UNIVERSITAT POLITÈCNICA DE VALÈNCIA

ESCUELA TÉCNICA SUPERIOR INGENIERÍA INDUSTRIAL VALENCIA

CHEMICAL ENGINEERING MASTER THESIS

STUDY OF GEOPOLYMER FILTERS COVERED WITH METAL-ORGANIC FRAMEWORKS, FOR THE RECOVERY OF RARE EARTH METALS IN WASTE STREAMS

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Academic year: 2020-21

ACKNOWLEDGEMENTS

I would like to take this opportunity to thank my LUT tutor Eveliina Repo and my partner Vitalii Kavun for their support. I would also like to thank the rest of my colleagues at the lab who have helped me so much inside and outside the university.

ABSTRACT

In the present project, different ways of synthesizing Metallic-Organic Frameworks (MOF) in ceramic filters manufactured in 3-D printers, and their adsorption capacity for rare earth elements (REE) will be studied.

REE are increasingly used in new technologies, so their recovery is of great importance. However, at present there are very few methods to achieve this goal, so research in this field is of great interest.

In this case, ceramic filters will be synthesized, using different variables, so that an optimal method can be found.

Keywords: Rare earth elements, Metallic-Organic Frameworks, Circular economy.

RESUMEN

En el presente proyecto, se van a estudiar diferentes maneras de síntesis de Metallic-Organic Frameworks (MOF) en filtros cerámicos fabricados en impresoras 3-D, y su capacidad de adsorción para elementos de tierras raras (REE por sus siglas en inglés).

REE son usados cada vez con mayor frecuencia en las nuevas tecnologías, por lo que su recuperación resulta de gran importancia. Sin embargo, hoy en día existen muy pocos métodos para alcanzar dicho fin, por lo que la investigación de este campo es de gran interés.

En este caso, se sintetizarán los filtros cerámicos, usando diferentes variables, de forma que se pueda encontrar un método óptimo.

Palabras Clave: Metales de tierras raras, Metallic-Organic Frameworks, Economía circular.

RESUM

En el present projecte, s'estudiaran diferents maneres de síntesis de Metallic-Organic Frameworks (MOF) en filtres ceràmics fabricats en impressores 3-D, i la seua capacitat d'adsorció per a elements de terres estranyes (REE per les seues sigles en anglès).

REE són usats cada vegada amb major freqüència en les noves tecnologies, per la qual cosa la seua recuperació resulta de gran importància. No obstant això, hui dia existeixen molt pocs mètodes per a aconseguir aquesta fi, per la qual cosa la investigació d'aquest camp és de gran interès.

En aquest cas, se sintetitzaran els filtres ceràmics, usant diferents variables, de manera que es puga trobar un mètode òptim.

Paraules Clau: Metalls de terres estranyes, Metallic-Organic Frameworks, Economia circular.

TABLE OF CONTENTS

CHAPTER 1.REPORT

1. Introduction

1.1. Related Work

The increase in the use of Rare Earth Elements (REEs) in recent years, as well as the ecological transition towards a circular economy, creates the need to recover these metals. Since their use is strongly related to new technologies, research is scarce, therefore the need for research in this field is urgent.

There are several industrial processes that produce waste containing rare elements such as phosphogypsum, bauxite residue, mine tailings, metallurgical slags, coal ash, incinerator ash and waste water streams according to *Binnemans, Koen, et al. (2015)* However, this master thesis focuses on waste water streams, where the most relevant research is as follows:

The research of *Li, Chaoran, et al. (2013)* suggests the use of Flowerlike Nano-$Mg(OH)_2$ to capture EWRs from waste water streams since adsorbents such as zeolites, clay or activated carbon are not effective in very diluted streams. Nanomaterials have a high specific surface area and many active centres, and Flowerlike Nano-$Mg(OH)_2$ has a high extraction capacity. However, the use of this material for uranium (U) recovery was very poor.

Another research was carried out by Ramasamy, *Deepika Lakshmi, et al. (2017)* where the use of modified mesoporous silica for the recovery of rare earth elements is proposed. Silica is a very powerful metal adsorbent with good mechanical stability, a high specific surface area and high thermal resistance. This study concluded that the method used was more effective than physical methods.

Barros, Oscar, et al. (2019) propose biosorption as a method to recover metals from wastewater. The advantages over chemical methods would be low operating costs, reduction of chemicals consumed and decrease of effluent toxicity. The results for supported biomass on zeolite are very similar to those with zeolite.

1.2. Objectives

The objective of this Master Thesis is the synthesis, under different conditions, of Metal-Organic Frameworks (MOFs) for their later use as adsorbent filters in order to recover Rare Earth Elements (REE). For this purpose, the formation of MOFs generated on the surface of geopolymer filters will be studied by varying the reaction time, the chemicals used and the modification of the filter surface.

With this Master Thesis the student will acquire experimental methodology and design capacity, sufficient for the achievement and development of the Master Thesis. Acquiring specific competences such as:

- The ability to carry out individual work that must be defended before a university tribunal, consisting of a project in the field of specific technology in Industrial Chemistry in which the competencies acquired are synthesized and integrated into the teaching.

- Manage the information coming from different sources and, if necessary, the computer tools for searching and classifying bibliographic resources or mono- or multimedia information.

- Analyzing and solving problems effectively, identifying and defining the significant elements that constitute them.

- Ability to design, synthesize, characterize and use nanoscopic, metallic and ceramic materials in various industrial applications and biomaterials in biomedical applications.

- To adapt to structural changes in society caused by factors or phenomena of an economic, energy or natural nature, in order to solve the derived problems and provide technological solutions with a high commitment to sustainability.

1.3. Document Structure

This Master Thesis is divided into three chapters: Report, Budget and Appendix.

In the report, it begins with a brief introduction to REEs and MOFs, as well as lists different methods for REE recovery in wastewater streams. The chapter continues by detailing the experimental methodology used for the trials of this research and ends with its results and conclusions.

In the chapter Budget the investment required to carry out this Master Thesis is shown. To obtain it, it is necessary to recognize all the materials, machinery and reagents that have been used in this project.

Finally, in the appendix, the results obtained in the experiment's BET attachment test are shown.

1.4. Rare Earth Materials

Rare-earth elements or rare-earth metals (REM) are defined as the fifteen lanthanides and the scandium (Sc) and yttrium (Y) due their similar chemical properties with the lanthanides and they are found on the same ore deposits as well. Those properties are based on the electronic configuration, offering a particulary stable 3+ oxidation state.

REE are divided in two groups: light rare earth elements (LREEs) and heavy rare earth elements (HREEs), although The International Union of Pure and Applied Chemistry (IUPAC) consider the REE from lanthanum (La) to gadolinium (Gd), including Sc, as LREE, and the elements from terbium (Tb) to lutetium (Lu), including Y, as HREE; Gd is usually considered as HREE by the common convention in industry. As there is not consensus in the division between LREE and HREE, in this work REE will be divided in three groups: LREE, HREE and intermediate REE.

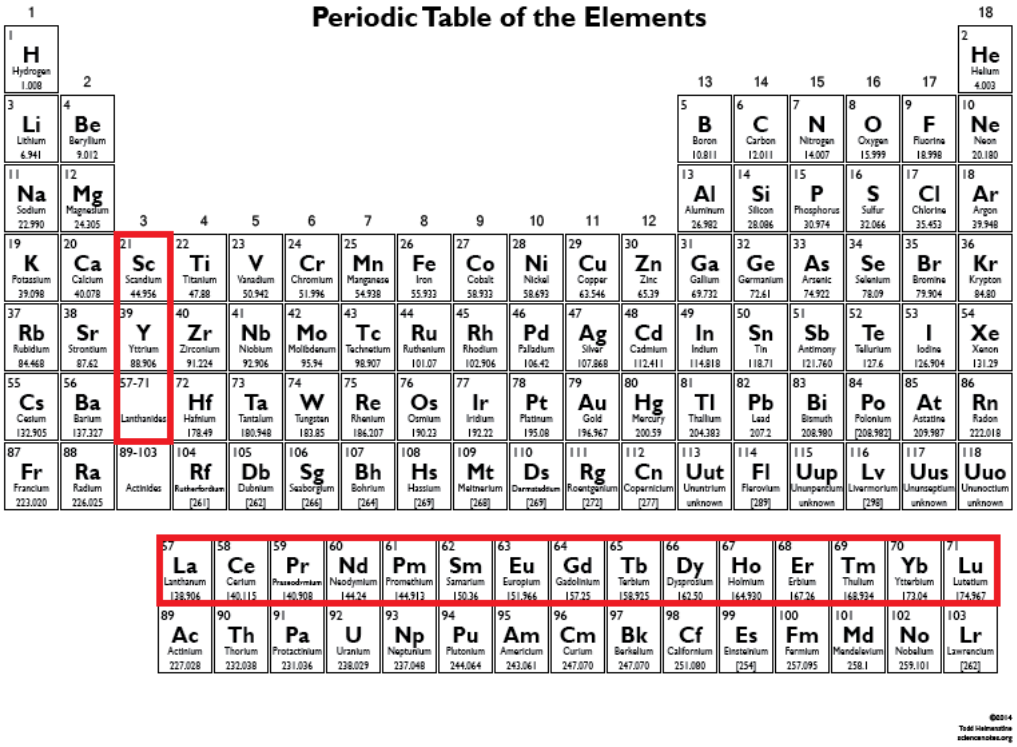

Fig. 1. Periodic Table, in which REE are pointed out with red.

Currently, the development of new technologies, especially in the environmental field, has generated an increase in the use of these metals since they are indispensable for almost all electric vehicles, as well as for renewable energy generators.

However, there are problems around the REE: On the one hand, the geopolitical problem derived from the low dispersion of metals around the world: China is the largest producer of SREs in the world, about 61% of the rare earth metals extracted from the earth's crust come from the Asian country.

On the other hand, the extraction of SEE has adverse effects on the environment: Since they are not pure metals and are not found in high concentrations in rocks, they are difficult to separate. Aggressive

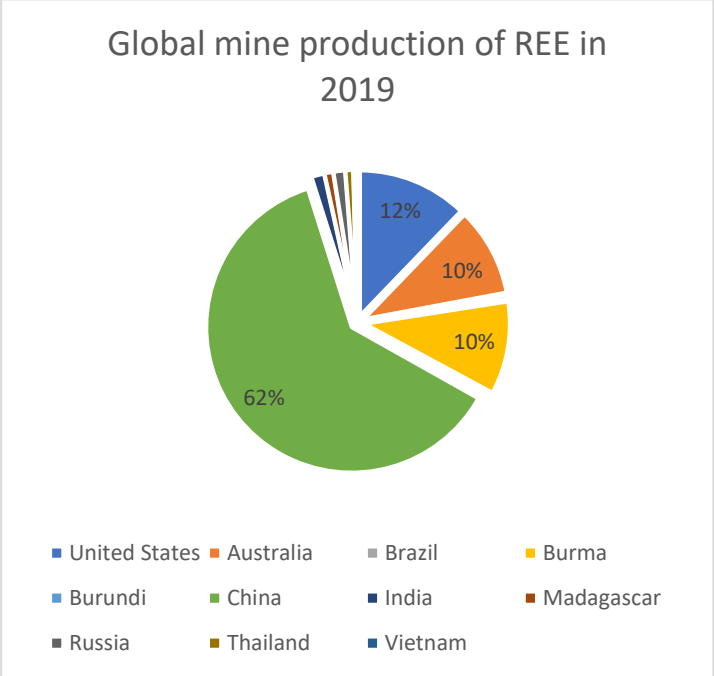

Fig. 2. Global mine production of REE in 2019.

Source: U.S. Geological Survey, Mineral Commodity Summaries, January 2020.

processes are needed to obtain them, such as extraction by organic solvents, magnetic separation or at high temperatures, around 1000 degrees. Some of the processes use acids for their separation and the high temperature combustion emits CO_2: in short, a very dirty process. In addition, rare earths usually have a radioactive element, thorium, as an impurity. They are not high concentrations it is not known how it can affect the environment and people who are close.

1.5. Metal-Organic Frameworks

Metal-organic frameworks are porous polymeric materials and are characterized by being formed by metal ions linked by organic molecules, ditopic or polytopic organic carboxylates, which act as bridges. This union forms two- or three-dimensional structures.

It is usually used in adsorption processes in extraction processes, although there are other applications: heterogeneous catalysis and gas storage. This is due to its high porosity and the ability to modify the size of these pores without changing the structure, due to the organic bonds. In addition, the pore size is not very diverse, so it provides selectivity in the process. In addition, MOFs are thermally and chemically stable. However, current uses of MOFs are not currently industrial.

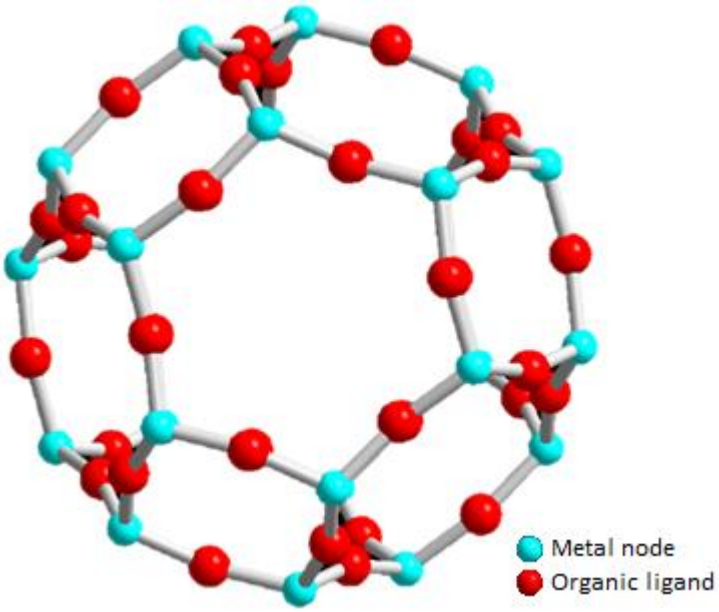

Fig. 3. Schematic illustration of a metal-organic framework (MOF)

2. Experimental Section

The synthesis process carried out on the designed filters is divided into two different steps: Surface modification and the synthesis of MOFs.

Before the surface modification, some samples were cut into four equal parts with a saw, but this experiment was carried out with both the cut filters and the entire filters.

2.1. Materials

-Geopolymers

-toluene (≥99.5%, VMR)

-(3-Aminopropyl)triethoxysilane (APTES, ≥98%, Sigma-Aldrich)

-terephthaloyl chloride (≥99%, Sigma-Aldrich)

-N_2

-aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, 99.9%, COMPANY)

-benzene-1,3,5-tricarboxylic acid (Trimesic acid, 98%, ACROS Organics)

-terephthalic acid (Benzene-1,4-dicarboxylic acid, H_2BDC, 98%, Sigma-Aldrich)

-ultra-pure deionized water (DI, 15 MΩ) was obtained from a CENTRA-R 60/120 system (Elga purification system, Veolia Water, Bucks, UK).

All chemicals were used as-received without further purification.

2.2. Silanization of the ceramic surface

The surface of a group of samples was initially modified in round bottom flasks, with 90 mL of toluene and 5 mL of aminopropyl triethoxylane (APTES), under a nitrogen atmosphere. Heated at 110 °C for 2 h under stirring. After that, the samples were washed with toluene for 40 min and dried at 90 °C overnight.

Half of the samples were saved for later characterization, being modified with amine groups on their surface.

The rest of the filters were modified again, in order to get a carboxyl group modification in their surface, in a round bottom flask, with 250 mg of terephthaloyl chloride dissolved in 60 mL of toluene and 350 µL of APTES, at 70 °C under stirring for 12 h. After cooling the samples to room temperature, the samples were washed with pure water and dried at 90 °C overnight.

2.3. MOF Crystallization

The synthesis was carried out using two different acids: benzene-1,4-dicarboxyl acid (H2BDC) and (Trimesic acid) Benzene-1,3,5-tricarboxylic acid. All of them, using all different species: without surface modification, amine group modification and carboxyl group modification; entire filters and cut filters.

For the synthesis of MOFs on the surface of the samples, PTFE autoclaves were used, the tests were carried out adding 0.36 g of acid to 25 mL of water and heated at 220 ℃ during a specific time. This paper studies the influence of the reaction time on the formation of MOFs, those different times were 6 h, 12 h, 16 h and 28 h. After cooled down to room temperature, the filters were washed with water.

