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Abstract

This study has investigated the solvent extraction of cadmium and lead ions from an aqueous solution in nitrate medium using aminooctyldiphosphonic acid (AODPA) as extractant in chloroform. In order to establish spectrophotometrically the concentration of metal ion in the aqueous phase before and after extraction, the Arsenazo III method was used. The effects of several extraction parameters on the extraction of these metals ions including volume ratio between the aqueous and organic phases (1–5), extraction kinetic time (0–30 min), molar ratio Q (1–5), addition of HNO_3 (pH =2–6), addition of KNO_3 (0.01 – 1M), temperature (10–40°C) and the synergetic effect by adding TOPO (solvating agent) were evaluated. Thermodynamic parameters including the Gibbs free energy (ΔG^0),enthalpy (ΔH^0), and entropy (ΔS^0) were calculated. Performed experiments showed that Pb (II) can be extracted till 73% when Cd (II) can be recovered completely after two cycles. The extraction of both metallic ions was spontaneous, endothermic and with a slight randomness. Positive synergetic effect was observed at a chelating agent/TOPO ratio of 3. It is a very encouraging result which can lead us to recover cadmium and lower the concentration of lead from wastewater.

Keywords

Aminooctylylphosphonic acid, solvent extraction, ion-exchange mechanism, Pb (II), Cd (II)

Introduction

The most rejected heavy metals are very polluting and dangerous. Lead and its inorganic derivatives are classified as category 2B (potentially carcinogenic to humans).[1] Lead modifies the cellular functioning by disrupting different physiological processes. It can thus cause blood anemia and renal effects (renal failure). Exposure to lead can affect the central nervous system (developmental delay, irritability, sleep disorders, loss of memory) and have long-term effects on fertility.[2] The effects of lead are generally amplified in the fetus and child (congenital abnormalities, persistent neurobehavioral deficits).[2,3] Cadmium, used in several industrial and agricultural processes as well as mining activities and designed carcinogenic by the United States (US) National Toxicology Program can increase the contamination of water and wastewaters around the world.[4,5] Cadmium can produce or increase the incidence of non-hereditary adverse effects in offspring.[6] Inhalation, ingestion or skin penetration, even in very small quantities, can cause irritation in the stomach, leading to vomiting and diarrhea, renal insufficiency and, at high doses, chronic bronchitis, fibrosis, emphysema, damage to the bone system, kidney stones and increased blood pressure.[7–10]

In order to eliminate or at least reduce the effects of these cations, many processes have been developed to face dangers towards human health and environment.

The use of the extraction process was widely used thus occupying a special place (for analytical purposes, in the processing of nuclear raw materials and in industries related to the fuel cycle). Solvent extraction consists of treating aqueous industrial waste before it is released into the environment. This process is a very efficient way of upgrading or rendering industrial wastes inert, and to treat discharges contaminated with lead and cadmium, and is generally aimed at recovering these metals, in order to reuse them and thus reduce their eco-toxicological impact.[11-13]

The aim of our work was to determine the optimal parameters, at which the extraction yield was maximum, of the solvent extraction of lead (II) and cadmium (II) from an aqueous solution in nitrate medium by a new chelating agent-aminooctyldiphosphonic acid (AAODMDP), dissolved in chloroform, synthesized under microwaves.[14]

Methods

Study design and setting

This study was conducted in April 2020 in our laboratory and LCMT Caen (France). The experimental procedure and metal cations analysis is detailed below. In brief after preparing aqueous and organic solutions, contact between the solutions was done. The two phases were separated gravimetrically, and 1 mL of aqueous solution was taken for UV/V analysis.

For synergetic effect, the organic phase was a mixture of our chelating agent (AODMDPA) and a solvating agent (tri octyl phosphine oxide) at different volume ratio.

Reagents and apparatus

The reagents used in this study (with supplier and catalogue number) were: Lead nitrate tetrahydrate Pb $(NO_3)_2$ $4H_2O$ (99%, Riedel De Haen, 10099-74-8), Cadmium nitrate tetrahydrate Cd $(NO_3)_2$ $4H_2O$ (99%, Riedel De Haen, 10022-68-1), Arsenazo III $C_{22}H_{18}AS_2N_4O_{14}S_2$ (99%, Aldrich, 216-788-6), Nitric acid (65%, Panreac, 7697 37 2), Acétic acid CH_3COOH (80%, prolabo, 64-19-7), Sodium Acétate CH_3COONa (98%, prolabo, 6131-90-4), Potassium nitrate KNO_3 (99%, Riedel De Haen, 7757-79-1),Chloroform $CHCl_3$ (99% Riedel De Haen, 67-66-3), Aminooctane $C_8H_{19}N$ (Aldrich, 111-86-4), Phosphorus acid (H_3PO_3, Aldrich, 13598-36-2), Hydrochloric acid (HCl, Riedel de Haen, 7647-01-0) , Formaldehyde (HCHO, Aldrich, 50-00-0), Acetone (C_3H_6O, Aldrich, 67-64-1), Tri octyl phosphine **o**xide TOPO (($C_8H_{17})_3$PO, 78-50-2) and aminooctyldiphosphonic acid (AODPA).[14] Microwave irradiations were performed using microwave oven Synthewave 402 (Prolabo) working at a frequency of 2450 MHz. Nuclear magnetic resonance (NMR) spectra were done on a Fourier Bruker AC multinuclear spectrometer. Ultraviolet–visible spectrophotometry (UV/Vis) spectra were obtained using the UV/Visdouble beam Optizen 3220UVspectrometer, a digital pH meter type Consort C863 to follow solution pH.

