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JACEK WIŚNIEWSKI^{*}, GRAŻYNA WIŚNIEWSKA^{*}

APPLICATION OF ELECTRODIALYSIS AND CATION EXCHANGE TECHNIQUE TO WATER AND ACID RECOVERY

Neutralization is a widespread method for the treatment of wastewaters from rinsing after metal etching. The process, however, is concomitant with the precipitation of environment-unfriendly sludges (metal hydroxides). The neutralized effluent carries a considerable load of salts which are very difficult to remove (if at all) by conventional treatment trains, thus undesirably affecting the receiving streams. Another drawback is the loss of two valuable components – water and acid.

The objective of the study was to recover water and acid from the after-etching rinse. The effluent contained hydrochloric acid (24 eq H^+/m^3), iron salt (99 g Fe_{tot}/m^3), nickel salt (2.66 g Ni^{2+}/m^3) and chromium salts (0.61 g Cr^{3+}/m^3). The experiments were run, using three alternative technological trains which involved electrodialysis (ED) and cation removal via ion exchanger. The ED process was investigated in a GOEMASEP 136 laboratory setup equipped with 20 pairs of cells with Neosepta AMX and CMX membranes. The diluate to concentrate ratio amounted to 27 dm³:1.8 dm³, which was equivalent to water recovery of 93.7%. Metal cations were removed, using a macroporous cation exchanger of Amberlyst 15 type.

The first technological train (cation removal–ED 1–ED 2) provided recovery of two products, i.e. water and acid. The water recovered via this route had only trace amounts of iron and nickel salts (0.02g met./m³), and a conductivity of 10 μ S/cm. The acid recovered by the ED 1 process had a concentration of 370 eq H⁺/m³ and contained small amounts of iron salt (18 g Fe_{tot}/m³). Overall energy demand for ionic transport amounted to 1.62 Wh/dm³.

The second technological train (ED 1–cation removal–ED 2) yielded water of slightly higher conductivity (23.0 μ S/cm) and the same content of iron and nickel salts (0.02g met./m³). An energy demand for the ED processes was equal to 0.54 Wh/dm³.

The water recovered with the third technological train (ED 1–ED 2) had a conductivity of 15.4 μ S/cm but higher iron salt content (0.18 g Fe_{tot}/m³). Energy demand for the ED processes amounted to 0.66 Wh/dm³ at optimal current densities.

Institute of Environment Protection Engineering, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

1. INTRODUCTION

Effluents from the rinse of metals after etching contain acid and metal salts. A widespread method of treating such wastewater involves neutralization of acid and precipitation of metal hydroxides. As the aforementioned method makes use of chemicals (lime), large amounts of troublesome sludges are produced in the course of the treatment process, and the neutralized effluent displays an increased salinity level. In terms of environmental safety and cost-effectiveness, the most desirable treatment effect is the recovery of two major components – acid and water, which makes it possible to abate not only amount of chemicals for neutralization but also the load of metal salts carried by the neutralized effluent. What contributes considerably to the cost-effectiveness of the process is the value of the acid recovered and high quality of the water obtained via this method.

Acid recovery can be regarded as cost-effective when the final product is of the purity desired (which means absence of metal salts) and has achieved an appropriate degree of concentration. In this context, preference is being given to the application of monoselective electrodialysis [1], [2]. Monoselective membranes with considerably reduced transport numbers of bivalent ions provide acid solutions of a comparatively high purity and higher concentration than that measured in the raw effluent.