To finish the synthesis, 0.82 g of Al $(NO_3)_3$, 0.18 g of acid was added to 25 mL of water and heated at 220 °C during the same time used in the previous step. After the reaction, they were washed with water and dried at 90 °C overnight. Some samples were synthesized two times, so the last two steps were repeated.

The synthesis was also modified using a bigger autoclave, but entire filters were only used with this different parameter, using the same concentration of acid and Al $(NO_3)_3$ in 50 mL of water, in this way, 0.72 g of acid were added to 50 mL of water and heated at 220 ºC for 12 h. After cooled down to room temperature, the filters were washed with water. Then, 1.64 g of Al $(NO_3)_3$ and 0.36 g of acid was added to 50 mL of water and heated at 220 °C for 12 h. After the reaction, they were washed with water and dried at 90 °C overnight.

3. Characterization

The surface of the filters after their modification was carried out using SEM, BET surface area and pore analysis, as well as the adsorption capacity via ICP. In this way, the morphology of the created MOFs, as well as their properties, could be observed.

3.1. SEM

Using the scanning electron microscope (SEM), the formation of MOFs on the surface of the geopolymers could be observed, helping to determine which MOFs synthesis methods were the most appropriate. The modified filters that were analyzed with SEM are shown in Table 1

Table 1. List of geopolymers analyzed with SEM. Where TPA is benzene-1,4-dicarboxyl acid and Trimesic acid is Benzene-1,3,5-tricarboxylic acid

Fig	Chemical	Size	Surf. Modif.	AC Volume (mL)	React. Time (h)	cicles
1	TPA	entire	NO	25	12	1
2	(2/3) TPA	entire	NO	25	12	1
3	TPA	entire	NO	25	12	2
4	TPA	entire	NO	25	16	1
5	TPA	entire	NO	50	12	1
6	TPA	cut (1/4)	NO	25	12	1
7	TPA	entire	NH	25	28	1
8	TPA	cut (1/4)	NH	25	12	1
9	TPA	cut (1/4)	COOCl	25	12	1
10	Trimesic ac.	entire	NO	25	12	1
11	Trimesic ac.	entire	NO	25	12	2
12	Trimesic ac.	entire	NO	25	16	1
13	Trimesic ac.	entire	NO	50	12	1
14	Trimesic ac.	cut (1/4)	NO	25	12	1
15	Trimesic ac.	entire	NH	25	12	1
16	Trimesic ac.	entire	NH	25	12	2
17	Trimesic ac.	entire	NH	25	28	1
18	Trimesic ac.	entire	NH	50	12	1
19	Trimesic ac.	cut (1/4)	NH	25	12	1
20	Trimesic ac.	entire	COOCl	25	12	1
21	Trimesic ac.	cut (1/4)	COOCl	25	12	1

The images offered by SEM are shown below. In them, the differences in the surfaces of the different filters can be observed after the synthesis of MOFs using different variables. Normal synthesis conditions are understood when the reaction time is 12 hours in a 25 mL autoclave.

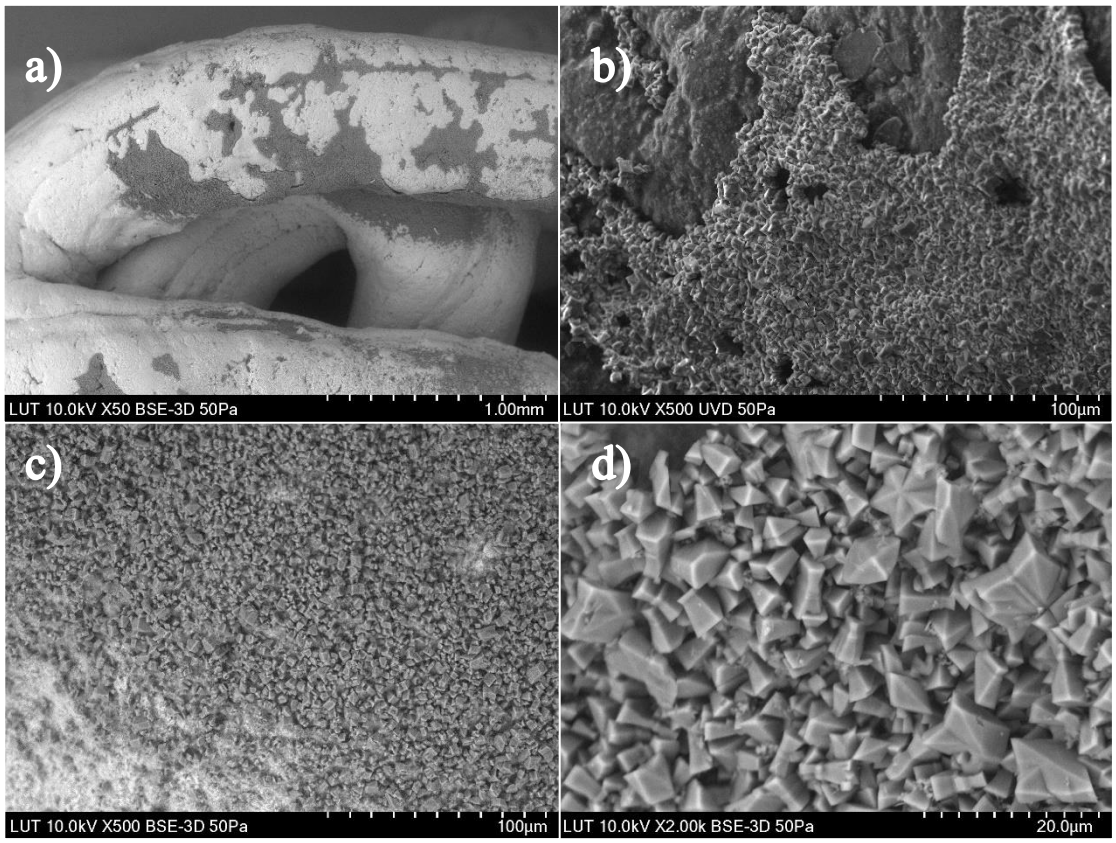

Fig. 4. Microstructure of MIL-96 crystallized on geopolymer entire filters synthesized with benzene-1,4-dicarboxyl acid without previous surface modification in a 25 mL autoclave volume during 12 h of reaction and one cycle. Amplification x50 (a), x500 (b) and (c), and x2000 (d).

Even though in Fig. 1 certain MOFs formed on the filter surface are observed, it is also possible to appreciate the poor distribution of them on the latter. Another data that the SEM images offer us about the result of the synthesis on this filter is the irregularity of the MOFs formed, which, despite having a certain geometric shape, are very irregular and with little similarity between them.

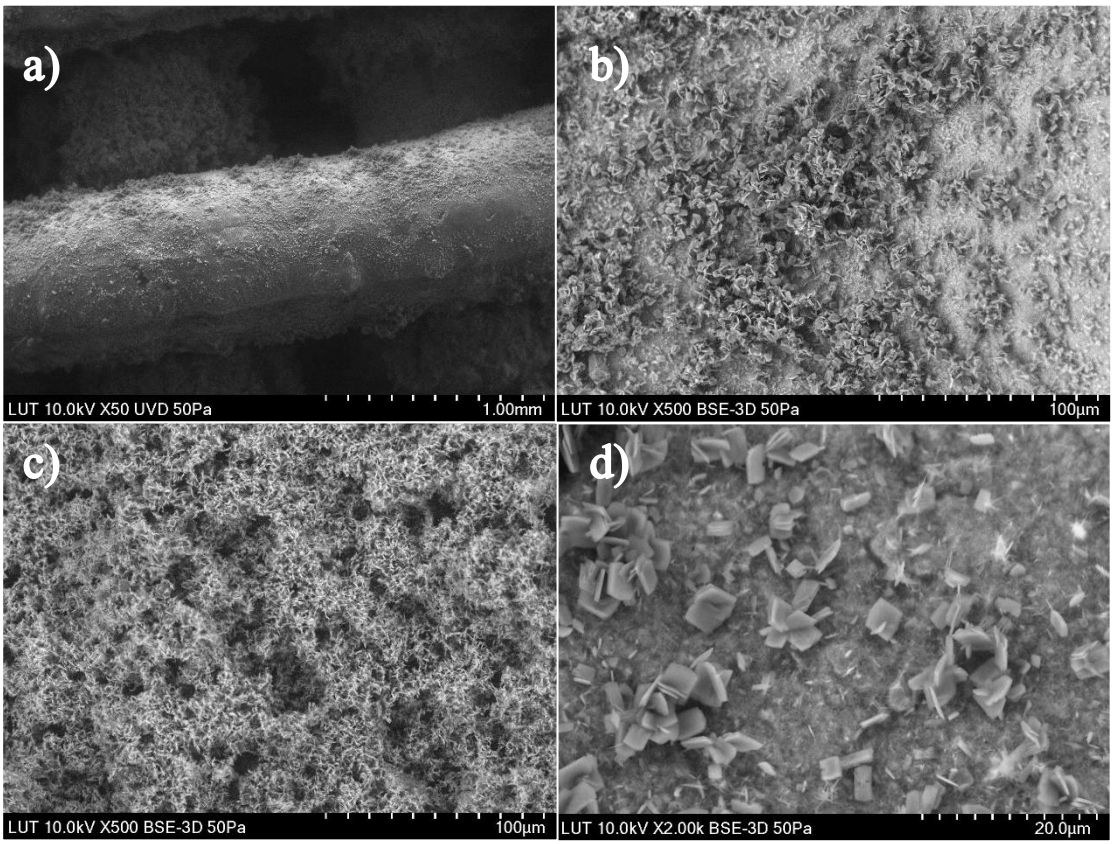

Fig. 5. Microstructure of MIL-96 crystallized on geopolymer entire filters synthesized with benzene-1,4-dicarboxyl acid in a proportion of 3/2, without previous surface modification in a 25 mL autoclave volume during 12 h of reaction and one cycle. Amplification x50 (a), x500 (b) and (c), and x2000 (d).

As can be seen, hardly any MOFs have been formed, instead, the surface has been covered with precipitated aluminum needles. Therefore, it is concluded that modifying the proportion of Terephthalic acid proportionally as a function of its functional groups, not only has a positive effect, but also considerably worsens the formation of MOFs. Therefore, this method is ruled out.

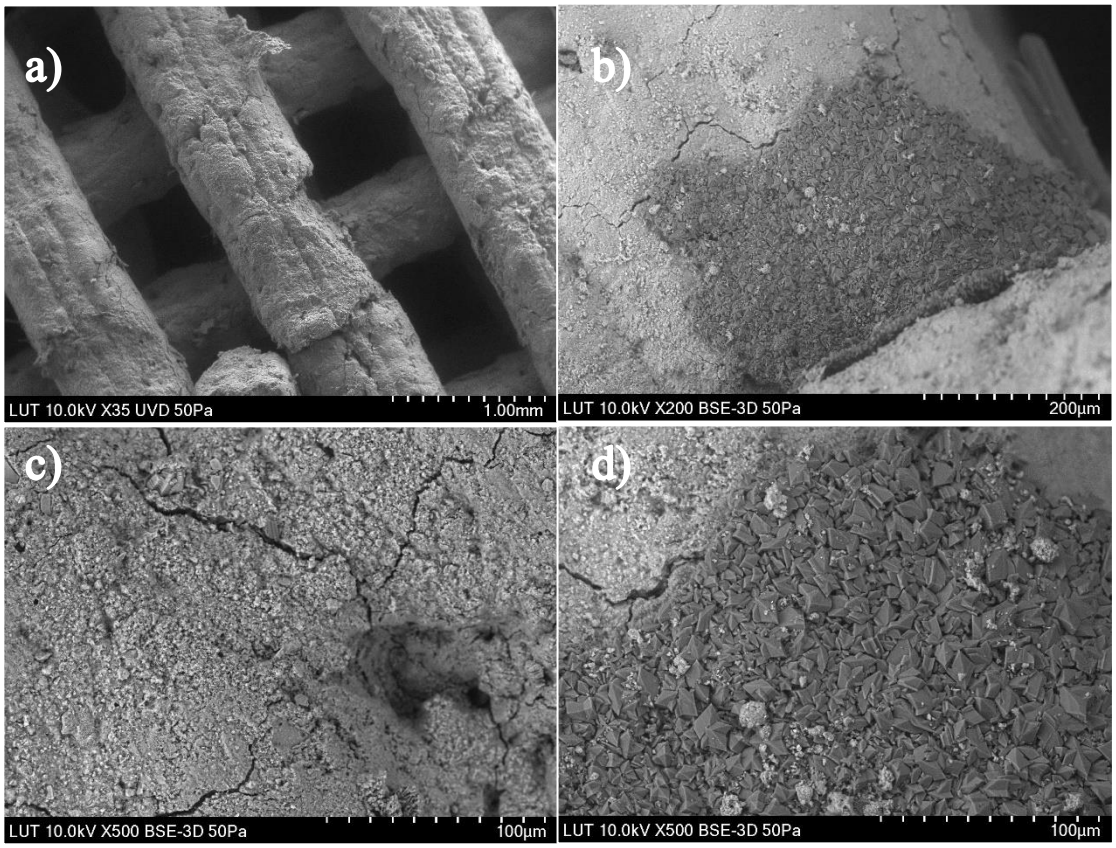

Fig. 6. Microstructure of MIL-96 crystallized on geopolymer entire filters synthesized with benzene-1,4-dicarboxyl acid without previous surface modification in a 25 mL autoclave volume during 12 h of reaction and two cycles. Amplification x50 (a), x200 (b) and (c), and x500 (d).

When performing a second reaction cycle for in normal synthesis conditions with benzene-1,4-dicarboxyl acid and without surface modification, the results are not very promising: although new MOFs are formed, the size and shape of these vary enormously. Furthermore, the mechanical properties of the geopolymer is completely compromised, it becomes extremely brittle, the surface fractures, losing much of the MOFs created by breaking.

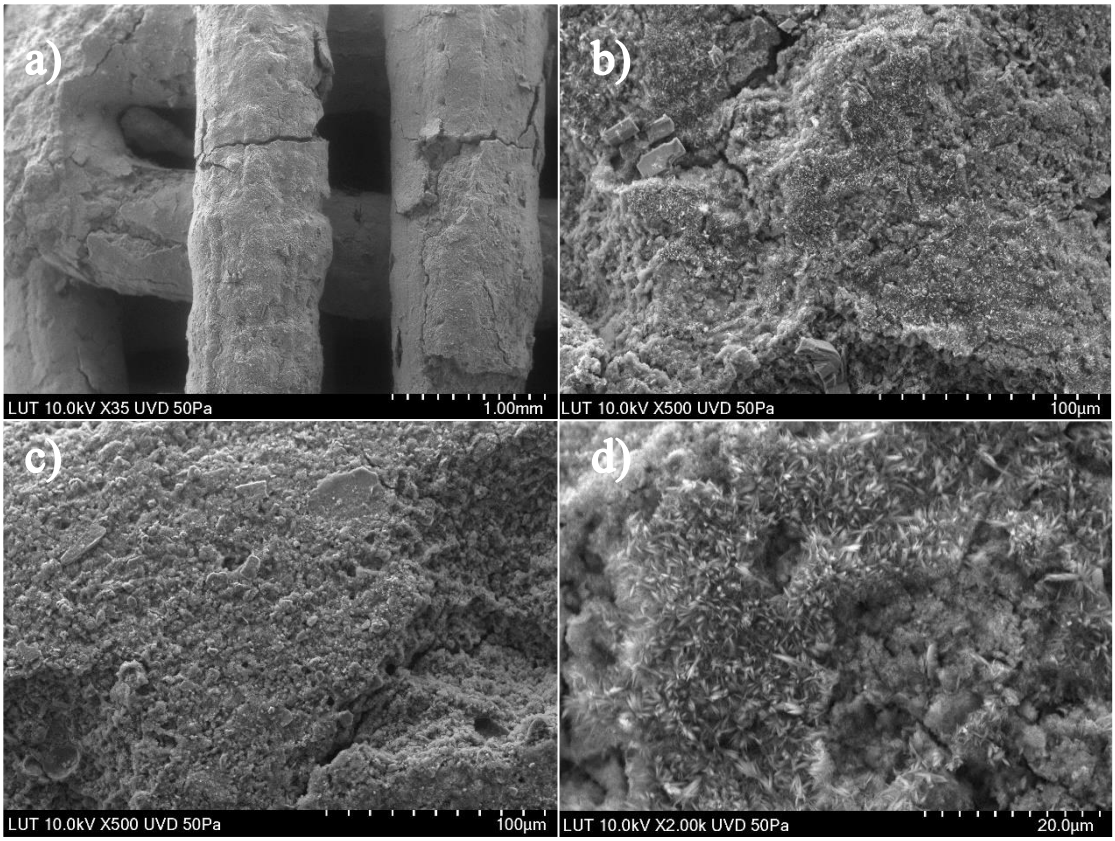

Fig. 7. Microstructure of MIL-96 crystallized on geopolymer entire filters synthesized with benzene-1,4-dicarboxyl acid without previous surface modification in a 25 mL autoclave volume during 16 h of reaction and one cycle. Amplification x35 (a), x500 (b) and (c), and x2000 (d).