Synthesis and characterization of Aminooctyldimethylene diphosphonic acid[14]

A mixture of aminooctane ($C_4H_{11}N$) (4.96 mL, 30.0 mmol), phosphorus acid (H_3PO_3) (5.02 g, 60.0 mmol), water (3.0 mL) and hydrochloric acid (HCL) 37% (3.0 mL) was irradiated (in a microwave oven) in a glass cylinder reactor fitted with a cooler at 240 W for 2 min. After adding formaldehyde (HCHO) 37% (4.8 mL, 64.46 mmol) rapidly, the mixture was irradiated for 12 min at 240 W. After cooling and evaporation for 5 min, the precipitate was filtered and the white solid was washed with acetone and water.

The product had the following properties: Yield (92 %), mp > 240°C, Formula: $C_{10}H_{25}NO_6P_2$, ^{1}H NMR (D_2O, Na_2CO_3):1.07 (t, 3H, **CH$_3$**), 1.15 (m, 12H, **CH$_2$**), 3.2 (d, $^2J_{HP}$ = 9,01 NC**H$_2$**-P), 3.46 (m, 2H, N-C**H$_2$**); ^{31}P NMR (D_2O, Na_2CO_3): d/H_3PO_4 (ppm) s, 6.7; ^{13}CNMR (D_2O, Na_2CO_3): 19 (s, C1), 25.4 (s, C2), 27.3(s, C3), 31.7 (s, C3),

51 (d, 2JCP = 137.7, NCH$_2$-P); **IR** (υ Cm^{-1})**:** 2925(vasCH), 1333 (Deformation of (CH$_2$)$_n$: n > 4) 1120 (vs P-OH), 1044 (vs P=O), 938 (vsCm υ P-O) (s:symetric, as: antisymetric); pKa: 2.75, 8.73, 9.35, (9.67). These values indicated that in the water–acetone media, the first proton was strong and the other protons were weak.

Extraction procedure

After dissolving aminooctyldiphosphonic acid in chloroform, the obtained organic solutions were used for extraction studies. Aqueous metal solutions were prepared by dissolving Pb (NO$_3$)$_2$ 4H$_2$O and Cd (NO$_3$)$_2$ 4H$_2$O in distilled water. The first stage consisted of achieving curves of standardization of the absorbance according to the concentration of Pb^{2+} and Cd^{2+}. The concentrations were in the range 10^{-6}-10^{-3} mol. L^{-1}. Pb^{2+} and Cd $^{2+}$ analyses in the aqueous phase after extraction was performed by the Arsenazo III spectrophotometric method which consists of using this chromogenic reagent to form ion-arsenazo III complex. After separation of the organic from the aqueous phase, Arsenazo III was added to the later to form Arsenazo-Ion complex, which was placed in a quartz cuvette after adjusting the aqueous solution pH with buffer solution. The absorbance was learnt at λmax = 610 nm for Pb^{2+} (pH = 4)[15] and λmax = 600 nm for Cd^{2+} (pH = 9.5),[16] the second stage involved optimizing factors of extraction. The volume ratio Vaq/Vorg (the two phases: aqueous and organic; were mixed with different volumes) was carried out to establish the optimal yield of extraction and avoid emulsions, followed by the extraction kinetics (the two phases were stirred for different time). This was carried out to determine the necessary optimal time to reach the extraction equilibrium and for which the yield is maximal. The effect of different concentrations of the extractant (10^{-3}M - 10^{-6}M) on the extraction of the metallic ions was studied. The effect of the ionic strength (a salt (KNO$_3$) was added to the aqueous phase) and medium acidity (adding an acid (HNO$_3$) to the aqueous phase at a specific pH) were investigated adding salt or acids to aqueous solutions respectively. Synergetic effect was investigated by adding a solvating agent (Tri octyl phosphine oxide) to the chelating agent (AODPA) in the organic phase then determine the synergetic coefficient.

