Aluminum extraction from a metallurgical industry sludge and its application as adsorbent

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Abstract

The aluminum industry produces a high amount of wastes that are concentrated in the sludge of their water treatment plants. This sludge is rich in aluminum, which could be extracted and purified. In this work, three extraction methods have been evaluated to recover the aluminum from the sludge samples provided by a metallurgical industry from Medellín, Colombia. The sludge has been characterized to confirm its high aluminum content. The Bayer extraction method has been carried out, using 1:10, 1:15 and 1:20 sludge/solution mass ratios, and HCl extraction, by using 1:15 and 1:20 ratios. The extraction with isopropanol has also been evaluated. The amounts of Al, Fe, Cu, and Ni present in the aqueous phase have been measured to determine the recovery of the metals, as well as the selectivity of the extraction method. The highest metal recovery (99.3%) is achieved by HCl extraction for a sludge/solution ratio of 1:20, while the Bayer method (1:15 ratio) has shown the best selectivity. On the other hand, the extraction with isopropanol has not been successful for any of the ratios evaluated. The extracted material has been tested as an adsorbent for the removal of chlorpyrifos (200 mg/l), where the removal percentages have been higher than 95% for all the weight ratios studied. Hence, this Al-enriched material shows good prospects to be used as an adsorbent in the treatment of polluted water.

Keywords: Aluminum extraction; sludge; Bayer process; isopropanol; hydrochloric acid; chlorpyrifos removal

1. Introduction

The aluminum industry is one of the most prosperous in recent years, being aluminum one of the most widely used non-ferrous metals worldwide. Its production has increased in the last decade from 37,606 thousand metric tonnes in 2009 to 63,697 thousand metric tonnes in 2019, showing a growth of 59% for this period [1]. The main applications include transportation, packaging, construction, and electrical engineering [2–4].

The extraction of aluminum from bauxite for the production of aluminum or alumina is usually carried out by the Bayer process, which consists of the solubilization of the aluminum species present in the bauxite in a hot solution of NaOH [5,6]. Aluminum reacts with the solution to form sodium aluminate, a soluble compound that, when diluted and cooled, precipitates as trihydrate alumina [5]. The precipitate is subsequently calcined to remove moisture impurities to obtain the desired compound.

Although the Bayer process is widely used, high pressure and temperature conditions are needed, giving way to high operating costs [7]. Additionally, some impurities (i.e. Na_2O, CaO, SiO_2, MgO, Fe_2O_3, etc.) are usually present in the final product [8]. On the other hand, extraction with HCl produces aluminum hydroxy chlorides (PACs), which, after additional treatments, could be used as flocculants in water treatment or in the cosmetic industry [9]. Extraction with isopropanol produces aluminum isopropoxide, a catalyst for reactions with aldehydes [10] which can be transformed, with additional treatments, to aluminum hydroxide, boehmite or pseudo-boehmite [7,9,11].

Once Al is extracted, the samples are subjected to different treatments, such as the anodizing process, which provides anticorrosive protection, but generates sludges composed of high alumina content and a variety of alkaline chemicals [2]. Anodized aluminum sludge is mainly composed of aluminum hydroxide, oxide-aluminum hydroxide, and aluminum oxides [11–13]. For every 1 tonne of anodized aluminum, 475 kg of sludge are generated, and it is estimated that the countries of the EU produce about 100,000 metric tonnes per year [14,15]. The disposal of these wastes in specific sanitary fills is currently an environmental problem, due to the high volume of wastes generated. Furthermore, transportation costs are estimated in 22-30 US$/tonne [15]. Attempts have been made to look for possible market applications in the cement, ceramic, and/or paper industries. However, few industries are available, which can only valorize ~20% of the overall waste generated [15].

Aluminum hydroxide ($Al(OH)_3$) is used in refractory materials, ceramics, polishing and abrasion applications, manufacture of zeolites, fire retardants and catalysts, among others [16]. These applications are possible due to the high alumina content of the sludge, with a composition almost constant over time, which makes its recycling process more attractive. These sludges have also been used in various inert matrices, such as concrete, glass, and ceramics [15,17].

This work aims to evaluate, by different extraction methods, the recovery of the aluminum contained in a wastewater sludge derived from a metallurgical industry. For this purpose, Bayer, HCl, and isopropanol extraction methods are compared for different reagent ratios. Besides, the extracted product has been evaluated for its application as adsorbent for the removal of an organophosphate pesticide (chlorpyrifos, CPS) from contaminated waters.

Similarly, a model of adsorption isotherms has been carried out from the isotherms proposed by Langmuir and Freundlich.

2. Experimental

The treated sludge sample (20 kg) has been provided by a company located in Medellín (Colombia), dedicated to the production of extraction, lamination, foil, and manufactured pieces. The sludge comes from the wastewater treatment plant, which must be neutralized before its disposal in a sanitary landfill. The sludge has been subjected to a mild drying process for 48 h at 40 ºC, so that the compounds contained would not degrade or react. The dried sludge has been crushed with a RETSCH® A7304184 jaw crusher and then passed through a 500 μm mesh screen.

2.1. Analytical methods

The elemental analysis for the quantification of N, C, S, H, and O has been carried out following the ASTM D5373-16 standard on the Elementar Vario Macro CHNS® (Elementar, Langenselbold, Germany). Additionally, X-ray Fluorescence (FRX) analysis have been performed on the raw sludge to identify and quantify the atomic species in a ZSX Primus Rigaku® (Rigaku, Tokyo, Japan) spectrophotometer. Likewise, an XRD analysis with Rigaku Ultima III (Rigaku, Tokyo, Japan) and SEM analysis were carried out through a microscope TESCAN LYRA3 FIB-SEM (TESCAN, Brno, Czech Republic) for the three samples, both the raw sludge, after being processed and when it was used as adsorbent.

The quantification of metal concentration has been performed using inductively coupled plasma optical emission spectrometry (ICP-OES) in an ICP-OES Thermo Scientific ™ ICAP6500 DUO kit (Thermo Scientific, Waltham, MA, USA) equipment. The Al content of

all the samples has been determined by this technique. Additionally, the samples derived from Bayer and HCl extraction have been analyzed for Cu, Fe, and Ni. Due to the high volume of the samples taken, all of them underwent a 1:10 dilution before digestion. The samples were digested following the EPA3015A standard [18] for liquid samples and EPA3051A [19] for solid samples. The analytical method was applied following Standard Methods standard 3120B [20] for aqueous samples and EPA standard 6010C [21] for solid samples. The measurement wavelength for aluminum was 308.2 nm. The physical properties of the extracted samples have been estimated by N_2 adsorption–desorption (Micromeritics ASAP 2010) at -196 ºC. The samples have been pretreated at 150 °C for 8 h under vacuum (10^{-3} mmHg), to remove possible impurities. The specific surface area (S_{BET}) has been calculated using the Brunauer, Emmett, Teller equation and the total pore volume (V_p) is based on the Gurvitch rule (for relative pressure $P/P_0 > 0.99$) [22,23]. The microporous surface (S_{micro}) and volume (V_{micro}) have been calculated using the t-plot method and mesoporous volume (V_{meso}) has been estimated by the difference between total and micropore volume ($V_{meso}=V_p-V_{micro}$). The pore size distributions have been determined by Barrer-Joyner-Halenda (BJH) method. The acidity and acid strength of the catalysts were measured by monitoring the adsorption-desorption of NH_3 by combining the techniques of thermo-gravimetric analysis and the differential scanning calorimetry, using a Setaram TG-DSC calorimeter connected online with a Thermostar mass spectrometer (Balzers Instruments) following the procedure previously reported in [24].