In the case of a 16-hour reaction with Terephthalic acid and without surface modification, the formation of strange needle-shaped crystals, possibly aluminum precipitated from the solution, is observed. No MOFs are found. In addition, cracks are seen in the filter.

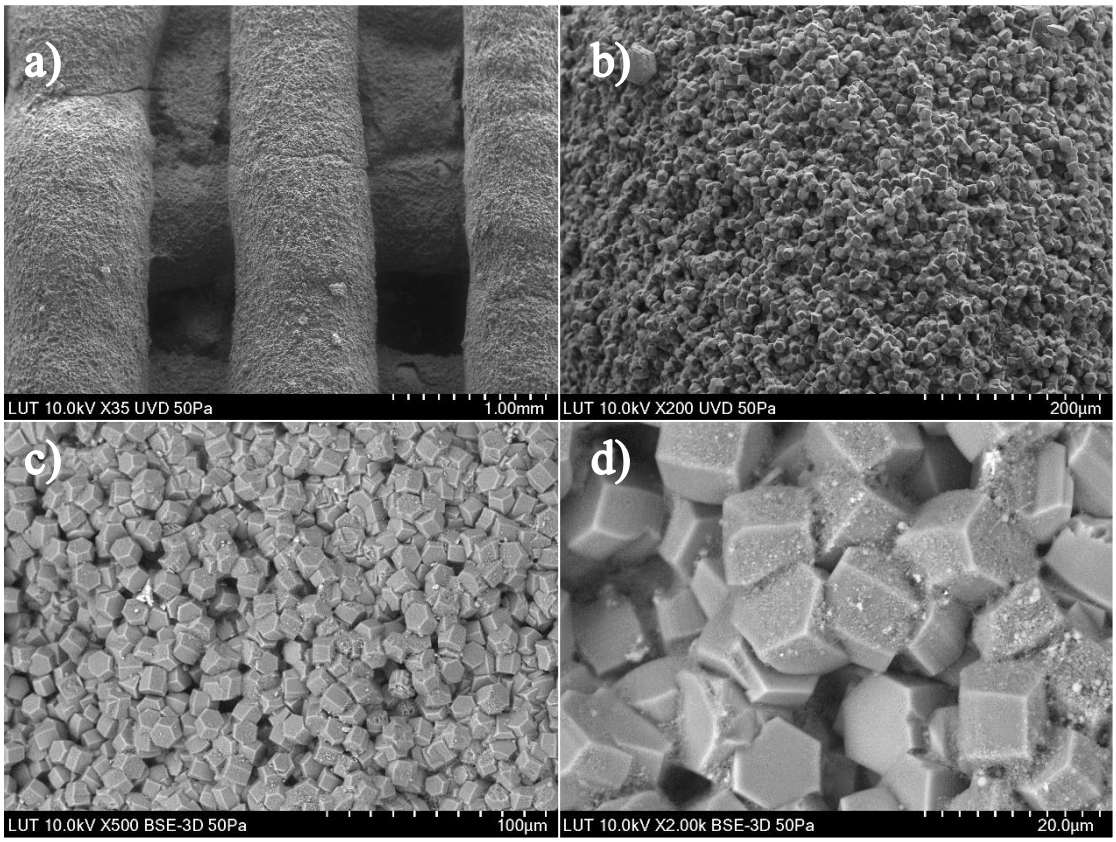

Fig. 8. Microstructure of MIL-96 crystallized on geopolymer entire filters synthesized with benzene-1,4-dicarboxyl acid without previous surface modification in a 50 mL autoclave volume during 12 h of reaction and one cycle. Amplification x35 (a), x200 (b), x500 (c), and x2000 (d).

In a reaction with a double-size autoclave, maintaining the concentration of the solutions during the reaction of formation of MOFs, the formation of said MOFs is observed for the first time homogeneously throughout the surface of the geopolymer. In addition, they have a hexagonal shape and an ideal size.

This is the only case in which Terephthalic acid has been used in which the results have been as expected during visual characterization via SEM. Later, other characteristics will be studied, especially the adsorption capacity of REE.

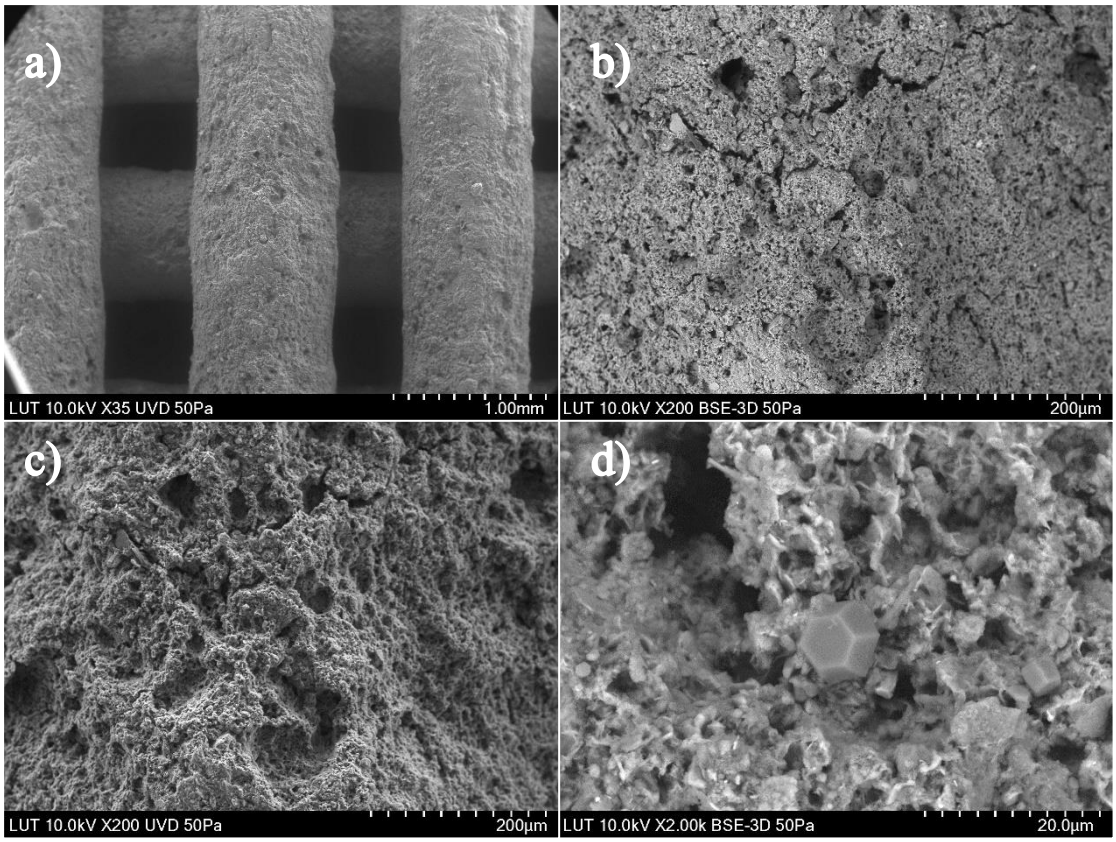

Fig. 9. Microstructure of MIL-96 crystallized on cut (1/4) geopolymer filters synthesized with benzene-1,4-dicarboxyl acid without previous surface modification in a 25 mL autoclave volume during 12 h of reaction and one cycle. Amplification x35 (a), x200 (b) and (c), and x2000 (d).

In the case of synthesis under normal conditions but using a filter chart, some scattered MOFs, of different sizes although in a 3D hexagonal shape, are observed again. As in the other cases where Terephthalic acid has been used in filters without surface modification, it cannot be considered a good result.

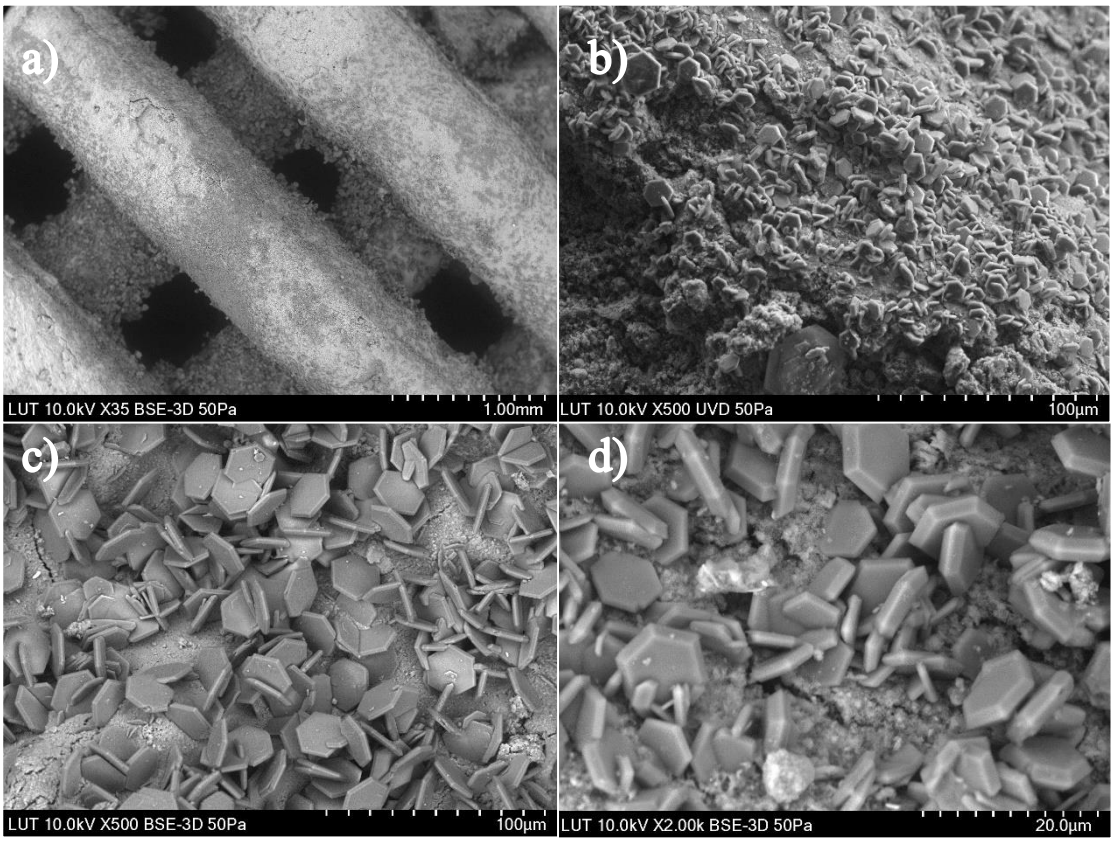

Fig. 10. Microstructure of MIL-96 crystallized on geopolymer entire filters synthesized with benzene-1,4-dicarboxyl acid with previous amine groups surface modification in a 25 mL autoclave volume during 28 h of reaction and one cycle. Amplification x50 (a), x500 (b) and (c), and x2000 (d).

Using a geopolymer with previous modification of the surface with amine groups, several tests were carried out, in this case the reaction time used was 28 hours.

Very flat hexagonal MOFs of similar size are observed; however, it does not homogeneously cover the filter surface.

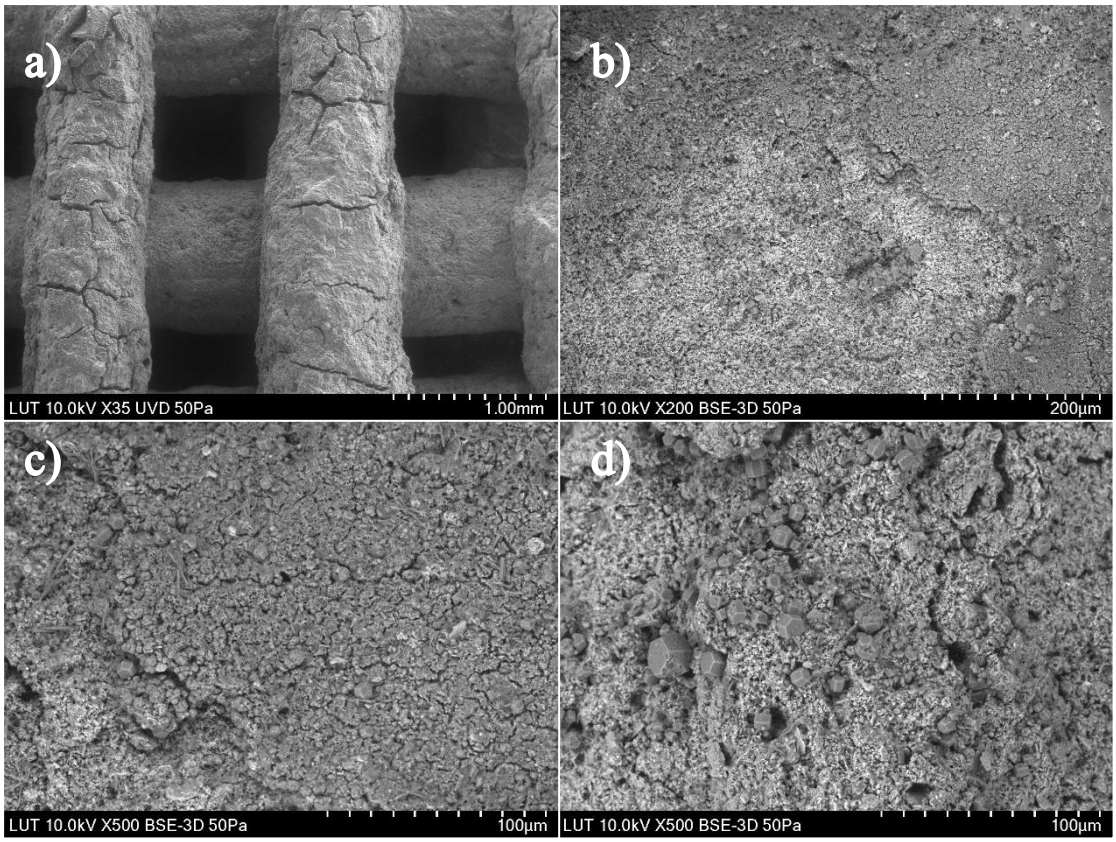

Fig. 11. Microstructure of MIL-96 crystallized on cut (1/4) geopolymer filters synthesized with benzene-1,4-dicarboxyl acid with previous amine groups surface modification in a 25 mL autoclave volume during 12 h of reaction and one cycle. Amplification x35 (a), x200 (b) and x500 (c) and (d).

The reaction was carried out under normal conditions using a quarter of a geopolymer filter with previous modification of the surface with amine groups.

In this case the result is far from expected, since the surface of the geopolymer is damaged, the MOFs created partially cover the surface and foreign bodies of amorphous shapes are observed on the surface.

