Removal of heavy metals from Water Rinsing of Plating Baths by Electrodialysis

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Abstract. During the chromic plating of parts, the baths become more and more poor in chromic acid and rich in metallic impurities such as Cu^{2+}, Zn^{2+}, Fe^{3+} and Cr^{3+} which makes the bath useless. Also, the water used to rinse parts contains chromic acid and metallic impurities. As it is known that chromic acid is relatively expensive and very toxic, so its recovery has double interest: economic and environmental. Its reuse is possible after removal of metallic impurities. In this work, we studied the possibility of metallic impurities elimination from the chromic acid. The influence of the current density and the circulating solution flow rate on the process efficiency has been studied. The elimination rates obtained in the presence of ion exchange textile are superior to those obtained in the absence of textile. The analysis of the results showed that for the three metallic impurities studied (Cu^{2+}, Fe^{3+} and Zn^{2+}), the purification rate increases versus the applied current density and solution flow rate. The importance of the elimination of the three metal cations is as the following order: $Cu^{2+} > Zn^{2+} > Fe^{3+}$.

Key words: Electrodialysis, Chromic Acid, Metallic Impurities, Recovery, Purification

Introduction

The surface treatment industry is a major consumer of water due to multiple rinses during the process. For example, during passage of the plating bath to rinse baths, chrome parts result in greater or lesser amounts of chromic acid and metal impurities in the rinse water. The chromic acid is one of the most hazardous components of waste water. Moreover, it is relatively expensive. We attach a special interest in its recovery. Generally known purification processes are relatively complicated, which also would deprive the recovery of profitability any character, such as methods of reduction – neutralization - precipitation generate a large volume of sludge, which leads to a displacement of pollution. The ion exchange can be applied to the recovery of chromic acid, however it has the constraint of regeneration cycles. The objective of this work is to study the possibility of purifying the rinse water contaminated by metallic impurities.

Materials and Methods

Laboratory cell and procedures

Electrodialysis has been implemented on a laboratory cell (figure 1) and tested with synthetic solutions of chromic acid containing a metal cation (Cu^{2+} or Zn^{2+} or Fe^{3+}). The cell is composed of four compartments: the power (A), anode electrode (EA), receiver (R) and cathode electrode (EC). The experimental setup that allowed to perform testing purification and by electrodialysis is presented in Figure 2. The solution to be treated flows through the feed compartment (A), while the pure chromic acid solution to concentrate flows through the anode electrode compartment (EA). In the receiver compartment (R), which had to transfer the metallic impurities, circulates a solution of sulfuric acid. In the cathodic electrode compartment (EC) also circulates a solution of sulfuric acid. At the ends of the cell are placed two electrodes, titanium plates in the compartment (EA) and graphite in the compartment (EC). The two electrodes are connected to a generator to power regular intensity (0-2.5A, 0-30V). We worked in galvanostatic mode to maintain constant current. Compartments and electrode materials are plexiglass.

The sealing of all joints is ensured by 1mm thick. The solutions studied were synthetic solutions of composition: 0.1M in CrO_3 + H_2SO_4 + 10^{-4} M to 10^{-2} M metal impurities (Cu^{2+} or Zn^{2+} or Fe^{3+}). At the end of follow changes in the concentrations of metallic
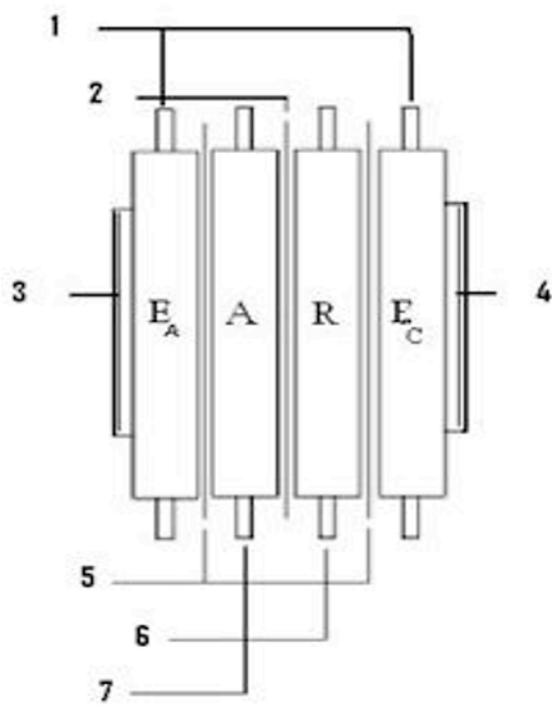
1 : Electrode compartment

2 : Cation exchange membrane   3: Anode

4: Cathode   5 : Anion exchange membrane

6 : Recevoir compartment   7: feed compartment

Fig. 1. Schematic of the electrodialysis cell with four compartments

impurities and chromic acid samples are taken in different compartments and concentrations were analyzed by atomic absorption (AA spectrophotometer SHIMADZU-62OO).

Results and Discussion

The analysis of the concentration of metallic impurities in the feed and receiver compartments was used to quantify the effectiveness of the solution purification and analysis of the concentration of chromic acid in the feed and anode compartments was used to quantify the reconcentrate of chromic acid.

