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AN INTEGRATED PROCESS FOR THE REMOVAL OF Cd AND U FROM WET PHOSPHORIC ACID.

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ABSTRACT

The application of fertilisers in intensive agriculture may cause some problems. Among others, the release of heavy metals contained in the phosphate fertilisers. Cadmium and Uranium are considered as special concern. Cd levels in agricultural soils have increased over the years and in some regions cadmium intake in food is approaching recognised limits of safety. U causes environmental problems due to its radioactive properties and for the same reason it is a strategic element with a high inherent value.

In this work, an integrated process based on the application of two membrane technologies for the selective recovery of the U and the Cd contained in wet phosphoric acid is presented. The process is based on the removal of U by ion exchange using the Purolite S940 resin as ion exchange resin followed by the selective removal of Cd by means of membrane assisted solvent extraction with Aliquat 336 as selective extractant. Working with acidic solutions containing initially 200 mg/l of U and 50 mg/l of Cd, the viability of the process for reduction of the U and Cd concentration below 2 mg/l has been confirmed and a simplified flow diagram of the integrated process for the removal of U and Cd from wet phosphoric acid, specifying inlet and outlet concentrations and the values of the design parameters is included.

This work is a partial result of the EC project entitled *Membrane Recovery of Metal Pollutants from Waste Waters of the Fertilizers Industry (MERMEP)* financed by the Avicenne Programme, with the objective of the research and development of five different membrane-based separation processes for the selective removal and recovery of heavy metals contained in acidic streams of the fertilisers industry. The participants in the project are: Universidad de Cantabria (Spain), Non-Dispersive solvent extraction; Atomic Energy Authority of Cairo (Egypt) Supported Liquid Membranes; Imperial College of Science, Technology and Medicine (U.K.), Emulsion liquid membranes; The Hebrew University of Jerusalem (Israel), Hybrid liquid membranes and EGE University (Turkey), Solid ion exchange membranes.

1. INTRODUCTION

The application of fertilisers can increase agricultural yields extraordinarily. However, intensive fertilisation brings other problems. Among others, the obtention process of wet phosphoric acid from the phosphate rock is accompanied by the solubilization of the major part of the heavy metals and radionucleides contained in the rock (Cd, U, Ni, Pb, Zn, Cr, Cu,…) due to the attack with sulphuric acid. Their content depends on the nature of the phosphate ore, which varies considerably from source to source. This process produces phosphoric acid that must be purified and concentrated for most uses.

Two elements have been considered of special concern, i) Cd that has been distinguished as a very dangerous substance because of its toxicity, persistence, bioaccumulation and carcinogenicity, and ii) uranium that causes environmental problems due to its radioactive properties and for the same reason it is a strategic element with a high inherent value.

Concerning the former, aware that cadmium levels in agricultural soils have been increasing over the years and in some regions that cadmium intake in food is approaching recognised limits of safety, several cadmium removal methods from phosphates and phosphoric acids has been investigated to reduce drastically the amount of Cd in the fertiliser. In this way, several techniques for the removal of cadmium from phosphoric acid are referred in literature, i.e., precipitation, flotation, ion exchange and liquid-liquid extraction (Hodge and Popovici, 1994, Hutton, 1983). Recently, non-dispersive solvent extraction has been shown as an alternative to the conventional extraction. (Hodge and Povonici, 1994; Alonso et al., 1997).