2.2. Procedure for extraction method

For the three aluminum extraction methods the same assembly has been performed. The vessel consists of a 2-neck flask, one for the reflux condenser, and the other for the thermometer or sampling, placed on a temperature-controlled heating blanket.

- *Bayer extraction process*

A NaOH (2M) solution has been used as the extraction substance. Three different tests have been performed for different sludge/solution ratios and a control sample composed only of the extraction solution has also been tested. In each test, 700 ml of the extraction solution is added to the flask, together with a certain amount of sludge,70.00 g, 46.67 g, and 35.00 g of sludge corresponding to 1:10, 1:15 and 1:20 sludge/solution mass ratios, respectively [25,26]. These tests are based on the methodology proposed in the literature [27,28], to assure the maximum recovery of aluminum. The mixtures have been brought to boiling point, corresponding to zero time. 20 ml aliquots have been taken from the flask mixture every 30 min up to 3 h for the analysis of metal content (by ICP-EOS, Section 2.1). Aliquots have been positive pressure filtered to remove solids.

It should be noted that the extraction of Al with NaOH in the aqueous phase involves a chemical attack on only part of the Al species, probably present in the mud. Corundum and spinel are not attacked by basic dissolution. Thus, the following reactions are likely to occur during this extraction process [29]:

$$2Al + 2NaOH + 6H_2O \xrightarrow{yields} 2NaAl(OH)_4 + H_2 \quad (1)$$

$$2AlN + 2NaOH + 6H_2O \xrightarrow{yields} 2NaAl(OH)_4 + 2NH_3 \quad (2)$$

$$Al_2(SO_4)_3 + 6NaOH \xrightarrow{yields} 2Al(OH)_3 + 3Na_2SO_4 \quad (3)$$

- *HCl extraction process*

Acid extraction allows the recovery of Al from the same species mentioned in the basic extraction, where it is suggested that the reactions that take place are as follows [30]:

$$Al + HCl \xrightarrow{yields} AlCl_3 + H_2 \quad (4)$$

$$AlN + 3HCl \xrightarrow{yields} AlCl_3 + NH_3 \quad (5)$$

$$Al_2(SO_4)_3 + 6HCl \xrightarrow{yields} 2AlCl_3 + 3H_2SO_4 \quad (6)$$

The same procedure followed for the Bayer extraction method has been carried out. In this case, a 2M HCl solution has been used as the extraction substance. Two tests have been carried out, by adding 700 ml of the extraction solution to the flask, and a quantity of sludge determined by the ratio corresponding to the test: 46.67 g and 35.00 g of sludge, corresponding to 1:15 and 1:20 ratios, respectively. The metal content has also been determined by ICP-EOS (Section 2.1).

- *Extraction process with isopropanol*

The Al recovery with isopropanol can occur according to the following reaction [31,32]:

$$2Al + 6C_3H_7OH \xrightarrow{yields} 2Al(C_3H_7O)_3 + 3H_2 \quad (7)$$

For this method, analytical grade isopropanol has been used as the extraction agent. The tests have been carried out based on the procedure proposed by Saiz et al. [7]. This process aims to obtain aluminum monohydroxide through the reaction between the sludge and the isopropanol to produce aluminum isopropoxide (Eq. (7)),

The different extraction tests are summarized in Table 1. One of the tests corresponds to a control sample in which aluminum has been used instead of the sludge. In each test, the catalysts composed of sublimated iodine (I_2), and mercury chloride ($HgCl_2$), have been dissolved in 50 ml of isopropanol at 70 ºC. The sludge has been added to the flask, then the isopropanol with the catalysts, and finally, the rest of the isopropanol. The mixture in the flask has been brought to a boil at 75 ºC (at 560 mmHg), corresponding to zero time. According to Saiz et al. [7] the reaction time depends on the catalyst used. In this work, using I_2 and $HgCl_2$ catalysts, reaction times between 3 and 11 h have been established. After each test, the content of the flask has been weighted, and the phases have been separated by positive pressure filtration. Retroevaporation distillation of the aqueous phase has been performed at 80 ºC for 3 h to reduce the amount of isopropanol. Finally, a metal analysis has been carried out on the aqueous phase of each test, as well as on the solid phase by ICP-EOS (Section 2.1).

Table 1. List of reagents used in each isopropanol extraction test.

Test	**Control**		**Test 1**		**Test 2**	
Time (h)	7		3		3	
Reagents/catalysts	Ratio (mol/mol Al)	Weight (g)	Ratio (mol/mol Al)	Weight (g)	Ratio (mol/mol Al)	Weight (g)
Sludge*	-	11.80	-	16.76	-	18.78
2-propanol**	6.00	155.69	6.00	133.89	6.70	77.84
I_2	0.01	1.15	0.00	0.15	0.01	0.39
$HgCl_2$	0.03	3.67	0.00	0.00	0.00	0.00
Sediment Measurement	No		No		No	
Test	**Test 3**		**Test 4**		**Test 5**	
Time (h)	7		11		11	
Reagents/catalysts	Ratio (mol/mol Al)	Weight (g)	Ratio (mol/mol Al)	Weight (g)	Ratio (mol/mol Al)	Weight (g)

Sludge*	-	43.83	-	69.50	-	69.49
2-propanol**	6.00	155.69	3.60	155.69	3.60	155.69
I_2	0.01	1.11	0.00	0.18	0.01	1.19
$HgCl_2$	0.03	3.58	0.00	0.18	0.02	3.79
Sediment Measurement	No		Yes		Yes	

* From the amount of the sludge the molar amount of A is calculated using the concentration characterization - ICP (Exception Test 1). ** The mass of 2-propanol is calculated from the added volume and the density of 2-propanol at 20 ºC (0.786 g/ml).

- *Recovery fraction (RF)*

In this work to clearly observe the extraction force of each method, the concept of the recovery fraction (RF) is used, which is defined as the fraction of the aluminum extracted with respect to the initial quantity [33].

