

Extraction and recovery of chromium from electroplating sludge

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Abstract

This work reports a study of the extraction and recovery of chromium from the wastes (class I dangerous) generated by a galvanic manufacturer. Commercial HCl at room temperature was employed, and the conditions of the extraction process were optimized according to a sequential experimental design, which also included the acid concentration and contact time as variables. The best extraction conditions (80% v/v; 30 min; 97.6% Cr) for the chromic sludge were chosen in order to make the recovery process economically feasible. After each extraction, the residue was submitted to leaching essays, to assess environmental risks. It was found that sludge could be characterized as no longer dangerous. In the recovery study, a simple and low-cost technique was evaluated for selectivity based on an oxidation step with hydrogen peroxide. A 2³ factorial design to assess the influence of oxidation time (min), temperature (°C) and peroxide amount (mol/L) was employed. The best conditions, yielding a chromium recovery of about 92%, were a time of 60 min, a temperature of 60 °C and 2.1 mol/L peroxide. Additional essays revealed that the same result could be obtained with more economic conditions (40 min, 1.4 mol/L peroxide and 60 °C). This technique proved not only effective in comparison with existing alternatives, but also low costing.
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1. Introduction

Residues discarded by industrial processes figure among the most important sources of environmental contamination. This is especially true of processes that use or yield dangerous chemicals, leading to potentially dangerous residues [1].

Many noxious residues are routinely treated for removal and recovery of heavy metals, with techniques that include conventional neutralization or precipitation, electrochemical reduction, ion exchange, reverse osmosis, membrane separation, and solvent extraction [2–4]. Precipitation of metal ions as hydroxides, under appropriate pH conditions, has been one

of the most used conventional methods [5]. This treatment, however, generates a heavy metal laden ‘slime’ or ‘sludge’.

The literature reports only few works on heavy metal recycling, and is scarce concerning chromium found in sludge resulting from chemical neutralization and precipitation. Since recovery of these metals with traditional separation procedures does not appear to be economically feasible, a search for safe alternative solutions for their final disposition is warranted [6]. One such possibility is using the metal sludge as an additive to cements and ceramic materials [7,8]. The main drawback of this approach resides in the fact that many people are allergic to heavy metals, and may exhibit skin edemas because of contact with the cement wet paste or with the ceramic artifact itself. Moreover, in addition to their toxic potential some sludge metals are economically valuable. This lends further motivation for investigating other recovery pro-

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cesses. Some hydrometallurgical techniques to treat sludge have been studied, with a view to obtaining maximum selectivity and recycling. Promising results have been obtained by combining relatively difficult and expensive methods like conventional liquid–liquid extraction, ion exchange, and/or electrochemical separations. These attempts, however, have not advanced beyond the laboratory or pilot plant scale [9,10].

In this work, we report on the treatment of galvanic sludge residues originating from a pre-treatment step in a production line for coated aluminum plates. This process consists of five stages: (1) alkaline degreasing at pH 2; (2) alkaline rinsing at pH 8.5–9.0; (3) chromium electrodeposition in a fluoridric/phosphoric medium; (4 and 5) two successive rinsing steps with industrial water at pH 3.0 and 5.0, respectively. After this treatment, the plates are ready to be taken for the coil coating step. All baths are carried out by spraying on both faces of the plates, with a nozzle pressure of 2 Kg/cm² and a line speed of 17–30 m/min, depending on plate thickness. The temperature is maintained at 35 ± 1 °C throughout the whole process. The effluent from the galvanic process is then neutralized and the metals precipitated by adding sodium hydroxide. The resulting sludge is finally treated by a simple, efficient and low-cost methodology for chromium extraction and recovery, evaluated in this work. This method's parameters were systematically varied according to sequential two-level factorial designs, to improve its extraction efficiency and to evaluate the selectivity of chromium oxidation by hydrogen peroxide. This methodology was preferred, instead of the widely used simplex optimization, because it usually requires less experimental runs.

2. Experimental

2.1. Classification of chromic sludge

A chromic sludge gross sample obtained from treatment of galvanic industrial effluents was subjected to leaching and solubilization, as previously described [11,12]. Chloride, cyanide, total chromium, fluoride, arsenic, barium, bismuth, chromium, mercury, nitrate, total phosphorus, sulfate, and surfactants were then quantified, following the methodology of [13].