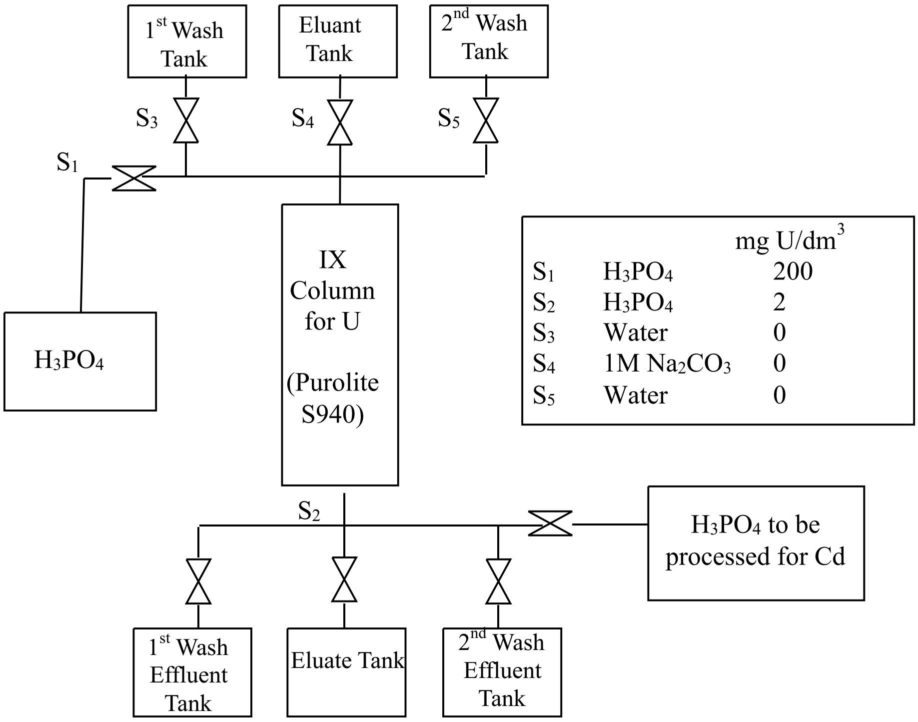
Uranium is found in natural phosphates in the concentration range 0.005%-0.02% U (Alonso et al., 1997). It was reported that 6.34 million tonnes of uranium exist in phosphates throughout the world (Naden and Streat, 1984). Several processes have been investigated for the recovery of uranium from wet process phosphoric acid. The first industrial trials were based on solvent extraction (Hurst and Crouse, 1971, 1972, 1973,1976, Hurst et al., 1974, Boin, 1985, Kouloheris, 1985). Later, ion exchange processes using the solvent-containing polymeric resins have been also tested (Gonzalez-Luque, 1982, Ketzinel et al., 1985). The aminomethylphosphonic resin Duolite ES 467 was found selective for the recovery of U from wet-process phosphoric acid (Gonzalez-Luque, 1982, Gonzalez-Luque and Streat, 1983a, 1983b, 1984). Kabay et al., 1998, published a study on the application of several chelating resins containing phosphonic or phosphinic groups to the recovery of U from phosphoric acid solutions. It was shown that the aminomethyl phosphonic resin Purolite S940 gives a promising sorption/elution behaviour working in small column extractions of U from phosphoric acid solutions.

Considering the importance of the removal of the referred elements from the phosphoric acid, this work presents an integrated process for the removal of Cd an U from wet phosphoric acid based on the application of two membrane processes, i.e., ion exchange resin, SIX, for the removal of U followed by non-dispersive solvent extraction, NDSX, for the removal of Cd.

2. EXPERIMENTAL

2.1. Removal of Uranium

The resin Purolite S940 (Purolite International Ltd., UK) used as ion exchange membrane contained aminomethylphosphonic acid as functional groups. Synthetic phosphoric acid solutions were prepared from 85% *o*-phosphoric acid. $UO_2(NO_3)_2.6H_2O$ (Merck) was added to the acidic samples. In the sorption studies phosphoric acid solutions (40%) containing $UO_2(II)$ (0.01 M) were delivered downward to the column at a flow rate of 10 bed volumes per hour. The breakthrough curves were obtained by analysis of successive fractions of the effluent. The columnar elution profiles of U were performed at a flow rate of 5 bed volumes per hour using 1 M Na_2CO_3 solution. Similar column sorption studies were performed using industrial phosphoric acid produced by the Turkish company Gubretas Co. (P_2O_5: 28-30%) with a uranium content of 135 mg/l following a preliminary filtration of acid through activated carbon, in order to validate the results previously obtained with synthetic acidic samples. The determination of U in the solutions were performed spectrophotometrically. Figure 1 shows a schematic diagram of the removal of U with resin Purolite S940.



		mg U/dm^3
S_1	H_3PO_4	200
S_2	H_3PO_4	2
S_3	Water	0
S_4	1M Na_2CO_3	0
S_5	Water	0

Figure 1: Schematic view of the experimental set-up for the removal of U.

2.2. Removal of Cadmium

Phosphoric acid kindly supplied by Fertiberia S.A. (Spanish company) was used as feed solution. The concentration of metals in the industrial grade phosphoric acid (Table 1) was analysed using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP). The initial content of cadmium in the industrial grade phosphoric acid was 1.42 x 10^{-4} M (16 mg/l). This concentration was increased to 50 mg/l in all experiments, by addition of $CdSO_4 \cdot 8/3H_2O$ (AnalaR, Probus).