During the Bayer and HCl extractions, 20 ml aliquots were taken every 30 min and were analyzed by ICP-EOS (Section 2.1) to determine the metal content. For these cases, the RF is the mass found in the aqueous phase, which is the dissolved mass inside the flask plus the mass removed in the aliquots, over the initial mass of Al. It is expressed as shown in Eq. (8) and Eq. (9):

$$V_i = V_0 - V_{Al}\left(\frac{i}{30}\right) \tag{8}$$

$$RF_i = \left(\frac{1g}{1000mg}\right)\frac{\left[C_i V_i + V_{Al}\sum_{j=30}^{i-30} C_j\right]}{\left(C_{sludge} m_{sludge}\right)} \tag{9}$$

where, *i,* is the sampling time (i = 0, 30, 60, 90, 120, 150, 180 min); RF_i, is the recovery fraction at time i (-); C_i, the concentration of the aqueous phase at time i (mg l^{-1}); V_i, the volume in the flask at time i (l); V_0, initial volume (V_0 = 0.7 l); V_{al}, aliquot volume (V_{al} = 0.02 l); C_{sludge}, initial sludge concentration (C_{sludge} = 27.8 wt%); m_{sludge}, the initial sludge mass (g).

In the case of isopropanol extraction, aliquots have been only taken in the final aqueous solution. Therefore, RF can be defined by Eq. (10), as follows:

$$RF_i = \left(\frac{1g}{1000mg}\right)\left(\frac{C_i V_i + Vol\sum C_i}{C_{sludge} m_{sludge}}\right) \quad (10)$$

2.3. *Chlorpyrifos (CPS) adsorption tests*

CPS has been used as a reference water pollutant for the adsorption tests, due to its wide use as a pesticide in agriculture, used indiscriminately especially in developing countries, such as Colombia. Its inadequate management and wide use have affected runoff and ground waters, generating health problems in the population. According to García-Reyes et al. [34] and Sharma and Kakkar [35] the maximum permissible limits of individual and total pesticide in drinking water are 0.1 and 0.5 ppb, respectively. For this study, a maximum pesticide concentration of 200 mg l^{-1} has been taken.

The adsorption tests have been carried out with different weights (0-5 g) of the precipitate obtained from the Bayer extraction process for a ratio of 1:15 (BES15). To check for reproducibility, all samples have been made in quadruplicate. The vials have been filled with 100 ml of the standard solution, the flasks have been shaken and the samples have been taken at 5, 30, 60, 90, 120, 150, 180, 210, and 240 mins. The vials are placed in a SIF 3000 model shaker (MAX QTM, Chandler, United States) at room temperature and 120 rpm. For lecture, 5 ml of the solution has been taken at each time and analyzed in a tube absorbance spectrophotometer using a Thermo Spectrophotometer UV Genesys (Thermo Fisher Scientific, Waltham, United States). Before analyses, calibration tests have been performed following ASTM-D3860-98. The equipment has been calibrated at different wavelengths with the problem solution. Similarly, the absorbance of the pollutant has been measured keeping the value of the wavelength constant, for the 20 solutions prepared with

concentrations from 0.5 to 400 mg l^{-1} of chlorpyrifos. A slope of 0.0107, an intercept of 0.0286, and an R^2 of 0.9972 has been obtained.

The most widely accepted models in the literature have been used to describe the adsorption isotherms [36]: Langmuir, Eq. (11); and, Freundlich, Eq. (12):

$$q_e = \frac{Q^0_{max} K_L C_e}{1 + K_L C_e} \quad (11)$$

$$q_e = K_F C_e^n \quad (12)$$

where Q^0_{max} (mg g^{-1}) is the maximum saturated monolayer adsorption capacity of an adsorbent, q_e (mg g^{-1}) is the amount of adsorbate uptake at equilibrium, K_L (l mg^{-1}) is the constant related to the affinity between an adsorbent and adsorbate, C_e (mg l^{-1}) is the adsorbate concentration at equilibrium, K_F (mg g^{-1})/(mg l^{-1}) is the Freundlich constant, n is the Freundlich intensity parameter, which indicates the magnitude of the adsorption driving [36–38].

Langmuir's principle assumes that there is a fixed number of accessible sites that are available on the surface of the adsorbent and that once the adsorbate occupies one site, no further adsorption can occur at that site. While Freundlich cannot describe the linearity ratio at very low concentrations nor the saturation effect at very high concentrations [39,40].

Likewise, the adsorption kinetics, which represents the dynamics of the adsorption process, have been analyzed by the mass balance of the adsorbate between the liquid and solid, and are described as follows:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (13)$$

$$\frac{dc}{dt} = \frac{-k_l a S(c - c_e)}{L} \quad (14)$$

$$\frac{dq}{dt} = k_L \alpha (c - c_e) \quad (15)$$

where q_e and q_t are the amounts of adsorbate uptake per mass of adsorbent at equilibrium and at any time t (min), respectively, and k_1 (min^{-1}) is the rate constant of the pseudo-first-order kinetic equation (PFO), k_L ($l\ m^{-2}\ min^{-1}$) is the mass transfer coefficient, a ($m^2\ g^{-1}$) the external surface area of adsorbent, L the volume of CPS solution and ρ_b ($kg\ m^{-3}$) the adsorbent bed density. $k_l a \rho_b$ represents the rate constant of the pseudo-first-order kinetic model.

The equilibrium parameters for the models of Freundlich and Langmuir, Eqs. (11) and (12), have been optimized, by minimizing an objective function, *OF*, defined as the sum of the squares of the differences between the values of the concentration of adsorbate in the liquid phase measured experimentally, c_{exp}, and the values calculated by the model, c_{cal}. For this, a calculation algorithm has been implemented in MATLAB, which uses the *ode* subroutine to solve the mass balance equations, Eq. (12), and the *fminsearch* subroutine, which calculates the without restrictions minimum of the objective function, based on the Nelder-Mead algorithm.

3. Results and discussion

3.1. Chemical characterization of the raw sludge

According to XRF results (Table S.1.), the content of Al (68.52%) outstands among other species, being the concentration levels similar to those found in other studies [3,41]. Therefore, this sludge shows a high concentration of Al, which has a high potential to be extracted and with little interference with other metallic species. The high concentration of S (28 wt%) observed may be due to the neutralization treatments carried out in the company at its place of origin.

Therefore, an ICP-OES analysis has been carried out to determine the metal concentration present in the sample (Table S.1.). For this specific work, Na was not quantified, since the Bayer extraction is carried out with NaOH, so it would not be possible to compare the initial characterization with the results of the extractions, in the same way, Ca was not quantified. It has been found that the concentration of Al determined by XRF is higher than that determined by ICP since the XRF technique quantifies the total Al present in the mud. The composition of the sludge is complex. However, it can be suggested that the total Al is provided by species, such as metallic Al, aluminum nitride (AlN), aluminum sulfate (Al_2SO_4), aluminum hydroxide ($Al(OH)_3$), aluminum oxides (Al_2O_3) and spinel ($MgAl_2O_4$) [29,42]. On the other hand, the Al determined by ICP corresponds to the Al species soluble in aqueous NaOH. Furthermore, some Al_2O_3 phases, such as corundum and spinel could be present in the sludge and would be insoluble [29].

