



Recycling of aluminum and caustic soda solution from waste effluents generated during the cleaning of the extruder matrixes of the aluminum industry

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ARTICLE INFO

Article history:

Received 22 September 2010

Received in revised form 12 January 2011

Accepted 12 January 2011

Available online 18 January 2011

Keywords:

Anodising

Aluminum hydroxide

Recovery

Recycling

Wastewaters

ABSTRACT

Anodising industries use a concentrated caustic soda solution to remove aluminum from extruder matrixes. This procedure produces very alkaline effluents containing high amounts of aluminum. The work reported here was focussed on recycling aluminum, as aluminum hydroxide, from these effluents and regenerating an alkaline sodium hydroxide solution. Briefly, the method comprises a dilution step (necessary for reducing the viscosity of the effluent and allowing the subsequent filtration) followed by a filtration to eliminate a substantial amount of the insoluble iron. Then, sulphuric acid was added to neutralize the waste solution down to pH 12 and induce aluminum precipitation. The purity of the aluminum salt was improved after washing the precipitate with deionised water. The characterization of the solid recovered, performed by thermogravimetric analysis, Fourier transform infrared spectroscopy and X-ray diffraction, indicated characteristics typical of bayerite. The proposal method allowed recovering 82% of the aluminum present in the wastewater with high purity (99.5%). Additionally, a sufficiently concentrated caustic soda solution was also recovered, which can be reused in the anodising industries. This procedure can be easily implemented and ensures economy by recycling reagents (concentrated caustic soda solution) and by recovering commercial by-products (aluminum hydroxide), while avoiding environmental pollution.

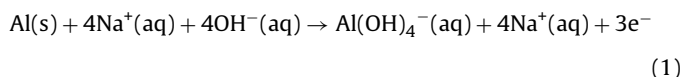
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1. Introduction

The finishing stage of the aluminum production consists of the extrusion of the billets (the aluminum material from which profiles are extruded) obtained by electrolysis and melting. The billet must be softened by heating (450–470 °C) prior to the extrusion. The heated billet is placed into the extrusion press, where the softened metal is forced through a precision opening, known as extruder matrix, to produce the desired shape. The process is quite similar to squeeze toothpaste from a tube.

In order to achieve good quality products, perfect cleanness of the internal surfaces of the extruder matrixes is essential [1]. To maintain the cleanness of the extruder matrixes, which are constituted of stainless steel, they are regularly dismantled and treated in a concentrated hot (100 °C) sodium hydroxide cleaning bath. Generally, this operation is performed after 3000 kg of aluminum has

been extruded, with an estimated loss of 1–2 kg of metal per matrix [2]. Typically, this process involves the dissolution of the aluminum from the extruder matrixes according to the following equation:



The concentration of tetrahydroxoaluminate, $\text{Al(OH)}_4^-(\text{aq})$, increases and the rinsing caustic solution loses its activity. As a consequence, a waste containing high amounts of aluminum is generated. In Europe, it is estimated that about at least 14,000 m³ of this residue is produced per year [2].

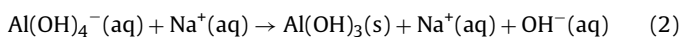
Conventionally, anodising industries use a small part of this alkaline waste stream by mixing it with part of the acid wastewaters coming from the anodising step, producing the so called anodising mud. This process causes a continuous loss of resource materials (aluminum and sodium hydroxide), as well as it results in generation of very large amounts of solid aluminum hydroxide anodising residues [3]. These residues are typically dewatered to reduce the volume of waste prior to being landfilled.

Removal of aluminum and its regeneration, as well as of the caustic soda solution, is important both environmentally and eco-

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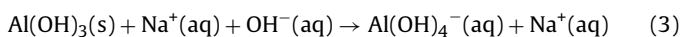
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nominally. Several techniques are available in the literature to recover and recycle aluminum or the caustic soda solution from the wastewater of the anodising industries. Emission reduction of aluminum anodising industry by the synthesis of several solid compounds from the acid [4,5] and the etching [6,7] wastewaters are described in the literature. On the other hand, the recovering and recycling of sodium hydroxide from the waste solution of aluminum etching operations has also been extensively studied [8–10]. Among them, caustic regeneration is a proven technology and has been in use in the United States and other countries for many years [11]. Such a system, based on the Bayer process, consists of adding fine crystals of aluminum hydroxide, $\text{Al}(\text{OH})_3$, which act as seeds to enhance crystallization, to the etching solution kept at a proper temperature. After some days, $\text{Al}(\text{OH})_3$ begins to precipitate, resulting in an increase of sodium hydroxide concentration in solution:



The principle of caustic regeneration process was applied for recovering aluminum from the etching wastewaters in the absence of aluminum complexing additives [6].