Table 1. Metallic content in the industrial grade phosphoric acid of Fertiberia

Metal	Wavelength (nm)	Detection limit (mg/l)	Concentration (M)
Cd	214.4	0.08	1.4 x 10^{-4}
Cr	205.6	0.2	56 x 10^{-4}
Cu	326.7	0.18	5.3 x 10^{-4}
Fe	238.2	0.15	360 x 10^{-4}
Ni	231.6	0.34	8.7 x 10^{-4}
Pb	220.4	1.43	0.3 x 10^{-4}
Zn	213.9	0.06	51.2 x 10^{-4}
U*	665	0.005	5.6 x 10^{-4}

* Determined with Arsenazo III using a Jasco spectrophotometer.

The extractant phase was a solution of Aliquat 336, a quaternary ammonium salt supplied by Henkel and used without further purification. Kerosene was used as diluent and isodecanol (Exxon) was added as modifier. Equal quantities in volume percentage of extractant and modifier, 30%, were added to the organic phase.

Cadmium phosphate in the phosphoric acid phase reacts with Aliquat 336 in its chloride form to generate a metal-extractant complex species in the organic phase (Urtiaga et al., 1999). The regeneration of the extractant was performed using water as stripping agent and therefore the Aliquat 336 was regenerated as its hydroxide form while cadmium chloride and some phosphoric acid were released into the aqueous stripping phase. A third step, equilibration step, was needed to convert the Aliquat hydroxide to the chloride salt needed for the extraction process, that was performed by contacting the organic phase with hydrochloric acid, 1M (Probus).

Figure 2 shows a schematic view of the experimental system for the removal of cadmium with Aliquat 336. Three modules of hollow fibres were used, one for the extraction, one for the stripping and the third one for the total regeneration of the Aliquat 336. The feed phosphoric phase and the stripping phase flowed in a continuous mode. The organic extractant phase was in a closed circuit flowing through the extraction, stripping and equilibration modules.

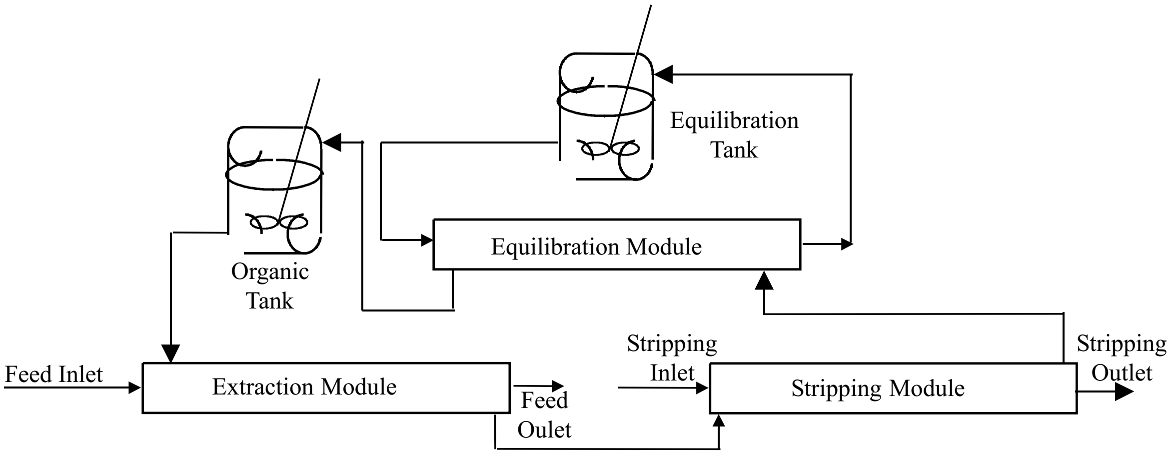


Figure 2: Schematic view of the experimental set-up for the removal of Cd.

3. RESULTS AND DISCUSSION

3.1 Removal of U by ion exchange resins

It was reported that chelating resin Purolite S940 containing aminomethylphosphonic acid groups gave promising sorption/elution behaviour for uranium recovery from phosphoric acid solution (Kabay et al., 1998). The investigation of kinetic behaviour of the resin for uranium removal from phosphoric acid solution has been performed by several kinetic models (Ortiz et al., 1999).

