Eco-friendly bench-scale zeolitization of an Al-containing waste into gismondine-type zeolite under effluent recycling

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Abstract

The feasibility of developing an eco-friendly bench-scale zeolitization process of NaP1 from an Al-containing waste and under recycling of effluents was evaluated. Prior lab-scale tests were performed to optimize the synthesis conditions. The mixture of effluents, i.e., mother liquors (ML) from the synthesis and rinse water (RW) from the cleaning step of the zeolites, was recycled several times to study the reduction of raw materials (NaOH and water) and accordingly the reduction of costs. The bench-scale process allows the complete transformation of the waste into NaP1 zeolite, reaching equivalent reaction yields (2.5 ton of zeolite per ton of waste) to the lab-scale process and avoiding the generation of new solid residues. The effect of the recycling of effluents on the physical-chemical properties of the resulting zeolites was investigated. NaP1 zeolite was the only crystalline phase obtained, showing morphological, textural and crystalline characteristics closely similar to NaP1 synthesized from fresh NaOH aqueous solutions and from pure chemical reagents. NaOH and water consumption savings of 80 and 67 %, respectively, were obtained, representing a cost reduction around 70 %. These results show that the bench-scale process to obtain NaP1 from an Al-waste with recycling of effluents can be a more sustainable alternative compared with the traditional synthesis methods.

Keywords: Aluminum waste; Eco-friendly zeolitization; Bench-scale; NaP1; Mother liquor recycling; High-CEC zeolite

1. Introduction

The development of environmentally friendly processes such as the re-use, recycling and recovery of metal-containing wastes generated in different industries is receiving significant attention due to the scarcity of certain primary raw materials employed in the preparation of diverse metal-containing products driven by the growing global demand. One of the priority objectives of the EU policies is focused on turning wastes into resources, with more prevention, re-use and recycling, and phasing out wasteful and damaging practices, for example landfilling, according to the General Union Environment Action Programme to 2020. Tsakiridis (2012) reviewed the aluminum salt slag recycling process, whose landfill disposal is forbidden in most of the European countries. Gil and Korili (2016) reported methods for the appropriate management of the saline cakes from aluminum industries. The increase of aluminum consumption leads to produce several millions of salt cake tons every year, about 95 % are landfilled, thus estimating a cost of 80 million euro. In those works, different synthesis methods of porous materials from the recovered aluminum are reported. The need for developing more sustainable alternatives is therefore essential in order to address the management of wastes generated, prevent and minimize their discharge as well as negative impacts on environment. Wastes, such as ferrochromium slag (Gencel et al., 2013), steel slag (Barca et al., 2014), aluminum dross (Murayama et al., 2006), fly and bottom ashes (Chareonpanich et al., 2011), etc., can be employed as low-cost "secondary raw materials" for the preparation of a wide range of valuable products with attractive applications in different fields, such as construction (Goñi et al., 2014), water remediation (Barca et al., 2014;

Chareonpanich et al., 2011), glass-ceramics (Gencel et al., 2013), etc. In this sense, a waste composed of a very fine aluminum powder, which is mainly generated in the slag milling process during the recovery of residual aluminum from aluminum slag and dross (Galindo et al., 2015a), can also be employed as a secondary raw material. This powder, highly rich in aluminum, is considered as a hazardous waste due to its small particle size and multiphase composition with different harmful substances, such as metallic aluminum, aluminum nitride, aluminum carbide, aluminum sulfide and heavy metals. In addition, this waste can react with water or humidity generating certain toxic gases, e.g., ammonia, methane and hydrogen sulfide, and/or inflammable and explosive gases like hydrogen. The content of aluminum (as oxide) in this waste represents about 53-81 % in weight (Galindo et al., 2015a), being still potentially valuable. Hence, it can be used as a non-conventional raw material for the production of different added-value materials. In previous studies, this waste was employed in various synthesis processes to obtain alumina (López-Delgado et al., 2012), hydrotalcites and glasses (Galindo et al., 2015b). Likewise, it has been also used as one of the aluminosilicate precursors for the synthesis of Na-zeolites, namely NaP1, SOD and ANA, by an one-step zeolitization process that achieves converting the whole waste into a zeolitic material (Sánchez-Hernández et al., 2016). The developed zeolitization process not only enables to reduce the amount of Al-containing wastes, which are generally disposed of in secure deposits, but also could preserve natural resources, hence helping the sustainability of environment.

The worldwide consumption of zeolites is growing every year as a result of the increasing use of these materials in numerous industrial applications, such as

water remediation (Gonzalez et al., 2015; Maretto et al., 2014), catalysis (Mazur et al., 2016), detergents, gas separation, membranes (Cundy and Cox, 2005; Yilmaz et al., 2012), etc. Zeolites can be obtained not only from chemical reagents, but also from diverse wastes, generally silica-rich precursors with very low alumina contents, such as fly ash (Deng and Ge, 2015; Querol et al., 2002), rice husk ash (Dey et al., 2012; Othman Ali et al., 2011), or kaolin-type precursors (Bessa et al., 2017) that, in general, involve pretreatments of the waste at high temperature to induce its conversion to more reactive products.

Zeolites present porous crystalline frameworks that allow the diffusion and adsorption/desorption of different molecules and ions through their channels or cavities (Maretto et al., 2014). Thus, zeolites are intensively being used in a variety of commercial applications, such as adsorbents, desiccants or detergent builders (Gupta and Ali, 2013; Yilmaz et al., 2012). For example, Franus et al. (2014) obtained several types of zeolites (NaX, NaP1, and sodalite), with different channel sizes, using fly ash and 3-5 M NaOH solutions at 75-95 ºC for 24 h. Such zeolitic materials were used in the removal of ammonium, zinc, radionuclides and CO_2 (Franus et al., 2015) and in the land-based petroleum spills cleanup (Bandura et al., 2015), showing good adsorption capacities. Among zeolites used as adsorbent materials in wastewater treatments, NaP1, i.e., gismondine-type zeolite (GIS), has been highly used due to its high cation exchange capacity (CEC) of 1.5-5.0 meq/g for commercial zeolitic products and about 2.0-3.1 meq/g for fly ash-based zeolites obtained by Querol et al. (2007). Its sorption properties allow the removal of heavy metals and ammonium from waters (Moreno et al., 2001; Querol et al., 2002) and the uptake of high water amounts (Sharma et al., 2016).

Although the literature on synthesis of zeolites by more environmentally sustainable processes has expanded continuously, only a few studies address issues related to the treatment of liquid wastes or mother liquors (ML), i.e., effluents that are generated in the synthesis processes and are usually discarded. For instance, ML used for the synthesis of FAU/LTA from lithium slag by the hydrothermal method can have a great influence on zeolite structure, leading to good adsorption capacities of calcium and magnesium (Lin et al., 2015). In addition to the generation of ML, other effluents are also produced in such zeolitization processes, for example, rinse water (RW) from the cleaning step for the removal of soluble species after the separation of ML and the zeolitic cake. For example, Behin et al. (2016) reported the synthesis process of NaP from coal fly ash under recycling of the effluents from filtration and washing steps. The quality of the resulting products was not modified with the recycling process. Recycling and reutilization of ML and RW into the zeolite synthesis can actually be one potential solution to treatment of the liquid wastes. Indeed, these effluents, in most cases, contain surplus reactants, such as inorganic elements (Si, Al, Ti, Na, etc.) and/or highly toxic organic compounds from structure directing agents that can be fed again to the synthesis process, thus minimizing the liquid discharge.