For cleaning the extruder matrixes, sodium hydroxide solutions at high concentrations are used in order to solubilise all aluminum, that remained in the dyes, as $\text{Al}(\text{OH})_4^-(\text{aq})$ species. Due to this, the final composition of these wastewaters is such ($\text{pH} \geq 15.5$) that the direct regeneration by caustic process is not feasible [12]. The method developed in this paper for recycling aluminum from the wastewaters of cleaning the extruder matrixes comprises a departure from the prior art methods where water or seeds of $\text{Al}(\text{OH})_3$ are added to the waste solution [6,9,12,13]. In U.S. Patent number 4,372,805 [13], a method for recovering sodium hydroxide and aluminum hydroxide from etching waste is shown; for this purpose, water is added to the solution containing dissolved aluminum to create a supersaturated solution of aluminum hydroxide and crystallize the aluminum hydroxide. On the other hand, $\text{Al}(\text{OH})_3$ was added to the spent aluminum etching as a seed crystal and fine nucleating agent in the agglomeration process [12]. In this work, due to the high pH of the wastewaters produced for cleaning the extruder matrixes ($\text{pH} \geq 15.5$), the addition of more $\text{Al}(\text{OH})_3$ would be solubilised as $\text{Al}(\text{OH})_4^-(\text{aq})$, according to the following equation:



Thus, this procedure is unfeasible to recover aluminum hydroxide from wastewaters with such high pH values. Thus, in the present paper we propose a slight neutralization of the waste solution, using sulphuric acid, enough to precipitate aluminum. So, the aluminum recovered with a high purity, as $\text{Al}(\text{OH})_3$, can be sold and re-used for different purposes; the remaining sodium hydroxide solution can be pumped into the cleaning bath of the extruder matrixes and reused after appropriate correction of the sodium hydroxide concentration.

2. Experimental

2.1. Materials

A representative sample of the effluent resulting from the alkaline washing of the extrusion dyes was provided by a Portuguese anodising factory.

All the acids used were of high purity, p.a. chloridric acid (HCl) was supplied by Merck (Darmstadt, Germany). The nitric (HNO_3) and sulphuric (H_2SO_4) acids were purchased from Panreac (Barcelona, Spain) and José M. Vaz Pereira (Lisboa, Portugal), respectively.

For atomic absorption spectroscopy with flame atomization (AAS), metal standard stock solutions with a concentration of 1000 mg L^{-1} were purchased from Merck and used as received. For atomic emission spectroscopy (AES), a standard solution of 1000 mg L^{-1} of sodium was prepared dissolving 0.6368 g of sodium chloride (NaCl) (99.8% anhydrous from Riedel-de Haën A.G. [Seelze, Germany]) in 250 mL of deionised water. Potassium nitrate p.a. (min 99%), from Merck, was added to the standard sodium solutions in order to suppress sodium ionisation.

For determination of sulphates, by the $450\text{-SO}_4^{2-}\text{-E}$ turbidimetric method [14], a stock standard solution containing 0.1479 g of anhydrous sodium sulphate (Na_2SO_4) p.a. from Merck, was dissolved in 1 L of deionised water. The buffer solution containing magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, Merck), sodium acetate (CH_3COONa , Merck), potassium nitrate (KNO_3 , Merck) and acetic acid (CH_3COOH , 100%, Merck) was prepared according to the method described [14]. Barium chloride (BaCl_2 , 99% purity), from Sigma–Aldrich (St. Louis, MI, USA), was used as received for precipitation of barium sulphate (BaSO_4).

All solutions were prepared with deionised water with resistivity higher than $14 \text{ M}\Omega \text{ cm}^{-1}$. All glassware was cleaned by soaking in 10% (v/v) HNO_3 during one day and then rinsing several times with deionised water.

2.2. Apparatus

Metal determinations were carried out by AAS and AES with a spectrophotometer AAnalyst 400 from Perkin Elmer (Norwalk, CT, USA). Previously to the samples readings, a calibration curve for each metal was performed.

The UV–vis absorbance for sulphate ions determination was recorded at 420 nm on a UV–vis spectrophotometer from Hitachi (Tokyo, Japan) using standard 1 cm glass cells. A calibration curve with sulphate concentrations from 1 to 100 mg L^{-1} was performed before the readings.

Determination of the inorganic carbon was done using a Shimadzu 5000 A Total Carbon Analyzer (Kyoto, Japan) with high temperature catalytic combustion and Pt alumina catalyst. For calibration, potassium diphtalate and anhydrous sodium carbonate were used as organic and inorganic standards, respectively.

Thermogravimetric analyses (TGA) of the solid $\text{Al}(\text{OH})_3$ recovered were carried out using a Thermobalance Mettler TA4000/TG 50. Fourier transform infrared spectroscopy (FTIR) analysis was performed using a Bomem MB-154 S spectrophotometer. X-ray diffraction (XRD) analyses were performed on a Philips X'Pert diffractometer, model MPD, using $\text{CuK}\alpha$ radiation.