For the design of an ion exchange column, the Thomas solution was used to find both *K* and *ka* fitting parameters to obtain more dependable and descriptive design data (Ortiz et al., 1999). Column sorption of UO_2(II) from phosphoric acid by the resin Purolite S940 was reported before (Kabay et al, 1998). In this study we used the breakthrough data (in 1, 3 and 6 M H_3PO_4) given in that report to get the fitting curves and design data. The parameters *K* and *ka,* ranging between 0.01 and 10, were used in the model of the Thomas solution. The sum of the square deviations between the experimental and calculated values of concentrations was found for the pairs of *K* and *ka* scanned. The optimum pair of parameters was taken as the one giving the minimum value for the sum of the square deviations. Thus, the mass action law constants *K* were obtained as 1, 1 and 1 for 1, 3 and 6 M H_3PO_4, respectively. Corresponding values of mass transfer coefficients *ka* were found as 0.05, 0.02 and 0.02 cm^3sln/cm^3bed.sec. Figures 3-5 show the breakthrough and fitting curves of uranium using these optimum values of the parameters, observing a satisfactory description of the experimental behaviour.

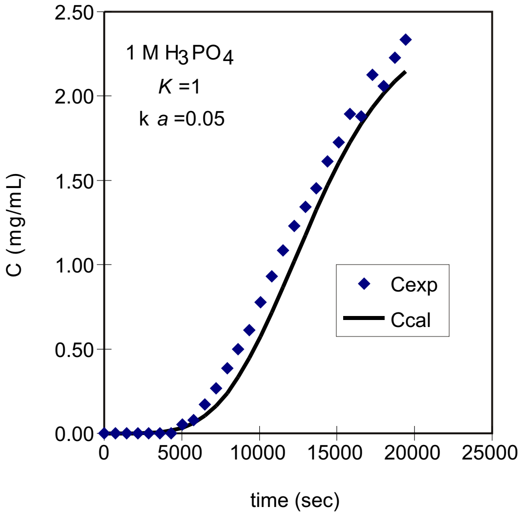


Figure 3. Breakthrough and fitting curve of uranium in 1 M H_3PO_4.

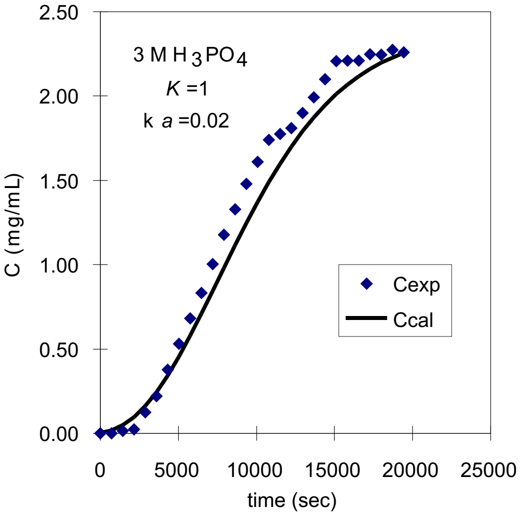


Figure 4. Breakthrough and fitting curve of uranium in 3 M H_3PO_4.

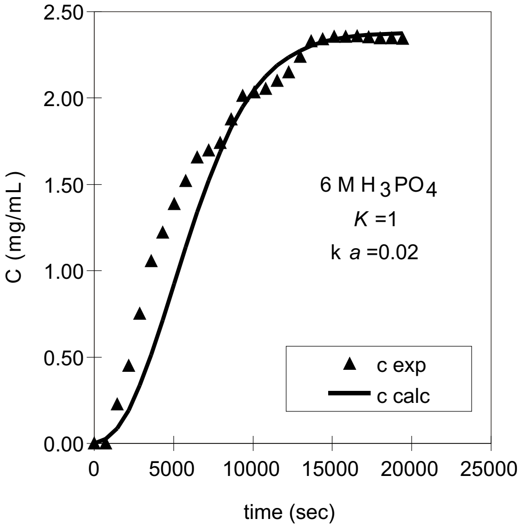


Figure 5. Breakthrough and fitting curve of uranium in 6 M H_3PO_4.

Next, with the obtained parameter values and for the feed of 6 M H_3PO_4 solution containing 200 mg U/dm^3 at a flow rate of 1m^3/h, columns at different lengths were designed, taking into account the concentration of industrial grade wet-phosphoric acid is almost 6 M. The breakthrough times for each column were found by considering the breakthrough concentrations as 2 mgU/dm^3. From this analysis, design alternatives for the removal of uranium from 6 M H_3PO_4 solution were obtained. The operational and equipment characteristics are presented in Tables 2-4.