2.2. Chemical composition of the chromic sludge

An amount of approximately 1 g of sludge sample was weighed and transferred to a porcelain crucible, mixed with 5 mL of concentrated HNO₃, and digested on the top of a heating plate. This procedure was repeated until the supernatant was clear. The material was then filtered into a 100 mL volumetric flask, and the volume completed with distilled water. A blank was prepared in the same way. The metals were quantified by inductively coupled optical emission spectrometry (ICP-OES).

Table 1

Sequential factorial designs used to evaluate the influence of acid concentration and contact time on heavy metal extraction

Run	HCl concentration (% v/v)	Contact time
1	60	24 h
2	80	24 h
3	100	24 h
4	60	5 h
5	80	5 h
6	100	5 h
7	60	3 h
8	80	3 h
9	100	3 h
10	30	1 h
11	60	1 h
12	80	1 h
13	100	1 h
14	30	30 min
15	60	30 min
16	80	30 min
17	100	30 min
18	10	10 min
19	10	30 min

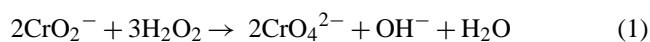
2.3. Acid extraction of metals from the sludge

Low-costing commercial HCl (Laborquímica) (US\$ 0.6/L) was used as the extracting agent, with the following characteristics: 25.8% purity, 1.13 g/mL density, 0.02 mg/L Zn, 0.03 mg/L Cr, 0.06 mg/L Al.

For metal extraction, 5 mL HCl was added to a residue sample weighing approximately 1 g, which was then stirred at 150 rpm. To find out improved extraction conditions, the influence of acid concentration and contact time was assessed with the four factorial designs given in Table 1, carried out sequentially. After each experiment, the heavy metal amounts were determined by ICP-OES. The residue left after each extraction was again subjected to leaching [11].

2.4. Chromium recovery

To assess chromium recovery, Cr(III) was oxidized to Cr(VI) with 30% hydrogen peroxide (US\$ 1.5), according to



A real sludge sample containing Cr (2424.5 mg/L), Al (1625.0 mg/L), Fe (1220.6 mg/L), Ca (157.1 mg/L), and Mg (155.3 mg/L) was employed for the analysis. The 2³ factorial design shown in Table 2 [14] was employed to achieve improved recovery conditions. The three factors in this design – concentration of H₂O₂, reaction time and temperature – were selected according to studies found in the literature [15,16]. The percent of oxidized Cr(III) was used as the response in the statistical analysis of the design results. The analysis of this first design indicated the need for the additional experiments given in the last five lines of Table 2. All

Table 2
Factorial designs used for studying Cr(III) oxidation conditions

Run	Time (min)	Temperature (°C)	[H ₂ O ₂] (mol/L)	Cr(VI) (mg/L)	Oxidized Cr(III) to Cr(VI) (%)
1	20	40	0.7	205.84	8.49
2	60	40	0.7	931.98	38.44
3	20	60	0.7	1421.48	58.63
4	60	60	0.7	1853.78	76.46
5	20	40	2.1	385.25	15.89
6	60	40	2.1	1894.75	78.15
7	20	60	2.1	1666.36	68.73
8	60	60	2.1	2253.57	92.95
9–11	40	50	1.4	1372.27, 1184.85, 1372.76	56.60, 48.87, 56.61
12	40	60	1.4	2253.57	92.95
13	40	60	2.1	2123.14	87.57
14	60	50	1.4	1772.31	73.10
15	60	50	2.1	1829.53	75.46
16	60	60	1.4	2172.35	89.60

The first design included a central point in triplicate (runs 9–11).

calculations were carried out with the ‘Statistica’ computational package [17].

2.5. Procedure for oxidizing Cr(III) to Cr(VI)

A 20 mL aliquot of the extract containing 2424.5 mg/L chromium was transferred to a 50 mL beaker and its pH was adjusted to 10 with NaOH, as indicated by the results obtained by [18,19]. The experiments were performed as specified by the level combinations given in Table 2. After each experimental run, the corresponding solution was cooled and filtered. The concentration of chromium(VI) in the filtrate was determined by the diphenylcarbazide method, using an UV–vis spectrophotometer, with absorbances recorded at 540 nm [13].