2.3. Procedure

2.3.1. Analytical determinations

The total metals and sulphates contents were determined directly in the residual solutions and in the original effluent (after previous dilution and filtration of the samples or after previous digestion of the samples with aqua regia); these last procedures allowed to quantify the amount of the chemical forms (soluble or insoluble plus soluble, respectively) of the various components present in the original effluent. The choice of the metals to be analysed was performed taking into account the composition of the aluminum alloys used in the billets and in the dyes (constituted of stainless steel), which were used in the extrusion process. Aluminum, chromium, copper, iron and manganese were analysed. Additionally, the same determinations were performed in the solid of $\text{Al}(\text{OH})_3$ recovered.

For acid digestion, 1 mL of the original effluent or 0.2000 g of the solid $\text{Al}(\text{OH})_3$ recovered were measured into a PTFE bomb and dampened with 0.5 mL water. To this, 3 mL of concentrated HCl

and 1 mL of concentrated HNO₃ were added. After any effervescence had subsided, the bomb was sealed, heated in a domestic microwave oven (850 W) for 50 s, and allowed to cool to room temperature. The heating–cooling cycle was repeated four times. After digestion, the samples were filtered (0.45 μm filters) into a standard flask and the solution made up to 25 mL with deionised water. This procedure was repeated at least two times with different aliquots. This digestion procedure has been previously validated and extensively used in our laboratory [15–17]. To validate the accuracy of the microwave acid digestion procedure, a CRM 601 reference material was used. Three replicates of the reference sample were digested. The results obtained for total metal concentrations were within the ranges of the indicative values based on the results of six laboratories (Davidson, personal communication).

Aluminum, chromium, copper, iron and manganese concentrations were determined by AAS and sodium content was determined by AES. A flame of air–acetylene was used for quantifying copper, iron, manganese and sodium. Aluminum and chromium were quantified using a flame of nitrous oxide.

Sulphates were measured using the turbidimetric method [14] by measuring the absorbance spectrophotometrically at 420 nm. With this method, sulphate ion was precipitated as barium sulphate (BaSO₄) in an acetic medium by the addition of barium chloride (BaCl₂) and the absorbance was read (A₁). For each sample, interference due to the presence of particles in suspension (e.g. aluminum hydroxide) was corrected by reading the absorbance of a blank (A₂), which contained all reagents unless the BaCl₂. Concentration of SO₄²⁻ was determined by comparison of the absorbance of sulphates (A₁ – A₂) readings against a calibration curve.

2.3.2. Procedure for recycling aluminum and sodium hydroxide

Firstly, in order to reduce the viscosity of the effluent, the original effluent was diluted (dilution factor: 2.5) and a subsequent filtration of the diluted suspension was performed with a filter of 0.45 μm of porosity. Then, concentrated sulphuric acid was added slowly and under agitation to the solution externally cooled with ice. Agitation was maintained during 2 h. Separation of the solid of aluminum hydroxide from the solution was performed by centrifugation during 4 min at 4500 rpm. After, the supernatant (first residual solution) was separated from the solid and the solid was washed with 20 mL of deionised water under agitation for 30 min. Then, the supernatant (second residual solution) was separated again from the solid by centrifugation during 4 min at 4500 rpm. The solid of aluminum hydroxide was washed two times more in a similar way as the previous ones; the third and four residual solutions were recovered for further analysis.

2.3.3. Characterization of the solid recovered

The solid recovered, after being washed three times, was characterized by TGA, FTIR and XRD. TGA of the precipitated solid was carried out in an open alumina crucibles in air atmosphere from 50 up to 900 °C at a heating rate of 10 °C min⁻¹. Disks of 100 mg of potassium bromide (KBr) containing 3% (w/w) of finely ground powder of the solid recovered were prepared and then analysed in a FTIR; the spectra were measured between 4000 and 650 cm⁻¹ and further treated with Win-Bomem Easy v3.04 level software. X-ray diffraction patterns were acquired at intervals of 0.06°, with a scan step time of 40 s, in the range 5° ≤ 2θ ≤ 115°.

3. Results and discussion

3.1. Chemical characterization of the original effluent

Firstly, chemical characterization of the original effluent coming from the anodising factory was performed. For this purpose, total metals (aluminum, chromium, copper, iron and manganese)

Table 1
Chemical composition of the original effluent.