In the elemental analysis high carbon content of 34.90 wt% has been identified in the original sludge, with smaller amounts of H (4.93 wt%) and N (0.60 wt%). The concentration of sulfur (0.66 wt%) quantified by elemental analysis is substantially lower than the one found by

XRF. The high concentration reported in the XRF analysis may be due to the fact that its analytical power is focused on the first layers of the sample. This implies that the concentration of S is higher at the surface since the neutralizing substance (H_2SO_4) acts on the surface of the particle. Instead, in the elemental analysis, the complete combustion of the sample is carried out, thus, the entire sulfur is oxidized to sulfur dioxide (SO_2), which allows quantifying the overall species [43]. Therefore, the S content provided by the elemental analysis has been taken as the characterization reference value.

Considering the results of ICP and elemental analysis, it can be concluded that the original sludge is rich in carbon and aluminum (Table 2). The remaining species (25.18%) mainly correspond to oxygen and traces of other metals. This implies that the metallic species have been mostly oxidized. Moreover, in accordance with the concentrations of C, H, N, and S, and considering the processes of the aluminum industry, it can be assumed that most of the compounds present in the sludge are inorganic [44,45]. In view of these, in Table 2 summarizes the results for the overall mass balance of the main species identified in the raw sludge (prior to extraction), determined by XRF, ICP, and elemental analyses.

Table 2. Characterization of chemical properties of the raw sludge.

Characterization	
Specie	**Concentration [%wt.]**
Carbon	4.90
Aluminum	27.80
Oxygen*	55.18
Hydrogen	4.93
Silicon	3.48
Calcium	0.96
Sodium	0.94
Nitrogen	0.60
Sulfur	0.66
Iron	0.36
Nickel	0.16

Copper	0.04
* Obtained from the remaining balance	

3.2. Extraction results

3.2.1. Bayer method

The results of the Bayer extraction throughout time are shown in Fig. 1, in which the recovery fractions (RFs), defined in Eqs. (4) to (6), for different sludge/NaOH mass ratios are plotted.

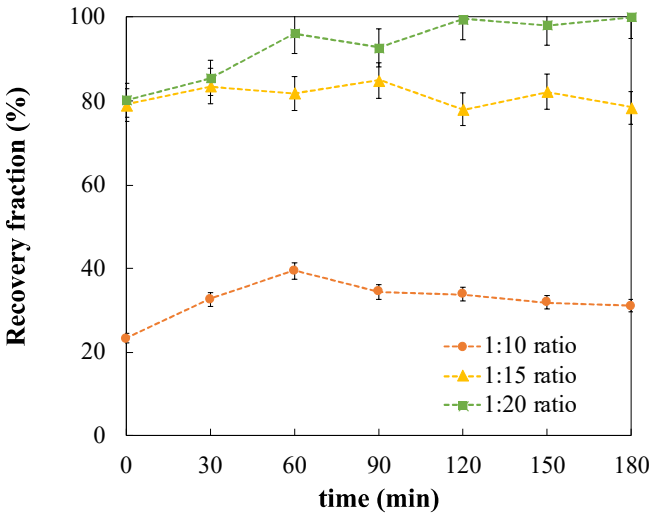


Fig. 1. Evolution of Al recovery fraction over time for different sludge/solution ratios during the Bayer extraction.

Overall, an increase in the sludge/solution ratio gives way to higher RF values regardless of the extraction time, being this effect more evident for an increase in the ratio from 1:10 to 1:15. However, at lower ratios, minor fluctuations are observed throughout time, due to a more limited amount of extraction solution [27,28]. For a 1:20 ratio, the highest extraction recovery fraction has been obtained, which shows an almost constant RF ~100% after 2 h.

Consequently, this ratio is the most suitable one in order to recover almost 100% of the Al content from the raw sludge.

A selectivity test of the extraction method according to the recovery fraction obtained for each compound has been performed and the results are shown in Fig. 2. This selectivity has been calculated as the ratio between Al-RF and other metals RFs average. It should be noted that the recovery fractions for Cu, Fe, and Ni are remarkably lower than that obtained for Al. Hence, it can be affirmed that these species will be mainly concentrated in the solution during the extraction process. This is mainly due to the electronegativity of the metals in question. Al is the least electronegative species (1.61), therefore, its willingness to join other complexes is greater than in the case of Fe (1.83), Cu (1.90), and Ni (1.91). Consequently, the method is more selective towards Al [29].

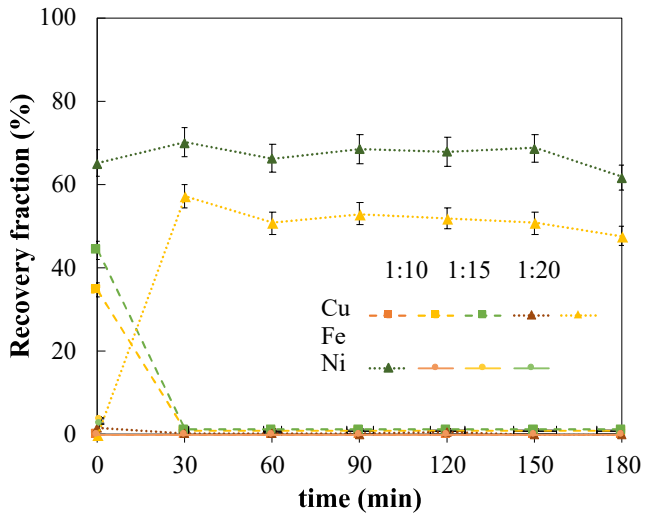


Fig. 2. Recovery fraction of other metals over time and for different sludge/solution ratios during the Bayer extraction.

At zero-time, Ni extraction does not exceed 3% regardless the sludge/solution ratio used. This could be attributed to the fact that Ni is a corrosion resistant species with caustic soda,

therefore, it hardly occurs in the aqueous phase [46]. For Cu, at zero time and for 1:20 ratio a fraction of 44% is recovered, while for the 1:15 ratio only 34% is recovered. This implies that the full extraction has occurred during the first boil. During the complete extraction process, its recovery varies between 0.99 and 1.26%, indicating that the extraction rate for different ratios does not vary significantly. Ni shows a constant recovery, which implies that the extraction occurred before boiling, similarly to Cu, without many differences between ratios. Both species, Ni and Cu, show the higher electronegativity among the four species analyzed. In the case of Fe, no extraction is observed for 1:10 ratio. The extraction using 1:15 ratio, shows a sharp increase in the recovery fraction up to 30 min, and then it remains almost stable for a value of 0.5% average. The highest Fe recovery fraction is achieved (~63%) for 1:20 ratio, from the beginning of the extraction. Contrasting the Al RF data with the RF of other metals, it is found that the 1:10 ratio has shown a better selectivity than the other ratios studied. A small extraction of Ni, Fe, and Cu is observed (Fig. 2), which in some cases reaches only up to 1%, while Al is up to almost 40% at 60 min. Therefore, the amounts of Cu, Ni, and Fe that passes into the aqueous solution are not significant compared to the mass of the extracted Al [47].