But monoselective electrodialysis was found to be inappropriate for water recovery. Much better effects were obtained by combining conventional electrodialysis with ion-exchange processes, because electrodialysis alone failed to provide water of the quality desired [3]. A combination of membrane techniques and ion-exchange processes is also advantageous in terms of the deionization costs. According to STRATHMANN [4], ion exchange is cost-effective at salt concentrations below 1 g/dm³, and electrodialysis at salt concentrations ranging from 1 to 10 g/dm³. However, the cost-effectiveness of the electrodialysis process was found to be primarily affected by the current density value. At increased current density, the membrane surface required can be noticeably reduced, but if the limiting value (i_{lim}) is exceeded, there will appear some undesirable implications such as increased energy demand, pH variations, and membrane destruction due to the rise in temperature. The equation derived by URANO et al. [5] enables determination of the i_{lim} value for an HCl solution with a defined acid concentration (C) and a defined flow velocity in the diluate cell (u). Hence we can write

$$i_{\rm lim} = 10C^{0.8}u^{0.78}$$
.

For the investigated after-etching rinse ($C = 24 \cdot 10^{-6}$ eq H⁺/cm³) and a constant flow rate in the diluate cell (u = 10 cm/s), the i_{lim} value calculated via the above route is 121 A/m².

The experiments were run, using three alternative technological trains which involved electrodialysis (ED) and cation removal via ion exchanger:

Train (I) – cation removal – ED 1– ED 2.

Train (II) – ED 1– cation removal – ED 2.

Train (III) - ED 1- ED 2.

Only train (I) provided recovery of two components: acid (by ED 1) and water (by ED 2). The other trains yielded water recovery alone.

2. EXPERIMENTAL

2.1. APPARATUS

The experiments were carried out on samples of after-etching rinsing bath, the etching agent being hydrochloric acid. The parameters of the effluent are listed in table 1.

Metal cations were removed using a macroporous, strongly-acidic cation exchanger of Amberlyst 15 type. Bed depth and filtration rate amounted to 0.5 m and 10 m/h, respectively. Cation removal was discontinued after a rapid rise of iron ion concentration in the effluent had been measured. The ion exchanger was regenerated with 10% HCl solution.

The ED process was run in a Goemasep 136 setup equipped with 20 pairs of cells comprising Neosepta AMX and CMX membranes, each of an effective surface area amounting to 36 cm^2 . The diluate volume to concentrate volume ratio was $27 \text{ dm}^3/1.8 \text{ dm}^3$. The ED process was carried out in a system with recirculation of the solutions, and was discontinued once when the desired efficiency of salt removal from the diluate had been achieved.

2.2. METHODS

In the course of the process, acid concentration and metal ion content were measured by titration and spectrophotometry (DREL 2000), respectively. Making use of the results of analyses, the following items were calculated (in the course of the ED process):

1. Efficiency of acid and metal salt removal from the diluate

$$\alpha = \frac{C_{dl}^{0} - C_{dl}^{t}}{C_{dl}^{0}} 100 \, [\%]$$

where C_{dl}^{0} and C_{dl}^{t} denote concentration of acid (or metal ions) in diluate, initial and after the time *t*, respectively; eq /m³ (g/m³).

| Parameter | Unit | Value |
|--------------|-------------------------------------|-------|
| pН | | 2.3 |
| Conductivity | mS/cm | 8.8 |
| Acidity | $eq H^+/m^3$ | 24 |
| Total iron | g Fe _{tot} /m ³ | 99 |
| Nickel | $g Ni^{2+}/m^3$ | 2.66 |
| Chromium | $g Cr^{3+}/m^3$ | 0.61 |

Characteristics of the effluent

2. Acid and metal salt enrichment in the concentrate

$$\varepsilon = \frac{C_c^{l}}{C_c^{0}}$$

where C_c^0 and C_c^t denote acid (or metal ion) concentration in the concentrate, initial and after the time *t*, respectively; eq/m³ (g/m³).

3. Energy demand

$$w_e = \frac{I \sum U \Delta t}{V_{dl}^t} \quad \left[\frac{Wh}{dm^3}\right]$$

where I denotes current intensity (A), U indicates voltage (V), t stands for duration of the process (h), and V_{dl}^{t} is the final volume of diluate (dm³).

4. Actual water recovery

 $R = 100(27 - \Delta V) / 28.8$ [%]

where ΔV is loss of diluate volume (dm³).