Results and discussion

In order to easily determine the different extraction factors, emulsions must be avoided. The distribution coefficient, D, and the extraction yield, Y, defined as follows,[10] will be used to discuss the extraction results:

$$D = \frac{Abs_{org}}{Abs_{aq}} = \frac{Abs_i - Abs_f}{Abs_f} \tag{1}$$

$$Y\% = \frac{Abs_{org}}{Abs_{aq}} = \frac{Abs_i - Abs_f}{Abs_i} \times 100 \tag{2}$$

With the variables being as follows: Ab$_i$, Ab$_f$ are the initial and final absorbance of aqueous solutions before and after extraction respectively.

Stirring speed effect

A parameter that appeared essential is the effect of the stirring speed. We noted that a medium stirring speed gave the highest extraction yield for both cations (Figure 1 and 2).[27] This can be explained by the fact that at the lowest speed, and
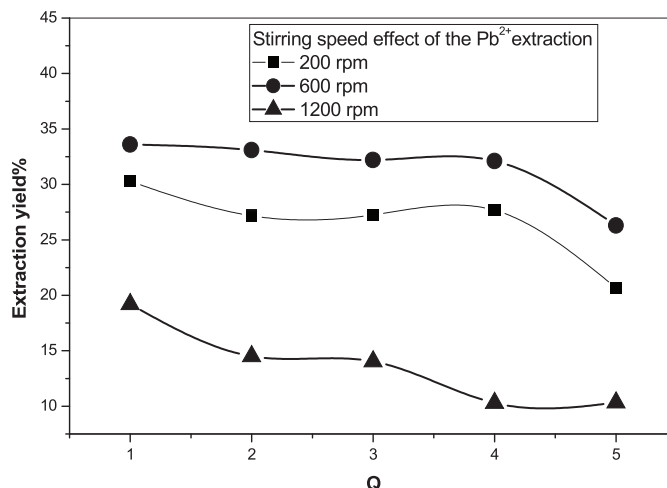

Figure 1. Stirring speed effect on Lead extraction. [Pb^{2+}] = 5 × 10^{-4} M, Vaq/Vorg = 1, T = 25°C. rpm = rotations per minute.
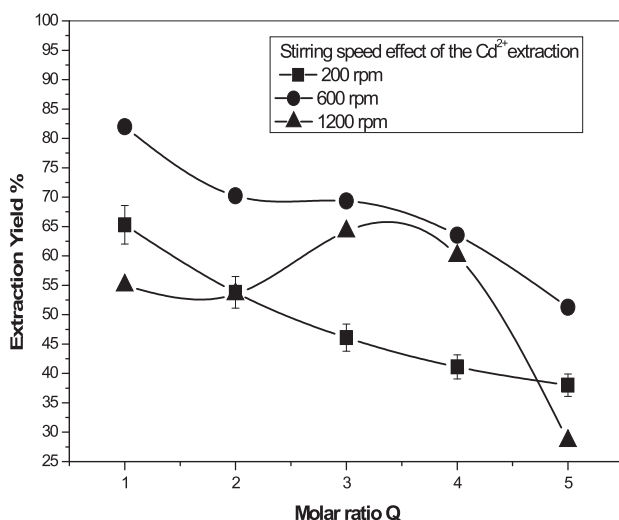
Figure 2. Stirring speed effect on Cadmium extraction. $[Cd^{2+}] = 5 \times 10^{-4}$ M, Vaq/Vorg = 1, T = 25°C.
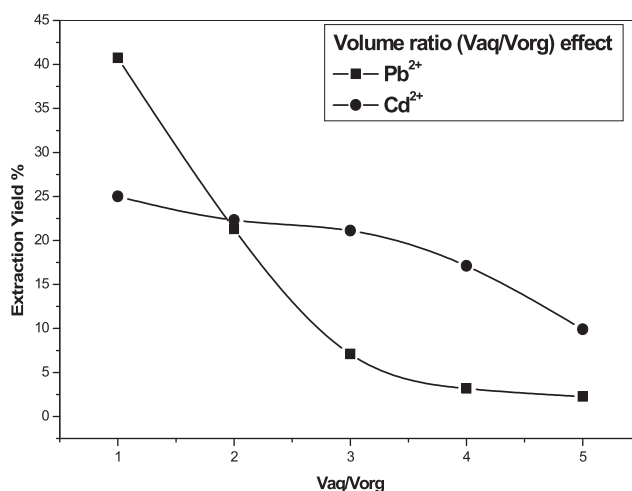

Figure 3. Effect of volume ratio on extraction yield of Cd^{2+} and Pb^{2+}. Organic phase [AODMDPA] = M, $[Cd^{2+}]$ = $[Pb^{2+}]$ = M, 600 rpm, T = 25°C.

taking into account the ionic radius of Pb^{2+} or Cd^{2+}, the mass transfer is not favored. Also, at the highest stirring speed, the two cations seemed to be des-extracted which will help us in the des-extraction process.