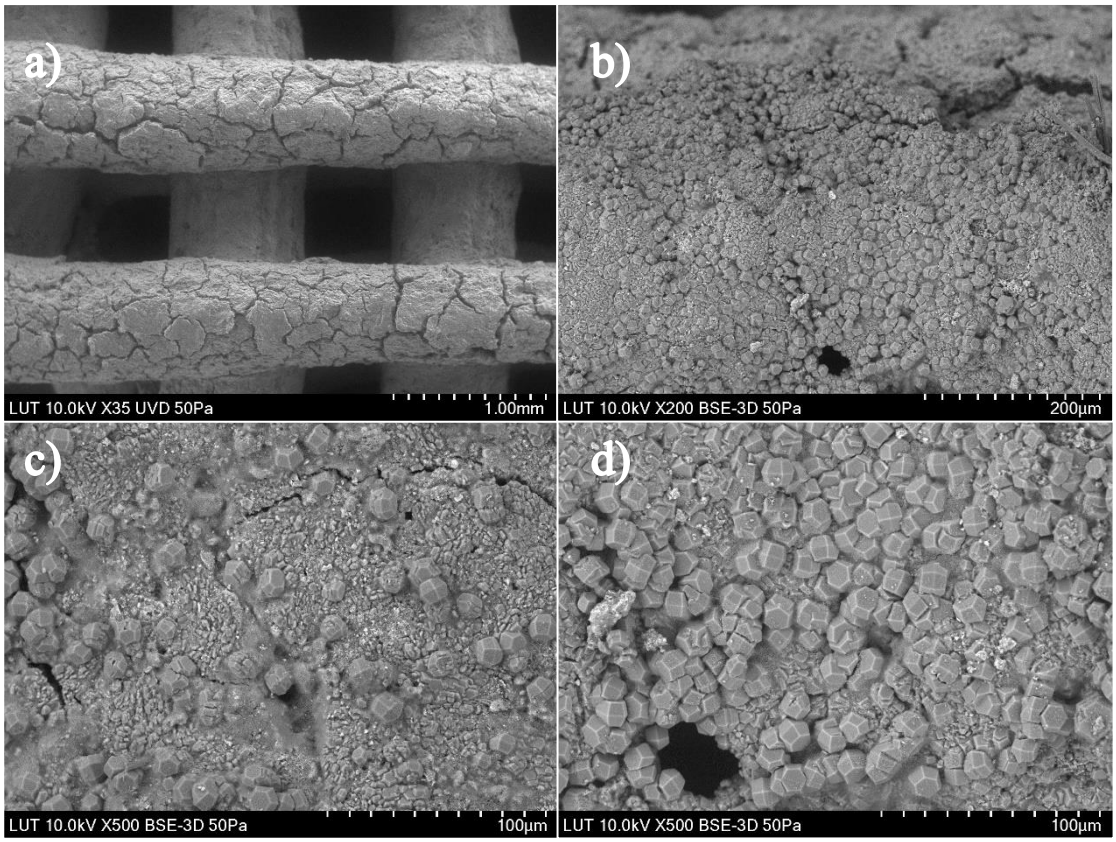

Fig. 12. Microstructure of MIL-96 crystallized on cut (1/4) geopolymer filters synthesized with benzene-1,4-dicarboxyl acid with previous carboxyl groups surface modification in a 25 mL autoclave volume during 12 h of reaction and one cycle. Amplification x35 (a), x200 (b) and x500 (c) and (d).

The reaction was carried out under normal conditions with previous modification of the surface with carboxy groups. Despite the formation of MOFs of similar size and hexagonal shape, the surface of the geopolymer is not homogeneously covered as might be expected, therefore. Furthermore, the filter surface has been severely damaged, and cracks are observed.

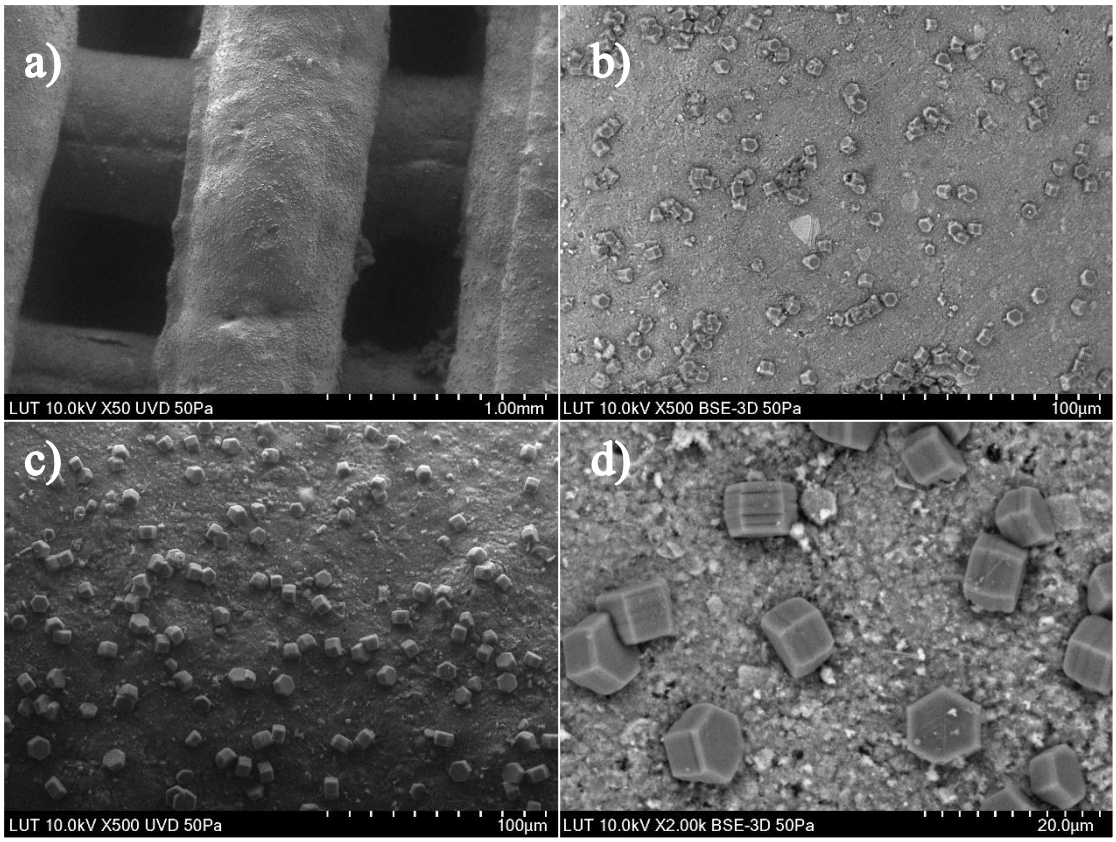

Fig. 13. Microstructure of MIL-96 crystallized on entire geopolymer filters synthetized with Benzene-1,3,5-tricarboxylic acid without previous surface modification in a 25 mL autoclave volume during 12 h of reaction and one cycle. Amplification x35 (a), x500 (b) and (c), and x2000 (d).

The following experiments have been performed using Trimesic acid instead of Terephthalic acid. In general, they offer better results, however, the reactions must be carried out with very specific variables.

In this case, the reaction was carried out under normal conditions and without modification of the surface. Cylindrical hexagonal MOFs with a homogeneous dispersion are observed, but hardly covering the surface. Layers are also observed in the same MOFs, as if they had formed as plates on top of each other.

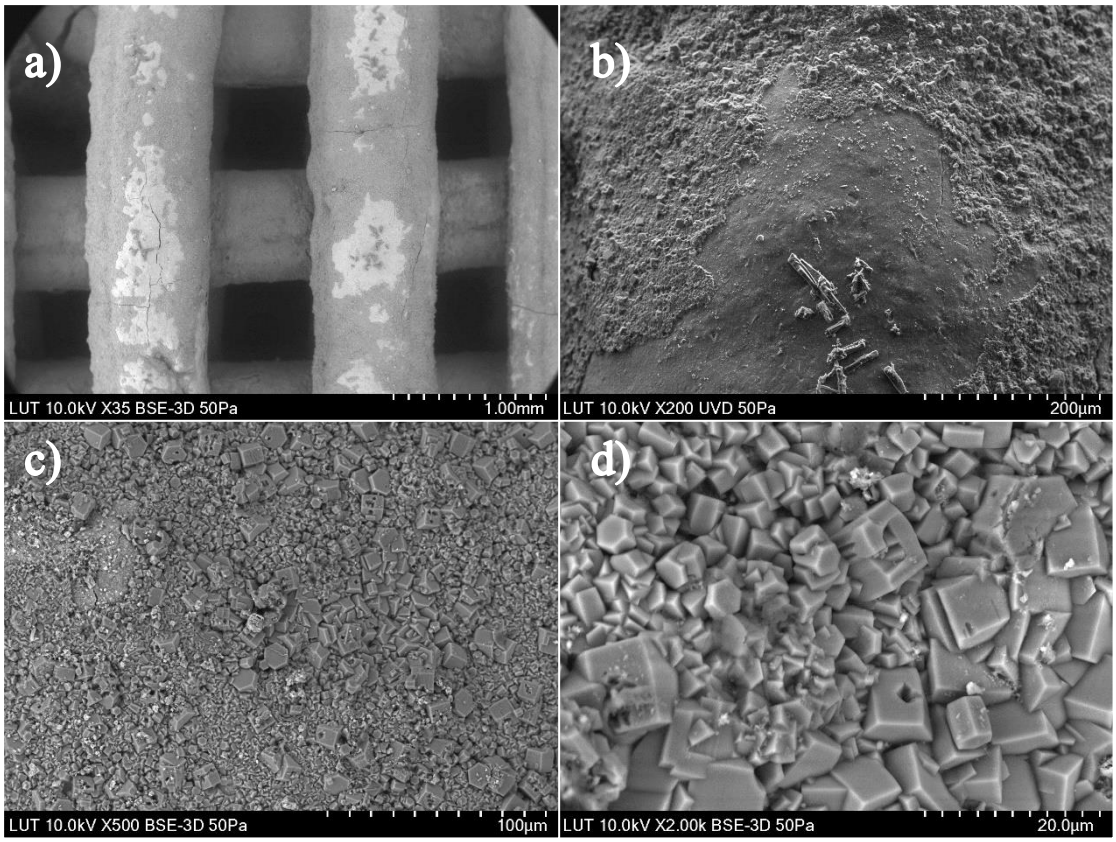

Fig. 14. Microstructure of MIL-96 crystallized on entire geopolymer filters synthesized with Benzene-1,3,5-tricarboxylic acid without previous surface modification in a 25 mL autoclave volume during 12 h of reaction and two cycles. Amplification x35 (a), x200 (b) and (c), and x2000 (d).

Under normal conditions, but repeating the reaction in a second cycle, it is possible to solve the problem of covering in much of the geopolymer, however, it is achieved at the expense of the other properties: the shape and size of the MOFs is very uneven and the mechanical properties of the filter are greatly diminished, making it easy to break, and consequently, MOFs are lost when the surface to which they were attached is lost.

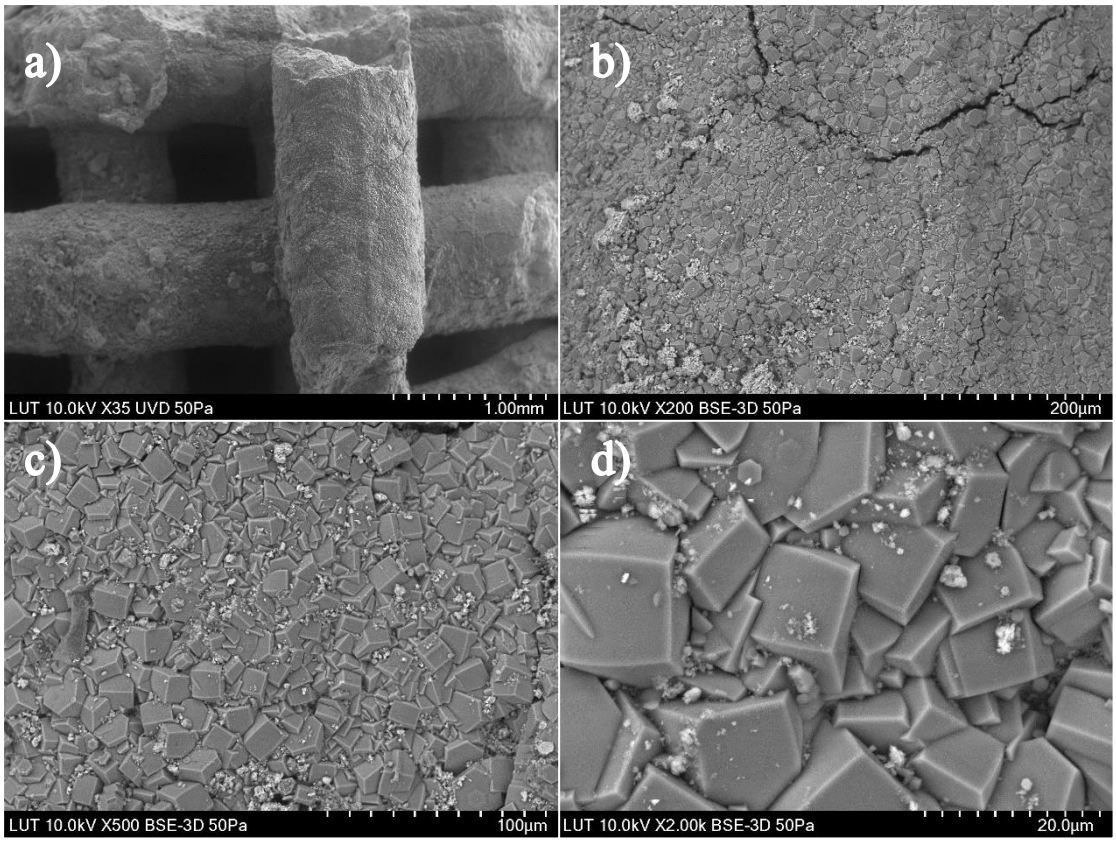

Fig. 15. Microstructure of MIL-96 crystallized on entire geopolymer filters synthesized with Benzene-1,3,5-tricarboxylic acid without previous surface modification in a 25 mL autoclave volume during 16 h of reaction and one cycle. Amplification x35 (a), x200 (b), x500 (c), and x2000 (d).

With the reaction time increased to 16 hours using Trimesic Acid, crystals of different size and shape are generated. The distribution and coverage is good, however the geopolymer has not supported the reaction and has become more brittle. It breaks very easily, losing the MOFs formed when the surface breaks.

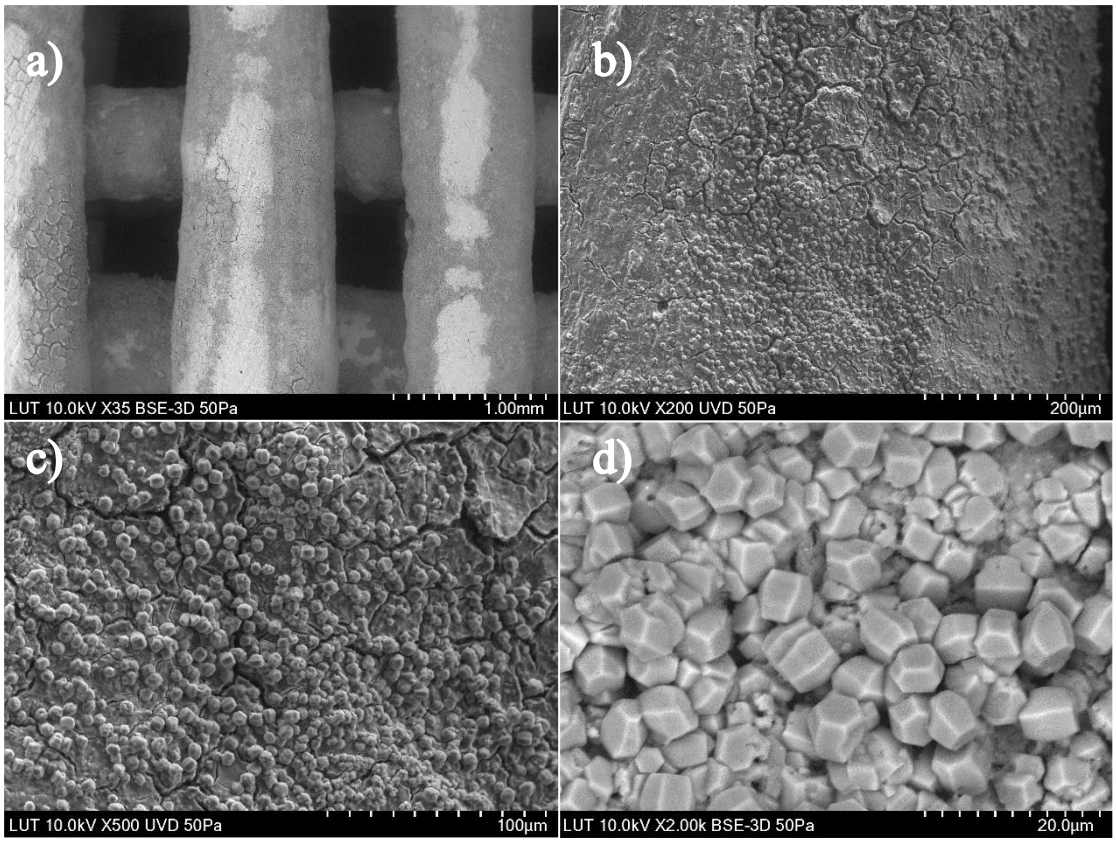

Fig. 16. Microstructure of MIL-96 crystallized on entire geopolymer filters synthesized with Benzene-1,3,5-tricarboxylic acid without previous surface modification in a 50 mL autoclave volume during 12 h of reaction and one cycle. Amplification x35 (a), x200 (b), x500 (c), and x2000 (d).

