperature

To investigate the effect of temperature on the extraction of cadmium from phosphoric acid a solution was prepared from a laboratory phosphoric acid with the following concentrations (KCl=100 gL^{-1}, P_2O_5= 28% wt, Cd=50 mgL^{-1}). The phase ratio was fixed at O/A=1 and the concentration of TOPO in kerosene was kept at 0.5 $molL^{-1}$. The temperature of extraction was varied from 20 ^{0}C to 46 ^{0}C. The results are presented in Table 3. The data in Table 3 are plotted in the form of Log D versus 1/T K as in Fig. 2. The results fit a straight line of the form:

$$\text{Log D} = 1020 / T - 1.905$$

With correlation factor R^2 =0.9458

The Van't Hoff equation can be represented after integration in the form:

$$\ln D = a - \Delta H/RT \qquad (3)$$

Therefore the enthalpy for the reaction ΔH= – 19.52 kJ mol^{-1}.

It is obvious that temperature has a negative influence on the extraction efficiency of cadmium.

Tab. 3. Effect of temperature on extraction of Cd

T K	293.16	303.16	308.16	319.16
1/T K^{-1}	0.0034	0.0033	0.0032	0.0031
D	37.46	26.78	25.32	17.52
Log D	1.57	1.43	1.40	1.24

3.3 Effect of chloride ion on Cd extraction

The results from factorial design experiment in Table 1 were fitted to the polynomial:

$$D = 77.23 - 58.41X1 + 43.84X2 + 46.38X3 - 32.47X1 \cdot X2 - 33.59X1 \cdot X3 + 24.20X2 \cdot X3 - 17.28X1 \cdot X2 \cdot X3 \qquad (4)$$

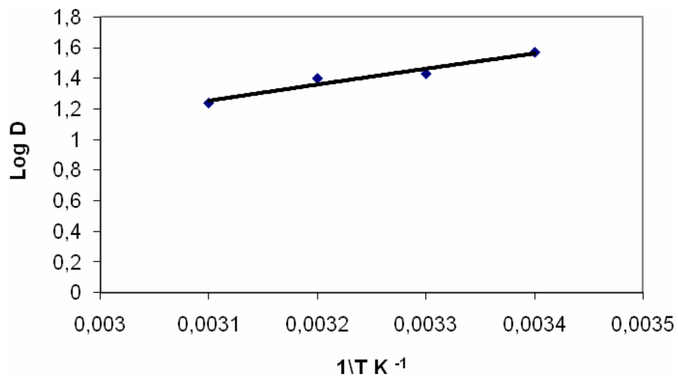

Fig. 2. Effect of temperature on extraction of Cd from phosphoric acid (P_2O_5= 28%wt , KCl=100 gL^{-1} , Cd=50 mgL^{-1} , [TOPO]=0.5 $molL^{-1}$, O/A=1)

Where

X1 = ([Cd]- 30) /20 or [Cd] = 20· X1 + 30,

X2 =([KCl] - 30)/20 or [KCl] = 20 · X2 + 30

X3 = ([P_2O_5]- 21)/7 or [P_2O_5]= 7 · X3 + 21

or

Data from Eq. (4) were plotted in Fig. 3 in the form of D *vs* [KCl] gL^{-1}. The results fit a straight line of slope 0.98 approximately. It is clear that extraction of Cd is enhanced by an increase in the concentration of [KCl]. This is in agreement with conclusions by other investigators [5]. This could be explained by complexion of Cd^{2+} with Cl^- before extraction according to :