Aqueous to organic phase volume ratio

The effect of volume ratio on the extraction yield of Pb^{2+} or Cd^{2+} was investigated using lead and cadmium nitrate aqueous solutions of 5×10^{-4} M. A concentration of 10^{-3} M of the organic phase was prepared by dissolving aminooctyl diphosphonic acid in chloroform. The results are indicated in Figure 3.

A volume ratio of 1 (which gave the maximum extraction yield) was used in the following experiences since the best-obtained yield of 40% and 25% were obtained, under this ratio, for Pb (II) and Cd (II) respectively. It is observed from Figure 3 that the higher the volume ratio, the lowest yield was, caused probably by a repulsion effect between the metal ions.

Extraction kinetics

The extraction kinetics results are shown in Figure 4. The variation of the stirring time between 0 and 30 minutes showed that the maximum yield of 32% was obtained for Pb^{2+} after 15 minutes, and 10 minutes was necessary for the Cd^{+2}. Thus, Pb^{2+} has greater resistance to mass transfer than Cd^{2+}. This can be explained according to the atomic properties of the ionic radius of lead (1.2 A°) compared to that of cadmium (0.97 A°)
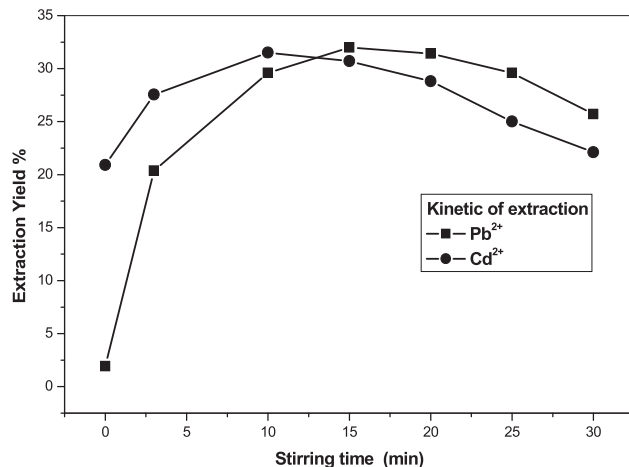
Figure 4. Kinetic of extraction of Lead and Cadmium, [AODMDPA] = M. $[Pb^{2+}] = [Cd^{2+}] = 5 \times 10^{-4}$ M, (Vaq/Vorg) = 1, 600 rpm, T = 25°C.
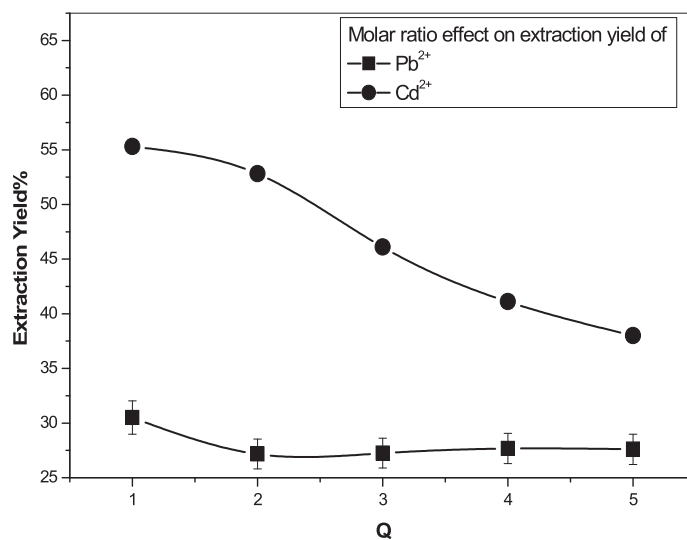
Figure 5. Molar ratio effect on the extraction of Lead and Cadmium as function of Q. $[Pb^{2+}] = [Cd^{2+}] = 5 \times 10^{-4}$ M, Vaq/Vorg = 1, 600rpm, T = 25°.

Molar ratio effect

The molar ratio, Q, was used to investigate the extraction yield of the two metal ions. It is expressed as:

$$Q = \frac{n_{\text{extractant}}}{n_{\text{metal ion}}}$$

It can be seen in Figure 5, that the extraction of the two metal cations decreases with increasing AODMDPA concentration in the organic phase. The best extraction yields obtained were 55 % and 32% for Cd^{2+} and Pb^{2+} ions, respectively, at a molar ratio Q = 1.

Ionic strength measures the electric field tension in a solution. To verify the influence of ionic strength on the output of extraction, we modified the aqueous phase by the addition of KNO_3 and HNO_3.