In this present work we report the feasibility of producing NaP1 from an Al-containing waste by a zero-waste hydrothermal zeolitization process performed on bench scale, and also the study of the influence of recycling of the effluents (ML and RW) on the resulting products. The objective was not only to minimize the raw materials consumption, but also to reduce the costs, amount of residual effluents to be treated as well as impacts of the process on environment. The

liquid/solid ratio in the initial synthesis process was studied on laboratory scale in order to optimize the experimental conditions of the bench-scale hydrothermal zeolitization process. Moreover, a simple cost estimation is presented for a better understanding of the developed zeolitization process under effluents recycling compared with the conventional synthesis method. The influence of the effluents recycling on the composition, crystallinity, morphology, structure, thermal stability and other properties of the products were studied by several techniques: XRD, SEM-EDS, FTIR, TG-DTA and ICP-OES. Moreover, the zeta potential, particle size distribution, specific surface area, and cation-exchange capacity (CEC) of the resulting materials were also determined.

2. Experimental

2.1. Materials

The Al-containing waste from metallurgical industry, used as the only aluminum source in the synthesis of NaP1 (GIS-type zeolite), consists of a grey fine powder with an Al_2O_3/SiO_2 molar ratio of 7.3. The main chemical composition of this waste was as follows: Al_2O_3 65.93 wt.%, SiO_2 5.34 wt.% and small quantities of MgO, TiO_2, CaO, Fe_2O_3, and Na and K chlorides (Sánchez-Hernández et al., 2016). The total content of aluminum in this waste (34.90 wt.%) is distributed in different crystalline phases, namely, metallic aluminum (12.84 wt.%), aluminum nitride (8.60 wt.%), corundum (7.04 wt.%), and spinel (6.43 wt.%). According to the metallic aluminum and aluminum nitride amount, in presence of humidity, toxic and hazardous gases, such as ammonia and hydrogen, can be generated, specifically, 160 and 71 Nm^3 per ton of waste,

respectively (Galindo et al., 2015a). The waste exhibits a heterogeneous morphology with a multiphase composition formed by crystalline and amorphous particles of different shape and size, as can be seen in Fig. 1. A more detailed characterization of the waste was described elsewhere (Galindo et al., 2015a; Sánchez-Hernández et al., 2016). The required Al^{3+} amount for the preparation of NaP1 was totally provided by this waste, which was directly used without any previous treatment. While the required Si^{4+} amount to balance the Al/Si ratio, was supplied both by the waste and by a 11 M Na_2SiO_3 neuter solution (water glass) due to the low silica content in the waste. The Na^+ amount was provided mainly by a 1 M NaOH aqueous solution prepared by dissolving NaOH pellets in distilled water for the lab-scale experiments, and by adding the needed amount of a 50 % (w/w) NaOH aqueous solution in water for the bench-scale synthesis experiments.

2.2. Methods

2.2.1 Lab-scale synthesis process: effect of the liquid/solid ratio

Firstly, the direct conversion of the waste into NaP1 zeolite was developed by the hydrothermal synthesis in the Na_2O-Al_2O_3-SiO_2-H_2O system on lab scale (Sánchez-Hernández et al., 2016). All the reactants, the solid waste (10 g), Na_2SiO_3 solution and NaOH solution, were mixed into a Teflon lined stainless steel autoclave reactor (Parr) of 1 L capacity. The synthesis was carried out with a fixed Si/Al molar ratio of 2.0, at 120 ºC for 6 h, under autogenous pressure and with continuous stirring. Different liquid/solid ratios (7.5, 15 and 25 mL/g) of the initial reaction suspension were tested in order to evaluate the most optimal conditions for a further synthesis with recycling of effluents (ML

and RW) on a larger scale. The liquid includes the volume of alkalizing agent (NaOH solution), water glass and distilled water, whereas the solid refers to the amount of the solid Al-waste. After the synthesis, the solid products were separated by filtration, washed with distilled water and dried in air at 80 ºC for 24 h. Hereinafter the samples obtained using a liquid/solid ratio of 7.5, 15 and 25 mL/g were named as R1, R2 and R3, respectively.

2.2.2 Bench-scale synthesis with recycling of effluents

In order to develop a process with zero effluents, the ML from the bench-scale synthesis of NaP1 was recycled up to three times to reduce raw material consumptions and the environmental impact of the process accordingly. ML can be reused due to their high basicity (pH ~ 13.6), approximately the same than the 1 M NaOH solution (i.e., alkalizing agent) used for the lab-scale hydrothermal process of NaP1 without effluents recycling. In addition, ML contains mainly elements such as Si, Al and Na considered as valuable elements for the zeolite synthesis. The larger-scale recycling experiments were developed following the same conditions as the previous lab-scale synthesis of NaP1 without effluents recycling: Si/Al molar ratio of 2.0, at 120 ºC for 6 h and under autogenous pressure of the reaction system. Thus, the solid waste (250 g) and all the reactants were added into a stainless steel reactor of 5 L volume (E. Bachiller B, S.A.) with temperature and pressure control and incorporated agitation system (Fig.2).

The effect of recycling on the products was studied reusing the ML to produce second, third and even fourth generations of NaP1. To maintain the same alkalinity and liquid/solid ratio (15 mL/g) used in the prior lab-scale experiments

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with liquid discharge, a certain ML volume (similar to 1 M NaOH), together with a small amount of fresh 1M NaOH (prepared from a 50 wt.% NaOH solution) were required. The total liquid volume to be recycled was also compensated by the addition of a small volume of the RW from the cleaning step of the zeolitic products. The RW pH is also equal to the ML pH, thus allowing even more the reduction in the liquid waste generated in the global process. The scheme of the recycling process of effluents to obtain NaP1 from the aluminum waste is shown in Fig. 3. Hereinafter the samples obtained by consecutive recycling of effluents (ML and RW) are named as Z1, Z2 and Z3, while Z0 corresponds to zeolite obtained with liquid waste discharge.

2.2.3 Characterization of samples

The study of the characteristics of samples, such as crystallinity, morphology, structure, thermal stability, cation-exchange and texture, were determined according to the same conditions and techniques of analysis described in our previous work (Sánchez-Hernández et al., 2016). The crystallographic phase identification of all samples was performed using the ICDD PDF reference pattern database. The relative crystallinity was calculated based on the five characteristic peaks of NaP1 (d_{101} at $12.54^{°}$, d_{200} at $17.74^{°}$, d_{112} at $21.74^{°}$, d_{301} at $28.24^{°}$ and d_{312} at $33.48^{°}$, according to the International Zeolite Association, IZA), designating the zeolite obtained in the synthesis without recycling as the reference. The chemical composition of the ML and RW (effluents) was determined by ICP-OES. The alkalinity of the effluents was calculated by titration with 0.1 N HCl using a TritoMatic titrator (Crison).

3.   Results and discussion

3.1.   *Effect of the liquid/solid ratio on the lab-scale synthesis of NaP1*

The influence of the volume of liquid per amount of solid (liquid/solid ratio) in the reaction system on the crystallinity of the resulting materials obtained by the lab-scale process was studied in order to assess the best synthesis conditions and to develop the scaling-up of a more eco-friendly process. The XRD patterns of the samples synthesized using 1 M NaOH solution and the different liquid/solid ratios (7.5, 15, 25 mL/g) at 120 ºC for 6 h on lab scale are shown in Fig. 4. The crystallographic properties of the zeolitic phases obtained were evaluated according to their XRD patterns. Table 1 collects the peak parameters, crystallite sizes and also the synthesis yield (expressed as kg of zeolite per kg of waste), as function of the different liquid/solid ratios tested. All the experiments led to the formation of NaP1 zeolite as the only crystalline phase according to the reference file (ICDD PDF 01-071-0962), identifying the most intense 301 reflection centered at 28.1° (Treacy and Higgins, 2007) for samples R1, R2 and R3. All samples showed well-defined XRD profiles, and shifts in the peak parameter values such as 2θ and FWHM were not observed. In addition, the crystallite size values for different liquid/solid ratios tested were very similar. It could indicate that the liquid/solid ratio in the reaction medium does not seem to modify the crystallite size. The most crystalline NaP1 was obtained for a liquid/solid ratio of 15 mL/g (sample R2), as shown its diffraction profile composed of well-defined and narrower peaks, resulting in the highest intensity value of the three main reflections (i.e., d_{101}, d_{112} and d_{301}).