Using Trimesic Acid under normal conditions, but in a 50 mL autoclave, the results are close to those expected. Well distributed MOFs have been formed over the entire filter surface, despite having not very homogeneous sizes and the shape differs slightly.

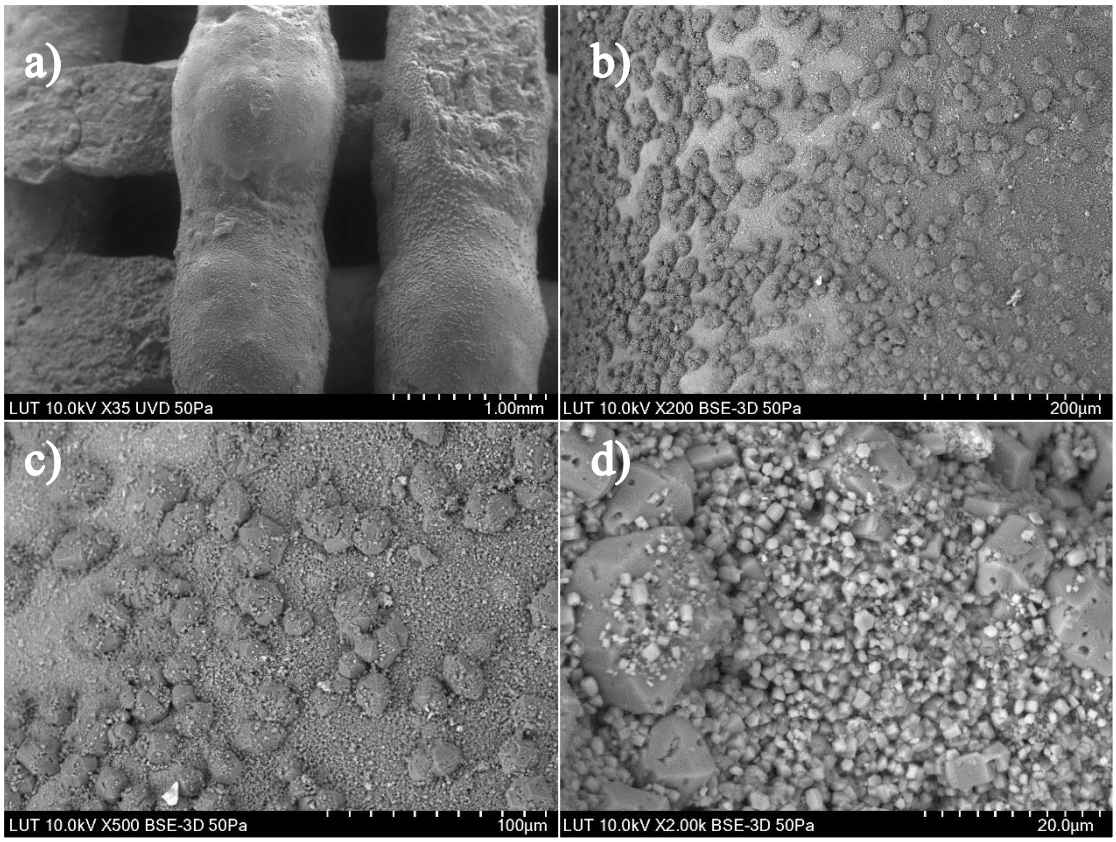

Fig. 17. Microstructure of MIL-96 crystallized on (1/4) cut geopolymer filters synthesized with Benzene-1,3,5-tricarboxylic acid without previous surface modification in a 25 mL autoclave volume during 12 h of reaction and one cycle. Amplification x35 (a), x200 (b), x500 (c), and x2000 (d).

Using a quarter of filter under normal conditions, the results shows a large difference in the sizes of the MOFs formed but a good distribution on the surface and in strange shapes.

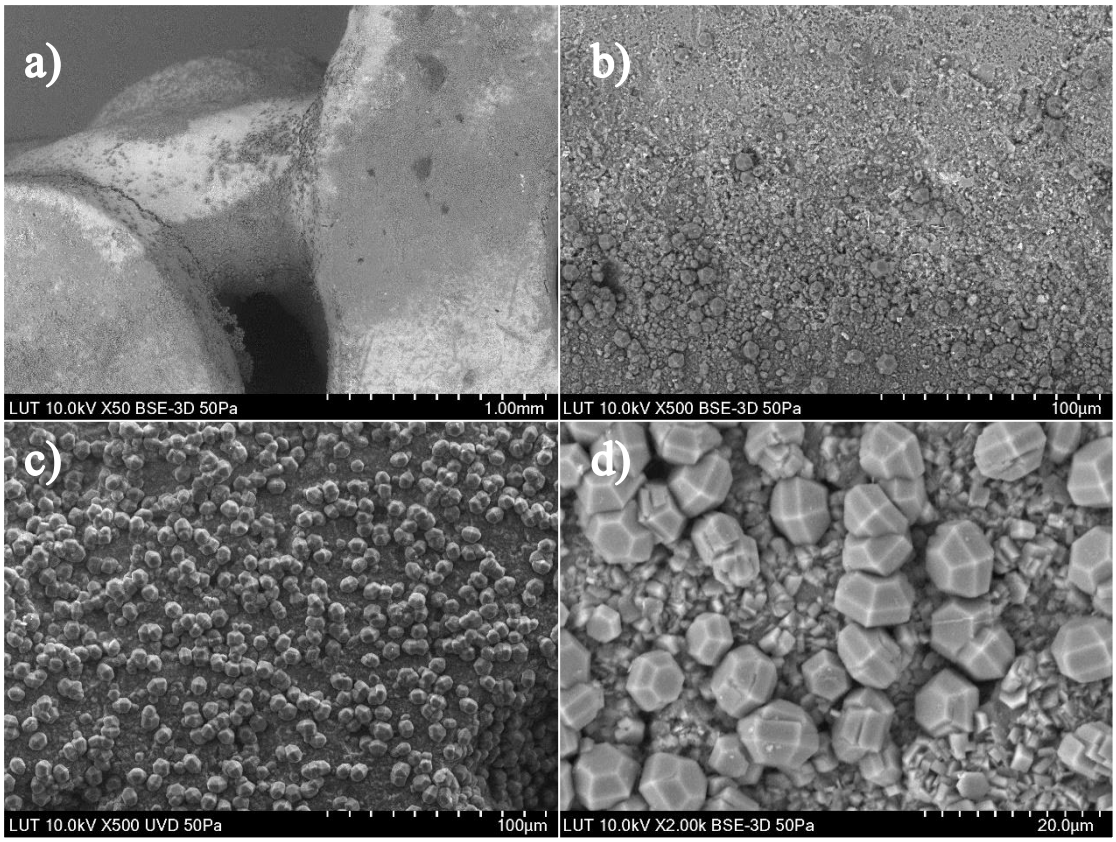

Fig. 18. Microstructure of MIL-96 crystallized on entire geopolymer filters synthesized with Benzene-1,3,5-tricarboxylic acid with previous amine groups surface modification in a 25 mL autoclave volume during 12 h of reaction and one cycle. Amplification x35 (a), x500 (b) and (c), x2000 (d).

As in the other reactions in which Trimesic Acid has been used in filters with the surface modified by amine groups, the distribution of MOFs is relatively good, but there are different sizes.

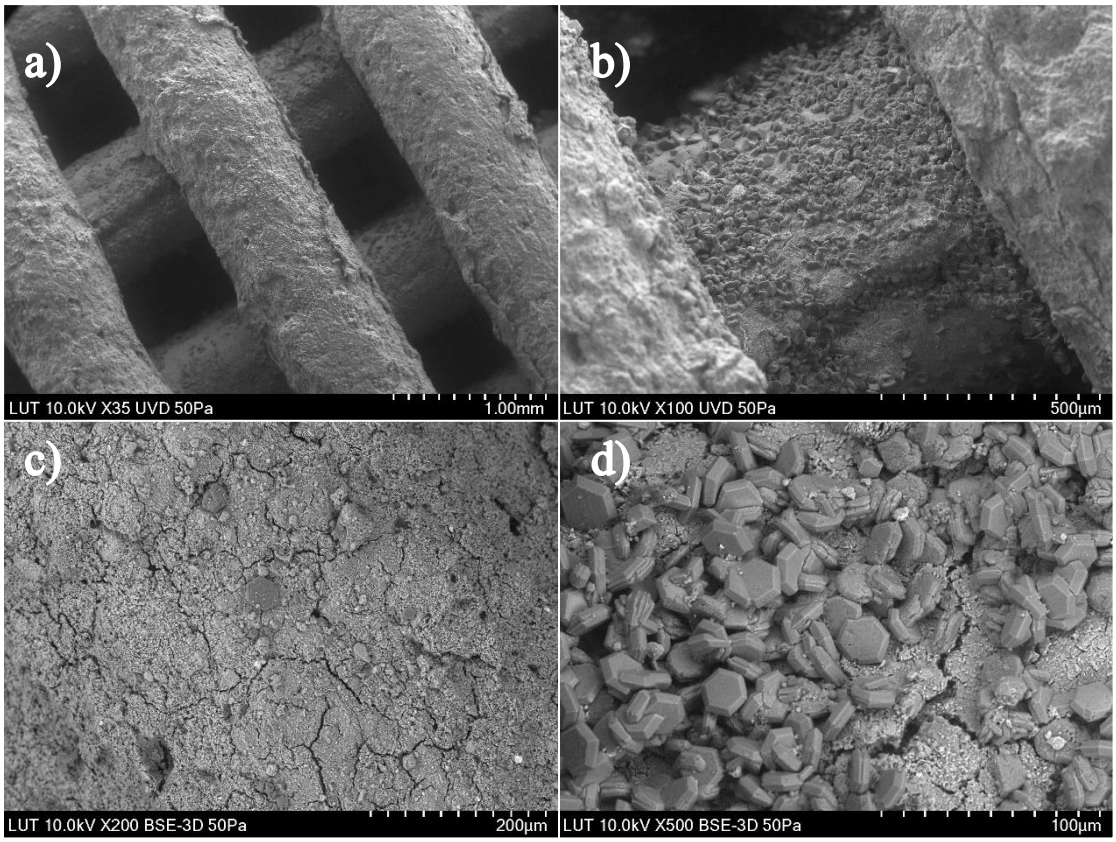

Fig. 19. Microstructure of MIL-96 crystallized on entire geopolymer filters synthesized with Benzene-1,3,5-tricarboxylic acid with previous amine groups surface modification in a 25 mL autoclave volume during 12 h of reaction and two cycles. Amplification x35 (a), x100 (b), x200 (c), and x500 (d).

As it has been observed in other tests, when repeating the reaction, the geopolymer filters are severely damaged. The mechanical properties are affected at levels that make the filter unusable for its intended use.

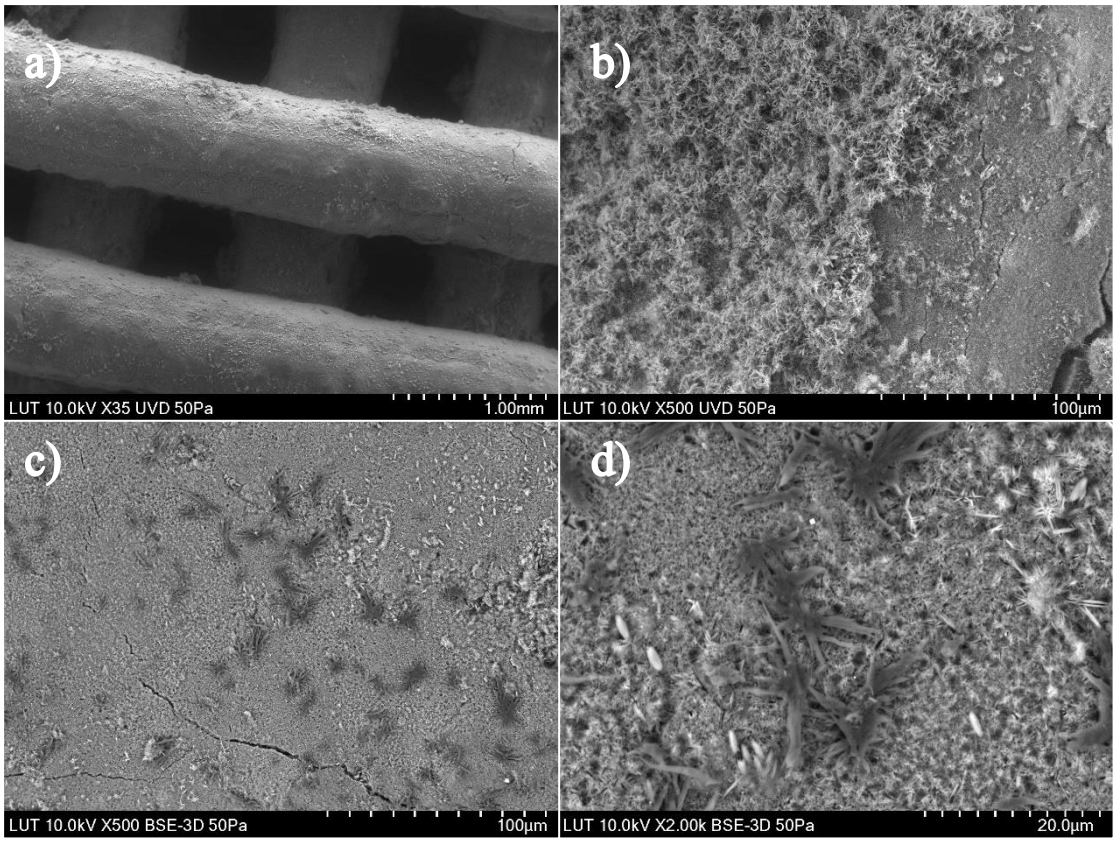

Fig. 20. Microstructure of MIL-96 crystallized on entire geopolymer filters synthesized with Benzene-1,3,5-tricarboxylic acid with previous amine groups surface modification in a 25 mL autoclave volume during 28 h of reaction and one cycle. Amplification x35 (a), x500 (b) and (c), and x2000 (d).

When carrying out the synthesis with a reaction time of 28 hours, in geopolymers previously modified with amine groups, the results are far from what was expected.

Formed needles are observed, possibly precipitated aluminum in various areas of the surface. There are no MOFs. As has already been seen in other methods, the increase in the reaction time is not favorable in the formation of MOFs.