Influence of the addition of potassium nitrate (KNO₃)

The concentrations of KNO_3 were taken equal to 0.01 M, 0.1 M and 1 M. The obtained results are shown in Figures 6 and 7. According to the results, we found that there was an increase in the extraction yield of Pb^{2+} ions whatever the quantity
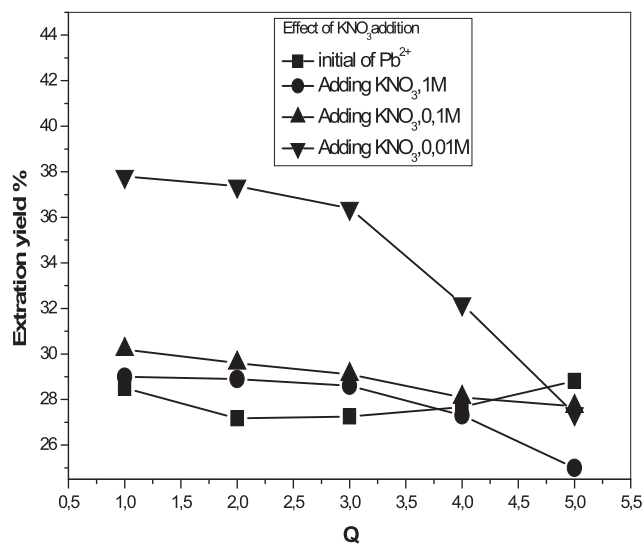
Figure 6. Evolution of the extraction yield of Lead according to Q with the addition of potassium nitrate KNO$_3$.
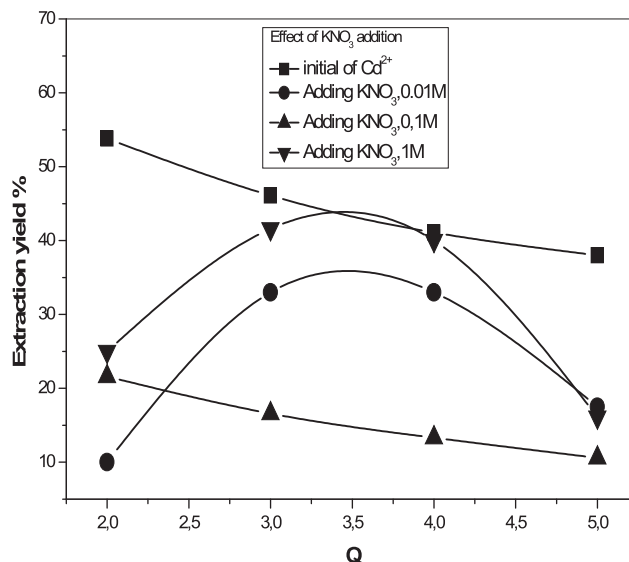[Pb^{2+}] = 5×10^{-4} M, Vaq/Vorg = 1, T = 25°C.

Figure 7. Evolution of the extraction yield of Cadmium according to Q with the addition of potassium nitrate
KNO$_3$. [Cd^{2+}] = 5 × 10^{-4} M, Vaq/Vorg = 1, T = 25°C.

of KNO$_3$ added to the system. A higher extraction percentage of lead ions in the presence of potassium nitrate can be attributed to the formation of stable complexes of Pb^{2+} in the aqueous phase in the presence of the latter salt.[17] However, Additions of KNO$_3$ reduce the extraction yield in the case of Cd^{+2}. This may be due to the competition between Cd^{2+} and K$^+$ ions, which is in accordance with the literature.[18]

Influence of the addition of nitric acid (HNO$_3$)