Constituents		Total concentration	Soluble concentration
Major constituents (g L ⁻¹)	Na	808	NA
	Al	199	194
	TC	NA	656
	IC	NA	574
Minor constituents (mg L ⁻¹)	Fe	310	18.2
	Cr	0.295	0.295
	Cu	7.05	7.03
	Mn	1.37	1.37

TC, total carbon; IC, inorganic carbon; NA, not applicable.

concentrations were quantified in the original basic suspension after microwave acid digestion with aqua regia and after previous dilution (dilution factor: 2.5) and filtration (filters of 0.45 μm of porosity). The dilution was mandatory due to the high viscosity of the basic suspension, which enables direct filtration. Total carbon (TC) and total inorganic carbon (IC) were also quantified in the filtrated solution; total organic carbon was calculated from the difference between the total and inorganic carbon. The results obtained are summarized in Table 1. The analysis of Table 1 shows that aluminum and sodium are the main elements present in the original effluent. Iron is also present, as a minor element, and mainly in the insoluble form. Total carbon is practically equal to the inorganic carbon; so, no significant quantity of organic carbon is present. In fact, taking into account the production process of the concentrated caustic soda suspension, described previously in Section 1, no organic carbon was expected to be present, as well as other inorganic ligands.

Table 1 shows that aluminum, chromium, copper and manganese are totally soluble. On the other hand, iron is mostly in an insoluble form. Considering the chemical composition of the original effluent described in Table 1, chemical equilibrium simulations for aluminum, copper and iron (Fig. 1) were performed using the MINEQL+ program [18]. Species distribution diagrams for aluminum (Fig. 1A) and copper (Fig. 1B) indicate that, at pH around 15.5, aluminum and copper are totally soluble as Cu(OH)₄⁻(aq) and Al(OH)₄²⁻(aq) species, respectively. Additionally, species distribution diagram for iron evidences that, at this pH, iron should be mainly in a insoluble form, as Fe(OH)₃(s) species (Fig. 1C), which is in agreement with the chemical characterization of the original effluent (Table 1).

In the case of sodium, all the total amount of sodium present in the wastewater (Table 1) resulted from the sodium hydroxide added to the cleaning bath (for further details see Section 1). Since about 84% of the amount of the hydroxide added is complexed, as Al(OH)₄⁻(aq), the remaining amount of sodium hydroxide present in the suspension (about 225 g L⁻¹) is much lower than its solubility, 1.11 kg L⁻¹ [19]. Thus, the total amount of sodium present in the wastewater corresponds to soluble sodium.

3.2. Aluminum recovery

3.2.1. Aluminum precipitation

The planned strategy for recovering aluminum was supported in its precipitation as Al(OH)₃. Therefore, it was important to predict if other metals could also precipitate and thus contaminate the aluminum precipitate. The iron concentration present in the original effluent is significant (310 mg L⁻¹) and would result in a significant contamination of the final solid of aluminum hydroxide. If we assume that the other metals (Cr, Cu and Mn) would precipitate totally, their contamination in the recovered aluminum hydroxide would be insignificant (lower than 0.003%).