3. RESULTS

3.1. RECOVERY OF ACID AND WATER BY MEANS OF TREATMENT TRAIN (I)

The treatment train involved cation removal, ED 1 and ED 2 and aimed at the recovery of two valuable components from the after-etching effluent – hydrochloric acid (by ED 1) and water (by ED 2). It was possible to achieve this, because the effluent was subject to pretreatment which allowed removal of iron ions and heavy metal ions.

At the initial stage of the study, the minimum HCl dose required for an efficient regeneration of the ion exchanger was determined. Thus, after the point of bed breakthrough by iron ions had been reached, the ion exchanger was regenerated with three acid doses: 350, 250 and 150 g HCl per dm³ of cation exchanger, respectively. The ion-exchange capacity of the bed was established in terms of the mass of iron ions, chromium ions and nickel ions removed from the effluent prior to breakthrough. Table 2 includes the ion-exchange capacity values for the bed regenerated with various HCl doses.

As shown by these data, the reduction of the HCl dose from 250 to 150 g per dm³ of cation exchanger decreased slightly (by about 10%) the ion-exchange capacity of the bed. Thus, it can be anticipated that the 150 g/dm³ HCl dose is sufficient to regenerate the cation exchanger.

Water and acid recovery by electrodialysis and cation exchange

Table 2

| with various HCl doses | | | | | |
|----------------------------|---------------------------------------|--------------------|--------------------|--------------------|--|
| HCl dose | Ion exchange capacity with respect to | | | | |
| g/dm ³ cat. ex. | Fe ²⁺ | Cr ³⁺ | Ni ²⁺ | Total | |
| | eq/dm ³ | eq/dm ³ | eq/dm ³ | eq/dm ³ | |
| 350 | 0.617 | 0.006 | 0.017 | 0.640 | |
| 250 | 0.630 | 0.005 | 0.024 | 0.659 | |
| 150 | 0.570 | 0.001 | 0.014 | 0.585 | |

Ion-exchange capacity of the cation exchanger regenerated with various HCl doses

Ion exchange provided removal efficiencies of 98.8%, 82.3%, and 93.4% for iron ions, nickel ions, and chromium ions, respectively. There was a concomitant increase in acid concentration as well as in the electrolytic conductivity of the solution. The parameters of the effluent following cation removal are listed in table 3.

Table 3

| Parameter | Unit | Value |
|--------------|-------------------------------------|-------|
| pН | | 2.05 |
| Conductivity | mS/cm | 10.4 |
| Acidity | $eq H^+/m^3$ | 27.0 |
| Total iron | g Fe _{tot} /m ³ | 1.2 |
| Nickel | g Ni ²⁺ /m ³ | 0.47 |
| Chromium | $g Cr^{3+}/m^{3}$ | 0.04 |

Parameters of the effluent following cation removal

After the metal ions had been removed, the effluent was sent to the ED 1 unit for acid recovery. The acid recovered in the course of the ED 1 process can be used in the preparation of a fresh etching bath.

Current density was found to have little effect (if at all) on the efficiency of acid removal, or residual iron salt removal, from the effluent (figure 1). Acid and iron salts were removed with an efficiency approaching 98% and 97%, respectively. Only at the highest current density applied in this study (150 A/m²) the efficiency of iron salt removal dropped to about 93%. There was, however, a slight contribution of current density to the acid enrichment in the concentrate, which varied from 11.7 (for i = 75A/m²) to 14.1 (for i = 150 A/m²). The plots are presented in figure 2. But with the increasing current density, the energy demand for ionic transport increased rapidly from 0.84 Wh/dm³ (at $i = 75 \text{ A/m}^2$) to 3.78 Wh/dm³ (at $i = 150 \text{ A/m}^2$), as shown by the plots in figure 3.