The effect of nitric acid addition to the aqueous phase before extraction was investigated, in the range of pH 2 – 3, on the extraction of 5×10^{-4} M of metallic cations. The results are shown in Figures 8 and 9. It was noted that the acidic medium disadvantages the lead ions extraction whereas, that of cadmium ions was seen to be favoured. Similar results were obtained in previous papers.[19,20]
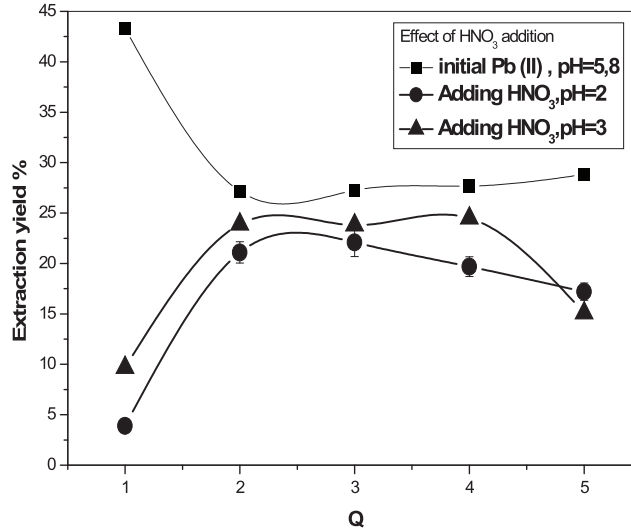
Figure 8. Evolution of the extraction yield of Lead according to Q with the addition of HNO_3. $[Pb^{2+}] = 5 \times 10^{-4}$ M, Vaq/Vorg = 1, T = 25°C.
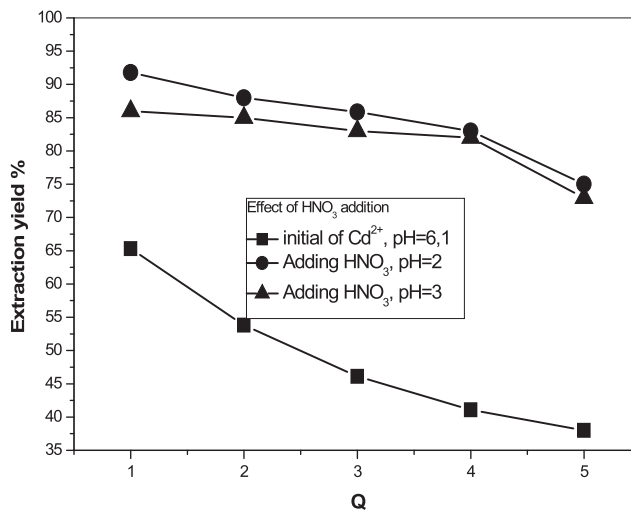
Figure 9. Evolution of the extraction yield of Cadmium according to Q with the addition of HNO_3 - $[Cd^{2+}]$ = 5×10^{-4} M, Vaq/Vorg = 1, T = 25°C.

Second extraction step

Another important variable affecting lead and cadmium recovery was studied. In Figures 10, 11, other extraction steps were realized. It was noted that Cd^{2+} can be recovered completely when Pb^{2+} reached 73% after two steps.

Temperature effect

The extraction yield was studied in the range of 10 to 40 ± 1°C. The results are given in Figure 12.

From Figure 8, it noticed that an increase in the temperature from 10°C to 40°C favoured extraction yield. It allows us to predict the Pb^{2+} and Cd^{2+} des-extraction at high temperatures. This may be associated with the increase in the release of water molecules upon dehydration of ions during extraction. This is in good agreement with the results found in the literature.[21,22]

Thermodynamic parameters calculation

Plots of the ln K values as a function of the inverse temperature [1/T (K)] in the range 283–313 K gave a straight line (Figure 13). The thermodynamic parameters can be determined by the following expressions[23]:

$$\Delta G^o = -RT \ln K \tag{1}$$

Figure 10. **Evolution of the yield according to the second cycle of Lead by AODMDPA.** $[Pb^{2+}] = 5 \times 10^{-4}$ M, Vaq/Vorg = 1, T = 25°C.
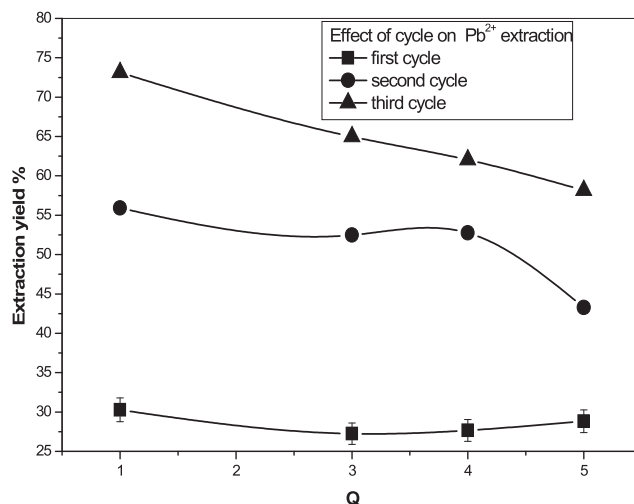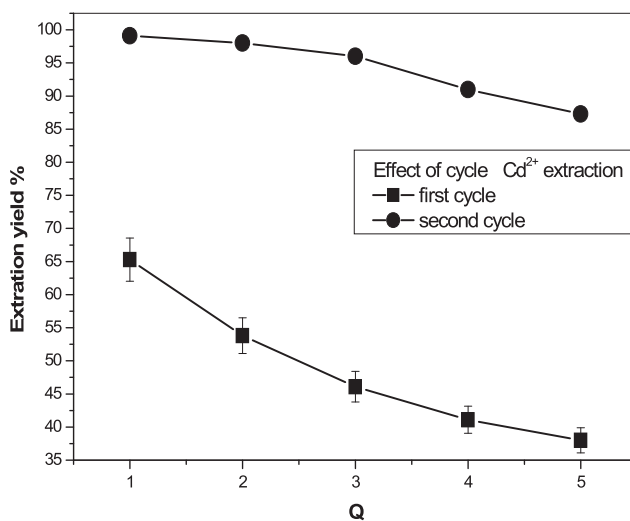

