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Simultaneous recovery of heavy metals (Pb, Cd, Zn) from diluted solutions by electroextraction technique

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Abstract. Cadmium is mainly used in galvanoplasty and stabilisation of plastic materials. It accumulates continuously in soils. The analysis of soil samples gave concrete evidence of increase of concentration of this element during the past centunary [1]. Furthermore Cd and Pb attack selectively the kidneys and the liver with enzymatic troubles. The work has enabaled to put into evidence the contribution of the presence of resin to the conventional electrodialysis process. The optimal conditions for the elimination of Cd^{++}, Zn^{++} and Pb^{++} ions were determined. These included influence of resin, imposed current density, flow rate of the feeding solution (diluat), different supporting electrolytes used during the electroextraction (HNO_3, HCl and H_2SO_4) and concentration of the solution to be treated [2-3-4]. Furthermore the competition between the electroextraction of the metallic cations Cd^{++}, $Zn^{++}$and Pb^{++} was investigated for different mixtures.

Key words: Electrodialysis, heavy metals, diluted solutions

Introduction

Electropermutation is an electroextraction process combining the conventional ion exchange with a modified electrodialysis procedure. It uses a central compartment of in a three compartment cell, separated by cation-exchange resins. In the central compartment, the polluted effluent flows continuously as single pass system. Under an applied current, the metal cations are fixed by the ion-exchange resins, substituted by protons provided by the acidic solution contained in the regeneration compartment and transferred into the receiver compartment where they are concentrated. The process feasibility is tested using low concentration solution of Pb^{2+}, Cd^{2+} and Zn^{++} ions. Solutions containing only one cation and mixtures of the cations are used under the same experimental conditions [5].

Materials and Methods

Electropermutation is an electroextraction process combining the conventional ion exchange with a modified electrodialysis procedure. It uses a central compartment of in a three compartment cell, separated by cation-exchange resins. In the central compartment, the polluted effluent flows continuously as single pass system. Under an applied current, the metal cations are fixed by the ion-exchange resins, substituted by protons provided by the acidic solution contained in the regeneration compartment and transferred into the receiver compartment where they are concentrated. The process feasibility is tested using low concentration solution of Pb^{2+}, Cd^{2+} and Zn^{++} ions. Solutions containing only one cation and mixtures of the cations are used under the same experimental conditions stopped [5]. by the anion exchange membrane. The ions present in the solution circulating in the central compartment will be able to be fixed onto the resin sites which are under the protonated form then they will again exchange and transferred into the receiver compartment.

Results and Discussion

The electroextraction of the metallic cations Pb^{2+}, Zn^{2+} and Cd^{2+} was studied with synthetic solutions prepared from nitrate salts. The efficiency of the process was analyzed for different operating parameters such as resin mass, nature of the regenerating acid, current density, flow rate and concentration of the studied solution. The feasibility of the process of electroextraction was first of all tested on simple systems corresponding to solutions containing only one metallic cation and in the second

stage the process was tested on mixtures of solutions containing several cations.

Electro-Extraction from Monocationic Solution:

Influence of the presence of resin on the process

Several experiments were carried out in the absence and presence of resin in the feeding compartment of the cell in which circulates the treated solution.

Table 1. Influence of the presence of resin on the solution concentration at the exit of the feeding compartment and the purification yield respectively.

	Pb^{2+}	Zn^{2+}	Cd^{2+}
$C^s(mgL^{-1})$, without resin	7.1	9	4
$C^s(mgL^{-1})$, with resin	0.3	1.1	0.7
T^E (%), without resin	82	77.5	90
T^E (%), with resin	99	97	98

In this table are assembled the concentrations of the exit solutions (Cs) and the corresponding purification yield (TE) which allows to quantify the contribution of the resin to the process. These latter values are clearly improved in the presence of resin since an increase from 8 to 20% depending on the cations.

Influence of Acid Regeneration

In the donor compartment circulates an acid solution called regenerating solution which provides protons to the feeding compartment. Hence it allows the continuous regeneration of the resin. Three acids were tested: HNO_3, HCl and H_2SO_4. The more acidic solution circulates in all compartments. The purification of the solution is not affected by the regenerating acids and its exit concentration remains low: Cs ≤ 3 mgL-1. On the other hand we notice a difference between the concentration values in receiver compartment which is in the order C^R (HNO_3) › C^R (HCl) › C^R (H_2SO_4).

Influence of the current density

This table allows the parameters related to the process efficiency to be compared: Concentration in the receiver and purification yield. The increase ion the current intensity favors the mass transfer in the receiver and the purification of the solution.

Table 2. Concentration in the receiver and purification yield as function of the current density, $(C^E)_{Pb}$ = 100 mg L^{-1}, $(C^E)_{Zn,Cd}$ = 40 mg L^{-1}, q = 1,5 mL mn^{-1}.

	Current density (mA cm-1)	1	2	4	7
Pb^{2+}	$C^R(mgL^{-1})$	65	70.7	80.1	88.2
	T^E (%)	92	98	97	97
Zn^{2+}	$C^R(mgL^{-1})$	21	36.4	42.1	53.6
	T^E (%)	92.5	95	96	98
Cd^{2+}	$C^R(mgL^{-1})$	49.9	78.3	85.5	94.3
	T^E (%)	92.5	98	98	99

Influence of the Feed Solution Flow Rate

The efficiency of the process as function of the feed solution flow rate may be deduced from Table 3.

Table 3. Concentration factor in the receiver and purification yield as founction of the flow rate, C^E = 40 mg L^{-1}, i = 2 mA cm^{-2}, t = 220 mn.

	Débit (mL mn^{-1})	1.5	5	10	15
Pb^{2+}	C_{conc}	1.2	1.8	2.3	4.3
	T^E (%)	99	92.5	85	82.5
Zn^{2+}	C_{conc}	0.9	1.9	2.2	3.4
	T^E (%)	95	50	37	20
Cd^{2+}	C_{conc}	2.0	2.6	3.2	4.1
	T^E (%)	98	77.5	67.5	52.5

The increase of the flow rate leads to an increase in the mass transfer in the receiver and consequently in the increase of the concentration factor. This result is predictable since the amount of cations entering the feed compartment is directly proportional to the solution flow rate. On the other hand, the purification yield (table3) decreases when the flow rate increases. Indeed, this parameter depends on the kinetics of exchange of the cations and the fixed sites on the resin and the membrane through which the transfer to the receiver is taking place.

Electroextraction of Mixtures of Metallic Cations

The experimental setup is similar to that used for the solutions containing one metallic cation. The analysis results obtained for the a mixture of three cations with one cation in excess.

Table 4. Fixation yield of cations on the resin for the mixture under investigation: Pb^{2+}/ Zn^{2+}/ Cd^{2+}

	Pb^{2+} (%)	Zn^{2+} (%)	Cd^{2+} (%)
Cations at same concentration	73	31	36
Pb^{2+} in excess	98	26	26
Zn^{2+} in excess	59	42	29
Cd^{2+} in escess	55	25	50

When a cation is in excess it concentration in the receiver compartment is important. Furthermore the concentration of Pb2+ is very high due to the affinity of the resin for this cation.

Conclusion

- The results obtained using the process of electroextraction on an ion exchange resin allows the efficient purification of diluted solutions in metallic cations even after saturation of resin.
- The present study has also demonstrated that it is possible to treat a mixture of metallic cations by electrozextraction with high yield (≥ 97%)

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