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Reverse osmosis applied to metal finishing wastewater

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Abstract

The electroplating industry is a great water consumer and, as a consequence, one of the biggest producers of liquid effluent. The metal finishing industry presents one of the most critical industrial waste problems. There is therefore growing interest in developing methods for reclaiming metals from plating waste stream and recovery of water using membrane technology [1,2]. The application of reverse osmosis (RO) to the global effluent from the electroplating industry has been studied in this paper. The results obtained show that there is 75–95% recovery of water and nearly total removal of metals in the permeate.

Keywords: Reverse osmosis; Electroplating wastewater; Pilot plant

1. Introduction

Various methods have been researched for the removal and/or recovery of metals from electroplating wastes [3,4]. These include neutralisation and precipitation, ion exchange, cementation, etc. Most of these processes are effective for removing specific metals from solution, but they do not produce the recovery of water and do not treat the global effluent produced by the electroplating industry.

The pieces used in the electroplating industry must be pre-treated in concentrate baths to remove grease and scaling before the electroplating process. There should be consecutive rinsing in the bath, and this water is the principal effluent produced. So, two types of waters are produced: acid waters (containing chromium VI) and alkaline waters (containing oils and fats and cyanide).

Reverse osmosis was shown to be ideally suitable for the treatment of metal finishing effluents. The process can purify plating rinsing waters and concentrate the plating ions up to levels where the recycling of the plating bath is economically interesting [5].

The main aim of this study has consisted in the achievement of the recovery of water in order

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to recirculate purified water to the production processes and reduce considerably the amount of polluted effluents which would be the concentrate produced in the membrane process. A global treatment of effluents has been established in order to reach these targets, while the segregation and treatment of the different types of effluents generated in this industry has been refused [6].

In order to obtain this aim several tests have been carried out in a pilot plant with a treatment capacity of 4 m^3/h, with different feeding concentration. In doing so, different phases have been simulated in a demonstration plant and will be installed in this industry.

The fouling of membranes must be considered. Therefore, several tests have been made and the results analysed. It is necessary to study the retrievement capacity of membranes and how the cleaning process affects membrane life.

2. Experimental study

There were four streams in the case of the industry studied: concentrate acid, dilute acid, dilute alkaline, and concentrate alkaline. Due to the cyanide contained in the concentrate alkaline mixed with the acid waters, the alkaline waters should be segregated in order to avoid the presence of HCN. It is necessary to pre-treat the alkaline waters destroying cyanides so as to mix these waters with the acid waters. Finally, the whole water is treated through the RO process.

2.1. Pilot plant test

Fig.1 shows the RO pilot plant where the experimentation has been made.The pilot plant has two different parts: (i) the feeding and (ii) the treatment group. The feeding system includes a tank with a feeding pump, and a filter element. The treatment group has two lines of membrane pressure vessels. In each line there are two membrane modules in series, with a total membrane filtration area of 24 m^2 per line. Only one line has been used for the present work, with a total of 4 membranes sized 4"×40".

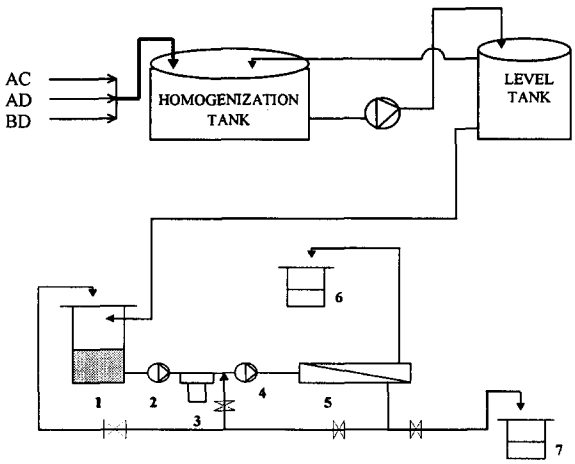


Fig.1. Diagram of RO system. 1 feed tank; 2 ultrafiltration pump; 3 pre-filter; 4 high pressure pump; 5 reverse osmosis membranes; 6 permeate tank; 7 retentate tank; AC concentrated acid; AD diluted acid; BD diluted basic.