The hydrothermal conversion of the waste into zeolite led to reaction yields (expressed as mass of obtained product per mass of waste) of ~2.50 kg of zeolite per kg of waste for the liquid/solid ratios of 15 and 25 mL/g, samples R2 and R3, respectively. On the contrary, the lowest zeolite amount was obtained using the lowest liquid/solid ratio of 7.5 mL/g (sample R1). It could be related to the lowest liquid volume used in the reaction medium, leading to the poorest homogenization of all the reactants during the synthesis, as well as, the lowest formation of crystal nuclei, and thus, resulting in the lowest reaction yield. The synthesis process using the highest liquid/solid ratio generated approximately 8.9 L of ML per kg of obtained zeolite, while the lowest ratio led to 1.3 L of ML per kg of zeolite. The ratio of 15 mL/g was considered as the optimal since it would not only allow the production of well-crystallized NaP1, but also the reduction in the waste effluent generation, resulting in 4.4 L of ML per kg of zeolite. Therefore, the ratio of 15 mL/g was selected to perform the bench-scale synthesis experiments with recovery and recycling of effluents.

3.2.   Effect of the effluents recycling on the bench-scale synthesis of NaP1

As above commented, the experimental conditions selected to perform the bench-scale experiments were 120 ºC for 6 h and a solid/liquid ratio of 15 mL/g. Fig. 5 shows the XRD patterns of the samples obtained using the fresh 1 M NaOH solution (sample Z0), and reusing both the ML (effluent generated in the synthesis) and the RW (water from the rinsing step) into the subsequent synthesis leading to the second, third and fourth zeolite generation (samples Z1, Z2 and Z3, respectively). The synthesis yield, amount of ML generated per kg of zeolite, crystallinity, peak parameters and crystalline sizes obtained in both the process with and without liquid discharge were studied (Table 2). NaP1

was obtained as the only zeolitic phase in all the experiments. The samples showed well-defined XRD profiles and no shifts in the 2θ and FWHM values were observed. The 301 reflection was centered at ~28º for Z0 prepared with a fresh 1 M NaOH solution and identical results were obtained for Z1, Z2 and Z3 prepared from effluents recycling. It is noteworthy that the recycling of effluents in the synthesis led to the complete dissolution of the silica and alumina amount present in the waste, resulting in highly pure NaP1. Although NaP1 zeolite is also usually synthesized from fly ash, the presence of unreacted quartz and mullite as a result of the lower solubility of these minerals in alkali solution is frequently observed (Deng and Ge, 2015; Querol et al., 2002; Szala et al., 2015; Wałek et al., 2008). Moreover, as observed in the XRD profiles, the crystallinity as well as crystallite sizes (~ 25-29 nm) of all samples did not vary significantly. It can be associated to the small quantities of NaP1 crystals present in the ML that act as seeds, thus favoring the heterogeneous nucleation and crystal growth of the zeolite. Although the process with recycling of effluents seems to decrease slightly the crystallinity, this parameter was maintained after each recycling cycle between 93 and 83 % for the recycled samples (Z1, Z2 and Z3) compared with the reference sample (Z0). The decrease of crystallinity could be related to the incorporation of other cations (e.g., K, Ca, etc.) from the liquid mixture of ML and RW to the framework. It could slightly distort the zeolitic structure as a result of the difference of cation sizes compared with the Na^+ ion. Table 3 shows the Life Cycle Inventory (LCI) analysis of the production of 1 ton of NaP1 zeolite by the bench-scale process with and without effluent discharge. LCI provides the data of inputs (sources of Na, Al and Si, synthesis process and cleaning water), recycled effluents, and

outputs (discharged RW after the zeolite cleaning) of the analyzed synthesis system. Due to the lack of data related to the industrial-scale production of zeolites, the LCI assessment was based on the mass flows from the lab and bench-scale experiments. The energy flow, not evaluated in this work, may oscillate around 21400-25200 MJ/t, according to the LCI for the production of zeolite A (Fawer et al., 1998). The reached reaction yields were quiet similar for all the samples, leading to ~2.5 ton of NaP1 zeolite per ton of waste after three consecutive recycling cycles. In addition, bench-scale synthesis involved the generation of the same volume of ML per kg of zeolite (~4 L/kg) in all the recycling cycles compared to that obtained in the lab-scale synthesis. Thus, the lab and bench-scale synthesis of NaP1 allowed getting materials with very similar crystallinities and equivalent reaction yields. These findings help emphasize the feasibility of the scaling-up of the zeolitization process using an Al-waste and under recycling of effluents.

As all the synthesis conditions (Si/Al ratio, temperature, time, and liquid/solid ratio) remain unchanged in each recycling cycle, the type of zeolite obtained, i.e., the crystallization of zeolitic products would depend on the reactant composition of the initial solution. In general, aluminosilicate zeolites are obtained under basic or strongly basic conditions in the Na_2O-Al_2O_3-SiO_2-H_2O system, where the alkalinity, defined as the concentration of base (H_2O/Na_2O), plays an important role in the zeolite crystallization (Xu et al., 2010). Thus, the alkalinity would significantly affect the nucleation and crystal growth of zeolites. In this sense, it should be pointed out that the amount of Na^+ cations and mineralizing agent (i.e., OH^- ions) in the initial solution would play an important role in the zeolite crystallization. The OH^- ion affects dissolution and

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polymerization/depolymerization reactions of aluminosilicates (Flanigen, 1973). Cations like Na^+ stabilize aluminosilicate ions via static electric and steric interactions, playing a remarkable structure-directing role, and determine their solubility regulating the concentration of aluminum in solution (Camblor and Pérez-Pariente, 1991) and accordingly helping the pH adjustment of the process (Xu et al., 2010). Some works reported that additions of alkali-metal cations like Na^+ in the initial solution involved an acceleration effect for the crystallization, facilitating the condensation or rearrangement of the structural building units of zeolites (Liu et al., 2014). Thus, the increase of the alkalinity by increasing the pH leads to a higher solubility of silicon and aluminum sources, favoring the crystallization of zeolites (Cundy and Cox, 2005; Flanigen, 1973; Xu et al., 2010). As the alkalinity of the reaction medium of the synthesis process under recycling of effluents must be adjusted, the pH and molarity values in each cycle were controlled. The molarity of recycled liquid mixture, ranged 0.86-0.80 M for ML and 0.54-0.37 M for RW, is somewhat insufficient for an adequate synthesis of NaP1, being necessary to add a certain amount of fresh 50 wt.% NaOH solution to reach 1 M, and accordingly to get the required alkalinity. Consumption savings of such fresh 50 wt.% NaOH solution of 80, 74 and 69 % were obtained in the first, second and third recycling cycle (Z1, Z2 and Z3, respectively), as shown Table 3. The amount of 50 wt.% fresh alkali solution should be increased only 5 % in each recycling cycle, thus saving costs in the preparation of NaP1. The volume of the recycled effluent mixture in each cycle contained ca. 83 wt.% of ML and 17 wt.% of RW. The process allows recovering the total volume of ML generated in each synthesis, and also around

33 % of the total water amount employed for the rinsing step to remove traces of soluble species in the zeolitic cake.

