

Application of the bipolar electro dialysis technique for the production of hydrochloric acid from wastewater regeneration of ion exchange resins

Xavier Córdova^a, Jhonny Valverde Flores^{a, b,*}

^aDepartment of Environmental engineering, University Cesar Vallejo – Lima Norte, C.P. 15314, Lima 39, Peru.

^bInstitute of Sciences and Engineering, Centre of Research and Training to the Regional Development (CINCADER). Lima 39, Peru.

jhoval1@yahoo.es

Resumen

Esta investigación tuvo como objetivo determinar cómo la aplicación de la técnica de electrodiálisis bipolar influye en la producción de ácido clorhídrico, a partir de la regeneración de resinas de intercambio iónico de aguas residuales en la urbanización Enace - Carabayllo, Lima, Perú. La técnica utilizada fue la electrodiálisis bipolar. Para ello, se construyó el módulo de electrodiálisis bipolar a escala de laboratorio con el fin de recuperar el ion cloro (Cl⁻) para la producción de ácido clorhídrico y la recuperación del ion sodio (Na⁺) para obtener un subproducto como es el sodio hidróxido de agua de regeneración residual de resinas de intercambio iónico. Los factores controlables se consideraron como: tensión aplicada a la celda de electrodiálisis (6, 12, 18 V) y flujo de alimentación (300 mL / min, 600 mL / min). Se obtuvo una recuperación después de 200 minutos, 18 voltios y un flujo de 600 mL/min, un porcentaje de 84,91% de ion cloro para la producción de ácido clorhídrico y 39,02% de ion sodio para un subproducto de hidróxido sódico

Palabras clave: ácido clorhídrico, electrodiálisis bipolar, recuperación, agua residual

Abstract

This research had as a goal to determine how the application of bipolar electro dialysis technique influences the production of hydrochloric acid, regeneration of ion exchange resins from wastewater in the urbanization Enace – Carabayllo, Lima, Peru. The technique used was electro dialysis bipolar. For this, the bipolar electro dialysis module was constructed at laboratory scale with the purpose of recovering the chlorine ion (Cl⁻) for the production of hydrochloric acid and the recovery of the sodium ion (Na⁺) to obtain a sub product as is the sodium hydroxide from residual regeneration water of ion exchange resins. The controllable factors were considered as: voltage applied to the electro dialysis cell (6, 12, 18 V), and feed flow (300 mL/min, 600 mL/min). A recovery after of 200 minutes, 18 volts and a flow of 600mL/min was achieved a percentage of 84.91% of chlorine ion for the production of hydrochloric acid and 39.02% of sodium ion for a by-product of sodium hydroxide.

Keywords: hydrochloric acid, bipolar electro dialysis, recovery, wastewater

1. Introduction

Electrodialysis (ED) is a separation process of ionic substances dissolved in an aqueous solution by applying an electric current in a direction perpendicular to selective ionic membranes, which allow a selective ion transport according to their cationic or anionic exchange (Medina, 2009). The bipolar membrane can be combined with ion exchange membranes producing acids and bases, they are alternately placed in series between two electrodes (Pilco, 2012).

Bipolar membranes are an evolution of those used in conventional electrodialysis, formed by an anion exchange membrane and a cation exchange membrane, which are in direct contact or separated by a porous medium. This intermediate region is called the transition region or interface (Ibáñez et.al, 2004). These membranes allow the dissociation of the water molecules by applying an electric field, generating protons and hydroxyls by the cationic and anionic side respectively, with a lower energy consumption than necessary reducing the voltage drop between poles, thus achieving energy yields and, being more compact, space is reduced by using them with respect to the homopolymer exchange membranes. Although the disadvantage is the higher acquisition cost compared to the homopolymers, as well as inferior durability, advances in the field of membranes suggest that work is being done to improve these two aspects. (Pilco, 2012).