The operating temperature can be adjusted and is controlled by a heat exchanger using cool or hot water. The inlet and outlet pressures of the membrane vessel are measured by two gauges control unit of pressures. The permeate and retentate flow rates are measured by two flowmeters.

2.2. Membranes

The RO membranes used for the treatment of wastewater are the spiral wound type, and have an effective membrane filtration area of 6 m^2. The specifications of this kind of membrane, fully aromatic polyamide advance composite membrane (ACM™), advise relationships of flow concentrate/permeate of 5:1. The pure water permeate flux is 8.7 m^3/d at 2000 ppm NaCl, 225 psi, and 25°C. Maximum operating pressure and temperature are 42 bar and 45°C, respectively.

2.3. Methods

Tests have been carried out in order to simulate different sections of a Demonstration Plant which

could treat the total volume of effluent generated by the industry. The different aspects considered are as follows:

- To ease up the fouling membranes, working with a 15% reject ratio, in order to study the behaviour system in extreme conditions of operation.
- To study the recovery capacity of membranes and how the cleaning processes affect life of membranes.

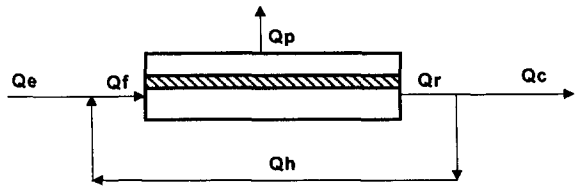


Fig. 2. Operation diagram used in the tests. Q_e effluent flow, l/h; Q_f feed flow, l/h; Q_p permeate flow, l/h; Q_r reject flow, l/h; Q_c concentrate flow, l/h; Q_h recycle flow, l/h.

Three types of tests (Fig. 2) have been carried out in order to reach these objectives:

1. A continuous purge of the circuit without recirculating any stream. The feeding goes across the system only once.

2. Some rejections come out of the system and some others are mixed in the feed tank with the effluent. All these tests have been carried out with external recirculation.

3. In order to obtain a higher energetic efficiency, similar to the previous tests but making the recirculation to reject in the way into the high pressure pump system. These tests are with internal recirculation.

3. Results and discussion

According to different operation conditions, several tests have been carried out in this study. In all cases the feed volume was 2 m³/h, the permeate flow was 1 m³/h, and the test was fulfilled in 8 h.

Starting from the effluents of electroplating industry, and carrying out the recirculations of the reject in the feeding circuit at the membrane, several feedings have been obtained. In doing so, various salt concentrations are obtained and different stages are simulated in a final industrial plant (Table 1).

3.1. Membrane efficiency

The capacity of separation of ions by a membrane is worked out by using the salt passage (SP) and salt rejection (SR) expressions. These are according with the selectivity of membrane in certain operation conditions [8].

$$SP = 100\% \times (C_p/C_f) \quad (1)$$

where C_p is the permeate concentration and C_f the feed concentration.

Table 1
Feeding used in all the tests (T-1 to T-6) obtained by recirculating the reject

	Q_e, l/h	Q_f, l/h	Q_h, l/h	Q_p, l/h	Q_c, l/h	Q_f/Q_c	Q_e/Q_c
T1	1825	1825	0	900	925	2	2
T2	1450	1975	525	950	500	4	3
T3	995	1595	600	790	205	8	5
T4	666	1373	708	525	141	10	5
T5*	1101	1899	798	916	185	10	6
T6*	791	1561	770	618	166	9	5

*Internal circulation

Tables 2–7
Efficiency values of salt rejection considering the feeding for all cases studied