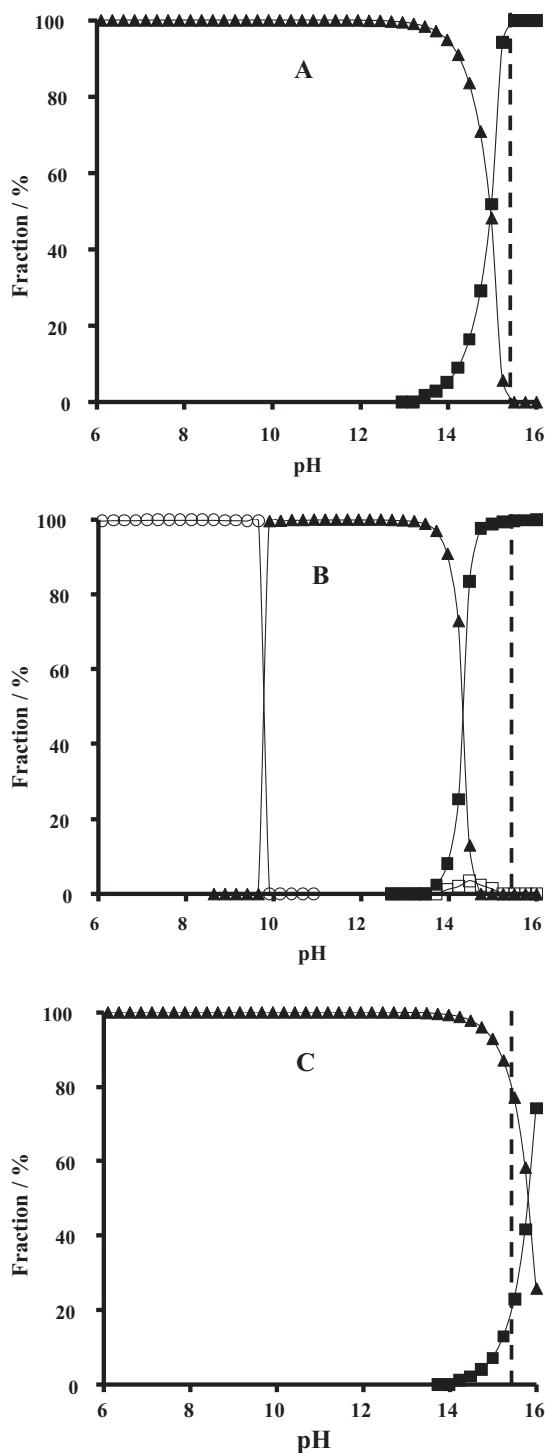


Fig. 1. Species distribution diagrams of 199 g L^{-1} of aluminum (A) 7.05 mg L^{-1} of copper (B) and 310 mg L^{-1} of iron (C) in the original effluent. The different species of metals in suspension were calculated with a chemical equilibrium computer program (MINEQL+) and assuming the total concentrations present in the original raw material. Aluminum(III) and iron(III) species: $\text{M}(\text{OH})_3$ (s) (\blacktriangle) and $\text{M}(\text{OH})_4^{(n-4)}$ (aq) (\blacksquare). Copper(II) species: $\text{Cu}(\text{OH})_2$ (s) (\blacktriangle), $\text{Cu}(\text{OH})_3^-$ (aq) (\square), $\text{Cu}(\text{OH})_4^{2-}$ (aq) (\blacksquare) and $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ (s) (\circ).

Since in the original effluent, aluminum is totally soluble, as $\text{Al}(\text{OH})_4^-$ (aq) species (Fig. 1A), and iron is mainly insoluble, as $\text{Fe}(\text{OH})_3$ (s) species (Fig. 1C), a previous filtration of the suspension allowed to remove the major part of the insoluble iron. The resulting filtrate was a clear, transparent and colourless solution.

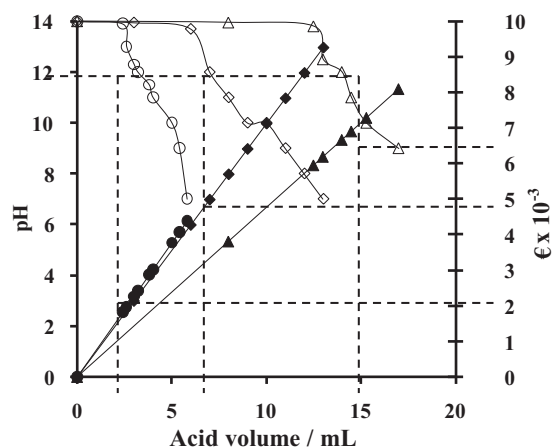


Fig. 2. pH titration of the diluted (dilution factor=2.5) basic solution with three inorganic acids: H_2SO_4 (\circ), HNO_3 (\square) and HCl (\triangle). Variation of the cost (closed symbols) with the volume of the acid added.

The planned strategy to recovery aluminum was a slight neutralization of the waste solution in order to convert the $\text{Al}(\text{OH})_4^-$ (aq) into solid $\text{Al}(\text{OH})_3$. For this purpose, pH titrations of the basic solution, diluted 2.5 times, using the three most common inorganic acids (hydrochloric, nitric and sulphuric acids) were performed (Fig. 2).

A simple analysis based in the consumption of the acids versus their costs revealed that sulphuric acid is the cheapest acid, as it is exemplified in Fig. 2: a volume of 3.2 mL of sulphuric acid was necessary for decreasing the pH of the basic solution to 12, corresponding to the lowest cost (2.4×10^{-3} euros) when compared with the other acids (Fig. 2). This analysis was based in the price values of the acids obtained from a Portuguese seller (data not shown).

Besides the cost analysis, one must not forget that sulphuric acid is largely used in the anodising industries. Usually, the anodization baths are made with sulphuric acid; this means that the use of sulphuric acid for aluminum recovery would not add a new raw material to the factory.

In order to design the cheapest and best experimental conditions for recovering aluminum efficiently with high yield, chemical simulations for predicting species distribution of aluminum were performed. Chemical simulation predicted that, at pH

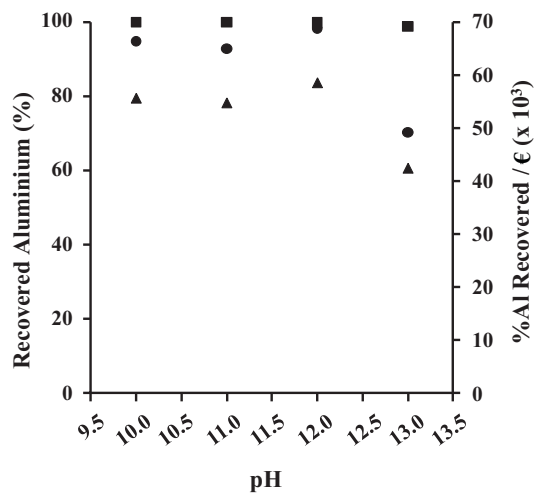


Fig. 3. Variation of the experimental (\bullet) and theoretical (\blacksquare) (calculated from chemical equilibrium simulations) aluminum recovered with the pH. Variation of the percentage of aluminum recovered per euros of acid consumed was also included (\blacktriangle).