3.2.2. HCl extraction

In Fig. 3 the Al RFs are plotted for different sludge/solution ratios. Similarly, to the Bayer process (NaOH extraction), the recovery fraction increases rapidly up to 90 mins and then slowly approaches asymptotically to a constant a value. A similar behavior is observed for both ratios. The highest recovery fraction (~100%) is attained for 1:20 ratio, which is consistent with the availability of HCl in the solution.

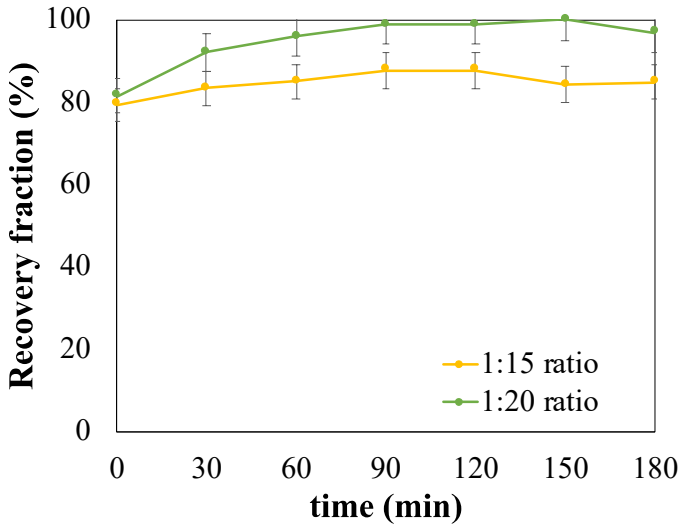


Fig. 3. Evolution of Al recovery fraction over time for different sludge/solution ratios during the HCl extraction

Likewise, the RFs of the remaining metals are depicted in Fig. 4. In other studies, Al removal efficiencies of up to approximately 96% have been reached. This study demonstrates that the removal of Al by means of HCl is an alternative technique to the Bayer process [48,49].

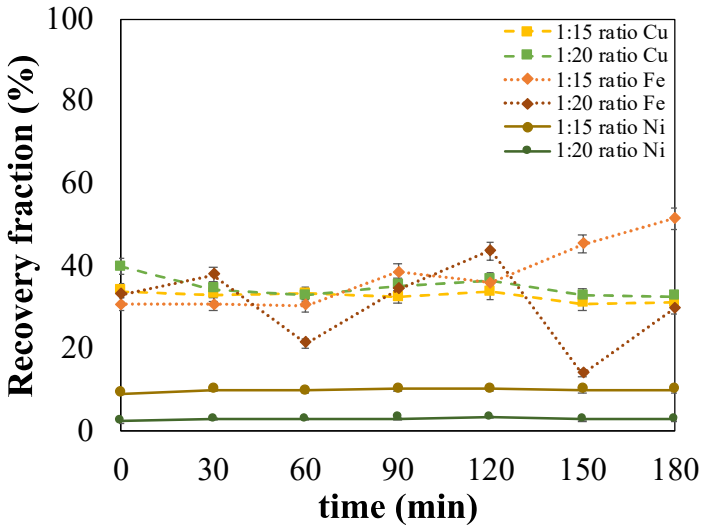


Fig. 4. Recovery fraction of other metals over time and for different sludge/solution ratios during the HCl extraction.

Fig. 4 shows that the extraction with HCl is more selective than with NaOH in short times but at long times it is not very selective with respect to the other compounds present in the sludge. The above, due the RF are less than 51% for Fe, 10% for Ni, and 40% for Cu. These values are lower than those shown for NaOH (Fig. 2). The extraction of Cu and Fe is much higher than the one for Ni. In the case of Cu, the maximum peak of extraction has been found with the 1:20 ratio at zero time, while for Fe this has been reached at 180 min with the 1:10 ratio. As with the NaOH extraction process, the extraction order has been the same, according to the electronegativity of the metals.

For Cu and Ni, similar stable behavior has been observed during the 180 min of extraction. This may indicate that extraction has been occurred prior to boiling. Fe shows a different behavior, with variations during the 180 min of the process, but with more variations in the 1:20 ratio. Contrasting the Al RF data with the RF of Ni, Cu, and Fe, it has been found that despite the fact that both ratios present similar selectivity, 1:20 ratio shows a greater recovery of Al with respect to the other metals. This is due to the fact that, for example, with the ratio 1:15, there is a higher percentage of Ni present in the sample, while with a 1:20 ratio, it is not. Also, it has been possible to consider for this study the 60^{th} minute, as the best conditions for the extraction of Al; since Cu, Ni, and Fe show lower RFs, and an RF of approximately 95% is achieved for Al. Similarly, other studies have reported the high removal efficiency with HCl. They have also found that as the liquid-solid ratio increases there is no significant improvement in the removal of Al [48–51].

3.2.3. Isopropanol extraction

Fig. 5 presents the RFs of each test. The RFs obtained are low, even the RF of the control performed is minor (4.56%). This can be attributed to the complex composition of the sludge,

shown in Table 2, in which different Al species are present. According to the Eq. (7), only metallic Al will react with isopropanol, while in the case of HCl and NaOH more species react (Eqs. (1) - (3)), and, thus, higher recovery percentages are observed. Another factor is the presence of water in the alcohol or in the reaction system, since aluminum isopropoxide hydrolyzes to aluminum hydroxide in the presence of water [9]. $Al(OH)_3$ is an insoluble white compound [52], that it can be formed during the reaction, and then, can be easily mixed with the remaining sludge. Since the system is not established under an inert atmosphere, the humidity of the environment could hydrolyze the product. Also, the alcohol has not been dried prior to the experiment, so any trace of water could favor this hydrolyzing too [53].

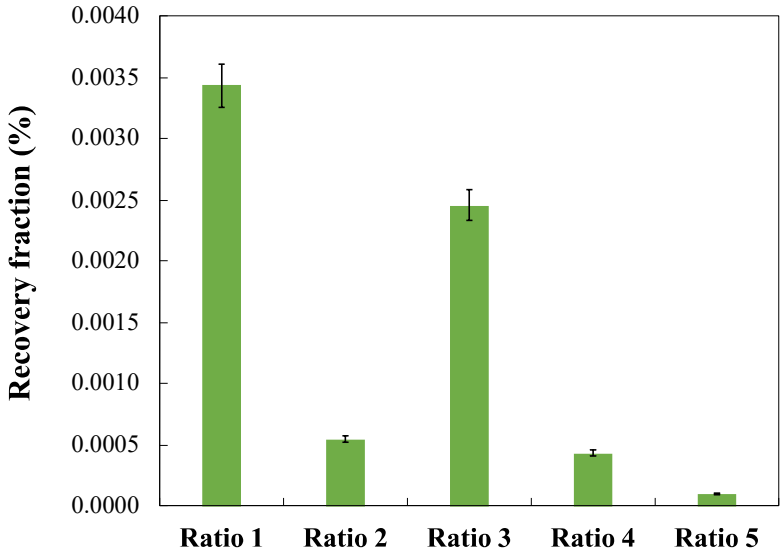


Fig. 5. Recovery fractions obtained by isopropanol extraction for different conditions (Table 1).