	T1					
	Ce (mg/l)	Cf (mg/l)	Cc (mg/l)	Cp (mg/l)	SR	CF
Cl^-	121.00	121.00	231.00	0.83	0.99	1.91
F^-	0.56	0.56	1.00	0.10	0.82	1.79
NO_3^-	16.90	16.90	34.10	0.42	0.98	2.02
PO_4^-	22.50	22.50	36.00	<0.10	1.00	1.60
SO_4^-	48.20	48.20	98.50	0.20	1.00	2.04
CN^-	3.00	3.00	3.90	2.70	0.10	1.30
Ca	6.30	6.30	12.00	0.50	0.92	1.90
Cr total	3.90	3.90	7.60	<0.20	0.95	1.95
Cu	1.80	1.80	3.60	0.12	0.93	2.00
Fe	1.10	1.10	1.50	<0.4	0.64	1.36
Ni	3.80	3.80	7.10	<0.17	0.96	1.87
Sn	<0.05	<0.05	<0.05	<0.05		
Zn	22.10	22.10	48.20	0.20	0.99	2.18
Na	87.80	87.80	202.00	1.40	0.98	2.30
TDS	338.96	338.96	686.50	6.47	0.98	2.03

	T2					
	Ce (mg/l)	Cf (mg/l)*	Cc (mg/l)	Cp (mg/l)	SR	CF
Cl^-	230.00	285.82	440.00	1.80	0.99	1.54
F^-	<0.1	0.18	0.31	<0.1		1.72
NO_3^-	15.50	19.86	31.90	0.32	0.98	1.61
PO_4^-	10.50	12.60	18.40	<0.1	0.99	1.46
SO_4^-	75.50	93.97	145.00	0.47	0.99	1.54
CN^-	14.30	14.86	16.40	13.90	0.06	1.10
Ca	16.70	18.29	22.70	0.40	0.98	1.24
Cr t.	6.05	9.28	18.20	0.40	0.96	1.96
Cu	27.50	32.44	46.10	1.80	0.94	1.42
Fe	0.60	0.60	0.60	<0.40	0.33	1.00
Ni	3.00	2.97	2.90	0.20	0.93	0.98
Sn	<0.05	<0.05	<0.05	<0.05		
Zn	43.10	54.08	84.40	1.60	0.97	1.56
Na	142.60	151.21	175.00	5.00	0.97	1.16
TDS	[illegible]	696.16	1001.91	25.59	0.96	1.44

*Calculated

	T3					
	Ce (mg/l)	Cf (mg/l)	Cc (mg/l)	Cp (mg/l)	SR	CF
Cl^-	135.00	326.10	643.00	3.00	0.99	1.97
F^-	<0.1	<0.1	1.43	<0.1		
NO_3^-	10.00	22.00	42.00	0.37	0.98	1.91
PO_4^-	<1	<1	<1	<1		
SO_4^-	73.00	176.00	351.00	0.50	1.00	1.99
CN^-	5.30	8.60	11.20	4.50	0.48	1.30
Ca	7.34	19.60	34.10	0.14	0.99	1.74
Cr total	20.10	17.50	26.90	0.23	0.99	1.54
Cu	17.20	28.80	46.90	1.70	0.94	1.63
Fe	1.15	1.24	0.90	<0.40	0.68	0.73
Ni	4.10	3.90	4.40	0.20	0.95	1.13
Sn	<0.05	<0.05	<0.05	<0.05		
Zn	20.77	46.05	79.50	0.40	0.99	1.73
Na	87.30	205.45	457.00	2.80	0.99	2.22
TDS	381.28	866.24	1698.33	13.84	0.98	1.99

	T4					
	Ce	Cf	Cc	Cp	SR	CF
Cl^-	64.00	167.00	263.84	0.50	1.00	1.58
F^-	2.85	7.62	12.35	0.34	0.96	1.62
NO_3^-	48.50	128.50	221.50	2.65	0.98	1.72
PO_4^-	<0.1	<0.1	<0.1	<0.1		
SO_4^-	90.00	262.00	524.00	0.95	1.00	2.00
CN^-	0.40	0.40	0.40	0.80	-1.00	1.00
Ca	9.00	26.15	45.00	0.15	0.99	1.72
Cr total	4.67	12.15	18.27	0.30	0.98	1.50
Cu	3.56	7.85	11.08	0.22	0.97	1.41
Fe	1.95	1.95	4.11	0.47	0.79	2.11
Ni	11.39	26.00	41.30	0.07	1.00	1.59
Sn	0.55	0.67	1.20	0.05	0.93	1.79
Zn	7.49	20.95	38.66	0.11	0.99	1.85
Na	68.60	209.00	343.80	1.75	0.99	1.64
TDS	312.98	970.24	1625.61	[illegible]	0.99	1.76