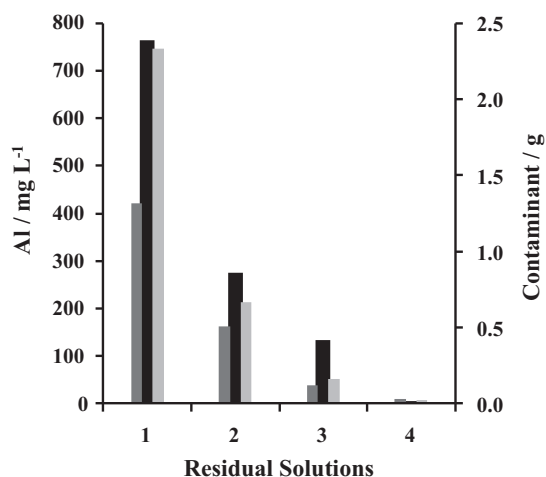


Fig. 4. Evolution of the decrease of aluminum, sodium and sulphates in the washing solutions. Amounts of aluminum (black bar), sodium (darker grey bar) and sulphates (lighter grey bar) present in the residual solutions.

13, aluminum should be almost totally transformed in solid aluminum hydroxide (98.8%) (Fig. 3). For lower pH values, chemical simulations predicted total recovery of aluminum (Fig. 3). Next, independent experiments, where the addition of sulphuric acid was done down to pH between 13 and 10, were performed. Acid was added slowly under stirring to the solution externally cooled with ice; after 2 h, a voluminous white precipitate of $\text{Al}(\text{OH})_3$ was obtained. After the solid has been separated by centrifugation and dried at 150 °C, an aliquot was acid digested and the amount of aluminum was controlled by AAS. The results were plotted in Fig. 3. At pH 13, the percentage of aluminum recovered was significantly lower (70%) than the value predicted theoretically (98.8%). In the range of pH between 12 and 10, the percentage of aluminum recovered ranged between 93 and 98, which is in good agreement with the values predicted theoretically by chemical simulation.

When we calculate the percentage of aluminum recovered per euros of acid consumed (Fig. 3), a maximum is obtained at pH 12, which indicates that this is the most favourable conditions for recovering aluminum.

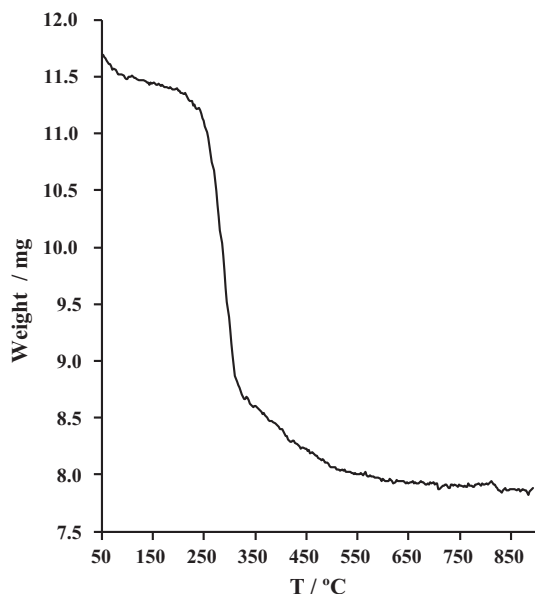


Fig. 5. TGA curves of the solid of $\text{Al}(\text{OH})_3$ recovered after the third washing step.

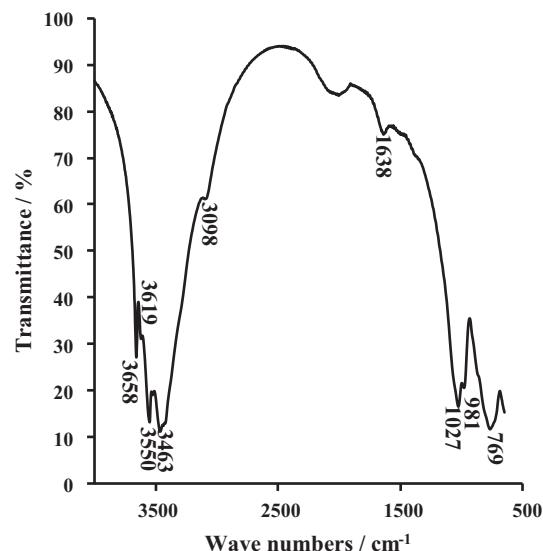


Fig. 6. FTIR spectrum of the solid of $\text{Al}(\text{OH})_3$ recovered after the third washing step and being dried at 100 °C until constant weight.