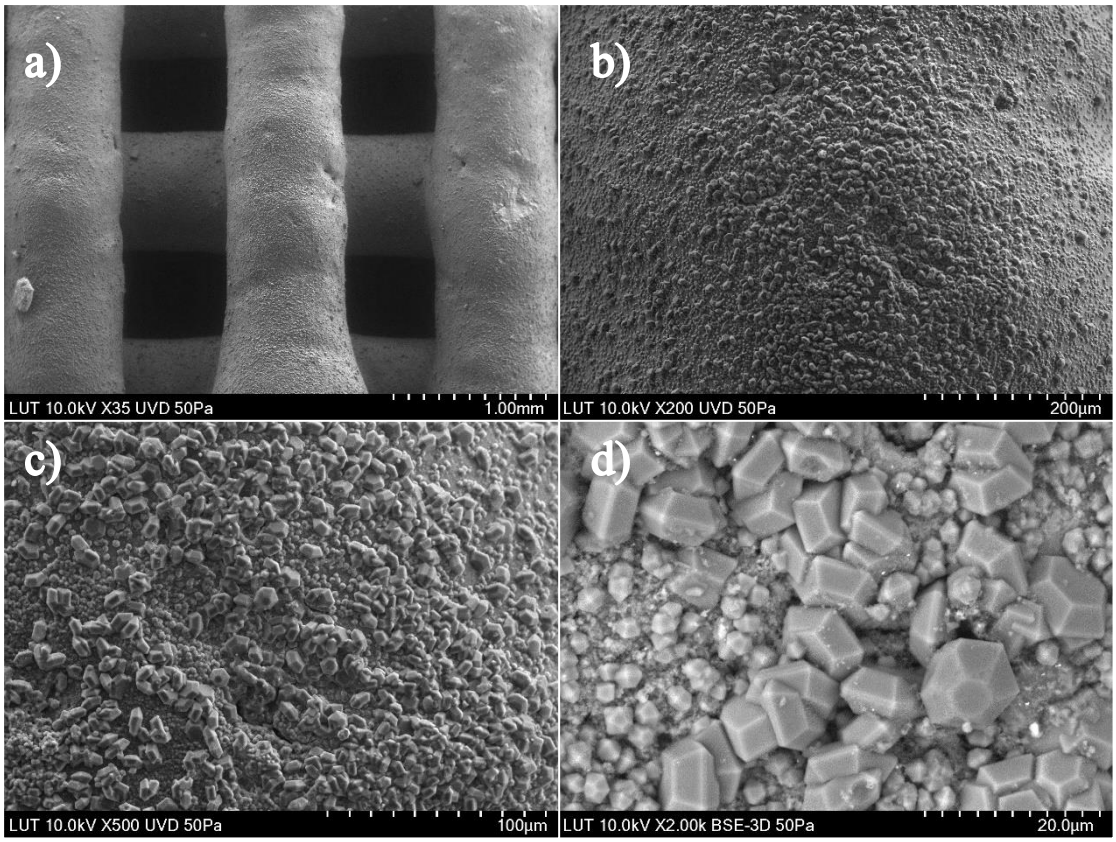

Fig. 21. Microstructure of MIL-96 crystallized on entire geopolymer filters synthesized with Benzene-1,3,5-tricarboxylic acid with previous amine groups surface modification in a 50 mL autoclave volume during 12 h of reaction and one cycle. Amplification x35 (a), x200 (b), x500 (c), and x2000 (d).

Using a 50 mL autoclave and filters with amine group modification on the surface gives quite good results. A very good distribution of MOFs is achieved over the entire surface, despite having different sizes. Furthermore, MOFs have a 3D hexagonal shape (rhombus type).

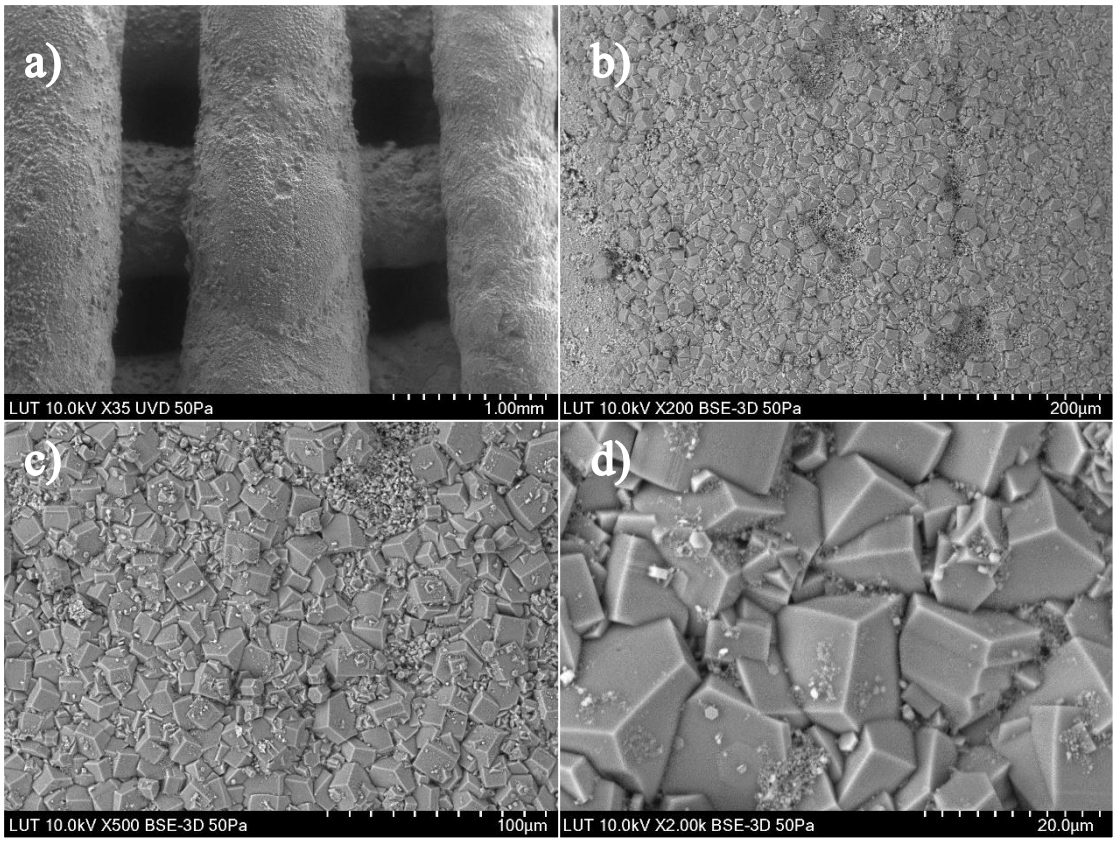

Fig. 22. Microstructure of MIL-96 crystallized on (1/4) cut geopolymer filters synthesized with Benzene-1,3,5-tricarboxylic acid with previous amine groups surface modification in a 25 mL autoclave volume during 12 h of reaction and one cycle. Amplification x35 (a), x200 (b), x500 (c), and x2000 (d).

In the case of a quarter filter, previously modified with amine groups on its surface, the results are good: A high distribution of synthesized MOFs is achieved despite having disparate size and shape.

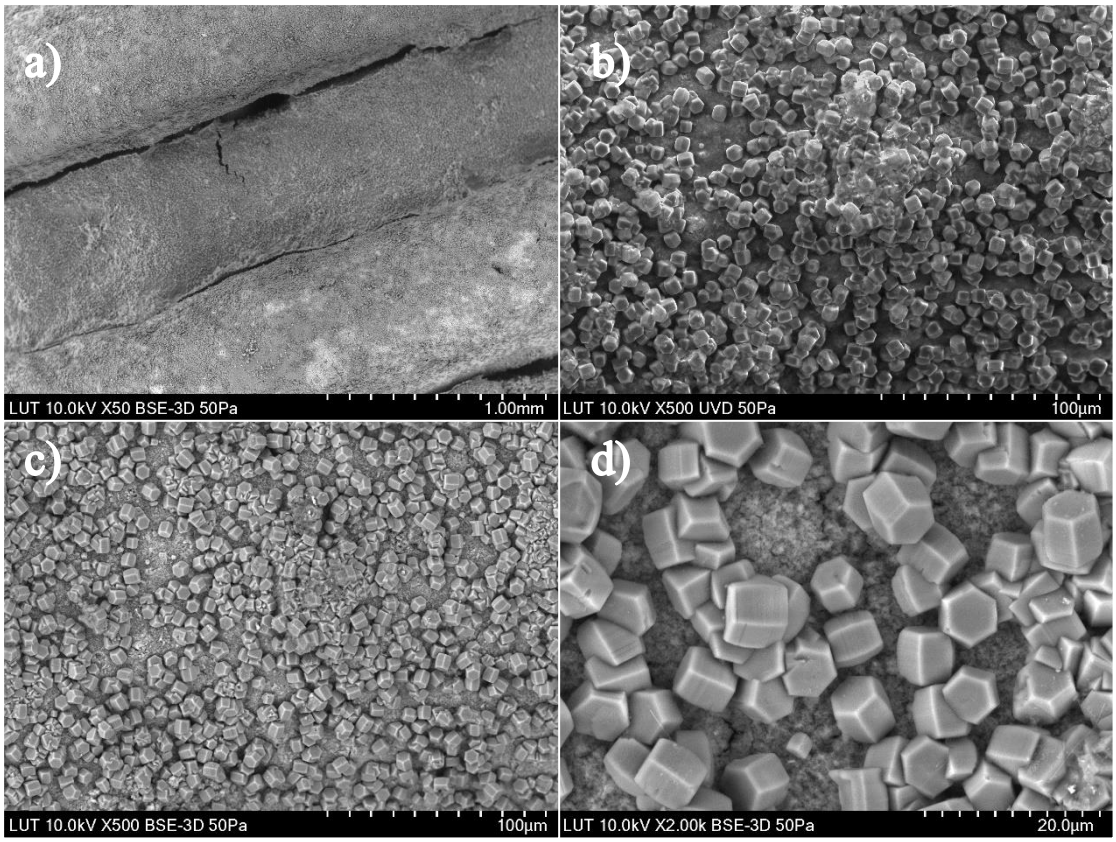

Fig. 23. Microstructure of MIL-96 crystallized on entire geopolymer filters synthesized with Benzene-1,3,5-tricarboxylic acid with previous carboxyl groups surface modification in a 25 mL autoclave volume during 12 h of reaction and one cycle. Amplification x35 (a), x500 (b) and (c), and x2000 (d).

When the surface is modified with carboxy groups, very good results are obtained. As can be seen in Fig. 23 MOFs are very homogeneously distributed on the surface, they have a very similar cylindrical hexagonal shape between them and they are very similar in size.

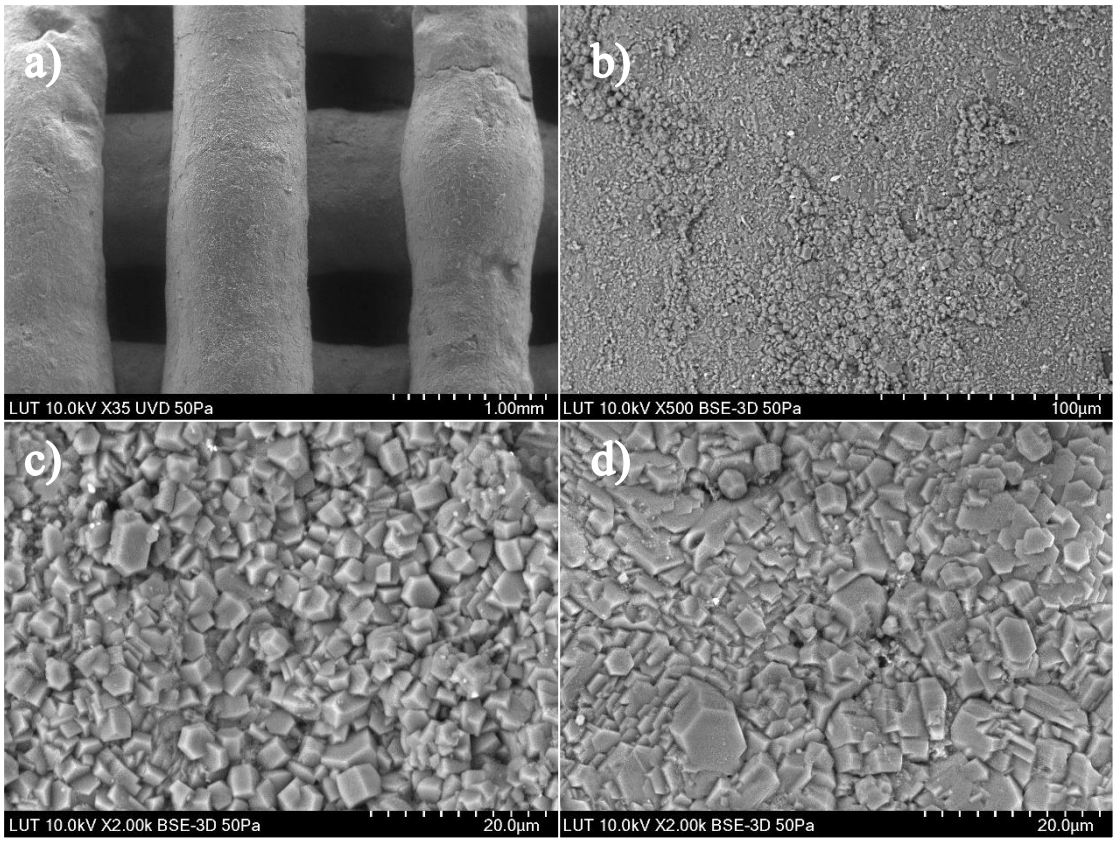

Fig. 24. Microstructure of MIL-96 crystallized on (1/4) cut geopolymer filters synthesized with Benzene-1,3,5-tricarboxylic acid with previous carboxyl groups surface modification in a 25 mL autoclave volume during 12 h of reaction and one cycle. Amplification x35 (a), x500 (b), and x2000 (c) and (d).

As with geopolymers cut with the modified surface of amine groups, in the case of having the surface modified with carboxy groups, embedded crystals are obtained, well distributed, of similar sizes but of strange shapes.

After analyzing different variables via SEM, it is concluded that the best conditions are:

- Reaction time 12 hours.
- 50 mL autoclave.
- Use of trimesic acid.

Where it is highlighted that the previous modification of the surface with amine and carboxyl groups produce even better results. However, tests will also be carried out with TBA synthesized in 50 mL autoclaves.

3.2. BET

Four samples were chosen for the BET porosity study, three of them synthesized with Trimesic acid: one initial, one without previous modification of the surface, one with modification with amine groups of the surface; and finally, with the surface modified with carboxyl groups. The results are shown in the Annex.

The isothermal adsorption curves of the different samples are shown in the index. According to Brunauer's classification, the istotherm is primarily of type II: non-porous and macroprosy, with condensation. This is the most common type of isotherm when the BET technique is performed. At low pressure, the micropores are filled with N^2. At intermediate pressures, the monolayer has formed, and the multilayer begins to form. Finally, at higher pressures, capillary condensation occurs.

The specific surface obtained is approximately 100 m^2/g for the three samples. This is very similar to the surface area of unmodified alumina. It is even a little lower, as the alumina would have a specific area of 129 m^2/g.

In addition, the pore size would also decrease. It follows that MOFs are generated in the larger pores, obstructing them in some cases. In this way, the pores would not be too deep, losing some specific surface area but not too much. In addition, it should be noted that MOFs, in theory, are capable of adsorbing REE, while untreated filters could not.

In conclusion, it can be said that the results of the BET analysis of the different samples, although not decisive, would follow the expected pattern, in which the synthesized MOFs have modified the surface and present potential to adsorb REE.

3.3. ICP

Finally, a test was carried out to obtain the adsorption capacity of the filters. For this, the samples were introduced in 50 mL bottles with a 33 ppm solution of Neodymium (Nd). They were kept under stirring for 24 hours and the final concentrations were measured by ICP. The results obtained can be seen in the Table 2.

Table 2. ICP results

Chemical	Size	Surf. Modif.	AC Volume (mL)	Dilution	Nd Conc. (ppb)	Adsorbed (ppb)	Filter Mass (g)	Volume (L)	Adsorbed (g)	Adsorption capacity (mg/g)
REE 40 ppb				1	40.21					
TPA	1/4	NO	25	5000	388.54	32825.2	0.44	0.05	1.64E-03	3.751
TPA	1/4	NH	25	5000	1960.33	31253.4	0.44	0.05	1.56E-03	3.572
TPA	1/4	COOCl	25	5000	4666.09	28547.6	0.44	0.05	1.43E-03	3.263
Trimesic ac.	1	NO	25	5000	3.53	33210.2	1.75	0.05	1.66E-03	0.949
Trimesic ac.	1	NO	50	5000	2673.85	30539.9	1.75	0.05	1.53E-03	0.873
Trimesic ac.	1/4	NO	25	5000	1836.70	31377.0	0.44	0.05	1.57E-03	3.586
Trimesic ac.	1	NH	25	5000	218.99	32994.7	1.75	0.05	1.65E-03	0.943
Trimesic ac.	1	NH	50	5000	8361.19	24852.5	1.75	0.05	1.24E-03	0.710
Trimesic ac.	1/4	NH	25	5000	3655.84	29557.9	0.44	0.05	1.48E-03	3.378
Trimesic ac.	1	COOCl	25	5000	211.92	33001.8	1.75	0.05	1.65E-03	0.943
Trimesic ac.	1/4	COOCl	25	5000	7944.32	25269.4	0.44	0.05	1.26E-03	2.888
Original dilution				5000	33213.70					

There is a clear difference between the whole and the cut pieces. Something logical, since the small ones have a larger surface. However, it would be interesting to study this phenomenon a little more in depth to determine if the formation of MOFs inside the filter pores is good.