A more exhaustive characterization of samples synthesized on bench scale was carried out in order to study their adsorption properties and to assess their potential applications in wastewater treatments.

The zeolitization process using either the fresh solution of alkalizing agent or the recycled effluents (ML and RW) resulted in highly crystalline zeolitic products with the same morphology, as shown in Fig. 6, which is characteristic of the GIS-type zeolite. This morphology consisted of "cauliflower-like" primary aggregates with well-defined cubic nanocrystals, ranged between 200 and 500 nm. Identical morphologies are presented by NaP obtained from chemical reagents by a hydrothermal method (Ali et al., 2015), and by microwave radiation (Zubowa et al., 2008). The hydrothermal conversion of fly ash into NaP with 2 M NaOH at 100 ºC for 24 h also showed this morphology (Qiu et al., 2015). According to the EDS analyses (Table 4), the average Si/Al ratio ranged between 1.6 and 1.8 for Z0, Z1, Z2 and Z3, values closely similar to the corresponding stoichiometric ratio (~1.67) of NaP1. Sodium was the main exchange cation in the structure of the obtained zeolites. Thus, for all the samples, Na/Al ratios between 0.8 and 0.9 were obtained, and, in general, other exchange cations were not observed, but scarcely, minor potassium content (with K/Na ratio < 0.03) was detected.

Fig. 7 shows the FTIR spectra of Z0, Z1, Z2 and Z3 recorded from 400-1200 cm^{-1}. All the samples exhibited the spectrum characteristic of NaP1 with the symmetric stretching vibrational mode of internal tetrahedron formed by two

strong bands centered at 747, and 608, and a very weak band at 668 cm^{-1}, and the tetrahedron bending mode attributed to the band at 433 cm^{-1}. These results agree with those found for NaP1 with high H$_2$ selectivity (Sharma et al., 2013) and good alkali-metal adsorption properties (Ali et al., 2015) synthesized from chemical reagents by hydrothermal methods. Similar FTIR bands were reported for NaP from other precursors like kaolin by a hydrothermal route at 100 ℃ for 48 h, showing good calcium adsorption capacities (Bessa et al., 2017).

The thermal behavior of all samples was studied from room temperature to 1000 ℃. Fig. 8 shows the corresponding TG-DTA curves recorded between 25 and 400 ℃. The TG-DTA curves follow the same profile for all samples. The total mass loss up to 1000 ℃ was related to the content of water released from the zeolite structure taking place in several steps for all the samples. Thus, Z0 involved a total mass loss of 13.4 wt.%, being almost similar as that obtained in the lab-scale synthesis of NaP1 from this Al waste at 120 ℃ for 6 h (Sánchez-Hernández et al., 2016). On the other hand, Z1, Z2 and Z3 showed slightly higher total mass losses of 15.1, 14.8 and 14.9 wt.%, respectively. Such mass losses can be associated with the content of water molecules present in the zeolite. It would involve 10 water molecules for Z0, and 11 water molecules for Z1, Z2 and Z3. These values are quite similar to the theoretical water content of NaP1 corresponding to 12 water molecules (Baerlocher and Meier, 1972). Lower and even higher mass losses between 12.5 and 18.0 wt.% were reported for NaP obtained from chemicals by a hydrothermal method at 100 ℃ for 4 days (Ali et al., 2015) and from MCM-22-type gels by microwave heating at 140 ℃ for 3 h (Zubowa et al., 2008). The strongest endothermic peak of NaP1 was determined at 107 ℃ for Z0 due to the highest heat flow (218.5 J/g) from the

release of water strongly adsorbed in the channels of NaP1. Sample Z1 showed the maximum water loss at 100 ºC resulting in water evaporation energy of 211.1 J/g. While Z2 and Z3 showed this water release with heat flows of 202.0 and 196.5 J/g at similar temperature values, 102 and 103 ºC, respectively. The cations from the recycled effluents could occupy the most internal voids to balance the zeolite charge, leading to lowest temperatures for the release of water from the zeolitic structure.

The textural properties, such as the specific surface area (S_{BET}), characteristic values (d_{10}, d_{50} and d_{90}) of particle size distribution, zeta potential (ZP) and cation-exchange capacity (CEC) of Z0, Z1, Z2 and Z3 are collected in Table 5.

The N_2 adsorption/desorption curves of all samples exhibited IV-type isotherm with a H3-type hysteresis loop at a relative pressure range between 0.45 and 0.99 (Fig. 9), indicating meso and macroporous behavior. Low S_{BET} values for all samples were obtained, which is likely due to the existence of macropores. These findings are similar to those found by Cama et al. (2005), who obtained NaP1 from fly ash by an alkaline treatment. The authors found higher S_{BET} values (18 ± 2 m^2/g) than that for a commercial zeolite (10 ± 1 m^2/g), and enhanced its porosity by an acid treatment that showed the highest S_{BET} (63 ± 3 m^2/g). Prior to N_2 adsorption experiments, the samples were outgassed at 140 ºC for 24 h. Ali et al. (2015) pSharma et al. (2016) obtained higher S_{BET} ranged 29-47 m^2/g (outgassing conditions: 250 ºC, 6 h) for NaP1 microspheres. Bandura et al. (2016) reported high S_{BET} around. 95 m^2/g (outgassing conditions: 250 ºC, 24 h) for NaP1 synthesized from fly ash, at 75 ºC for 24 h. The low S_{BET} values of NaP1 from the Al-waste could be caused by the low outgassing temperature (< 100 ºC) what could hinder the adequate cleaning of

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the zeolite surface. Although the repared NaP1 from chemicals at lower temperature (100 ⁰C) and for a longer time (4 days), also leading to low porosity, 6 -14 m^2/g (samples outgassed at 200 ⁰C). Huang et al. (2010) reported even lower values than 5 m^2/g (outgassing conditions: 250 ⁰C, 10 h) for NaP from conventional reagents. The authors stated that these results were related to the high crystallization of NaP and its small pores. On the other hand, nitrogen adsorption/desorption is considered as a standard textural analysis, this technique could lead to inaccurate values for the assessment of materials with relatively small microspores as is the case of GIS-type zeolite with 8 membered-rings (Ali et al., 2015; Huo et al., 2012; Sharma et al., 2016). The particle size distribution from 0.1 to 100 μm of all samples showed a quasi-unimodal and narrow distribution centered at 16.57, 22.49, 26.20 and 22.49 μm of particle diameter for Z0, Z1, Z2 and Z3, respectively, as can be seen in Fig. 10. These results fit well to those found in the literature for NaP1 obtained from fly ash (Bandura et al., 2016). The parameters of PSD for the samples prepared using fresh solution of NaOH (Z0) and the first recycling (Z1) were very similar, while the second and third recycling samples (Z2 and Z3, respectively) showed slightly higher values. It could be related to a particle aggregative behavior as a consequence of the recycling process of effluents. All samples presented negative values of ZP, resulting in materials with negatively charged surfaces. The results showed that slightly more negative charges were available in the samples obtained from the zeolitization process without effluent discharge (Z1, Z2 and Z3), and hence, a higher electrostatic attraction between positive charges and the active sites of NaP1 can be found, but these differences are scarcely significant. Therefore, the samples prepared by the synthesis with

recycling of effluents present the same textural characteristic than the sample obtained with fresh solution, and all of them might be used in water remediation applications to adsorb different cations. The mild conditions employed in the synthesis under recycling of effluents allowed for high-CEC zeolites, resulting in 2.3-2.4 meq NH_4^+/g for all samples. These results coincide with that obtained for sample Z0 and to those CEC values found in the literature for NaP1 obtained from fly ash (Querol et al., 2002), and also prepared by the lab-scale synthesis using this Al-containing waste (Sánchez-Hernández et al., 2016).