Fig. 1. Efficiency of the acid (α_{H^+}) and iron salt (α_{Fe}) removal vs. current density (*i*) for the effluent after cation removal



Fig. 2. Acid enrichment (ε) in the concentrate vs. current density (*i*)



Fig. 3. Energy demand (w_e) vs. current density (i) in the ED 1 process

On considering the acid concentration in the concentrate achieved in the course of the process, as well as the energy demand involved, we anticipated that the optimum current density for the process was 100 A/m². With such a current density we obtained a slightly acid diluate (0.6 eq H⁺/m³) with low-iron concentration of salt (0.04 g Fe/m³), and a highly acid (370 eq H⁺/m³) concentrate with small amounts of iron salts (18 g Fe/m³) at an energy demand amounting to 1.33 Wh/dm³.

To recover high-quality water, the diluate obtained by ED 1 was sent to the ED 2 unit. We found that, in the investigated range (10, 20 and 30 A/m²), current density had little effect on the quality of the recovered water. In every instance, the efficiency of residual acid removal was 100%, whereas that of residual iron salt removal ranged from 50% (at 10 A/m²) to 75% (at 30 A/m²). On comparing the energy demand for ED 2 and the parameters of the recovered water, we assumed that the most advantageous current density value was i = 20 A/m². The water recovered with this current density contained trace amounts of iron salts (0.02 g Fe_{tot}/m³) and nickel salts (0.02 g Ni²⁺/m³), and had a conductivity of 10 μ S/cm; energy demand for ionic transport amounting to 0.29 Wh/dm³.

Analysis of the concentrate obtained by ED 2 showed that its parameters were similar to those of the effluent after cation removal (conductivity, 5.1 mS/cm, acidity, 11.0 eq H⁺/m³; Fe_{tot}= 0.5 g Fe/m³). This finding substantiates the potentiality for using the concentrate obtained by ED 2 as the feeding concentrate of ED 1. At such approach, water recovery by ED 1 and ED 2 may amount to 93.75%. In reality, however, this value is lower because of the water transport from the diluate to the concentrate, which is mainly induced by the osmosis phenomenon and by the hydration layer transfer. Water transport was found to occur only in the course of the ED 1 process (because of the high concentration gradient and high current density). At optimal current density, actual water recovery by ED 1 and ED 2 totalled 93.4%, whereas overall energy demand for ionic transport amounted to 1.62 Wh/dm³.

3.2. RECOVERY OF WATER WITH TREATMENT TRAIN (II)

The treatment train involved ED 1, cation removal and ED 2 as unit processes, and provided only water recovery from the after-etching effluent. The water recovered via this route was of high quality. The concentrate produced in the course of the ED 1 process was a waste material – a mixture of acid and metal salts. A major advantage of the treatment train was that the operation of the cation exchanger (up to break-through) could be extended considerably due to the removal of metal salts in the course of ED 1.

In the investigated range of current density (40–75 A/m²), the efficiency of acid removal approached 96% and varied only slightly as shown by the plots in figure 4. But there was a noticeable relation between current density and the removal of metal salts. Once the current density value had exceeded 50 A/m², the values of α_{Fe} , α_{Ni} and

 α_{Cr} decreased rapidly (figure 4). The optimum value of current density approached 50 A/m², and was found to be the one resulting from the intersection of the α_{H+} and α_{Fe} curves (HCl and metal salts being the main components of the untreated after-etching effluent). At 50 A/m², the energy demand for ionic transport was only 0.40 Wh/dm³. The parameters of the effluent from the ED 1 process are listed in table 4.