Figure 11. Evolution of the yield according to the second cycle of Cadmium by AODMDPA. $[Cd^{2+}] = 5 \times 10^{-4}$ M, Vaq/Vorg = 1, T = 25°C.
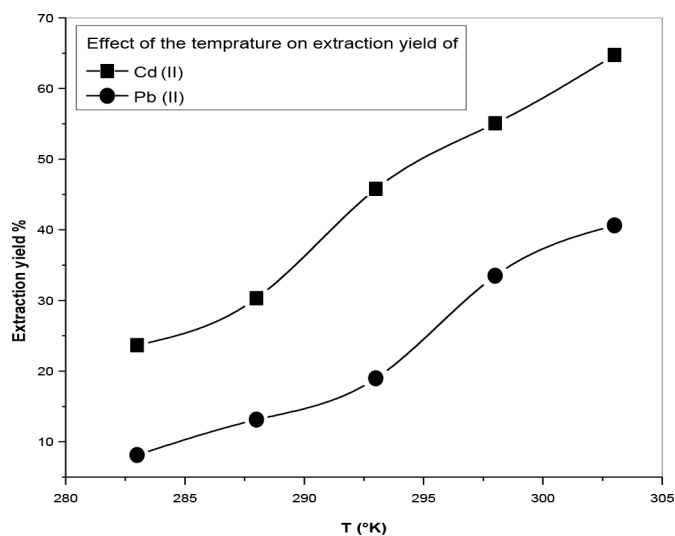

Figure 12. Effect of temperature of the extraction yield of Lead and Cadmium, [AODMDPA] = 10^{-3}M $[Pb^{2+}]$ = $[Cd^{2+}] = 5 \times 10^{-4}$ M, (Vaq/Vorg) = 1.
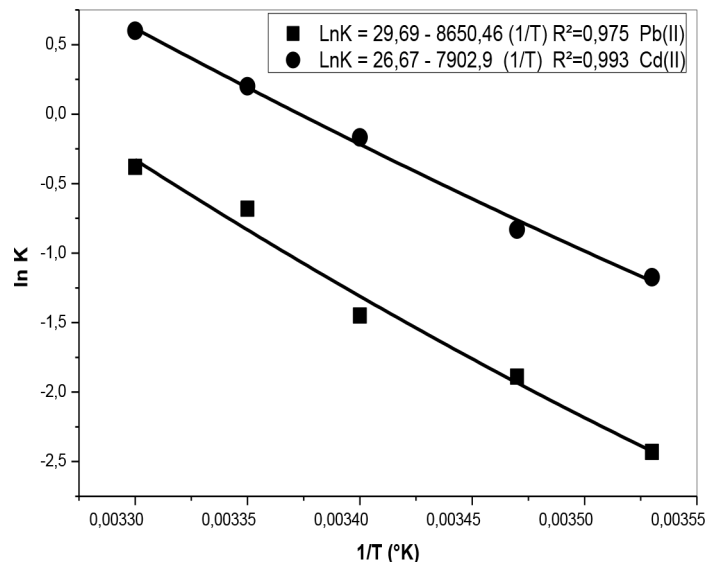
Figure 13. Variation in Ln Kin function 1/T for Lead and Cadmium extraction with AODMDPA.

Table 1. Thermodynamic parameters of the lead and cadmium at 298 K.

Cation	$\Delta G°$ (Kcal/mol)	$\Delta H°$ (Kcal/mol)	$\Delta S°$ (Cal/mol.K)
Pb^{2+}	− 0.526	+ 17.30	+ 59.82
Cd^{2+}	− 0.091	+ 15.80	+ 53.34

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{2}$$

From these equations (1) and (2) we pull the following equation (3) to calculate $\Delta H°$ and $\Delta S°$ while drawing the curve LnK according to the temperature.

$$\text{Ln K} = \Delta S^o/R - \Delta H^o/RT \tag{3}$$

The numerical values of ΔH^0, ΔS^0 are computed from the slope.[24] The negative value of Gibbs free energy as shown in Table 1 indicates the spontaneous nature of extraction, while positive value of ΔH^0 reflects the endothermic extraction behavior. The positive value of ΔS^0 may be due to the increase in randomness around the chelating function.[25]
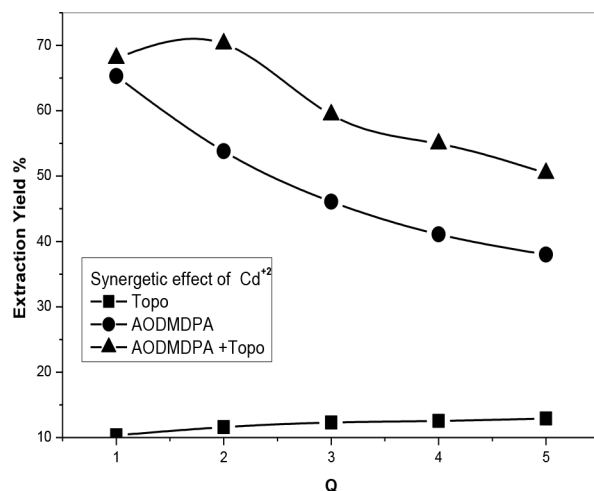