This is partly consistent with the results of the Al concentrations present in the sediment of the Tests 4 and 5 (16% and 13.5%, respectively), since the mass of the hydroxyl group per mole of Al is greater than that of the oxy group (2.1 times more weight). This implies that

the Al has been transformed from Al_2O_3 to $Al(OH)_3$, increasing the weight of the sediment and decreasing the Al concentration of the solution. It is important to consider that isopropoxide is soluble in isopropanol, hence it has not been deposited on the sludge. Additionally, its boiling point is about 140 ºC at 8.0258 mmHg [54], therefore, it was hardly dragged into the distillate during the distillation process.

Comparing the results, it can be perceived that an increase in time has not necessarily improved the extraction. Tests 4 and 5, have been carried out for a duration of 11 h, which have shown the lowest extraction percentage; while the highest extraction has been obtained, with those tests (Test 1 and 2) performed at 3 hours. In addition, higher recovery fractions have been obtained for lower amounts of catalyst (0.001 mol mol^{-1} Al). Furthermore, the addition of $HgCl_2$ has not significantly improved the extraction. For the Test 3, a good extraction is obtained using high amounts of catalyst, both I_2 and $HgCl_2$, after 7 h.

The results with isopropanol have not been as expected, meanwhile, the extraction should improve over time thus providing more energy and giving a long period for the formation of the desired compound. Also, the addition of more catalysts should enhance the reaction, to break any oxide barrier so that the reaction can take place on the surface.

3.2. Comparison of the three extraction processes

In this study has only sought to compare the three extraction systems based on some assumptions. Therefore, it has been recommended for isopropanol extraction, to carry out more tests and replicates to obtain specific statistical evidence to be able to conclude that this method is effective in removing Al. Another problem so that the isopropanol extraction was

not efficient has been the temperature used, which in other studies has shown that at high temperatures there is a greater formation of these aluminum gels [53,55].

HCl extraction has shown higher recovery percentages (+ 22.77% at 90 min) than the Bayer process for short recovery times, but for longer times a similar recovery has been observed in both treatments. This has possibly occurred due to the higher electronegativity of the chloride ion compared to the electronegativity of the hydroxyl group. The Bayer method has been more selective, since the extraction of Cu, Ni, and Fe is, on average, several times greater in the extraction of HCl than in the Bayer process (Cu: 27 times greater, Fe: 3 times greater, Ni: 17 times greater). In view of these results, the Bayer process for a 1:15 ratio (BES15) has been the most selective extraction method and the samples recovered have shown the highest Al content.

The obtained product (BES15) has been characterized by N_2 adsorption-desorption and TPD of NH_3, following the procedure described in Section 2.1. BES15 sample shows a BET surface of 35.4 $m^2 g^{-1}$, a microporous surface of 1.8 $m^2 g^{-1}$, and mesopore volume of 0.14 $cm^3 g^{-1}$. The results are similar to those obtained in other works with BET surface areas of 32.9% and 39.0 [56–58]. However, BES15 sample did not show any acidity. Hence, the BES15 has been used as an adsorbent in the removal of CPS.

3.3. Chlorpyrifos removal from BES15 obtained by Al extracting

Fig. 6 shows the removal of CPS with the precipitate using BES15 as adsorbent (Eqs. (11)-(12)). It can be observed that high removal rates are obtained after the initial contact of CPS solution with BES15, by reaching a removal up to 96% after 5 mins of contact for all the weight ratios analyzed. Immediately, the CPS solution comes into contact with BES15. After,

this behavior is kept constant throughout time, indicating that BES15 is a good adsorbent to be used for the removal of organophosphate contaminants such as CPS. These results are similar to those obtained in other studies published in the literature with CPS concentrations between 100 μg l^{-1} and 500 mg l^{-1} [39,59–62]. The results of this study are better than those found with other types of adsorbents, such as zinc oxide nanoparticles, which after 40 mins of contact a removal of 70% was achieved [63]. It has been demonstrated that regardless the amount of precipitate mass, high removal efficiencies have been achieved.

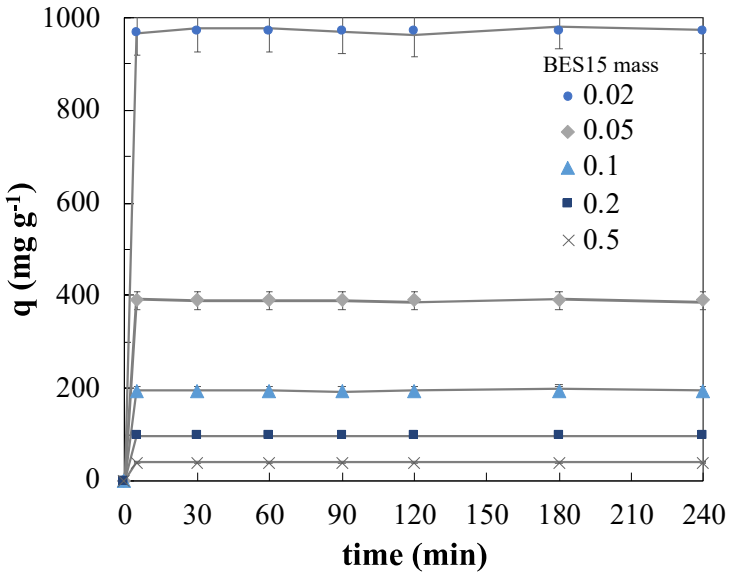


Fig. 6. CPS removal by BES15 synthesized adsorbent for different precipitated mass. Operating conditions: 23 ºC, 240 min.

Fig. 7 shows the parity graph corresponding to the two models used described in Section 2.3. The values obtained in the fitting of the experimental data using the two adsorption models are summarized in Table 5. Both models have been adjusted correctly, however, the Langmuir model, which considers the formation of a single layer of adsorbate on the surface, achieves the best adjustment for all the precipitated mass evaluated. Consequently, the *OF*

value of the Langmuir model ($4.55 \cdot 10^{-22}$) is 12 orders of minor magnitude, in comparison to the one obtained for the Freundlich model ($1.72 \cdot 10^{-8}$). These results are not decisive to conclude that the deposition of the CPS on the surface of BES15 could correspond to a physical (physisorption) or chemical (chemisorption) mechanism, but they contribute a better understanding of the process. Many authors argue that this mechanism cannot be assigned based only on adequate kinetic models, but that different analytical techniques such as FTIR, SEM, Raman spectroscopy, among others, must be performed. [36,64–66].