Fig. 4. Efficiency of the acid (α_{H^+}) and metal salts (α_{Fe} , α_{Ni} , α_{Cr}) removal vs. current density (*i*) for raw wastewater

Table 4

Parameters of the effluent from the ED 1 process ($i = 50 \text{ A/m}^2$)

| Parameter | Unit | Value |
|--------------|-------------------------------------|-------|
| рН | _ | 2.7 |
| Conductivity | mS/cm | 0.43 |
| Acidity | eq H ⁺ /m ³ | 1.1 |
| Total iron | g Fe _{tot} /m ³ | 3.2 |
| Nickel | $g Ni^{2+}/m^3$ | 0.095 |
| Chromium | $g Cr^{3+}/m^3$ | 0.02 |
| | - | |

The efficiency of cation removal by ion exchanger was found to be good as the concentrations of iron ions, nickel ions and chromium ions decreased to the level of 0.08 g Fe_{tot}/m^3 , 0.014 g Ni^{2+}/m^3 and 0.01 g Cr^{3+}/m^3 , respectively. It should be noted that ca. 97% efficiency of iron salt removal achieved in the ED 1 process multiplied the volume of the wastewater which had been filtered to the moment of bed break-through. We determined this volume by making use of the ion-exchange capacity of the cation exchanger with respect to iron ions (0.570 eq/dm³ of cation exchanger) as

well as the initial and final concentrations of Fe_{tot} (3.2 g Fe/m³ and 0.08 g Fe/m³, respectively). The value obtained by this method was 5.135 dm³ per dm³ of cation exchanger. In the case of untreated effluent (where the concentration of Fe_{tot} ions decreased from 99 g Fe/m³ to 1.2 g Fe/m³ as a result of ion exchange), the wastewater volume which had been filtered up to the breakthrough point amounted only to 163 dm³ per dm³ of cation exchanger.

Since cation removal brought about a rise in acid concentration, the final stage of the treatment process included ED 2. In the water recovered via this route, acid and chromium salts were absent, whereas iron salts and nickel salts occurred in trace amounts only (0.02 g Fe_{tot}/m³ and 0.01 g Ni²⁺/m³, respectively). Conductivity totalled 23 μ S/cm.

Current density had little effect on the efficiency of desalination; but as current density increased, so did energy demand (from 0.14 Wh/dm³ at i = 10 A/m² to 0.46 Wh/dm³ at i = 30 A/m²). That is why we adopted the current density value of 10 A/m² as best suited for the needs of the process.

The concentrate obtained by ED 2 had an acid concentration of 32 eq H^+/m^3 and 8.8 mS/cm. Hence, the concentrate from ED 2 could be used in ED 1. Under such conditions, the efficiency of water recovery by ED 1 and ED 2 (including osmotic transport) totalled 93.3% at an overall energy demand for ionic transport of 0.54 Wh/dm³.

3.3. WATER RECOVERY WITH TREATMENT TRAIN (III)

The treatment train included ED 1 and ED 2, and the objective of the study was to find out whether or not a two-stage electrodialysis process would yield the recovery of high-quality water. The treatment effect obtained by means of ED 1 was reported in



Fig. 5. Efficiency of metal salt removal ($\alpha_{\text{Fe}}, \alpha_{\text{Ni}}$) vs. current density for the effluent after ED 1

section 2. The ED 2 process brought about a complete removal of residual acid concentration, irrespective of the current density applied (10, 20 or 30 A/m^2). But as the current density increased, the efficiency of iron salt removal showed a tendency to decrease (figure 5). Thus, the best desalination effect (95%, 78% and 100% efficiency of iron salt removal, nickel salt removal and chromium salt removal, respectively) was achieved with the lowest current density applied (10 A/m²). The water recovered by ED 2 had a conductivity of 15.4 μ S/cm; total iron content and nickel concentration amounting to 0.18 g Fe_{tot}/m³ and 0.02 g Ni²⁺/m³, respectively. Energy demand for ionic transport in the ED 2 process totalled 0.26 Wh/dm³.

The parameters of the concentrate obtained by ED 2 (22 eq H^+/m^3 , 22 g Fe_{tot}/m^3 , and 6.1 mS/cm) allowed its reuse in the ED 1 process. That is why the theoretical recovery of water amounted to 93.75%, whereas the real efficiency of water recovery (including osmotic transport) obtained with the treatment train (III) was 93.3%. Energy demand for ionic transport in ED 1 and ED 2 reached 0.66 Wh/dm³.