	T5					
	Ce (mg/l)	Cf (mg/l)*	Cc (mg/l)	Cp (mg/l)	SR	CF
Cl^-	131.17	404.82	782.50	2.03	0.99	1.93
F^-	1.22	3.46	6.55	0.11	0.97	1.89
NO_3^-	12.33	34.67	65.50	0.50	0.99	1.89
PO_4^-	<0.1	<0.1	<0.1	<0.1		
SO_4^-	72.66	227.52	441.25	0.57	1.00	1.94
CN^-	3.26	5.64	8.93	1.69	0.70	1.58
Ca	8.99	33.37	67.01	0.10	1.00	2.01
Cr total	2.95	7.69	14.23	0.40	0.95	1.85
Cu	15.89	50.18	97.51	1.37	0.97	1.94
Fe	<0.4	<0.4	<0.4	<0.4		
Ni	2.37	6.70	12.67	<0.17	0.97	1.89
Sn	<0.05	<0.05	<0.05	<0.05		
Zn	16.23	50.96	98.89	1.11	0.98	1.94
Na	70.90	224.66	436.87	2.20	0.99	1.94
TDS	337.97	1049.65	2031.91	10.06	0.99	1.94

*Calculated

	T6					
	Ce (mg/l)	Cf (mg/l)*	Cc (mg/l)	Cp (mg/l)	SR	CF
Cl^-	785.67	2246.22	3733.33	14.33	0.99	1.66
F^-	5.30	13.67	22.20	<0.1	0.99	1.62
NO_3^-	59.00	168.16	279.30	1.77	0.99	1.66
PO_4^-	<1.00	<1.00	<1.00	<1.00		
SO_4^-	408.67	1131.10	1866.67	4.70	1.00	1.65
CN^-	9.85	11.36	12.90	2.07	0.82	1.14
Ca	67.67	191.96	318.50	0.53	1.00	1.66
Cr total	10.40	20.00	29.78	0.23	0.99	1.49
Cu	89.52	211.80	336.31	3.82	0.98	1.59
Fe	<0.4	<0.4	<0.4	<0.4		
Ni	12.32	33.07	54.20	0.10	1.00	1.64
Sn	<0.05	<0.05	<0.05	<0.05		
Zn	93.60	259.68	428.77	0.96	1.00	1.65
Na	422.54	1164.41	1919.77	6.26	0.99	1.65
TDS	[illegible]	5451.44	[illegible]	34.77	0.99	[illegible]

*Calculated

Salts rejection is the opposite of salt passage, and is defined by Eq. (2).

$$SR = 100\% - SP \quad (2)$$

The efficiency values of salt rejection considering the feeding in all the cases studied are shown in Table 2–7.

It is possible to check that the membrane selectivity for each ion shows practically the same values. In case of the cyanide this crosses more easily the membrane, and the efficiency is lower than other anions with a higher molecular weigh.

3.2. Concentration factor

The relation between the composition in the feeding and the salts rejection by the membrane, is determined by the concentration factor [9], shown in Table 3, and it is defined as

$$CF = C_r/C_f \quad (3)$$

where, CF is the concentration factor, C_r the reject concentration and C_f the feed concentration.

Similar factors for ions suggest that the membrane selectivity is analogous. In this case the membrane chosen for these tests presents a uniform behaviour regarding the time of operation and working conditions.

3.3. Experimentation summary

The values represented in Table 8 correspond to the total dissolve solid, from each stream that intervenes in the membrane process.

As a consequence of these results, the two following points should be taken into account:

- The efficiency of the operation is higher than 95% in all the tests made.
- The relationship of rejection and feeding added to the system (E_{fm}), are higher than 97% and 99% on an average.