Therefore, after three consecutive effluent recycling cycles, the resulting zeolites retained high crystallinity as well as morphological, textural and adsorption properties as compared to the zeolite obtained in the initial experiments where a fresh 1M NaOH solution was used as the alkalizing agent.

Thus, the synthesis scaling-up shows quite similar results compared with those found in the lab-scale synthesis of NaP1 from the same Al-waste (Sánchez-Hernández et al., 2016), involving a good reproducibility of the process.

The chemical composition, pH and conductivity of the ML recycled during the hydrothermal synthesis of Z1, Z2 and Z3 are collected in Table 6. The main elements detected by ICP-OES were Na, Si, K and Al. All these elements constituent the zeolite frameworks, and therefore, ML could have a profitable effect on the synthesis of zeolites. Likewise, the pH and conductivity values of ML are very similar to the 1M NaOH solution (Sánchez-Hernández et al., 2016), thus confirming that ML can be recovered and fed into zeolitization processes, and saving NaOH and water consumptions.

3.3. Feasibility of industrial-scale zeolitization process

To assess the feasibility of industrial-scale production, a cost estimation (Table 7) was calculated according to the LCI, showing the production of one ton of NaP1 from the Al-waste by the process using fresh NaOH solution (Z0) and by the improved process after three consecutive recycling cycles (Z3). Moreover, the conventional synthesis process (without recycling) of NaP1 from commercial aluminum sources like Al_2O_3 was evaluated, considering the same amount of aluminum oxide present in the waste (*ca.* 66 wt.%). The price of commercial NaP1 depends on the manufacturer and may be ranged 600-1325 €/ton of zeolite, according to data provided by some members of the European Zeolites Producers Association. The lifetime of NaP1 varies according to the pH, being of 2 years at near neutral pH and less than 10 days at below pH 3 (Cama et al., 2005). As commented above, the process under effluents recycling led to a considerable decrease in the amount of fresh 50 wt.% NaOH of 80, 74 and 69 % for Z1, Z2 and Z3, respectively, compared with the synthesis of Z0. Concerning the total water amount required for the synthesis of Z3, only RW was required since all the ML volume from the synthesis of Z2 together with a certain amount of RW were recycled for the preparation of Z3. It involved a water consumption saving of 67 % when it is related to the total water amount (i.e., fresh water for the synthesis and RW for the rinsing step) used for the synthesis of Z0. The effluent recycling process represented a cost reduction of 68 and 70 % for water and NaOH, respectively. In addition, the reuse of Al-containing wastes would involve a significant cost reduction when it is compared with the cost of the aluminum sources commonly used in the zeolite synthesis, such as sodium aluminate, pseudo-boehmite, aluminum hydroxide

and aluminum isopropoxide (Xu et al., 2010). The use of Al-wastes in the synthesis process can also save the costs of deposit authorized landfill (around 109 € per ton of waste). Moreover, the concerns derived from their disposal because of their hazardousness are also minimized.

Thus, the zero liquid discharge process implies not only an economical opportunity respect to the process without re-used of effluents (ML and RW), but also an environmental improvement. It would help to handle and reduce the generation of effluents from the zeolitization process, saving the raw materials consumption.

4.   Conclusions

This work addresses the development of a bench-scale zeolitization process with recycling of effluents to obtain NaP1 from an aluminum waste with zero liquid discharge. The waste from the aluminum slag milling process is usually stored in secure deposits, becoming an environmental hazard. Thus, this Al-waste was used as the only Al-source for the synthesis of NaP1. Prior lab-scale experiments led to establish the adequate experimental parameters for the scaling-up (i.e., the liquid/solid ratio in the initial reaction suspension, among others). The mixture of effluents, formed by ML from the synthesis and RW from the cleaning step of zeolites, was recycled several times in order to study its effect on the resulting zeolites, as well as, to reduce the consumption of raw materials, i.e., NaOH and water, and also the costs. The zeolitization process with recycling of effluents enables the physical-chemical properties of the resulting products to be maintained. In addition, the bench-scale process allows the complete transformation of the waste into zeolite, reaching equivalent

reaction yields (2.5 ton of zeolite per ton of waste) in each effluents recycling cycle. The obtained NaP1 zeolites showed morphological, textural and crystalline characteristics similar to those synthesized from fresh NaOH solutions and from pure chemical reagents. The zeolitization process under effluents recycling led to consumption savings of NaOH and water of 80 and 67 %, respectively, compared with the process with liquid discharge. This implied a cost reduction of 70 and 68 % for NaOH and water, respectively.

Therefore, the zeolitization process from a hazardous Al-waste with recycling of ML and RW represents a green and feasible alternative to the traditional zeolite synthesis from other raw materials. Besides, it contributes to preserve the natural water resources.

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Table 1

Effect of the initial liquid/solid ratio on the synthesis yield and the crystallinity of the zeolites synthesized from aluminum waste on laboratory scale.

Sample	Liquid/solid ratio (mL/g)	Yield (kg$_{zeolite}$/kg$_{waste}$)	Phase	Intensity (counts) [a]	FWHM (º) [b]	2θ (º) [b]	D$_{hkl}$ (nm) [b]
R1	7.5	2.29	NaP1	826	0.26	28.06	32
R2	15	2.46	NaP1	1204	0.27	28.11	31
R3	25	2.47	NaP1	1018	0.28	28.08	29

[a] Sum of the intensities of the three most intense XRD peaks (d$_{101}$, d$_{112}$ and d$_{301}$).

[b] Peaks parameters (FWHM, 2θ) and crystalline size (D$_{hkl}$, calculated by Scherrer equation) were determined according to the most intense reflection (d$_{301}$).

Table 2

Effect of the recycling on the crystallinity of the zeolites synthesized from aluminum waste on bench scale.

Sample	Liquid/solid ratio (mL/g)	Phase	Crystallinity (%)	2θ (º) [a]	FWHM (º) [a]	D$_{hkl}$ (nm) [a]
Z0		NaP1	100	28.07	0.33	24.83
Z1	15	NaP1	92.6	28.07	0.30	27.32
Z2		NaP1	83.0	28.09	0.28	29.27
Z3		NaP1	83.6	28.09	0.29	28.26

[a] Peak parameters and crystalline sizes associated to the most intense reflection of NaP1 (d$_{301}$).

Table 3

LCI of the production of 1 ton of NaP1 by the bench-scale process with and without liquid discharge.

Yield ($t_{zeolite}$/t_{waste})		Input (kg/$t_{zeolite}$)					Recycled effluent[a] (kg/$t_{zeolite}$)		Output (kg/$t_{zeolite}$)
		Al waste	Water glass	NaOH 50 wt.%	H_2O synthesis	H_2O cleaning	ML	RW	Discharged effluent
Z0	2.45	408	1470	390	4898	2449	4080	816	1633
Z1	2.49	402	1450	80	-	2410	4110	804	1606
Z2	2.46	407	1460	100	-	2439	4030	813	1626
Z3	2.52	397	1430	120	-	2381	-	-	6281

[a] Mixture formed by ML 83 wt.% and RW 17 wt.%, where the total amount of ML and a certain amount of RW are recycled. The amount of recycled effluent for the synthesis of Z1, Z2 and Z3 is equivalent to the amount of fresh water used for the preparation of Z0.