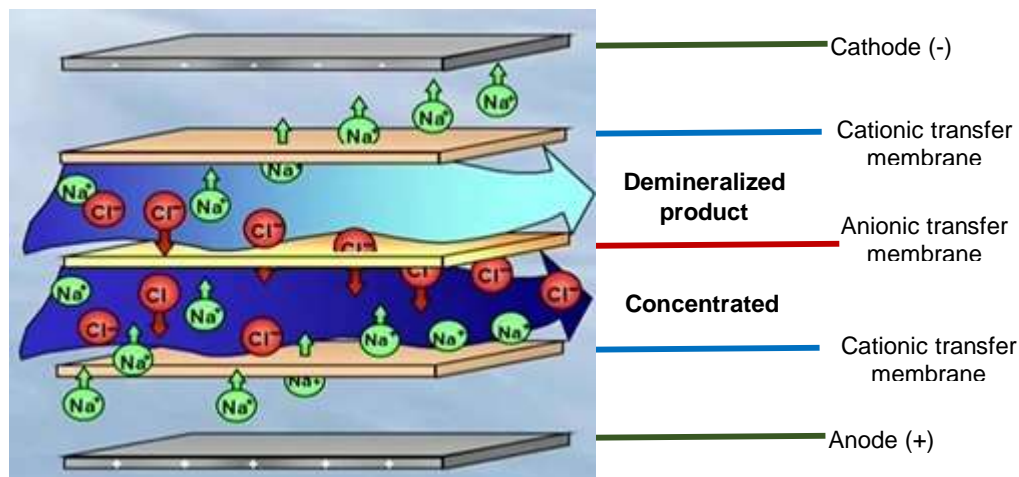


Figure 1. Transport of chlorine ions in electrodialysis

Properties of ion exchange membranes

The physical and chemical properties of ion exchange membranes can be conditioned for a particular application. The main properties to consider when selecting an ion exchange membrane for a given process are:

a) Ionic selectivity

The selectivity is the ability of the membranes to pass or discriminate an ion depending on the load. The fixed charges define the ion selectivity.

b) Chemical Stability. It is essential that it be high, because during its application the membranes are subject to oxidizing and reducing substances, pH changes and presence of organic solvents.

c) Mechanical Resistance. The membranes must have a high mechanical resistance and a small variation of their dimensions to avoid their rupture as a result of the forces that must be supported when placed in the electrodialysis modules. The matrix of the polymer defines the mechanical strength.

- d) Electrical resistance. It is extremely important that it be kept as low as possible in order to minimize energy consumption. The electrical resistance depends on the type of ion exchange groups and on the thickness of the membranes, the electrical resistance of 2.5, 3.5 (Ω / cm^2)
- e) Thermal Resistance. It depends on the base polymer as well as the polymeric reinforcing material. Perfluorinated membranes are stable up to 100 °C, while commercial non-perfluorinated membranes generally can not work at temperatures above 60 °C.
- f) Low diffusion coefficient for solute and solvent. Unfortunately ion exchange membranes are permeable to some extent to non-ionized molecules. These can pass through diffusion, especially small ones.

Technical requirements of the Electrodialysis with Bipolar Membranes (EDBM)

For Pilco A. (2012) the technical requirements that an EDBM module must meet are the following:

- The minimum distance between the membranes must be between 0.5 and 1 mm to reduce the electrical resistance.
- The hydrodynamic conditions must be adequate according to the specifications of the module used, guaranteeing a high surface speed.
- The ratio of the area of the membrane to the volume of the EDBM module should be high.
- Leaks between different compartments should be avoided.
- Short circuits and other possible points of malfunction of the electrical circuit must be reduced.
- Between the membranes can be arranged separators in charge of directing the currents of the different solutions.

2. Materials and Methods

The research used Inductive - Deductive method. The research design was pre-experimental with pretest and post-test to a single group. 10 liters of water were used as a sample for 6 tests.