Figure 14. Synergetic effect of the extraction yield of Cadmium according to Q. $[Cd^{2+}] = 5 \times 10^{-4}$ M, (Vaq/Vorg) = 1; (AODMDPA: TOPO = 3: 1), T = 25°C.
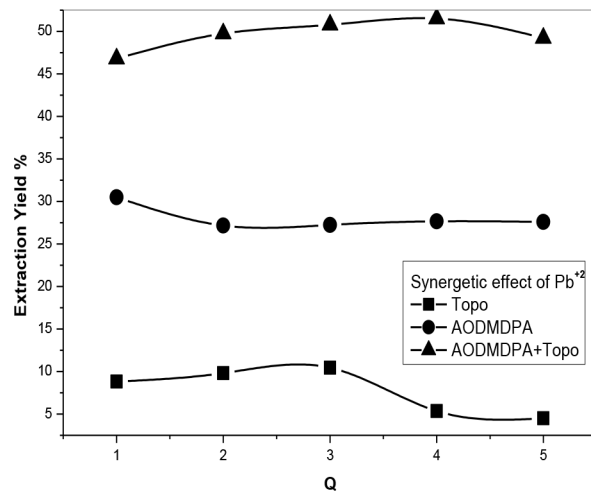
Figure 15. Synergetic effect of the extraction yield of Lead according to Q. $[Pb^{2+}] = 5 \times 10^{-4}$ M, (Vaq/Vorg) = 1; (AODMDPA: TOPO = 3: 1), T = 25°C.

Table 2. Different synergetic coefficients of Tri octyl phosphine oxide and phosphonic Acid (TOPO/AODMDPA) according to molar ratio Q. Q: molar ratio Q_1: Q = 1, Q2: Q = 2, Q3: Q = 3, Q4: Q = 4, Q5: Q = 5. D_1: Distribution factor using TOPO alone. D_2: Distribution factor using AODMDPA alone. S: Synergetic factor $S = \log \frac{D_{1+2}}{D_1+D_2}$.

Cation	Molar ratio Q	Q1	Q2	Q3	Q4	Q5
Pb (II)	**D_1** TOPO	0.096	0.108	0.116	0.056	0.047
	D_2 AODMDPA	0.44	0.377	0.375	0.383	0.381
	D_{1+2} (AODMDPA +TOPO)	0.879	0.989	1.031	1.063	0.969
$S_1 > 0$ (positive synergy)		**0.214**	**0.309**	**0.322**	**0.384**	**0.354**
Cd (II)	**D_1** TOPO	0.115	0.131	0.140	0.143	0.148
	D_2 AODMDPA	1.882	1.164	0.885	0.699	0.614
	D_{1+2} (AODMDPA +TOPO)	2.130	2.363	1.461	1.220	1.017
$S_2 > 0$ (positive synergy)		**0.028**	**0.26**	**0.166**	**0.161**	**0.125**

Synergetic effect

In order to study the synergetic effect, Tri octyl phosphine **o**xide TOPO (solvating agent) was added to our extractant (chelating agent) at 298 K. The synergetic coefficients were obtained as described by M. Taube and al.[26]

Different phosphonic/TOPO volume ratios were tested presenting negative coefficients maybe because of steric and competition phenomena in the organic phase. The best synergetic coefficient was obtained at a phosphonic acid/TOPO volume ratio of 3 (Figures 14 and 15). The synergistic enhancement is attributed to the formation of complexes with the two extractants. Different positive synergetic coefficients are gathered in Table 2 showing that whatever the molar ratio, a positive synergetic coefficient was obtained.

Conclusion

A new phosphonic acid extractant named aminooctylphosphonic acid easily synthesized under microwave using low-cost chemicals. Complete achievement of Cd^{2+} can be reached when Pb^{2+} extraction reaches 73% after two cycles. A positive synergetic effect was observed at an AODMDPA/TOPO ratio of 3. It is a very encouraging result that can lead us to recover Cd^{2+} and lower the concentration of Pb^{2+} from wastewater.

Data availability

Open Science Framework: Spectrophotometric study of Solvent extraction of Pb (II) and Cd (II) by aminooctyldiphosphonic acid. https://doi.org/10.17605/OSF.IO/FMHT4.[27]

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