Table 4

EDS analyses of the NaP1 zeolite synthesized on bench scale.

Sample	Atomic %				Si/Al
	Na	Al	Si	O	
Z0	9.91	11.34	18.64	59.63	1.64
Z1	9.71	11.25	18.95	59.82	1.69
Z2	7.72	11.54	19.64	60.68	1.70
Z3	8.67	10.95	19.71	60.34	1.80

Table 5

Specific surface area (S_{BET}), particle size distribution (PSD), zeta-potential (ZP) and cation-exchange capacity (CEC) of NaP1 zeolites synthesized on bench scale.

Sample	S_{BET} (m^2/g)	PSD (µm)			ZP (mV)	CEC (meq/g)
		d_{10}	d_{50}	d_{90}		
Z0	13	1	12	27	-70.9	2.37
Z1	12	1	17	29	-77.5	2.37
Z2	10	2	21	40	-79.2	2.25
Z3	11	4	16	30	-76.2	2.27

Table 6

Chemical composition, pH and conductivity (CE) of the mother liquors (ML) obtained after the synthesis using fresh NaOH solution (MLZ0), first (MLZ1) and second (MLZ2) synthesis with the previously corresponding ML recycling.

Mother liquor	Chemical composition				pH	CE (mS/cm)
	Na (mg/mL)	K (mg/mL)	Si (mg/mL)	Al (µg/mL)		
MLZ0	20.21	0.32	0.98	25	13.6	134
MLZ1	24.33	0.30	0.89	20	13.7	126
MLZ2	24.79	0.31	0.64	25	13.7	127

Table 7

Cost estimation based on the production of one ton of NaP1 by zeolitization process from an Al-containing waste with and without liquid discharge.

Inputs [a]	Developed process with recycling ($€_{2016}$/ton$_{zeolite}$) [b]	Developed process without recycling ($€_{2016}$/ton$_{zeolite}$) [c]	Conventional process without recycling ($€_{2016}$/ton$_{zeolite}$)
Al_2O_3	-	-	2430
Water glass	1329	1367	1367
NaOH 50 wt.%	75	252	252
Fresh H_2O	1	4	4
Total	1405	1624	4054

[a] Chemical reagent prices based on Manuel Riesgo, S.A. Spanish supplier: 9.01 $€_{2016}$ per kg of commercial aluminum source (Al_2O_3) used for the conventional synthesis of NaP1, 158.45 $€_{2016}$ per 125 L of water glass, and 63.50 $€_{2016}$ per 50 kg of NaOH pellets; 0.5486 $€_{2016}$ per m^3 of water (Madrid, Spain).

[b] The consumption of water only involves the fresh water used in the rinsing step of the zeolite Z3.

[c] The consumption of fresh water involves the fresh water fed to the synthesis process and used in the rinsing step of the zeolite Z0.

Figure captions

Fig. 1. SEM image of the Al-containing waste used for the NaP1 synthesis.

Fig. 2. Bench-scale synthesis set up. 1) Reactor and thermal fluid heating and agitation system. 2) Control system of synthesis parameters: temperature, pressure and agitation.

Fig. 3. Scheme of the eco-friendly bench-scale process to obtain NaP1 from an aluminum waste under recycling of mother liquor (ML) and rinse water (RW).

Fig. 4. XRD patterns of NaP1 zeolite obtained with different liquid/solid ratios of the reaction suspension: 7.5 mL/g (R1), 15 mL/g (R2), and 25 mL/g (R3) on lab scale.

Fig. 5. XRD patterns of the NaP1 zeolite synthetized by using fresh NaOH solution (Z0), and with effluent re-used: first, second and third recycling cycle (samples Z1, Z2, and Z3, respectively) on bench scale.

Fig. 6. SEM images at different magnifications of NaP1. Sample Z0 obtained using fresh alkalizing agent (a), and samples Z1, Z2, and Z3 prepared after the first (b), second (c) and third (d) effluent recycling cycle, respectively.

Fig. 7. FTIR spectra of NaP1 synthetized with liquid discharge (Z0) and with effluent recycling (Z1, Z2, and Z3) on bench scale. Wavenumber values shown for Z0.

Fig. 8. TG (- - - dash line) − DTA (— solid line) for NaP1 zeolite obtained via fresh alkalizing agent (Z0), and via the first (Z1), second (Z2) and third (Z3) effluent recycling on bench scale.

Fig. 9. Nitrogen adsorption/desorption isotherms of zeolite NaP1 synthesized with fresh NaOH solution (Z0) and with effluent recycling (Z1, Z2, and Z3) on bench scale.

Fig. 10. Particle size distribution of the synthesized NaP1 zeolites with fresh alkalizing agent (Z0), and with effluent recycling (Z1, Z2, and Z3) on bench scale.
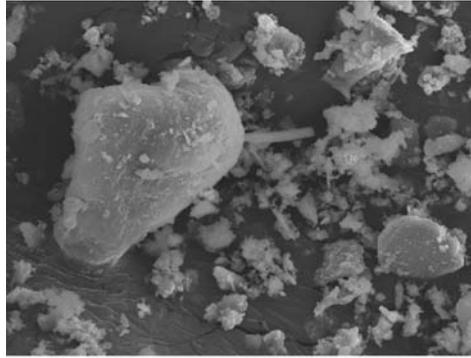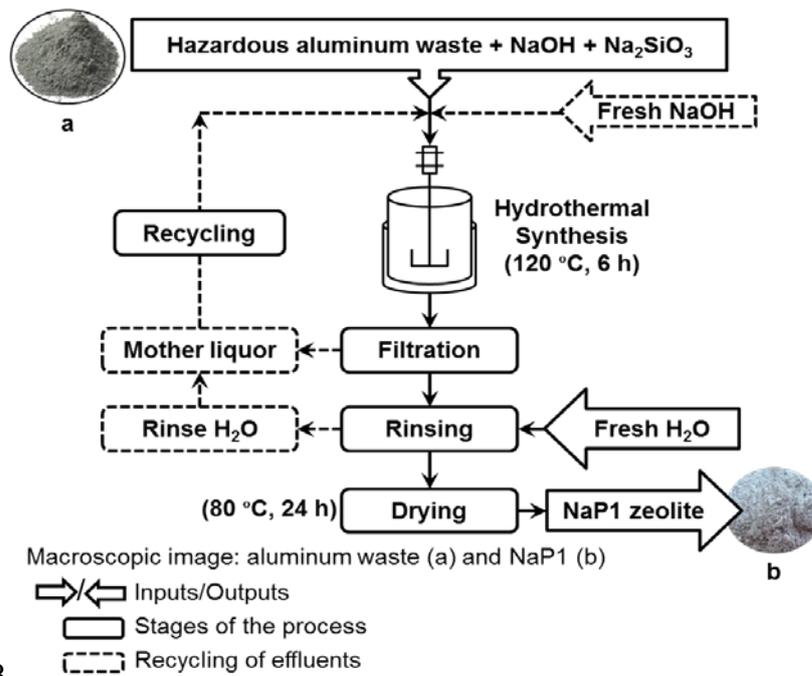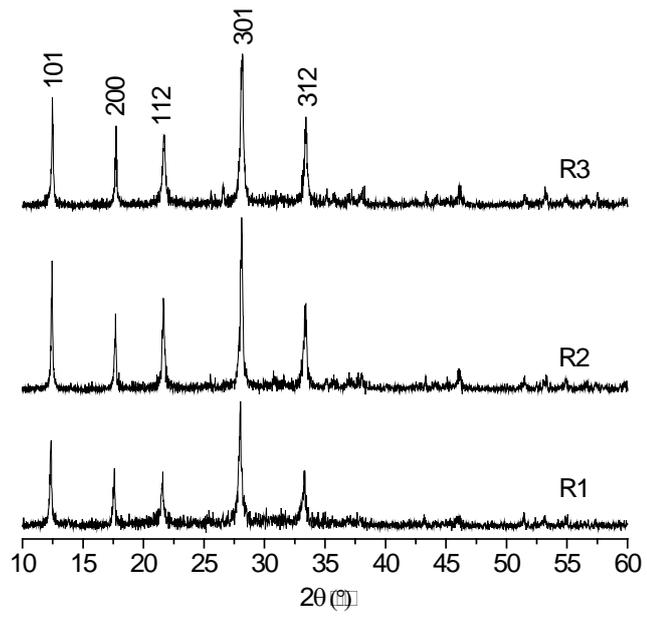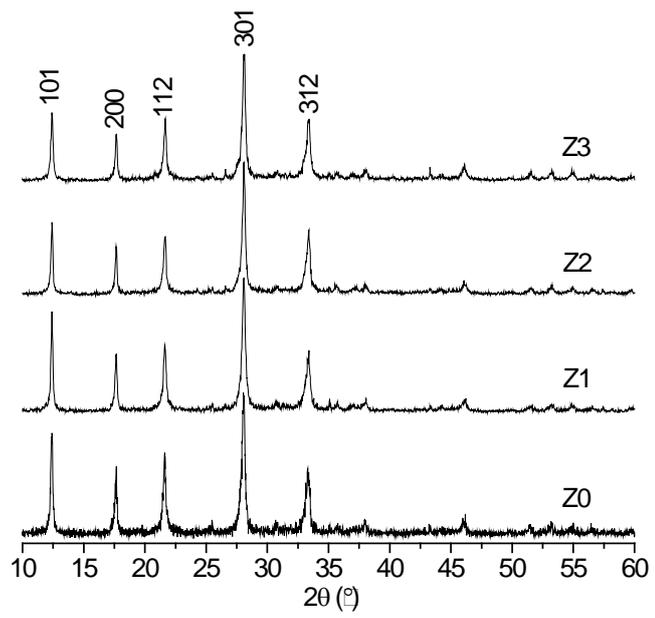
Fig. 1