Another fact to consider is the difference between the MOFs synthesized with benzene-1,4-dicarboxyl acid and with trimesic acid: There is a slight increase in adsorption capacity on the TPA species compared to the trimesic acid. Based on the results obtained in the previous tests, the results are unexpected, since a better adsorption capacity was expected from MOFs formed with trimesic acid. In the same way, geopolymers with a previously modified surface have a lower adsorption capacity than without modification. Once again, we get contrary data.

In summary, a relationship between the adsorption capacity of REE with the MOFs generated at the surface cannot be demonstrated. It is possible that there are other variants that affect it, such as the contact time, which could be greater than 24 hours.

A future article will study the adsorption capacity of MOFs in depth.

4. Conclusions

From the results obtained we can conclude:

Firstly, small modifications in the reaction time cause big changes in the MOFs synthesis. Being 12 hours the optimal time for their formation. Other modifications of the variables are also influential: Performing more than one reaction cycle causes the loss of mechanical properties of the filters, fracturing them in many cases; and generating several different sizes of MOFs, so it is not recommended to perform more than one reaction per filter.

Second, modification of the surface of geopolymers not only changes the coating of MOFs on the filter, but also modifies their shape. Within which, the use of Amine and carboxyl groups generate the most homogeneous MOFs in terms of coating, shape and size.

Third, the synthesized MOFs also differ depending on the acid used. Benzene-1,3,5-tricarboxylic acid is the one that generates the most homogeneous MOFs.

The dilution of reagents and the size ratio of the filter-autoclave also influence the synthesis. A different dilution than the one used in this Master Thesis has a negative influence on the formation of MOFs . On the other hand, by maintaining the dilution but increasing the size of the reactor, better results are obtained.

Finally, it should be noted that although filters with more MOFs generated and with greater homogeneity do not offer better results in terms of Neodynium adsorption. In a second part of the study carried out by LUT, the adsorption capacity of geopolymers covered by MOFs will be studied in more detail.

5. Bibliography

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CHAPTER 2. BUDGET

This section reflects the investment required to carry out this Master Thesis. To obtain it, it is necessary to recognize all the materials, machinery and reagents that have been used in this project.

1. PARTIAL BUDGETS

Chapter 1 shows the personnel required to carry out both the experimental trials and the search for information and conduct of the study.

CHAPTER 1 - Personnel

Designation	Amount		
	Price (€/hr)	Quantity (hr)	TOTAL (€)
Chemical Engineer	30.00	250	7,500.00
		Total :	**7,500.00**

Chapter 2 details the machinery used in the laboratory during the experimental stage of the end of grade work.

CHAPTER 2 - Equipment

Designation	Amount				
	Price (€)	Quantity	Lifetime (h)	Use (h)	TOTAL (€)
Analytical balance Cobos JT -220AI	2,268.00	1	65745	15	0.52
Dryer without plate	303.33	1	175320	240	0.42
Nalgene Drying Plate	89.99	1	175320	240	0.12
IKA heating plate c-mag HS-7	525.00	2	65745	12	0.19
ASEM gas extraction hood	10,495.00	1	87660	30	3.59
Stove Gallur	1,250.00	1	131490	210	2.00
				Total:	**6.84**

Chapter 3 details the expenses necessary to provide the laboratory with basic and auxiliary materials.

CHAPTER 3 - Materials

Designation	Amount		
	Price (€)	Quantity	TOTAL (€)
Dräger FFP2 mask 1720+ v	2.11	2	4.22
Ceramic capsule f/flat, 169x68 mm	38.27	12	459.24
Lab Timer	11.50	1	11.50
Gloves box 100 pcs	6.47	1	6.47
Lab coat	18.84	1	18.84
Safety footwear	39.75	1	39.75
Beaker 25 mL	3.30	4	13.20
50 mL beaker	2.29	4	9.16
Beaker 100 mL	3.28	4	13.12
250 mL beaker	3.11	4	12.44
1000 mL beaker	16.84	2	33.68
Class A pipettes 5mL	31.00	1	31.00
Class A graduated pipettes 10mL	31.74	1	31.74
Class A pipettes with 10mL volume	39.02	1	39.02
Class A graduated pipettes 20mL	55.27	1	55.27
Class A pipettes, 50mL volume	96.29	1	96.29
Class A pipettes, 100mL volume	101.91	1	101.91
Erlenmeyer wide mouth 250mL	6.42	6	38.52
Lab spatula/spoon	3.21	2	6.42
Ring support with nut	5.30	1	5.30
Universal laboratory stand	11.90	1	11.90
Polystyrene bucket of 1 cm. (100pcs)	75.82	1	75.82
Burette 50 mL	76.41	1	76.41
Volumetric flask A 50 mL	31.58	8	252.64
Volumetric flask A 100 mL	32.99	2	65.98
Volumetric flask A 1000 mL	79.52	2	159.04
Volumetric flask A opaque 100 mL	42.86	2	85.72
Distilled water bottle 1L	11.91	10	119.10
		Total	**1,873.70**

Finally, the costs associated with the reagents used in Chapter 4 are represented.

CHAPTER 4 - Chemicals

Designation	Amount		
	Price (€)	Quantity	TOTAL (€)
Toluene (≥99.5%, VMR) 2L	163.00	3	489.00
APTES (≥98%, Sigma-Aldrich) 100mL	58.60	1	58.60
Terephthaloyl chloride(≥99%, Sigma-Aldrich) 250g	35.70	1	35.70
$Al(NO_3)3{\cdot}9H_2O$, (99.9%, COMPANY) 500g	68.50	1	68.50
Trimesic acid, (98%, ACROS Organics) 250g	20.80	1	20.80
H2BDC, (98%, Sigma-Aldrich) 500g	31.70	1	31.70
		Total:	**704.30**

2. EXECUTION BUDGET

With the sum of the partial budgets, the Material Execution Budget is obtained.

Budget of material execution

Chapter 1 Personnel		7,500.00 €
Chapter 2 Equipment		6.84 €
Chapter 3 Materials		1,873.70 €
Chapter 4 Chemicals		704.30 €
	Total…….	10,084.84 €

The material execution budget is increased to the amount of TEN THOUSAND EIGHTY-FOUR EUROS AND EIGHTY-FOUR CENTS

By adding the project's general expenses (electricity consumption, maintenance, cleaning, etc.) and the industrial profit, the Contract Execution Budget is calculated.

Contract execution budget

Chapter 1 Personnel		7,500.00 €
Chapter 2 Equipment		6.84 €
Chapter 3 Materials		1,873.70 €
Chapter 4 Chemicals		704.30 €
Budget of material execution		10,084.84 €
10 % Overheads		1,008.48 €
8 % Industrial profit		806.79 €
	Total…….	11,900.11 €

Finally, the Bidding Base Budget is calculated by adding 24% VAT to the Contract Execution Budget, which expresses the final cost of the project.

Bidding budget

Chapter 1 Personnel		7,500.00 €
Chapter 2 Equipment		6.84 €
Chapter 3 Materials		1,873.70 €
Chapter 4 Chemicals		704.30 €
Budget of material execution		10,084.84 €
10 % Overheads		1,008.48 €
8 % Industrial profit		806.79 €
Amount		11,900.11 €
24 % VAT		2,856.03 €
	Total…….	14,756.13 €

The total budget amounts to the expressed amount of FOURTEEN THOUSAND SEVEN HUNDRED AND FIFTY-SIX EUROS AND THIRTEEN CENTS

CHAPTER 3. APPENDIX

Appendix 1: BET result. White Filters

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3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 3 | Page 1 of 17

Sample: OC-0-25ml-1
Operator:
Submitter:
File: C:\3Flex\data\RepoEvelina\000-510-OC-0-25ml-1.SMP

Started:	11/1/2019 10:07:01 AM	Analysis adsorptive:	N2
Completed:	11/1/2019 7:25:20 PM	Analysis bath temp.:	77.302 K
Report time:	11/5/2019 11:15:50 AM	Thermal correction:	Yes
Sample mass:	0.0536 g	Warm free space:	21.1605 cm³ Measured
Cold free space:	63.7502 cm³	Equilibration interval:	5 to 10 s
Low pressure dose:	None	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63

Summary Report

Surface Area

Single point surface area at P/Po = 0.159691793:	129.8823 m²/g
BET Surface Area:	136.7560 m²/g
t-Plot Micropore Area:	10.3554 m²/g
t-Plot external surface area:	126.4006 m²/g
BJH Adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter:	117.6885 m²/g
BJH Desorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter:	138.6777 m²/g

Pore Volume

Single point adsorption total pore volume of pores less than 193.4646 nm diameter at P/Po = 0.990000000:	0.379725 cm³/g
Single point desorption total pore volume of pores less than 193.4646 nm diameter at P/Po = 0.990000000:	0.404092 cm³/g
t-Plot micropore volume:	0.003153 cm³/g
BJH Adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter:	0.397197 cm³/g
BJH Desorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter:	0.405720 cm³/g

Pore Size

Adsorption average pore diameter (4V/A by BET):	11.1067 nm
Desorption average pore diameter (4V/A by BET):	11.8194 nm
BJH Adsorption average pore diameter (4V/A):	13.4999 nm
BJH Desorption average pore diameter (4V/A):	11.7025 nm

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3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 3 | Page 1 of 17

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\ArbonaJa...\000-569-0-0.SMP

Started:	1/27/2020 4:42:28 PM	Analysis adsorptive:	N2
Completed:	1/28/2020 2:00:13 AM	Analysis bath temp.:	77.264 K
Report time:	2/4/2020 10:51:11 AM	Thermal correction:	Yes
Sample mass:	0.0800 g	Warm free space:	21.1394 cm³ Measured
Cold free space:	63.7252 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63

Summary Report

Surface Area

Single point surface area at P/Po = 0.139805188:	93.1466 m²/g
BET Surface Area:	98.5746 m²/g
t-Plot Micropore Area:	4.9054 m²/g
t-Plot external surface area:	93.6691 m²/g
BJH Adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter:	48.8578 m²/g
BJH Desorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter:	64.5593 m²/g

Pore Volume

Single point adsorption total pore volume of pores less than 166.4084 nm diameter at P/Po = 0.988348185:	0.141487 cm³/g
Single point desorption total pore volume of pores less than 166.4084 nm diameter at P/Po = 0.988348185:	0.141487 cm³/g
t-Plot micropore volume:	0.001302 cm³/g
BJH Adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter:	0.118211 cm³/g
BJH Desorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter:	0.126110 cm³/g

Pore Size

Adsorption average pore diameter (4V/A by BET):	5.7413 nm
Desorption average pore diameter (4V/A by BET):	5.7413 nm
BJH Adsorption average pore diameter (4V/A):	9.6779 nm
BJH Desorption average pore diameter (4V/A):	7.8136 nm

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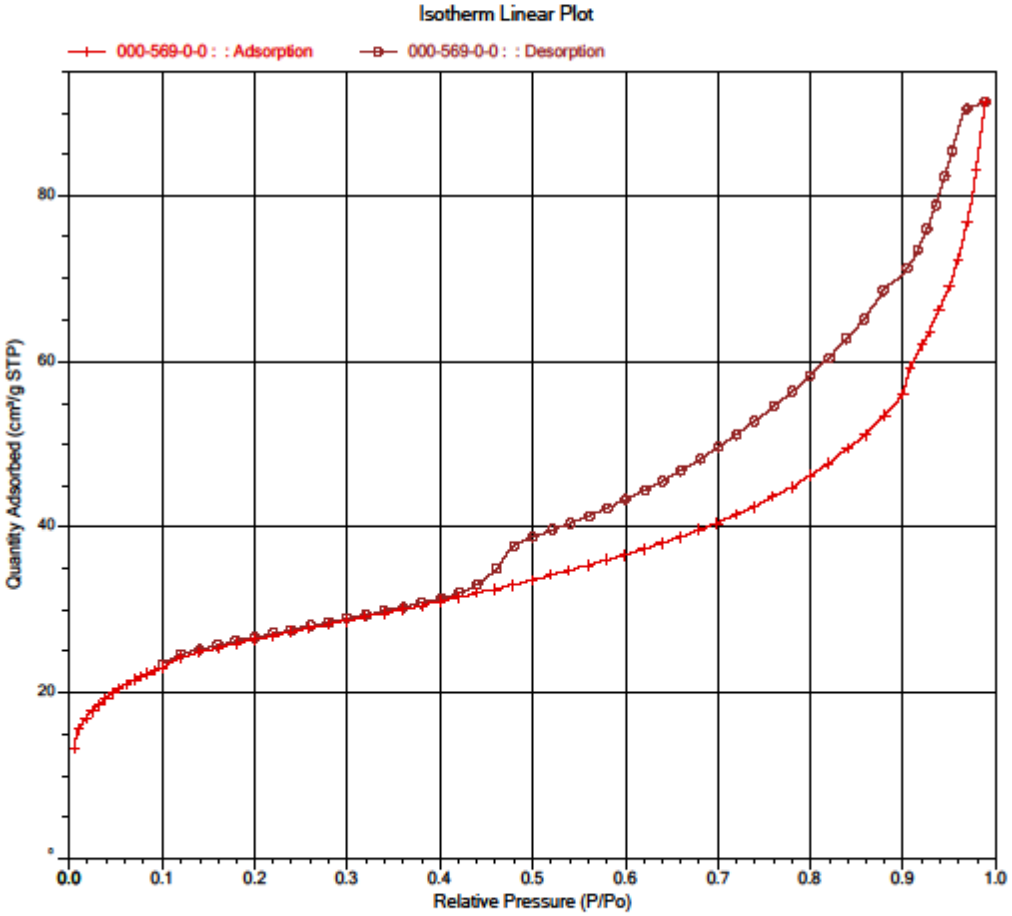
3Flex 4.02 | 3Flex Version 4.02 | Page 5 of 17

Serial # 826 Unit 1 Port 3

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEvelina\Arbona\a...\000-569-0-0.SMP

Started:	1/27/2020 4:42:28 PM	Analysis adsorptive:	N2
Completed:	1/28/2020 2:00:13 AM	Analysis bath temp.:	77.264 K
Report time:	2/4/2020 10:51:11 AM	Thermal correction:	Yes
Sample mass:	0.0800 g	Warm free space:	21.1394 cm³ Measured
Cold free space:	63.7252 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63



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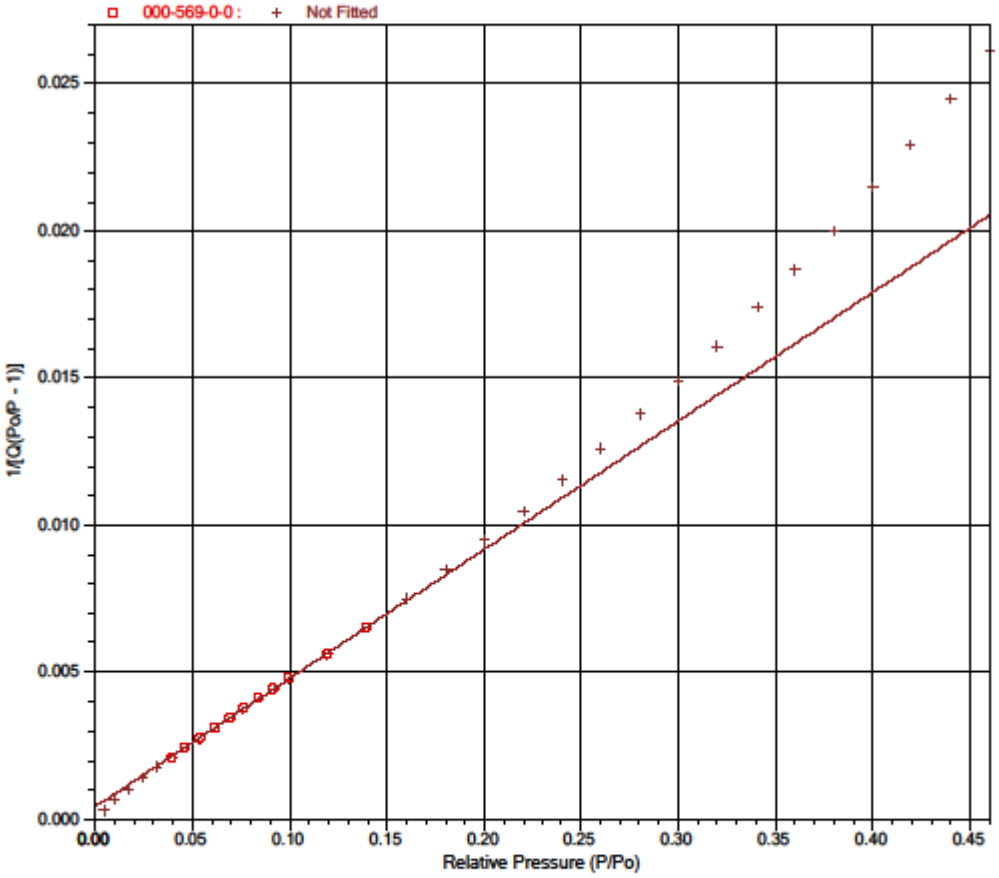
3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 3 | Page 7 of 17