Components of a bipolar electrodialysis cell

a) Electrodes:

Composed of two rectangular metallic plates, resistant to the corrosion, formation of oxides and deposition of nonconductive organic films, and the most usual is platinized Titanium. In the geometric center two cylinders must be welded to connect the edges of the power supply. The function of the electrodes is to provide the electric field necessary for the process to be carried out. One of the critical factors when configuring an EDBM module is the corrosion resistance of elements such as electrodes, as well as the price of such elements. Stainless steel is the most economical solution for the anode and cathode and can be used in neutral or slightly basic aqueous electrolytes.

Other more expensive options are the nickel electrodes. They are used when a greater passivity is required a great resistance of a metal against the corrosion. Titanium electrodes, which have excellent passivity against acids and bases, are reserved for applications where the concentrations are extremely high.

The electrodes used in bipolar electrodialysis equipment are of the following materials:

Cathode: The material to be used is platinized titanium. The reduction reactions that occur in it are relatively moderate and produce hydrogen gas evolution, these depend on the pH, the material used was 316 stainless steel 30cm x 3cm.

Anode: very aggressive oxidation reactions occur in the anode, that materials as Ir / Ti, PbO₂ / Ti can tolerate in the bipolar electrodialysis equipment as platinized titanium anode of 30cm x 3cm.

b) Spacers: They are plastic structures that have a mesh shape, and are placed to separate each pair of membranes. The functions that they fulfill within the process are to promote turbulence, to avoid the deposition of materials on the surface of the membranes, as well as to seal the cells and to cause the homogenization of the concentration.

c) Cells: It is the basic element for the construction of a bipolar electro dialysis cell, which comprises the ion exchange membranes, cationic and a bipolar membrane, diluted and concentrated spacers and the concentration cell, with a total area of 90 cm² each membrane.

Cationic Membrane. A cationic membrane is composed of a polyethylene laminate charged with the radical SO₃ that it can be hydrophilic (water-loving compound), the ion being the most hydrophilic so that it will prevent dissolved solids adhere colloid.

Anionic Membrane. It is a membrane composed of a solid base which contains a positively charged radical that attracts anions, such as the quaternary ammonium anion. This contains the opposite of the cationic membrane since by having positive charge all the colloids are going to adhere like a magnet so it gets dirty very quickly This radical is very weak, it breaks to extreme pH, with time it is lost, the bonds are broken and the ions go to the water, for it has to replace sheet.

Membrane bipolar. It contains the bipolar (positive and negative) poles and is the union of both an anionic and cationic membranes through this we obtain as a result a bipolar membrane that is responsible for dissociating H₂O (H + OH⁻).

d) Concentration cell:

At the passage of the electric current, the ions pass through both the anionic and cationic membranes and form a concentrated electrolytic solution that passes through the concentration cell and proceeds to the union with the ion (H + OH⁻) forming HCl or NaOH.

e) Dilution cell: When the electrolyte solution is formed concentrated solution that is directed to the concentration cell to form HCl or NaOH, also by dilution cell move diluted or product.

f) Centrifugal pumps: Centrifugal pumps are very useful for the operation of the electro dialysis equipment, because they recirculate the feed.

g) Solution tanks: During the electro dialysis process four solution tanks are used, one for the concentrate, one for the diluted and two for the washing of the electrodes. Each tank has a capacity of 1 liter.

h) Electrical source: The power supply must provide continuous current to the process manipulated in a range of 0 to 30 volts from the source.

Procedure of treatment

The procedure was the following:

The sample obtained from resin regeneration water was selected. An initial sample is carried out before the pretreatment. Then it is carried out to the pretreatment process and obtain percentage of sedimentation of Calcium, Magnesium and Sulfates of water. Water is then passed through the bipolar electro dialysis equipment, where the independent variables (flow and voltage) are manipulated, finally the product obtained (HCl and NaOH) are analysed and calculated the percentage recovery of ions from chlorine ions.