3. Results and discussion

3.1. Characterization of chromic sludge

The chemical composition of chromic sludge is determined by the process used for treating industrial effluents, chromium, aluminum, iron, calcium, and magnesium being the elements present in the largest amounts. The usual treatment consists in using sodium bisulfite to reduce the Cr(VI) ions resulting from the painting process of aluminum plates to Cr(III), after which the highly insoluble chromium(III) hydroxide is precipitated with NaOH. Several other metals also precipitate in this step from the effluent, where they are present in the following amounts: Fe (1850.0 mg/L), Al (1891.7 mg/L), Ca (225.1 mg/L), Mg (212.9 mg/L), Mn (1.8 mg/L), and Zn (5.0 mg/L).

After the chromic sludge was subjected to leaching according to the [11] procedure, it was found that fluoride was still present in a concentration of 249.0 mg/L, well above the maximum level allowed by legislation, 150.0 mg/L. Therefore, the residue is classified as dangerous, class 1 [1].

3.2. Sequential experimental design for the chromic sludge

Several studies with sludge resulting from the treatment of effluents have been reported. Within these, Macchi et al. obtained 90% chromium recovery using concentrated H₂SO₄ and a contact time of 24 h [18]. Taking these results as starting point, in the first experiments the contact time was kept at 24 h and the concentration of commercial hydrochloric acid (used instead of the more expensive sulfuric acid) was set at three different levels: 60, 80 and 100% (v/v). These experiments led to chromium recoveries in the 89.9–99.6% range. Moreover, almost all the residue was dissolved, rendering the fluoride leaching determination unnecessary.

With a view to reducing process costs, shorter contact times (5 and 3 h) were then tried. Chromium recovery in these experiments remained high, from 87.5 to 99.7%, and again practically all the sludge dissolved.

In the third design, the acid concentration was varied from 30 to 100%, and the contact time from 30 min to 1 h. Recovery values between 75.1 and 99.5% were then obtained. The concentration of leached fluoride was determined only for recovery values under 81.0%, where it was found in the 30.6–36.1 mg/L interval, well within the range allowed by the regulation [1].

In the last design, the acid concentration of acid was reduced to 10% and the contact time was varied from 10 to 30 min. These levels yielded recoveries from 55.5 to 61.8%. Even though, in the cases when a residue was left, the largest leached fluoride concentration was 47.7 mg/L, still in compliance with legislation. These relatively low amounts may be explained by the low solubility of Cr(III) in water. A 3D plot of the results of all experiments is shown in Fig. 1. As the acid concentration and the contact time increase, the amount of recovered chromium also increases. This may be explained by an increase in dissolving power as the acid concentration is raised. This is an important factor, because Cr(III) is insoluble in water. Longer contact times also lead to increased

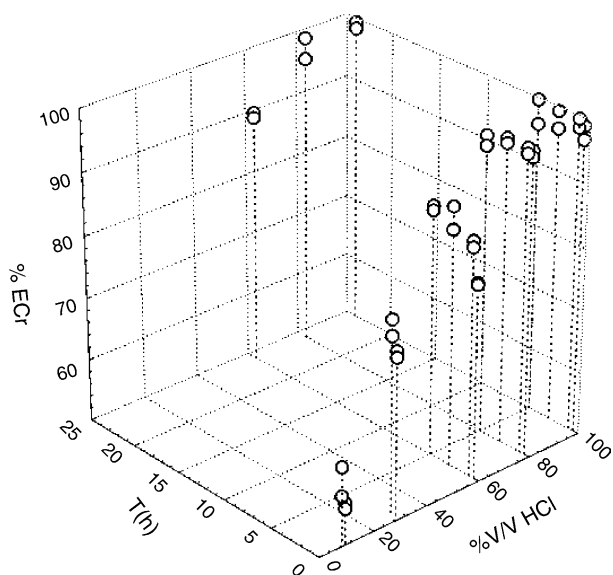


Fig. 1. Percent chromium recovery in chromic sludge at several concentrations of commercial hydrochloric acid (5, 10, 30, 60, 80, and 100%) and contact times (10 min \cong 0.17 h, 30 min \cong 0.5, 1, 3, 5, and 24 h).

recovery, but this effect is not very significant for concentrated solutions.