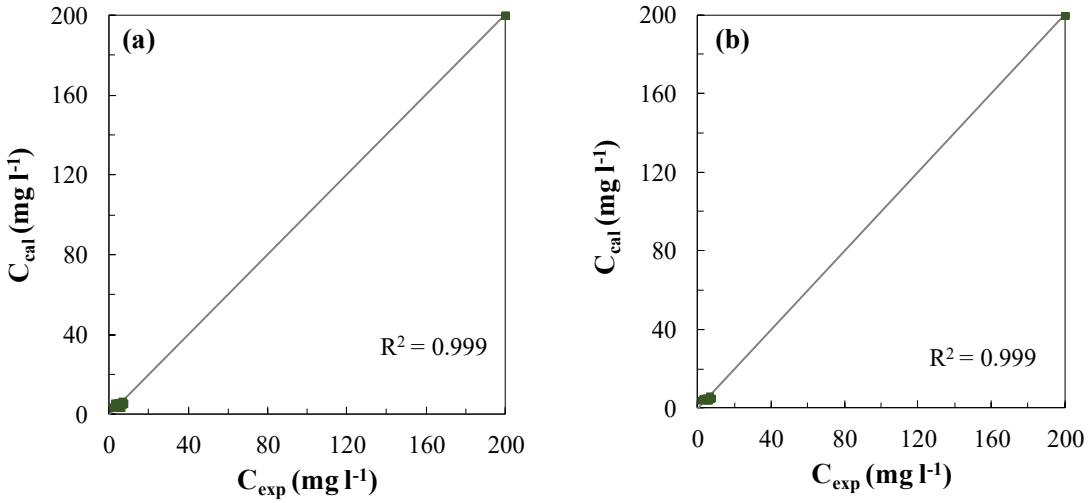


Fig. 7. Parity charts of the tested adsorption isotherm models. (a) Langmuir and (b) Freundlich.

The value of $K_L \alpha \rho_b$ (Table 5, 1.06 min^{-1}) obtained for the Langmuir model is equal to that found by Moussavi et al. [67] in the tests carried out with amoxicillin solutions of 10 mg l^{-1} on NH_4Cl-induced activated carbon. Several studies have been carried out for the removal of CPS on zinc oxide nanoparticles and bagasse biochar, in which lower values (0.025 min^{-1} and 0.1205 min^{-1}, respectively) were obtained [61,63].

Table 5. Balance parameters and mass transfer coefficient calculated for the models evaluated

Parameter	Langmuir	Freundlich
$k_L a \rho_b$ (min^{-1})	1.06	-
OF	$4.55 \cdot 10^{-22}$	$1.72 \cdot 10^{-8}$
K_L (l mg^{-1})	8.23	
q_m (mg g^{-1})	40.27	
K_F		1.53
n		0.45

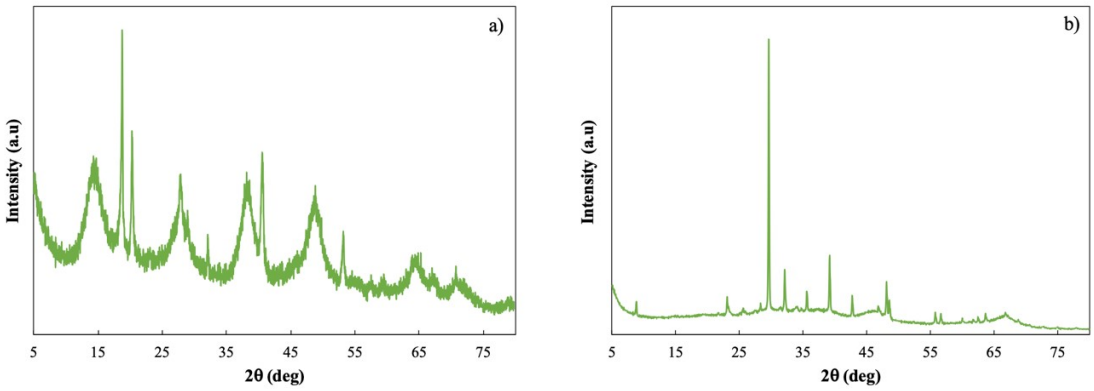
The value for q_m of 40.27 mg g^{-1}, is similar to that found by ul Haq et al. [63] (47.85 mg g^{-1}) using zinc oxide nanoparticles, while this value is higher than that found by Jacob et al. [61] (4.26 mg g^{-1}) using bagasse biochar. In the case of K_F, 1.55 and 2.50 mg g^{-1} were found, similar to those found in this work.

Therefore, the results obtained in our study on BES15 show good prospects, since this less sophisticated adsorbent can be obtained as a by-product of the treatment of hazardous sludge wastes derived from the metallurgical industry.

It must be considered that, according to European legislation, the individual concentrations of this pollutant must not exceed 0.1 ppb. This work has been carried out for the removal of a concentration of 200 ppm, which implies that BES15 could be used as a support in conventional filtration systems due to its high removal rates.

3.4. XRD and SEM Characterization

In Fig. 8 it can be seen that after carrying out the Bayer process to the crude sludge, a crystallinity of the material was achieved, thus showing that the Bayer process improves the sample's crystallinity. The above is reflected in the angle 2θ at 29º that corresponds to aluminum. Furthermore, it is shown that after BES15 is used as an adsorbent, CPS considerably affects the crystallinity of the material, because it is adsorbed on the surface of the material, thus verifying the results of the Langmuir model, which is also observed in the SEM images (Fig. 9c). This behavior is also observed in the increase in carbon on the surface of the adsorbent after the CPS removal process (Table 6). In the XRD analyzes of the sludge, compounds such as boehmite, bicchulite, calcite, calcium and bayerite were identified. In the case of BES15, aluminum oxide was mainly identified at the angle 2θ at 29º. While for the BES15-CPS sample, aluminum oxide and other minor compounds such as carbon and chlorine that can be associated with CPS were identified.