Table 8
Experimentation summary

		T-1	T-2	T-3	T-4	T-5	T-6
	Total Dissolve solid (TDS)						
	Cf(mg/l)	338.70	696.10	855.20	870.20	1050.00	5451.40
	Cp (mg/l)	6.50	25.90	13.80	8.40	10.10	34.80
	Cc (mg/l)	685.50	1001.90	1685.70	1525.50	2031.90	9001.70
WORKING PRESSURE (Bars)		18.00	21.00	26.00	26.50	24.70	26.80
OPERATION	EFFICIENCY Efo=QcXc/QeXe=1-(QpXp/QeXe)	0.99	0.97	0.97	0.98	0.98	0.99
	CONCENTRATION FACTOR CF=Cr/Ce	2.03	1.71	4.45	4.87	6.01	4.58
	% CONVERSION R=100*Qp/Qe	49.32	65.52	79.40	78.89	83.19	78.83
MEMBRANES	EFFICIENCY Efm=QrCr/QfCf=1-(QpCp/QfCf)	0.99	0.98	0.99	1.00	1.00	1.00
	CONCENTRATION FACTOR CF=Cr/Cf	2.03	1.44	1.99	1.75	1.94	1.65
	% CONVERSION R=100*Qp/Qf	49.32	48.10	49.53	38.24	48.25	39.60

Both parameters show us that the membrane chosen presents a good behaviour with these effluents.

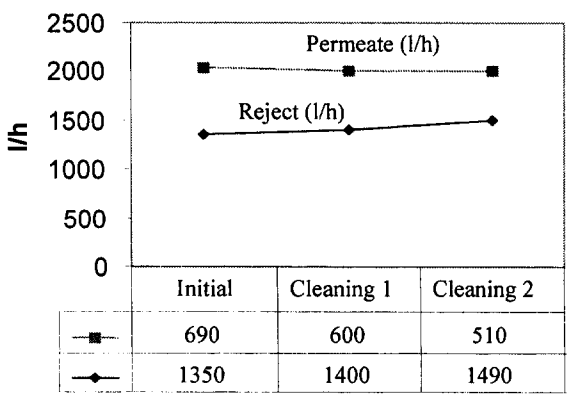
3.4. Membrane fouling

This is a key factor in a membrane process, because the cleaning stage forces the sequential outage of the operation in the plant and generates the quick ageing of the membranes.

A rinse mode was made by totally opening the rejection valves and reducing the system pressure. These conditions generate a turbulent rise and pull a large amount of solids deposited in the membrane surface.

According with the membrane specifications, a chemical cleaning was made. It consists in removing the metallic oxides by treatment them with citric acid, and eliminating oil and greases using an abluent. Due to the fact that this experimentation was not continuous, the period of time necessary to clean the membranes is not representative to the real situation.

Once the cleaning process was made, a comparative study of the membrane abilities was done and the recovery of membrane capacities was adequate and similar to the original. These results show evidence the efficacy of the chemical cleaning, as Fig. 3 shows.



	Initial	Cleaning 1	Cleaning 2
■	690	600	510
◆	1350	1400	1490

Fig 3. Permeate flow before and after the membrane cleaning.

4. Conclusions

Membrane technology can be used to treat the global effluent from the electroplating industry. Previously it is necessary to make the following pre-treatments:

(1) Oxidising the cyanides contained in the basic stream that contents this pollutant.

(2) Eliminating solid by using a 5 μm filter.

(3) Adjusting the pH in the inlet of effluents that feeds the membrane system. The minimum pH will be according to the chosen membranes.

The permeate obtained presents a quality as the deionized water, and it is possible to incorporate it into the production process. The physical and chemical characteristics of this permeate are better than the water used in these industries.

The percentage of recycled water is about 75–95% depending on the pollutants contained in the initial effluent.

The pollutants contained in the rejection, approximately 15–25% of volume of the steam fed, can be recovered and put away in a dump as solid wastes.

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