Fig. 2

Fig. 3

Macroscopic image: aluminum waste (a) and NaP1 (b)

Inputs/Outputs
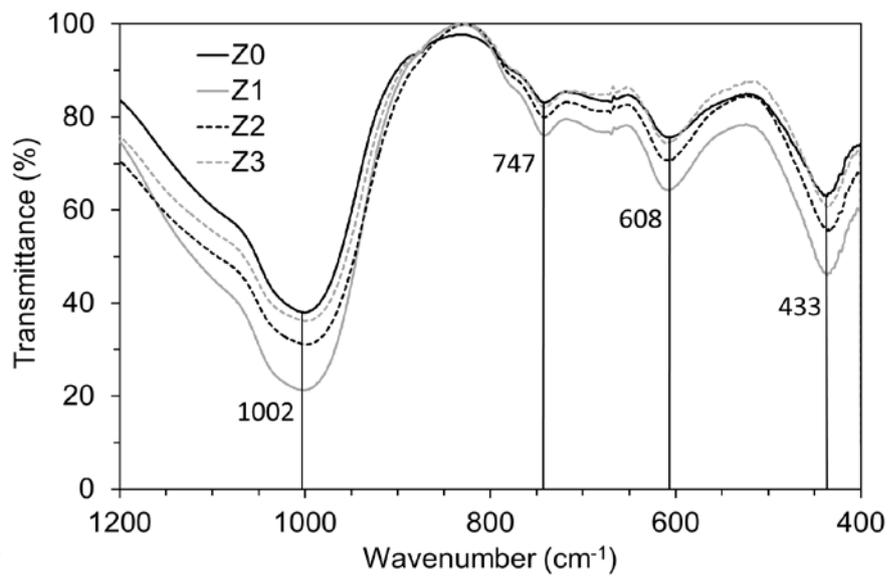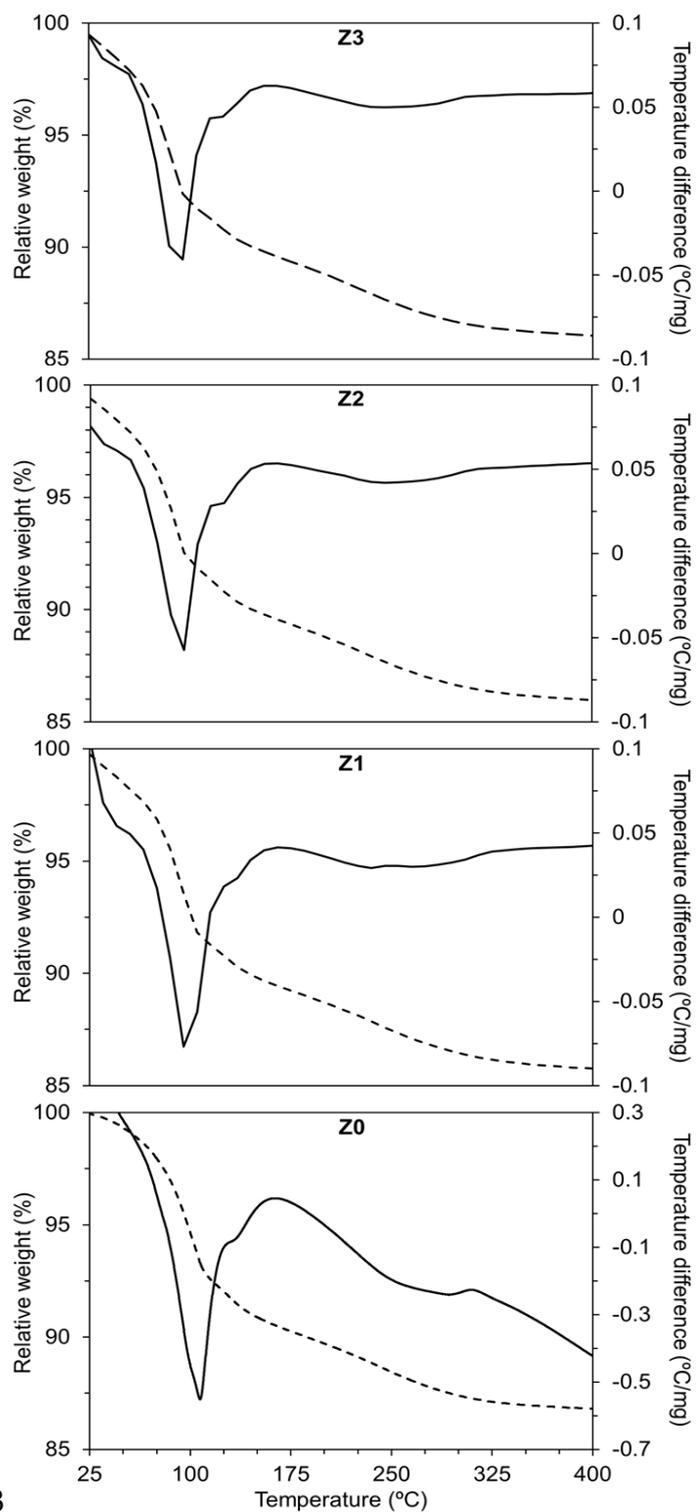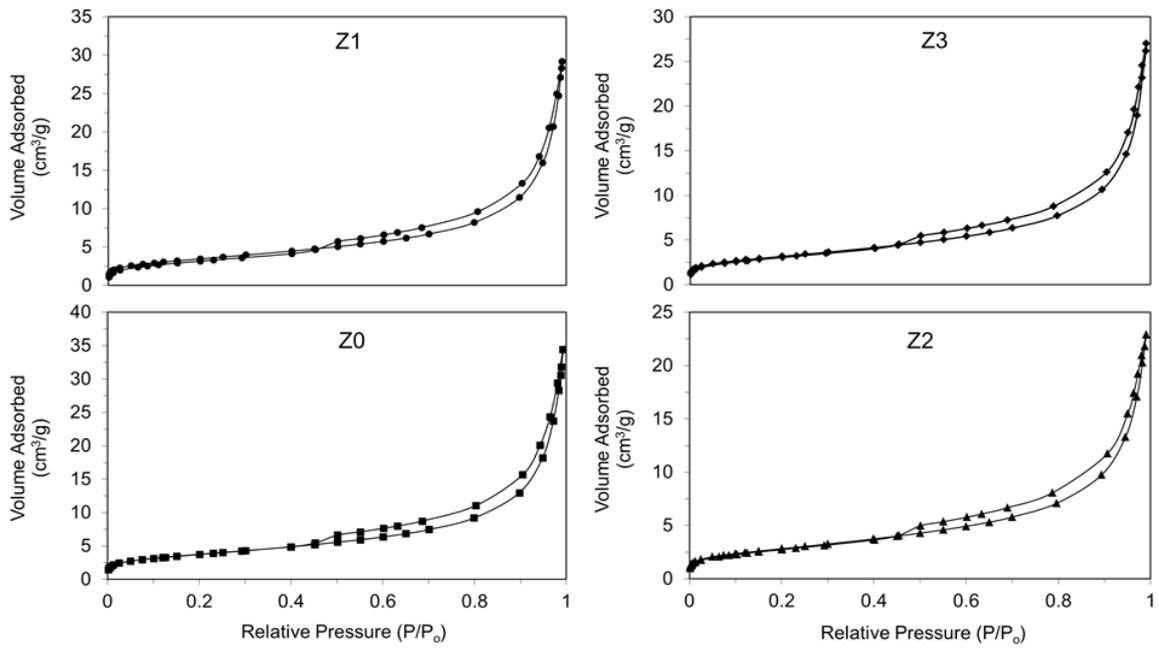Stages of the process
Recycling of effluents