3.2.2. Removal of contaminants

The solid recovered after sulphuric acid neutralization down to pH 12 was centrifuged. After, the supernatant was filtered through 0.45 μm and the residual solution (first residual solution) retained for aluminum, sodium and sulphate determinations. Then, the solid was washed thoroughly with deionised water (20 mL each time) to eliminate sodium and sulphate contaminants. Firstly, only one washing step was used and then two and three washing steps were also assayed; second, third and fourth residual solutions coming from these additional washing steps were collected for aluminum, sodium and sulphate determinations. Fig. 4 shows the variation of the amount of sodium and sulphates present in each residual solution. This figure evidences that the major amount of contaminants was removed in the first washing step. Second and third washing steps also allowed a significant removal of contaminants. The fourth washing step had a marginal effect on the removal of contaminants (elimination of 1.5 and 0.8% of sodium and sulphates,

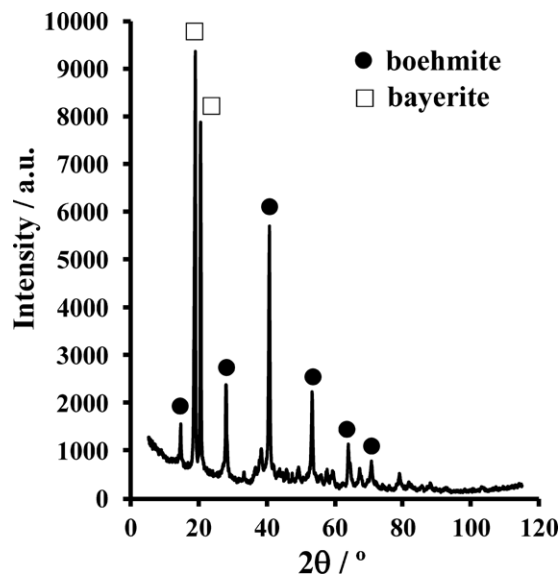


Fig. 7. X-ray diffraction pattern (CuK α radiation, $I = 50$ mA, $V = 40$ kV) of the solid of $\text{Al}(\text{OH})_3$ recovered after the third washing step and being dried at 100 °C until constant weight.

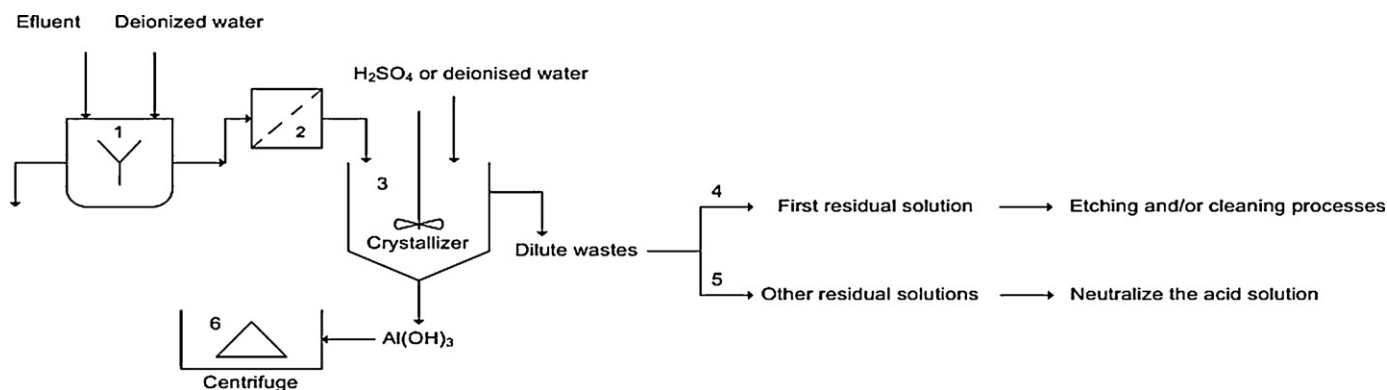


Fig. 8. Proposal flow sheet for the treatment process of the caustic concentrated suspension.

respectively). Fig. 4 also shows the impact of successive washing steps on the leaching of aluminum from the solid recovered. The total amount of aluminum leached from the solid in the four residual solutions was only 1.1% of the aluminum present in the original effluent, being the higher amount leached in the first washing step. This fact is well understood due to the high insolubility of aluminum hydroxide, $\log K_{ps} = -33.7$ [20], and shows that the successive washing steps had a minor impact on the losses of aluminum and thus in the final yielder of the solid recovered.