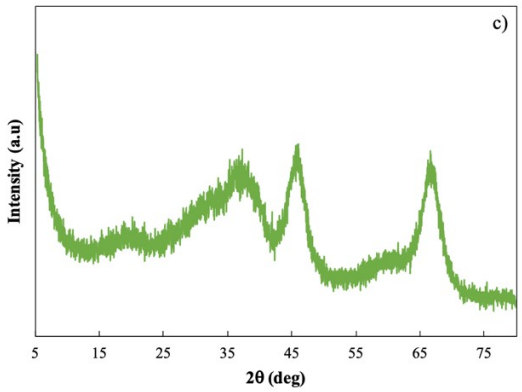
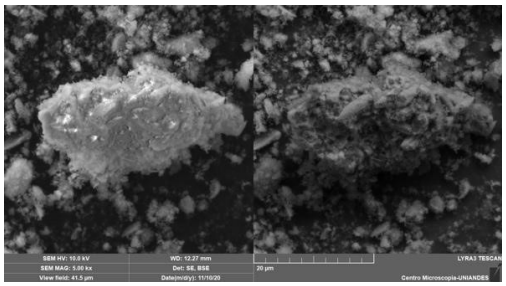
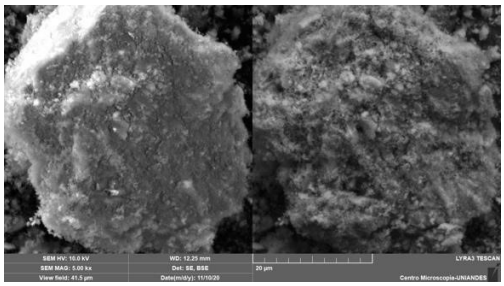


Fig. 8. XRD diagram of the evaluated samples. a) sludge, b) BES15 and c) BES15-CPS.

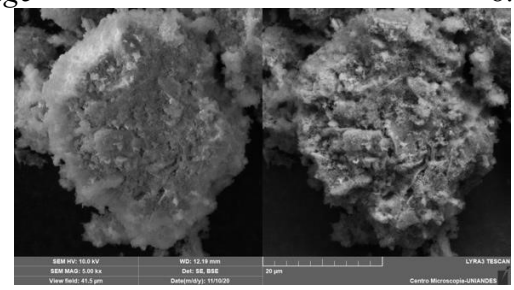
In Fig. 9 the SEM images are shown, it is observed that while the sludge there is little consolidation and a typical sample of sludge from wastewater treatment is evident. After the aluminum extraction process in the BES15 sample, a consolidation of the sample with slightly more defined crystals and porosity in the sample was observed. Finally, after the adsorption process, a layer is observed that can be attributed to the CPS carbon and that the pores are saturated.



a. Sludge



b. BES15



c. BES15-CPS

Fig. 9. SEM images of the different samples. a) sludge, b) BES15 and c) BES15-CPS.

Table 6 shows that in the sample of BES15-CPS there is the presence of compounds associated with the removed insecticide such as chlorine and carbon (Fig. 8 and Fig. 9). While the other minor CPS compounds are not detected by the equipment due to its low content and the resolution of the equipment (> 0.1%).

With the EDS analysis it can be observed how after carrying out the aluminum extraction process through the Bayer process the Na content increases considerably, because the reaction of the process involves NaOH, then in the adsorption process it decreases considerably. This behavior can be due to the fact that Na reacts and can be released in the aqueous sample and leave as NaOH.

Table 6. Elemental content of the different samples (SEM-EDS)

Element	BES15 (Atomic %)	BES15 (Atomic %)	BES15-CPS (Atomic %)
C	6.81	-	9.53
O	67.46	0.24	51.25
F	1.28	3.44	2.94
Na	0.51	11.49	1.65
Al	23.70	27.64	33.89
Si	-	0.31	-
S	0.24	1.87	0.54
Cl	-	-	0.21
Total	100.00	100.00	100.00

4. Conclusions

In this work, we have successfully applied and compared three extraction methods for the removal of Al from sludge wastes derived from the aluminum industry. It should be mentioned that these extraction methods have been scarcely investigated for the removal of these types of wastes. Therefore, we have contributed to their suitable valorization in order to avoid an inappropriate disposal in landfills, by lessening their high environmental impact, and by the proposal of an alternative application as adsorbents to remove CPS pollutants, which are widely used in agriculture, especially in developing countries.

Among the different Al extraction methods analyzed, the Bayer method has been the most feasible one, especially for 1:15 and 1:20 sludge/NaOH ratios, where an Al recovery of 80% and 100%, have been obtained, respectively. However, the selectivity for 1:20 ratio has been substantially lower than the one obtained for 1:15 ratio. In addition, an average recovery of 60% iron, 40% copper, and 2.5% nickel have also been obtained with 1:20 ratio.

The Al extraction with HCl is also a feasible method. For a sludge/HCl ratio of 1:20 a stable Al recovery of 99.32% has been achieved after 90 mins. However, this method is considerably less selective than the Bayer method. In this case, an average recovery of 34.56% of iron, 34.21% of copper and 6.54% of nickel have been obtained.

The Al extraction with isopropanol has not shown promising results, even when high amounts of catalyst were added or $HgCl_2$ was used. Similarly, extraction was not improved over time. This could be attributed to the hydrolysis of the product to aluminum hydroxide, as well as to its slow reaction rate and energy requirements.

Based on these results, the Al samples extracted by the Bayer method with a ratio of 1:15 (BES15) have been tested for the CPS adsorption, in which a removal of 99% has been

attained for 5 to 240 mins, by showing a stable performance, with no evidence of desorption. A good fit has been established for the adsorption process, according to Langmuir isotherm, in which a single layer is formed at the beginning of the process.

The results shown above highlight the good prospects of these waste materials to be used as an economic adsorbent in filter columns. Furthermore, it must be considered that the CPS removal has been performed for higher concentration levels than those required by legislation, which makes these results promising for its commercial application.

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data file has been provided.

NOMENCLATURE

α	External surface area of adsorbent ($m^2\ g^{-1}$)
ρ_b	Adsorbent bed density ($kg\ m^{-3}$)
c_{cal}	Values calculated by the model
C_e	Adsorbate concentration at equilibrium ($mg\ l^{-1}$)
c_{exp}	Phase measured experimentally
C_i	concentration of the aqueous phase at time I (mg l-1)
C_{sludge}	initial sludge concentration (% wt)
i	sampling time
k_1	Rate constant of the PFO equation (min^{-1})
K_F	Freundlich constant, ($mg\ g^{-1}$)/($mg\ l^{-1}$)
K_L	Constant related to the affinity between an adsorbent and adsorbate ($l\ mg^{-1}$)
k_L	Mass transfer coefficient ($l\ m^{-2}\ min^{-1}$)
$K_L \alpha \rho_b$	represents the rate constant of the pseudo-first-order kinetic (PFO) model
L	Volume of CPS solution (l)
m_{sludge}	initial sludge mass (g)
n	Freundlich intensity parameter(dimensionless)

Q^0_{max}	Maximum saturated monolater adsorption capacity of an adsorbent, (mg g^{-1})
q_e, q_t	Amounts of adsorbate uptake per mass of adsorbent at equilibrium
RF	Recovery fraction
RF_i	Recovery fraction at time i
S_{BET}	BET specific surface area (m^2 g^{-1})
S_i	Product selectivity (%)
S_{micro}	Micropore area (m^2 g^{-1})
t	Time (min)
V_0	initial volume (l)
V_{al}	aliquot volume (l)
V_i	Volume in the flask at time I (l)
V_{meso}	Mesopore volume (cm^3 g^{-1})
V_{micro}	Micropore volume (cm^3 g^{-1})
V_p	Pore volume (cm^3 g^{-1})

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