During the process in the pilot plant of bipolar Electro dialysis the determined parameters were:

Limit Current Density:

The different voltages of the worked sample were recorded as: 6 V, 12 V and 18 V according to flow and experience for each sample. The limiting current was then determined at different flow rates, such as 300 and 600 mL/min, for a time of 200 minutes. In addition, electrical conductivity data were taken in parts per million. Ten tests every 20 minutes were taken up to 200 minutes for both hydrochloric acid production tanks and sodium hydroxide by-product.

Operational Parameters

During the process of bipolar Electro dialysis, data were recorded of the operational parameters using a tab, in which the flow, concentration and electrical potential were recorded.

3. Results

Description of the pilot water treatment plant

The pilot water treatment plant has parts to ensure the EDBM, which are:

Tanks. Eight acrylic tanks were used in order to facilitate the transport and reception of the water in the different stages of the process. See table 1.

Table 1. Description of tanks in EDBM

Tank number	Description
Tank 01.	It receives the water of ion exchange resin regeneration to later offer the pretreatment with capacity of 20 liters
Tanks (02, 03, 04)	These tanks have the capacity of one liter two hundred milliliters of water, designed with the purpose of using a liter of water to dilute to the solution. These solutions are driven by a pump with a drip system for precipitation. Tank 02 (Na_2CO_3 solution is found for precipitation of calcium ion, Tank 03 (NaOH solution is found for precipitation of magnesium ion) and Tank 04 (BaCl_2 solution is found for precipitation of sulfate ion)
Tanks (05, 06 y 07)	These tanks have a capacity of three liters of water to achieve the precipitation of the Mg^{2+} , Ca^{2+} , SO_4^{2-} ions found mainly in the water's regeneration of ion exchange resins. Tank 05 (Receives Na_2CO_3 solution for precipitation of calcium ion), Tank 06 (receives NaOH solution for precipitation of magnesium ion) and Tank 07 (Receives BaCl_2 solution for precipitation of sulfate ion)

Water Pump. Three fish tank pumps were used for the recirculation of water with chemical content to achieve the sedimentation of water hardness, at a potential of 110V. To obtain this potential a transformer was used for each pump.

Valve. A small valve to regulate the continuous flow of ion exchange resin regeneration water in each tank was used.

Drip system. Three irrigation system drippers were used on three tanks (02, 03, and 04) to be dripping to the tanks (05, 06, 07) by means of the drip system.

Hoses. Hoses with a diameter of 10 millimeters were used to transport the water to different tanks.



Figure 2. pre-treatment equipment for water of resin regeneration for the production of hydrochloric acid

Description of bipolar electro dialysis pilot plant

a) Membranes. The cell contains two bipolar membranes (cationic and anionic) and bipolar with an effective area of 90 cm² each.

- Bipolar membranes. They are responsible for dissociating water (H₂O) in H⁺ and OH⁻ to facilitate the production of hydrochloric acid and the sub-product sodium hydroxide.
- Anionic membranes. Allow only passage of the positively charged ion and prevent its return.
- Cationic membranes. Allow only passage of the negatively charged ion and prevent its return

b) Electrodes. The anode and cathode are platinized titanium of 30 cmx3 cm, the same material was used due to the change of polarity that will be made during the process.

c) Spacers. Three spacers made of plastic material in mesh form were used diluted and concentrated solutions flow through these channels, sealing the cells, being the support of the membranes and generating turbulence for the increase of chemical transport.