Fig. 4

Fig.5
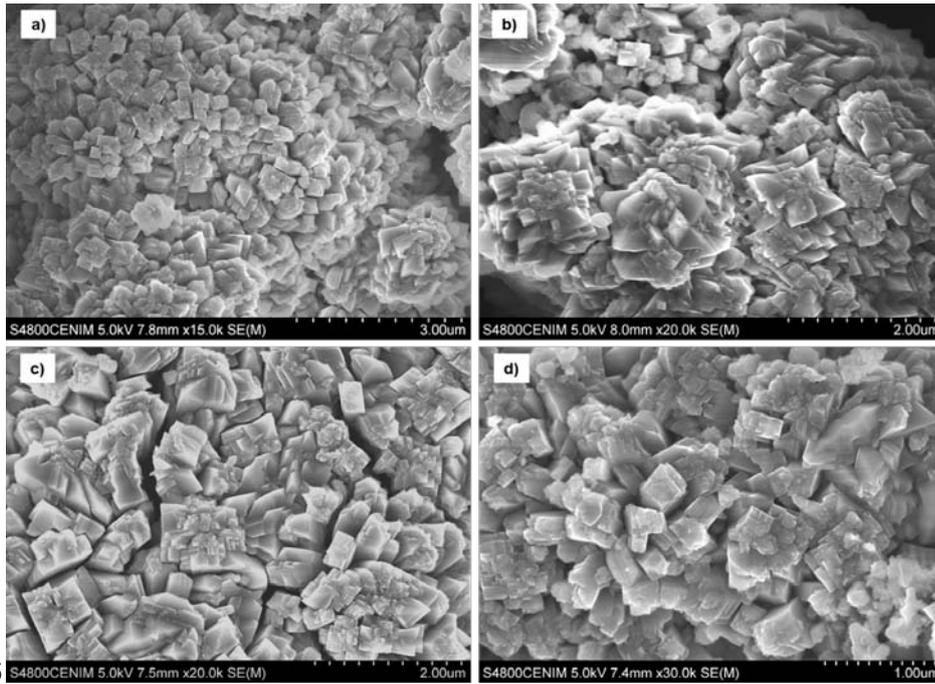
Fig. 6

Fig. 7

Fig. 8

38

Fig. 9

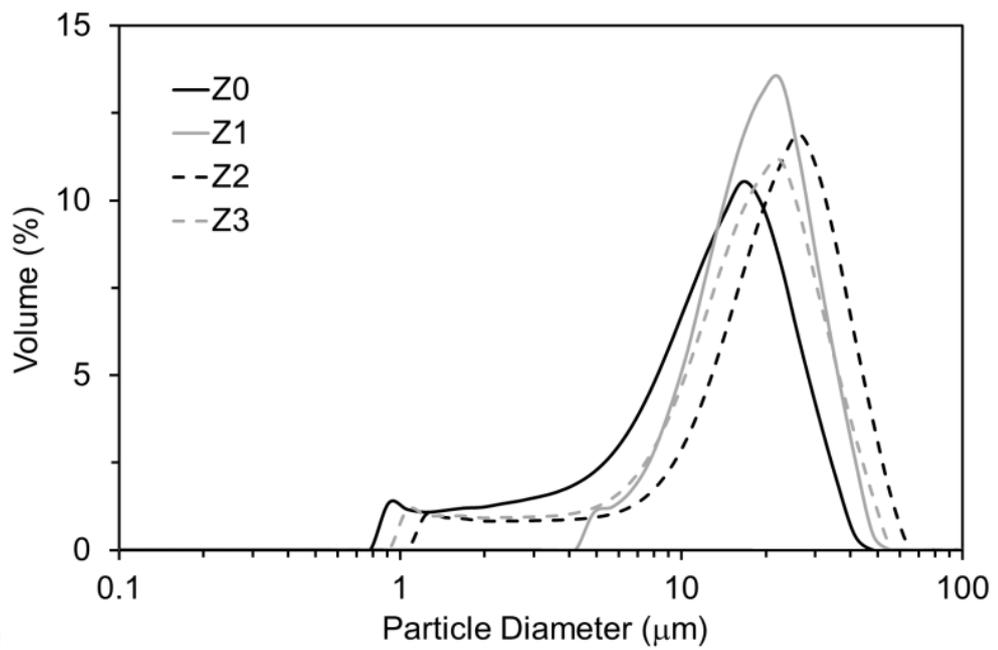
Fig.10

Graphical Abstract

Hazardous aluminum waste + NaOH + Na$_2$SiO$_3$

Fresh NaOH

Recycling

Hydrothermal synthesis

Mother liquor ← Filtration

Rinse H$_2$O ← Rinsing ← Fresh H$_2$O

Drying → NaP1 zeolite

→ / ← Inputs/Outputs
▭ Stages of the process
┅ Recycling of effluents