Table 2. Operational characteristics for U removal.

Operational data	Unit/symbol	Value
concentration inlet/outlet	mg/L	200/2
mass action law constant	K	1
mass transfer coefficient	κa, cm^3 sln/cm^3 bed sec	0.02
particle size range	mm	0.355-0.500
average particle diameter	mm	0.4275
number of columns	unit	2
void fraction of the bed	ε	0.28
bulk density of the resin	g/cm^3	0.358
Reynolds number	Re	0.0854

Table 3. Common column parameters.

Property	Value
Feed flow rate	1 m^3/hr
Density of solution	1.2583 g/cm^3
Viscosity of solution	3.15 cP
Column diameter	0.60 m
Cross sectional area	0.282 m^2
Superficial velocity	0.05 cm/s
Mass flux	0.63 kg/m^{2}s

Table 4. Design alternatives for U removal.

Length cm	Sorption time hr	NTU	ΔP (k Pa)	Amount of resin kg
100	64.0	40	30.64	100.956
150	110.0	60	45.96	151.434
200	152.0	80	63.05	201.912

The operational data on the steps of first washing, elution and second washing are obtained by sharing the sorption time among the three steps. Table 5 contains the features of the tandem columns designed. 1 M Na_2CO_3 solution was accepted as an eluting agent, considering that the uranium loaded onto Purolite S 940 is quantitatively eluted with 1 M Na_2CO_3 (Kabay et al., 1998). Figure 6 shows the elution profiles reported in a previous study (Kabay et al., 1998). The uranium concentration in the eluate reaches 36.5 g/L, 15.3 times higher than that of the initial solution (0.01 M UO_2(II)) in 1 M H_3PO_4. The respective concentration values are 20 times for 3 M H_3PO_4 solution and 6.55 times for 6 M H_3PO_4 solution. Bearing this in mind, the concentration value of uranium in the eluate (see Fig.9) was given as 2800 mg U/L, which is about 14 times the initial concentration of 200 mg/L. Value 14 was the average of the values obtained in the cases of 0.01 M UO_2 (II) in 1, 3 and 6 M H_3PO_4.

Table 5: Washing and elution conditions for U.

	First washing	Elution	Second washing
Solvent	Water	Water	Water
Solute	Water	Na_2CO_3	Water
Concentration, M	55.5	1	55.5
Time, hr	21-50	21-50	21-50
Flow rate, m^3/hr	1	1	1

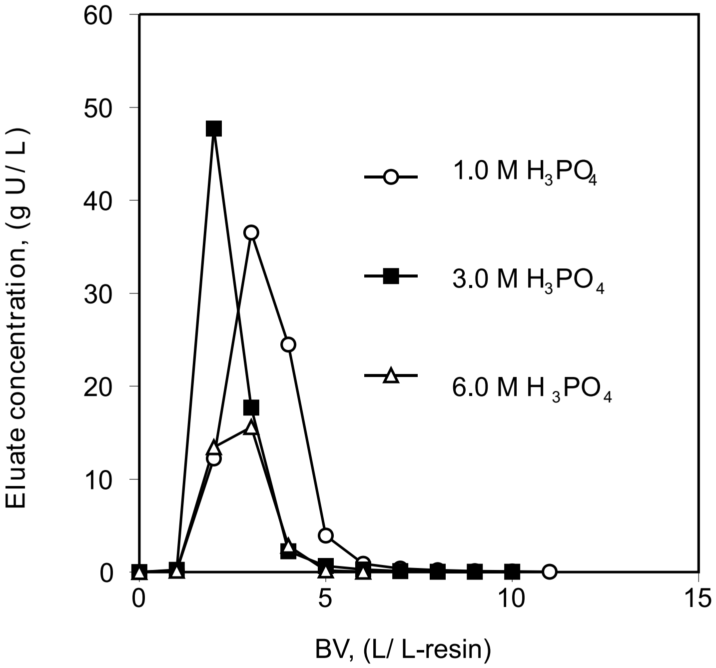


Figure 6. Elution curves of uranium in 1, 3 and 6 M H_3PO_4.

3.2. Removal of Cd by NDSX

The operation conditions of the experiments are shown in table 6.

Table 6: Operation conditions of the experimental runs.