The cell has two acrylic plates two inlets and two outlets for flowing solutions at the ends. These plates have the function of giving stability and resistance to the bipolar electro dialysis battery.

d) Centrifugal pumps. it was used four centrifugal pumps at a potential of 110V for recirculation of each solution separately. Three transformers were used to obtain this potential.

e) Solution Tanks. Four transparent acrylic tanks of 1 liter contain solutions of concentrate, and wastewater washing regeneration ion exchange resin. These are connected directly to the bipolar electro dialysis cell.

f) Electrical Supply. From 5 to 30 volt of 5 amp in power supply was used to provide direct current to the Equipment.

g) Flow control valves. Two small valves were added to the pretreatment.

h) Valves. Four valves were installed to each tank to facilitate expulsion of solutions.

i) Hoses. Hoses with a diameter of 10 millimeters were used in order to transport the water to the different parts of the equipment.



Figure 3. Bipolar Electro dialysis Pilot plant for production of hydrochloric acid through wastewater regeneration of ion exchange resins

Initial Laboratory Analysis

10 liters Collected of waste water from washing regeneration of ion exchange resin in a storage tank were mixed to achieve a homogeneous mixture. In a jar of 500mL a sample was taken in order to know the initial concentration of salts (sodium and chlorine) and hardness content (magnesium calcium and sulfates) before to the pre-treatment process.

Pretreatment application

Water was pumped to tank 5 with a constant flow of 6 mL/min by means of which the different chemical compounds were added to each tank.

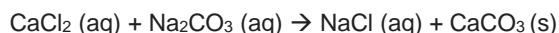
Chemical Precipitation

It consists of a rinse water purification of the regeneration of ion exchange resins, the aim of the treatment is to eliminate the contaminants that affect the electrodes, the process performance or the quality of the product. The elements to be eliminated are Mg^{2+} , Ca^{2+} , SO_4^{2-} and Ba^{2-}

The first stage precipitates the calcium, magnesium and sulfate ions.

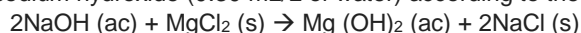
Addition of Na_2CO_3 for removal of calcium ion

The calcium ions are mainly found as $CaCl_2$ to precipitate it is treated with an aqueous solution of sodium carbonate (Na_2CO_3) 0.20 gr/L of water under controlled stirring conditions, resulting in the formation of insoluble carbonate salts.



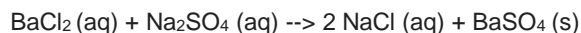
Addition of NaOH for removal of magnesium ion

Magnesium ions are generally found in the form of magnesium chloride ($MgCl_2$), to precipitate it is treated with aqueous solution of sodium hydroxide (0.30 mL/L of water) according to the following reaction



Addition of $BaCl_2$ to precipitate sulfate ion

Sulphate ions are present in form of calcium-, sodium- or magnesium- sulfate. For the removal of the sulfate ions, a solution of barium chloride is added, at a concentration of 0.05gr/L of water, in acid medium pH (3-4), obtaining the following reaction



The effective precipitation of calcium and magnesium salts should occur while maintaining an excess of the reactants and with agitation.

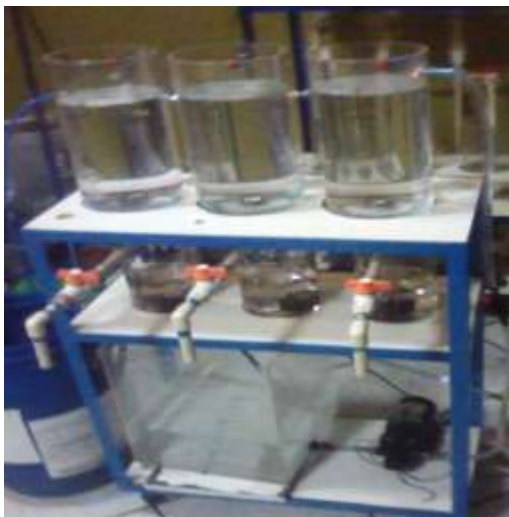


Figure 4. Application of pre-treatment to ion exchange resin regeneration water (Chemical Precipitation)

Results of the post-pretreatment laboratory analysis

A sample of ion exchange resin regeneration water was then collected in a flask of 500 mL in order to know the sedimentation rate of magnesium calcium and sulfates.