$$Cl^- + Cd^{2+} = CdCl^+$$

$$CdCl^+ + Cl^- = CdCl_2$$

$$CdCl^+ + Cl^- + TOPO = CdCl_2.TOPO$$

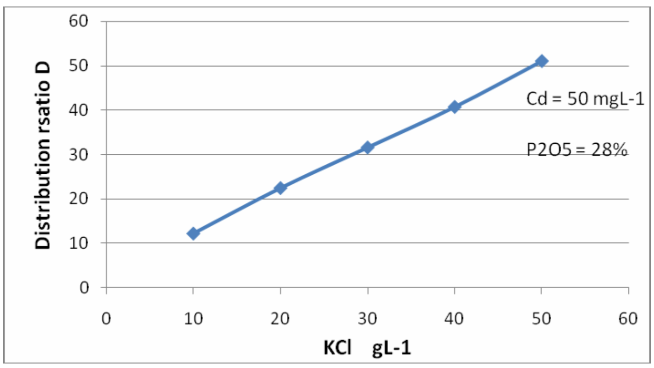

Fig. 3. Effect of Cl^- anion on Cd extraction. Cd= 50 mgL^{-1}. T=20 ^{0}C , P_2O_5=28%

3.4 Effect of P_2O_5 concentration on Cd extraction

Eq. (4) is plotted in the form of D *vs* [P_2O_5] % as shown in Fig. 3. The results fit a straight line with slope of 2.98. It is obvious that concentration of P_2O_5 has a strong positive influence on the extraction of Cd from phosphoric acid.

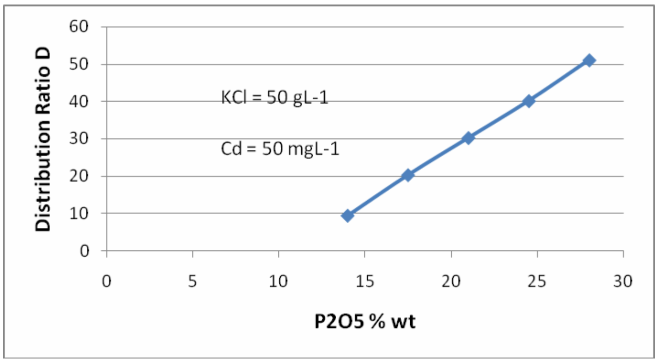

Fig. 4. Effect of P_2O_5 concentration on Cd extraction. Cd= 50 mgL^{-1}. T=20 ^{0}C , KCl=50 mgL^{-1}

3.5 Effect of Cd concentration on Cd extraction

Data from Eq. (4) is plotted in the form of D *vs* [Cd]. The results as shown in Fig. 5 are represented by a straight line with a slope of -7.03 approximately. It is clear that [Cd] has a strong negative influence on the extraction of Cd by TOPO/kerosene solvent.

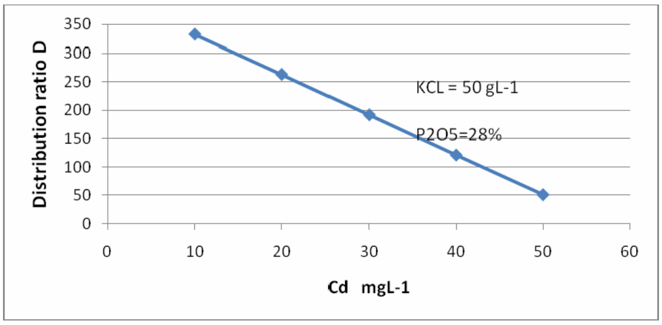

Fig. 5. Effect of Cd concentration on Cd extraction. KCl = 50 gL^{-1} , P_2O_5= 28%. T= 20 ^{0}C

4 Conclusions

From the results it is clear that cadmium in phosphoric acid could be extracted by TOPO solvent in kerosene diluent. The extraction is influenced by many factors :

- Temperature has a negative influence decreasing the extraction efficiency by increasing the temperature so it is better in practice to extract the cadmium after cooling the phosphoric acid.
- Presence of Cl^- in the acid has a positive influence on the extraction of Cd since it complexes with it. But this has no practical application since Cl^- in the acid is an impurity and it is not recommended to add extra Cl^- to it .
- The extraction of Cd is increased by increasing the concentration of phosphoric acid. So it may be better to extract the Cd using the hemihydrate method to produce the acid or after concentrating the acid in the dihydrate method. This is because the acid produced by the hemihydrate method has a higher concentration than the one produced by the dihydrate method .
- Extraction is influenced also by the concentration of Cd and it decreases by the increase of Cd concentration.

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