	I	II	III
Feed Flow rate	9.0×10^{-4} m^3/h	3.6×10^{-3} m^3/h	7.2×10^{-3} m^3/h
Organic Flow rate	3.1×10^{-3} m^3/h	4.2×10^{-3} m^3/h	3.8×10^{-3} m^3/h
Stripping Flow rate	0.6×10^{-3} m^3/h		
Equilibration Flow rate	3×10^{-2} m^3/h		
Organic Volume	718×10^{-6} m^3		
Equilibration Volume	1×10^{-3} m^3		
Inlet Feed Concentration	0.495 mol/m^3	0.467 mol/m^3	0.437 mol/m^3
Inlet Stripping Cadmium Concentration	0 mol/m^3		
Initial Organic Cadmium Concentration	0 mol/m^3	0 mol/m^3	Final organic cadmium concentration of experiment B
Run Time	65 h	56 h	26 h

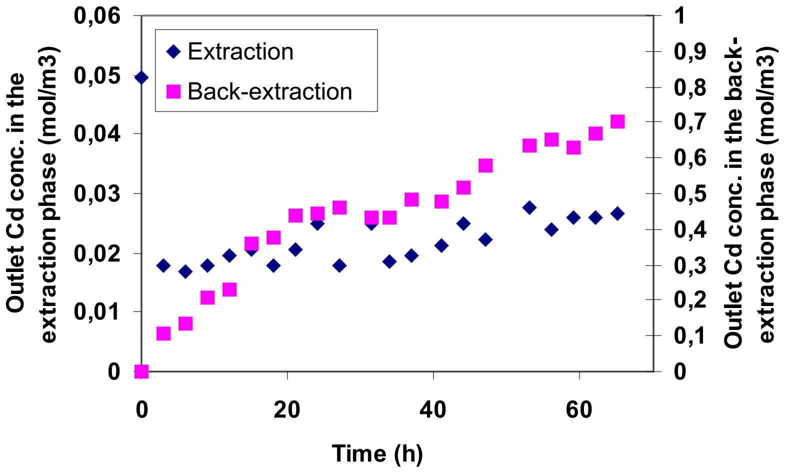


Figure 7. Experimental results of run I

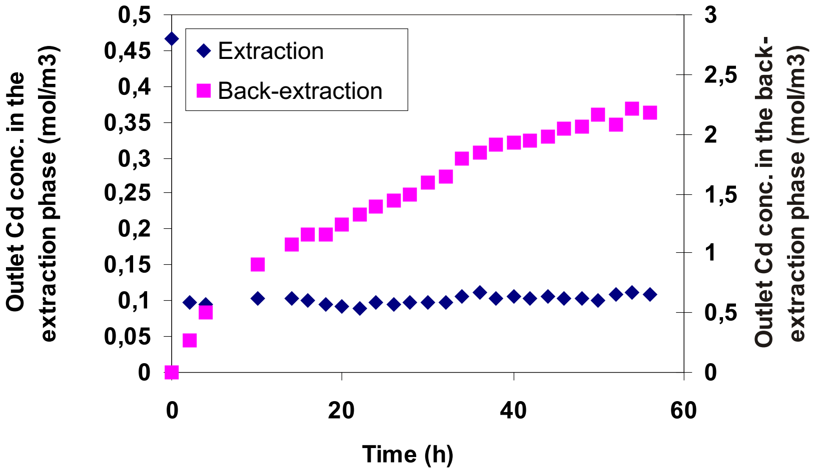


Figure 8. Experimental results of run II.

Concerning the concentration of Cd in the back-extraction solution it is observed that it increases rapidly in the three experiments. The final concentration depends on the initial organic cadmium concentration, the inlet feed concentration and the feed flowrate. A maximum value of 3.3 mol/m^3 is obtained in the third run.