4. SUMMARIZING COMMENTS

1. In terms of water and acid recovery, the most effective treatment train for the effluent from rinsing of metals after etching was the one involving cation exchange, ED 1 and ED 2. The treatment train provided recovery of acid (concentrate of ED 1) and recovery of deionized water (diluate of ED 2). The acid solution (370 eq H^+/m^3 , with a small amount of iron salts) can be reused as a component of fresh etching bath, whereas the water recovered via this treatment train (conductivity, 10 μ S/cm; trace amounts of iron and nickel salts) may be of utility in final rinsing (after etching of metals). Real recovery of water by ED 1 and ED 2 was 93.3%, and energy demand for ionic transport totalled 1.62 Wh/dm³.

2. The treatment train consisting of ED 1, cation exchange and ED 2 provided only water recovery from the after-etching effluent. The flux of deionized water (conductivity, 23 μ S/cm; trace amounts of iron and nickel salts) accounted for 93.3% of the overall flux of the treated wastewater. Energy demand for ionic transport in ED 1 and ED 2 amounted to 0.54 Wh/dm³ only. Compared to the treatment train described in item 1 a major advantage of the present treatment train was the 30 fold increase of the wastewater volume which had been filtered through the cation exchanger up to the breakthrough point.

3. The treatment train including a two-stage electrodialysis process, ED 1 and ED 2, yielded recovery of water which had a low conductivity (15.4 μ S/cm) and slightly increased iron salt content (0.18 g Fe_{tot}/m³). Real efficiency of water recovery by ED 1 and ED 2 totalled 93.3% at an energy demand for ionic transport of 0.66 Wh/dm³.

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ZASTOSOWANIE ELEKTRODIALIZY I JONITOWEJ DEKATIONIZACJI DO ODZYSKU WODY I KWASU

Podstawową metodą oczyszczania ścieków z płukania po trawieniu metali jest neutralizacja. W procesie tym jednakże powstają uciążliwe dla środowiska osady.

Przedmiotem badań był odzysk wody i kwasu ze ścieków z płukania metali po trawieniu. Ścieki zawierały kwas solny (24 eq H^+/m^3), sole żelaza (99 g Fe/m³), sole niklu (2,66 g Ni²⁺/m³) i sole chromu (0,61 g Cr³⁺/m³). Eksperymenty prowadzono w trzech różnych układach technologicznych, w których stosowano elektrodializę (ED) i jonitową dekationizację. Proces elektrodializy prowadzono w laboratoryjnym elektrodializerze GOEMASEP 136, składającym się z 20 par komór z membranami Neosepta AMX i CMX. Stosunek objętości dyluatu do koncentratu wynosił 27 dm³:1,8 dm³. Jony metali usuwano za pomocą makroporowatego kationitu Amberlyst 15.

W układzie technologicznym (I) (kationit–ED 1–ED 2) prowadzono odzysk dwóch produktów – wody i kwasu. Odzyskana w ten sposób woda zawierała śladowe ilości soli żelaza i niklu (0,02 g met./m³), a jej przewodność wynosiła 10 μ S/cm. Roztwór kwasu natomiast miał stężenie 370 eq H⁺/m³ i był nieznacznie zanieczyszczony solami żelaza (18 g Fe_{og}/m³). Zużycie energii na transport jonów w procesach ED wynosiło 1,62 Wh/dm³.

W układzie technologicznym (II) (ED 1-kationit-ED 2) uzyskano wodę o nieco wyższej przewodności (23 mS/cm) i porównywalnej zawartości soli żelaza i niklu (0,02 g met./m³). Zużycie energii w procesach ED wynosiło 0,54 Wh/dm³.

Zastosowanie układu technologicznego (III) (ED 1–ED 2) umożliwiło odzyskanie wody o przewodności 15,4 µS/cm, lecz o wyższej zawartości soli żelaza (0.18 g Fe_{og}/m³). Zużycie energii w procesach ED wynosiło 0,66 Wh/dm³.