3.3. Characterization of the solid recovered

The solid recovered, after being washed three times and dried at 100 °C until constant weight, was characterised by TGA, FTIR, XRD and chemical analysis (aluminum, iron, sodium and sulphates).

The TGA indicated a weight loss of about 35% when the solid was heated up to 900 °C (Fig. 5). The small weight loss, which occurred up to 100 °C, can be mainly due to non-structural water desorption [21]. Most of the weight loss occurred between 200 and 500 °C. This thermal stability behaviour expresses the decomposition reaction of aluminum trihydroxide due to steplike removal of constitutional water. No significant weight loss was observed above 500 °C. The thermal evolution described suggests that the solid recovered is consistent with gibbsite or bayerite structures since the dehydroxylation to transitional alumina (η -form) occurs at about 300 °C, while the dehydroxylation of boehmite to transitional alumina (γ -form) requires about 475 °C [21,22].

The FTIR spectrum of the solid recovered is presented in Fig. 6. In the bending region for Al–O–H, two bands were observed at 981 and 1027 cm^{-1} . These infrared peaks can be attributed to the bending of the Al–O–H bonds in bayerite and gibbsite [23], respectively. In addition, the arrangement of the absorption bands in the region of the stretching vibrations (resonances above 3000 cm^{-1}) suggests a bayerite structure [23,24]. The presence of two small broad bands at 1638 and 3098 cm^{-1} indicates an impurity of boehmite [24,25].

According to the XRD analysis, bayerite was the dominant (94%) crystalline phase present in the solid recovered (Fig. 7); minor amounts (6%) of boehmite were also detected. These results are in good agreement with the FTIR spectrum analysis.

The chemical analysis of the aluminum hydroxide revealed that the solid was recovered with high purity (99.5%), containing only sodium and sulphates as minor contaminants (0.3 and 0.2%, respectively). The amount of iron detected was lower than 0.009%.

3.4. Proposal of treatment process

Here, we propose the treatment of the original effluent, the concentrated caustic soda suspension, in a discontinuous basis. The flow sheet of the process treatment is given in Fig. 8.

Firstly, the effluent coming from the cleaning of extrusion dyes is sent to a settling and storage tank (1) and diluted with deionised water (a dilution factor of 2.5 is necessary for reducing the viscosity of the effluent and allow the following filtration). Next, the supernatant of this suspension is filtered (2) to remove the solid unsettled of iron hydroxide. Then, filtered concentrated caustic soda solution is transferred to the crystallizer vessel (3), where sulphuric acid is slowly added under stirring to decrease the pH down to 12 and promote aluminum hydroxide precipitation (about 0.1 mL of concentrated sulphuric acid, 95–97% and $\rho = 1.84$, per mL of effluent). Hydrated alumina precipitates from the solution and settles to the bottom of the crystallizer. The first overflow from the vessel (4) (first residual solution), with reduced aluminum (about 760 mg L^{-1}) and sufficiently free caustic levels (about 110 g L^{-1} of sodium at pH 12), can be pumped into the etching bath and reused or pumped into the cleaning bath of the extrusion dyes and reused after appropriate correction of the sodium hydroxide concentration. The other residual solutions (5), which result from washing the crystals with deionised water, can be joined and used for neutralizing the acid waste effluents also produced in aluminum anodising industries. Crystals of hydrated alumina are withdrawn periodically from the bottom of the crystallizer and dewatered with a centrifuge (6).

4. Conclusions

In this work, a simple economical and nearly closed cycle for treating the alkaline ($\text{pH} \geq 15.5$) wastewaters generated during the cleaning of extruder matrixes from the anodising industries was developed for the first time. Analysis of the chemical composition of the raw material has shown high concentrations of aluminum, as tetrahydroxoaluminate, and sodium hydroxide. Minor amounts of iron (mostly present as an insoluble form) and vestigial amounts of chromium, copper and manganese were also present.

The developed process comprised four steps: (1) a dilution step for reducing the viscosity of the effluent; (2) a filtration to eliminate insoluble iron; (3) precipitation of aluminum, as aluminum hydroxide, after decreasing the pH of the solution down to 12; (4) washing the crystals of aluminum hydroxide with deionised water. With this process, 82% of the aluminum present in the wastewater was recovered with high purity (96.9 or 99.5% when two or three washing steps were used, respectively).

The high purity of the aluminum hydroxide recovered allows selling it; the remaining alkaline sodium hydroxide solution can be pumped into the cleaning bath of the extruder matrixes and reused after appropriate correction of the sodium hydroxide concentration.

Acknowledgment

The authors wish to thank Professor José L.C.C. Figueiredo from the Faculty of Engineering from the University of Porto for the use of analytical facilities (thermobalance).

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