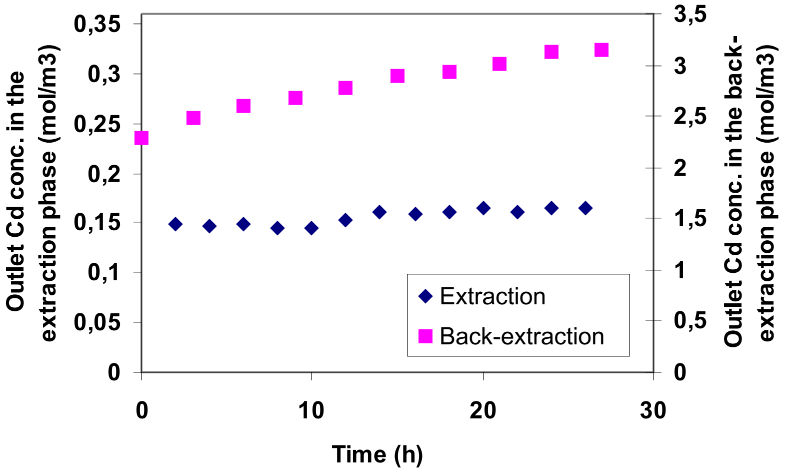


Figure 9. Experimental results of run III.

A mathematical model consisting in mass balance equations for cadmium considering a homogeneous composition in the fluid flowing through the shell side of the hollow fibre modules is used to simulate the experimental results (Ortiz et al, 1996, 1999). The value of the parameters of the model and their deviation from the experimental data are shown in table 7 where K_m represents the membrane mass transfer coefficient and K_t represents the apparent mass transfer coefficient.

Table 7. Optimum values of the parameters and deviations for the proposed models.

Parameters		Deviation
K_t =1.04 x 10^{-2} m/h	K_m =3.40 x 10^{-5} m/h	1.07

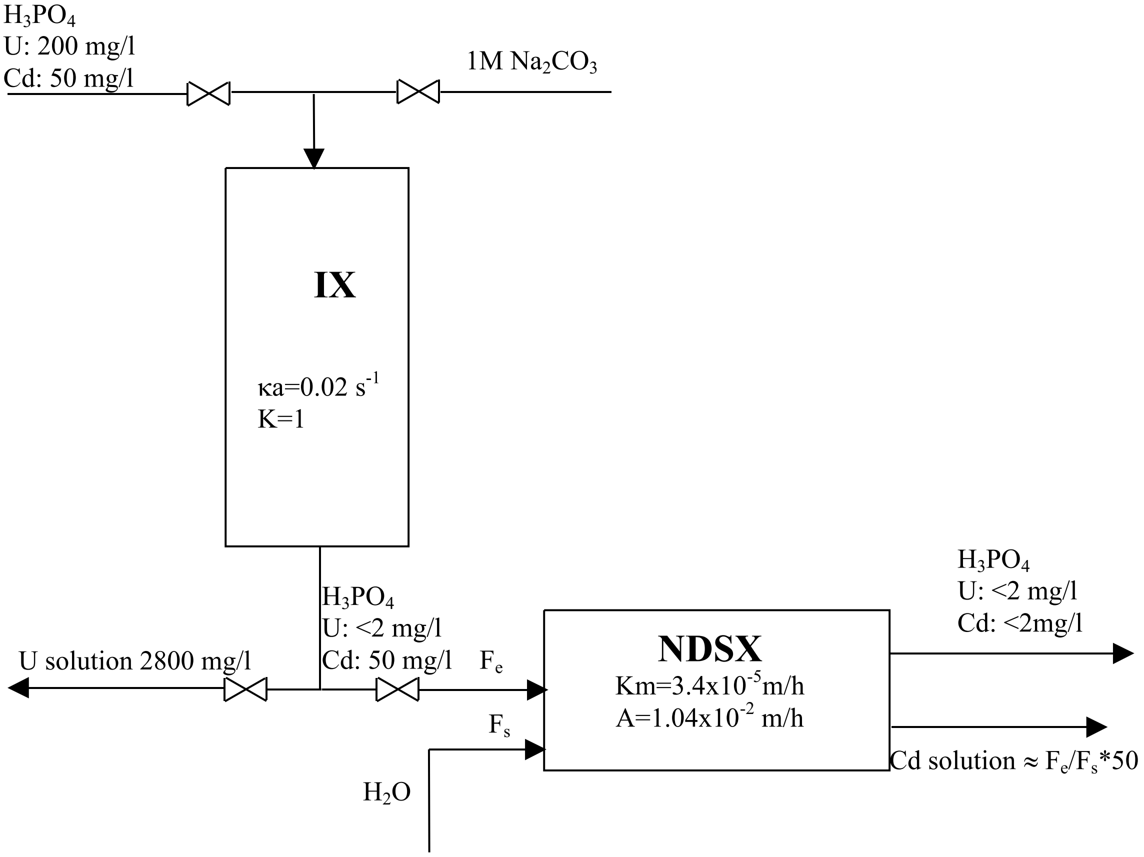


Figure 10: Flow diagram of the integrated process for the removal of Cd and U from wet phosphoric acid.