Treatment of the multicationic solution

In order to improve the effectiveness of treatment we have tested a technique that combines electrodialysis with ion exchange. In the central compartment or feed compartment delimited by two ion -exchange membrane is insert a sheet of ion-exchange textile. The effectiveness of the technique combining electrodialysis and ion exchange can be improved by optimizing parameters such as current density, traffic flow rate, the concentration of the solution and the pH.

Removal of metallic impurities by electrodialysis and electrodialysis associated with ion exchange

Analysis of the cation concentration in the solution at the outlet of the feed compartment allowed us to calculate the elimination rate. The elimination rates (table 2) obtained in the presence of textile are superior to those obtained in the absence of textile. For the three metal cations studied, the greatest difference was observed with Fe^{3+} cations.

Table 2. Values of elimination rate (%)

Element	Cu^{2+}	Zn^{2+}	Fe^{3+}
Electrodialysis	32,24	30,64	22,70
Electrodialysis- Ion exchange	50,94	53,5	46,5

Influence of some parameters

In order to improve the effectiveness of treatment we have tested a technique that combines electrodialysis with ion exchange. In the central compartment or feed compartment

Influence of current density

To see the influence of current density on the transfer of metallic impurities from the feed compartment to the receiver compartment, we conducted experiments acid purification, lasting one hour at different current densities. Figure 3 shows that when the current density increases the number of transferred moles of metal cations into the receiver compartment increases. A current density 20 mA cm^{-2} chosen as optimal density in previous studies, the numbers of moles Cu^{2+} and Zn^{2+} are equal and superior to that of Fe^{3+} cations.
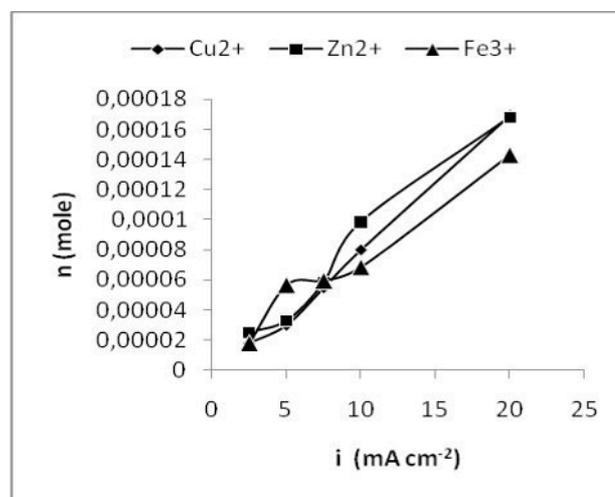

Fig. 3. Variation in the number of moles as a function of current density

Influence of flow rate

The performance of the method according to the flow rate of the feed solution can be analyzed from the results in table 3. The elimination rate of fall drastically significantly (more than 4 times) when the flow rate increases from 0.4 to 8 ml min^{-1}. The increased flow rate of 8 to 30 mL min^{-1} causes a decrease less sensitive than the first. The value of flow rate 0.4 mL min^{-1} was already chosen in the study purification and re-concentration of acid by electrodialysis as the optimal value.

Table 3. Elimination rate versus flow rate

Flow rate (mL min^{-1})	0,4	8	15	30
		T^E (%)		
Cu	50,94	11,18	9,19	8,88
Zn	53,5	11,39	10,73	10,20
Fe	46,50	14,39	12,38	9,61

Influence of pH

As the studied solution is very acidic can expect a competitive transfer across the membrane between the metal cations and protons. A late highlight the influence of the concentration of protons we have performed experiments at different pH values. Examination of the solutions prepared at different pH values for a solution (Fe^{3+}: 8 10^{-4} M, Cu^{2+}: 10^{-2} M, Zn^{2+}: 10^{-2} M), showed that from pH 2 precipitation begins. The results of purification solutions at different pH were used to calculate the clearance rate. Table 4 shows that indeed when the pH increases the clearance rate increases. The increase in the average treatment of 53 (pH 1.1) to 78% (pH 1.7) illustrates the competition between metal cations and protons.

Table 4. Elimination rate at different pH values.

pH	1,1	1,28	1,45	1,70
Cu^{2+}	52,31	56,50	61,52	79,12
Zn^{2+}	54,94	57,51	66,78	80,38
Fe^{3+}	53,34	59,17	60,53	75,89

Influence of initial concentration of metal ions in the feed solution

The results are expressed in Table 5. It is observed that the values of elimination rates (Table5) show that the process efficiency decreases drastically when the concentration of the feed solution increases. At the lowest concentration the elimination rate of the three metal cations are similar.

Table 5. Rate of treatment with different concentrations of the feed solution

C	0,08	0,16	0,33	0,5	1
Cation			T^E (%)		
Cu^{2+}	74,40	70,00	68,7	55,00	50,94
Zn^{2+}	72,30	61,26	57,6	49,40	53,5
Fe^{3+}	71,50	67,00	65,5	61,00	46,50

Conclusion

The results of the study focused on the elimination of metal cations from chromic acid solutions by electrodialysis have shown that it is possible to separate metallic impurities from wastewater containing chromic acid. The electroextraction of metal cations depends on the applied current density, flow rate and pH of the solution to be treated. The elimination rates obtained in the presence of ion exchange textile are superior to those obtained in the absence of textile.

References

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