3.3. Chromium recovery from the sludge

Since chromium is not the sole metal ion present in the sludge, hydrogen peroxide was employed to oxidize Cr(III) to Cr(VI), to avoid interference of other species in its recovery. Chromium in sludge usually appears as part of insoluble hydroxides. To separate it from other metals, several oxidizing agents have been used. Mathew used sodium hypochlorite, ozone and hydrogen peroxide to oxidize chromium in electroplating sludge [19]. Even with excess sodium hypochlorite, chromium oxidation required a medium set at pH 10, heating to 50 °C and stirring for 1 h, and no more than 85% chromium was recovered as chromate. Duffey obtained complete Cr(III) recovery from an iron-containing sludge, also using sodium hypochlorite [20]. It was suggested, in this case, that the ferric ion remains insoluble as ferric hydroxide, instead of ferric chromate, and therefore does not compete with chromium. Despite being a very efficient oxidizing agent for Cr(III), sodium hypochlorite may exhibit some undesirable environmental effects. During the oxidation of Cr(III), the organic matter in the sludge may react with chlorine in the hypochlorite to yield harmful organochlorinated compounds [18,21]. Human exposure to these compounds may

Table 3

Analysis of the 2^3 design corresponding to runs 1–11 in Table 2

Main Effects			Interactions			
<i>t</i>	<i>T</i>	[H ₂ O ₂]	<i>tT</i>	<i>t</i> [H ₂ O ₂]	<i>T</i> [H ₂ O ₂]	<i>t</i> [H ₂ O ₂]
33.6	38.9	18.4	-12.5	9.71	-5.1	-6.5

All effects have a standard error of $\pm 3.1\%$. Statistically significant values are shown in boldface.

lead to headaches, skin thickening, haemorrhage, testes atrophy, embryonic alterations, and kidney cancer [22]. Ozone is a stronger oxidizing agent than hypochlorite is, but its production cost is considerably higher. Mathew [19] used ozone to oxidize Cr(III) in sludge, but obtained only 67% recovery thus concluding that using stronger oxidants did not necessarily lead to increased recoveries.

The effects calculated for the 2^3 design corresponding to runs 1–11 in Table 2 are shown in Table 3. Only the main effects were found significant. They are all positive, indicating that higher recovery values will be obtained when all three design factors are set at their higher levels. Complete chromium oxidation was not achieved. The maximum recovery was 92.5%, which is comparable to the 84% value reported by [19]. These authors argued that this limitation might be due a polymer formed by Cr(III) and Cr–O–Cr, and/or to Cr–OH–Cr bridges, or even to the presence of iron, which may compete with chromium and preclude the latter's oxidation. According to [23], oxidation of these polymers by hydrogen peroxide is hard to achieve.

In an attempt to find more economical recovery conditions, we decided to perform additional runs at level combinations beyond those specified by the starting 2^3 design, and displaced toward the region associated with higher recovery values. The results of these runs are shown in the last five lines of Table 2. In these new experiments, a maximum of 92% chromium recovery was obtained with run 12, which corresponds to the settings of $t = 40$ min, $T = 60$ °C, and [H₂O₂] = 1.4 mol/L. The same value was obtained with the best run of the starting design (no. 8), which, though carried out also at 60 °C, required more time (60 min) and peroxide concentration (2.1 mol/L). This probably means that at the higher temperature the factors contact time and [H₂O₂] become relatively secondary, and can be used at reduced settings, without significantly affecting chromium recovery.

Since most metals precipitate as hydroxides, all metal amounts found after the oxidative process (Zn, Mn, Fe, Al, Ca, and Mg) were very low, and did not compromise the purity of the process solution (Table 4). Residual iron was very easily removed at pH 7–10. Even with the increased

Table 4

Chemical composition of the sludge solution, before and after the oxidative process (mg/L)

Metal	Zn	Mn	Fe	Cr	Al	Ca	Mg
Before	5.0	1.4	1220	2424	1625	157	155
After	0.005	0.001	0.035	2287	5.6	1.8	0.025

solubility of aluminum at pH 10 as $\text{Al}(\text{OH})_4$, most of the aluminum was removed. All precipitated metals were separated by filtration.

4. Conclusions

Sequential designs were used to find satisfactory experimental conditions for chromium recovery from electroplating sludge. A recovery of 97.6% was attained with 30 min contact time and 80% (v/v) HCl (US\$ 0.6/L). In every case the leached fluoride levels were high enough to characterize the residuals as dangerous, class 1. Hydrogen peroxide (US\$ 0.9/L) was employed at 30% because of its fast kinetics in relation to O_2 [24], and because it decomposes to oxygen and water, which are not environmentally damaging [18]. With the oxidative process it was possible to attain a 92% recovery of metallurgical grade chromium at 40 min, 60 °C and 1.4 mol/L. The methodology reported here is simple, economical and environmentally sound, since it requires only low-cost reagents and little energy.

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