Finally, the analysis of the five membrane technologies under investigation in the project led to an integrated process considering two different alternatives for the removal of Cd and U from wet phosphoric acid that are possible from the technological point of view (figure 11). Selection between the two options should consider additional aspects, such as risk analysis, scale-up and continuous operation and generation of waste effluents (Urtiaga et al., 2000).

CONCLUSIONS

This work presents a new process integrating two membrane operations for the removal of U and Cd contained in wet phosphoric acid: ion exchange separation using the resin Purolite S940 for the removal of U contained in the acid followed by a non-dispersive solvent extraction process using Aliquat 336 as selective extractant and water as back-extraction agent for the removal and recovery of cadmium.

Concerning the SIX process, the breakthrough data collected from column experiments were used by fitting them to the solution of Thomas in order to find design parameters. By computer simulation, breakthrough time, NTU, pressure drop and resin amount were calculated for the columns of different lengths.

Concerning the non-dispersive solvent extraction process, the values of the parameters K_m which represents the membrane mass transfer coefficient and K_t which represents the apparent mass transfer coefficient were obtained: K_m = =3.40 x 10^{-5} m/ and K_t =1.04 x 10^{-2} m/h.

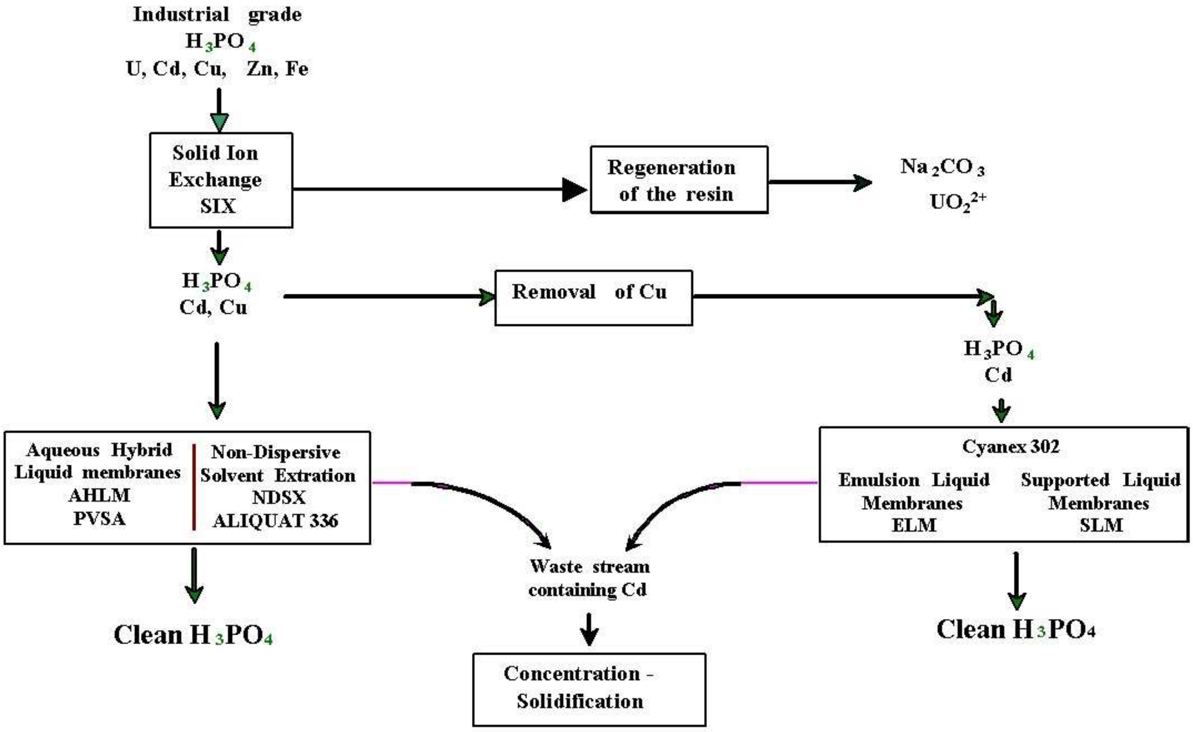


Figure 11. Integration of membrane based technologies for the purification of wet phosphoric acid.

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