Table 3: Laboratory results of Magnesium-, Calcium-, and Magnesium Sedimentation of

concentrations	Mg (ppm)	Ca (ppm)	SO ₄ ²⁻ (ppm)
Initial concentrations	34.4	2294.6	2903.5
sedimented Concentration	19.15	1597.45	260.01
Percentage of sedimentation	55.67%	69.62%	91.04%

In Table 3 shows the percentage of sedimentation Magnesium, calcium and sulfate achieved through the pre-treatment equipment for the production of hydrochloric acid and the sub product sodium hydroxide.

Manipulation of variables in the bipolar electro dialysis process

Six tests were performed in the bipolar Electro dialysis equipment at pilot level and operating parameters as Flow (300 mL/min and 600 mL/min) and Electrical Potential (06 V, 12 V and 18V), regulated with the help of the electric source, all the experiments were a time period of 200 minutes.

Two liters of ion exchange resin regeneration wastewater was used in tanks 2 and 3. For each test one liter was used for each tank and one liter of distilled water was added in tank 1 for the HCl production and in tank 4 for NaOH. Conductivity and parts per million were monitored in tank 1 and tank 4, which was performed by extracting 50mL in a precipitated vessel every 20 minutes.

The samples were measured by Atomic Absorption Spectrophotometer SHIMAZU AA-7000 and Triode Reflowable Electrode de pH Orion 9157BNMD. Results are shown in the following table.

Table 4. Recovery rate of chlorine and sodium ion for the production of hydrochloric acid and its by-product sodium hydroxide

Recovery	Cl (ppm)	Na (ppm)
Initial concentrations	33998.77	13122.74
recovered Concentration	28868.4	5120.01
Percentage of recovery	84.91%	39.02%

The Table 4, shows the percentage recovery of the chlorine ion for the hydrochloric acid production and of sodium ion for the by-product sodium hydroxide. The recovery percentage of order of the chlorine ion is 84.91%, and 39.02% of the sodium ion.

Table 5. Results of values of the operational parameters of the flow and electrical potential

Volume	N°	6 Volts				12 Volts				18 Volts			
		T01 NaOH (ppm)	T04 HCl (ppm)	T01 NaOH (µs)	T04 HCl (µs)	T01 NaOH (ppm)	T04 HCl (ppm)	T01 NaOH (µs)	T04 HCl (µs)	T01 NaOH (ppm)	T04 HCl (ppm)	T04 HCl (µs)	T01 NaOH (µs)
300 mL/min	1	10	10	33.8	17.8	30	10	45.2	18.3	13.6	20	35.4	10
	2	90	60	103.3	85.7	180	50	83.1	256	173.2	230	341	173.2
	3	120	102	260	280	310	120	437	200	232	320	465	232
	4	210	260	450	580	450	270	653	367	800	750	1200	450
	5	320	430	630	850	540	440	781	632	1267	1250	1800	880
	6	480	650	940	1279	730	720	1033	1041	2020	1460	2610	1880
	7	625	840	1254	1550	910	1010	1310	1495	3130	1840	3800	2480
	8	820	1080	1580	1950	1200	1600	1696	2290	4230	2330	5200	3050
	9	1035	1310	1885	2320	1532	2133	1976	4310	5140	2877	6350	3655
	10	1250	1580	2121	2700	1912	3465	2390	6450	5720	3287	7390	4287
600 mL/min	1	20	18	34.2	32	40	170	97.3	253	10	10	33.8	17.8
	2	1750	2188	2860	3410	420	460	602	692	1070	1500	1200	612
	3	2170	2800	3200	3720	650	1050	961	1512	1900	2600	2500	1893
	4	2270	3400	3800	4360	960	1540	1334	2070	2500	3500	4500	2930
	5	2840	3830	4070	5500	1440	2570	2060	3620	3300	4850	6230	4250
	6	3150	4470	4500	6380	2100	3760	2940	5380	4510	6800	9200	6170
	7	3450	5250	4940	7480	2820	5290	4140	7550	5910	9280	13280	8450
	8	3750	5964	5360	8370	3720	7060	5340	10050	7410	11800	17490	10600
	9	4240	6790	6080	9700	4760	9190	6800	13120	8534	14536	21750	13300
	10	4500	7350	6450	10480	5700	11350	8180	15550	9854	17534	26450	15900

Table 5 shows the results obtained using the conductivity meter with the fluxes of 300mL/min and 600mL/min of ion exchange resin regeneration residual water obtained with the application of different volts (06 , 12 and 18) of electrical potential obtained every 20 minutes for 200 minutes in tank 1 (NaOH) and tank 4 (HCl).

Table 6: Results of values of the operational parameters: 600 mL/min of flow and 6 Volts of electrical potential

Volume	N°	T01 NaOH (ppm)	T04 HCl (ppm)	T01 NaOH (μ s)	T04 HCl (μ s)
600mL/min	1	20	18	34.2	32
	2	1750	2188	2860	3410
	3	2170	2800	3200	3720
	4	2270	3400	3800	4360
	5	2840	3830	4070	5500
	6	3150	4470	4500	6380
	7	3450	5250	4940	7480
	8	3750	5964	5360	8370
	9	4240	6790	6080	9700
	10	4500	7350	6450	10480

According to the results of the table shown in Table 6, it can be seen that the recoveries of the chlorine and sodium ion for the production of HCl and the sub product NaOH, as the electro dialysis process continues, there is a continuous increase as it progresses time. The same behavior was observed in all other experiments, therefore, it is confirmed, the effectiveness of the method to recover H- and Na+ ions for the production of hydrochloric acid and of the sub product such as NaOH.

4. Conclusions

- It is concluded that the bipolar electro dialysis method allows to recover the chlorine and sodium ions, obtaining a recovery of 84.91% of the chlorine ion for the production of hydrochloric acid and 39.02% of the sodium ion for the production of sodium hydroxide confirming so, it is an appropriate technology for the production of hydrochloric acid and a by-product of sodium hydroxide from ion exchange resin water regeneration wastewater.
- It is concluded that the voltage affects the recovery of chlorine ion for the production of hydrochloric acid by bipolar electro dialysis, through ion exchange resin regeneration wastewater and the highest percentage of recoveries was achieved with 18 volts.
- It is concluded that the flux affects the recovery of chlorine ion, for the production of hydrochloric acid by bipolar electro dialysis, through ion exchange resin regeneration wastewater as a higher percentage of recoveries was achieved with 600mL/min

Acknowledgments

We gratefully acknowledge to the Department of Environmental engineering, University Cesar Vallejo – Lima Norte, for giving facilities in environmental issues. We also thank to the Institute of Science and Engineering, Centre of Research and Training to the Regional Development, (In Spanish, Centro de Investigacion y Capacitacion para el Desarrollo Regional-CINCADER) for allowing us to share technical experiences.

Reference

- Ibáñez, R. [et.a], "Electrodialysis with bipolar membranes. Fundamentals and applications.
- Medina, J. 2009. Development of Electrodialysis Modules for Desalination of Salable Waters, determination of Physical Parameters and Experimental Evaluation of Diffusional Model, Peru, (Master's Thesis). Available in http://cybertesis.uni.edu.pe/uni//medina_cj/pdf/medina_cj.pdf
- Mier, M.; Ibáñez R.; Ortiz, I.; Rivero, M., 2004, Chemical Engineering Journal, Spain. ISSN 0210-2064, no. 418, pp. 166-182.
- Pilco Núñez, A. 2012. Separation of nickel ions from galvanic liquid effluents using an electrodialysis module (Master Thesis, National University of Engineering). (Accessed on September 28, 2012).