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\ArbonaJa...\000-569-0-0.SMP

Started:	1/27/2020 4:42:28 PM	Analysis adsorptive:	N2
Completed:	1/28/2020 2:00:13 AM	Analysis bath temp.:	77.264 K
Report time:	2/4/2020 10:51:11 AM	Thermal correction:	Yes
Sample mass:	0.0800 g	Warm free space:	21.1394 cm³ Measured
Cold free space:	63.7252 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63

BET Surface Area Plot



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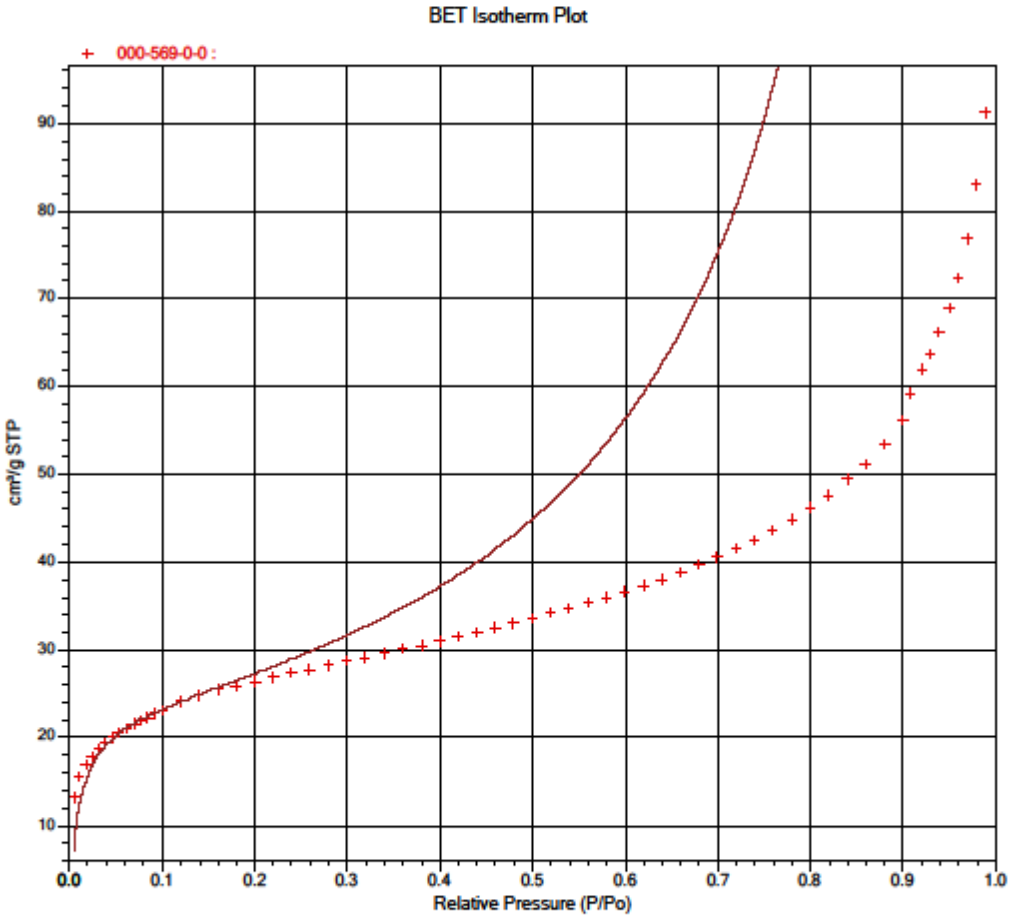
3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 3 | Page 8 of 17

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\ArbonaJa...\000-569-0-0.SMP

Started:	1/27/2020 4:42:28 PM	Analysis adsorptive:	N2
Completed:	1/28/2020 2:00:13 AM	Analysis bath temp.:	77.264 K
Report time:	2/4/2020 10:51:11 AM	Thermal correction:	Yes
Sample mass:	0.0800 g	Warm free space:	21.1394 cm³ Measured
Cold free space:	63.7252 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63



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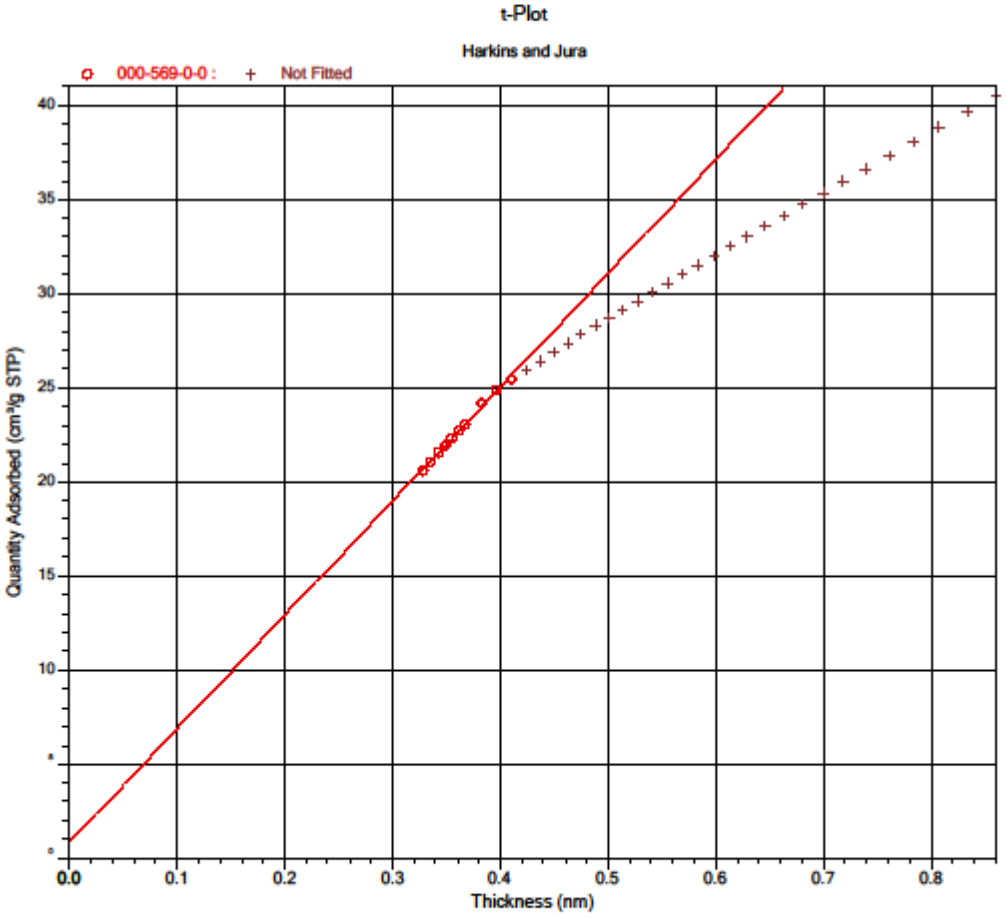
3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 3 | Page 11 of 17

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\ArbonaJa...\000-569-0-0.SMP

Started:	1/27/2020 4:42:28 PM	Analysis adsorptive:	N2
Completed:	1/28/2020 2:00:13 AM	Analysis bath temp.:	77.264 K
Report time:	2/4/2020 10:51:11 AM	Thermal correction:	Yes
Sample mass:	0.0800 g	Warm free space:	21.1394 cm³ Measured
Cold free space:	63.7252 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63



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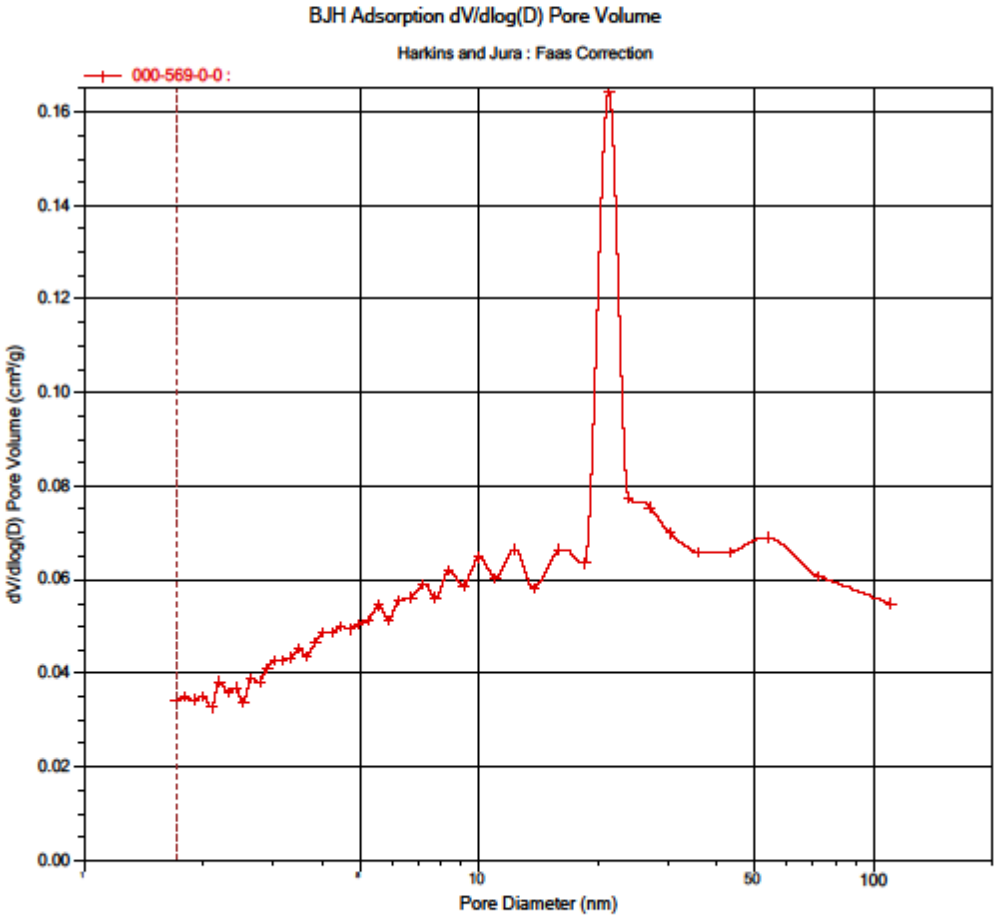
3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 3 | Page 14 of 17

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\ArbonaJa...\000-569-0-0.SMP

Started:	1/27/2020 4:42:28 PM	Analysis adsorptive:	N2
Completed:	1/28/2020 2:00:13 AM	Analysis bath temp.:	77.264 K
Report time:	2/4/2020 10:51:11 AM	Thermal correction:	Yes
Sample mass:	0.0800 g	Warm free space:	21.1394 cm³ Measured
Cold free space:	63.7252 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63



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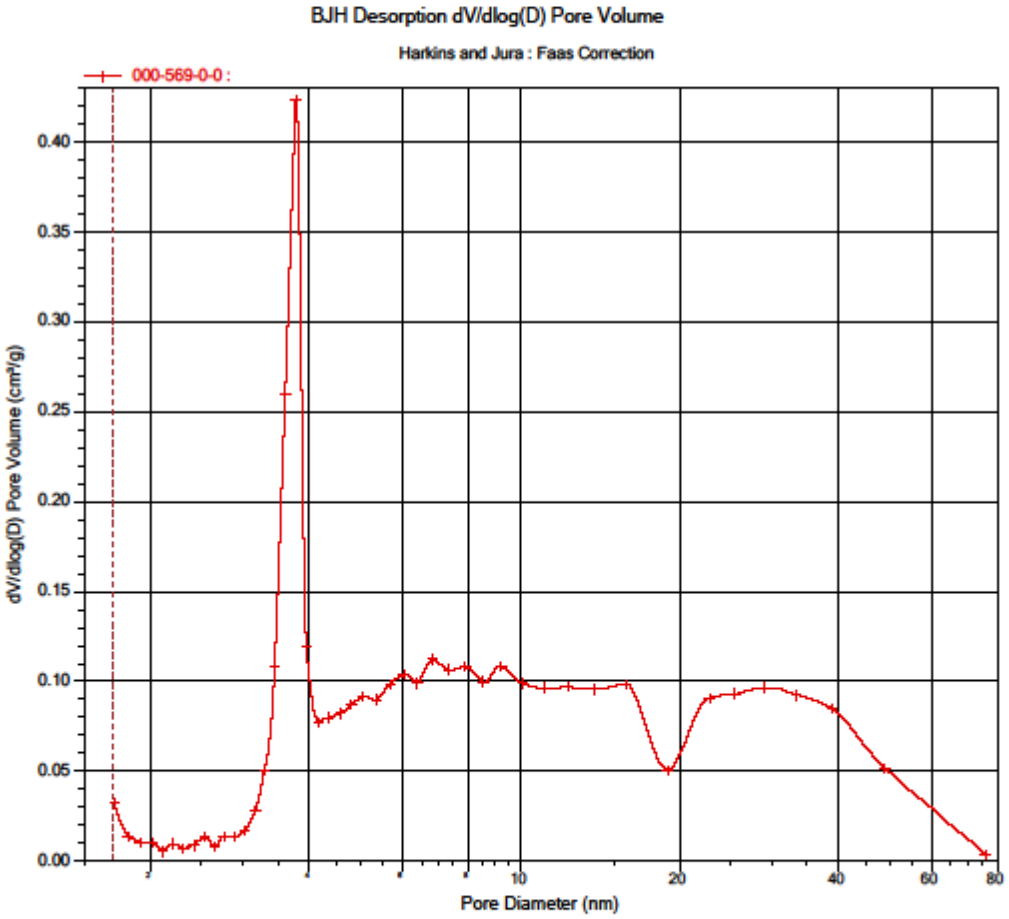
3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 3 | Page 17 of 17

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\ArbonaJa...\000-569-0-0.SMP

Started:	1/27/2020 4:42:28 PM	Analysis adsorptive:	N2
Completed:	1/28/2020 2:00:13 AM	Analysis bath temp.:	77.264 K
Report time:	2/4/2020 10:51:11 AM	Thermal correction:	Yes
Sample mass:	0.0800 g	Warm free space:	21.1394 cm³ Measured
Cold free space:	63.7252 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63



Appendix 2: BET result. Filters with MOFs. No surface modification

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3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 2 | Page 1 of 18

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\ArbonaJ...\000-568-NH-0.SMP

Started:	1/27/2020 4:42:28 PM	Analysis adsorptive:	N2
Completed:	1/28/2020 2:00:13 AM	Analysis bath temp.:	77.258 K
Report time:	2/4/2020 10:51:08 AM	Thermal correction:	Yes
Sample mass:	0.0379 g	Warm free space:	21.3546 cm³ Measured
Cold free space:	64.0011 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63

Summary Report

Surface Area

Single point surface area at P/Po = 0.139915434:	113.8539 m²/g
BET Surface Area:	122.8074 m²/g
t-Plot Micropore Area:	8.8000 m²/g
t-Plot external surface area:	114.0074 m²/g
BJH Adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter:	54.8310 m²/g
BJH Desorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter:	84.4404 m²/g

Pore Volume

Single point adsorption total pore volume of pores less than 171.7089 nm diameter at P/Po = 0.988713363:	0.153390 cm³/g
Single point desorption total pore volume of pores less than 171.7089 nm diameter at P/Po = 0.988713363:	0.153390 cm³/g
t-Plot micropore volume:	0.001294 cm³/g
BJH Adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter:	0.119214 cm³/g
BJH Desorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter:	0.136862 cm³/g

Pore Size

Adsorption average pore diameter (4V/A by BET):	4.9961 nm
Desorption average pore diameter (4V/A by BET):	4.9961 nm
BJH Adsorption average pore diameter (4V/A):	8.6968 nm
BJH Desorption average pore diameter (4V/A):	6.4832 nm

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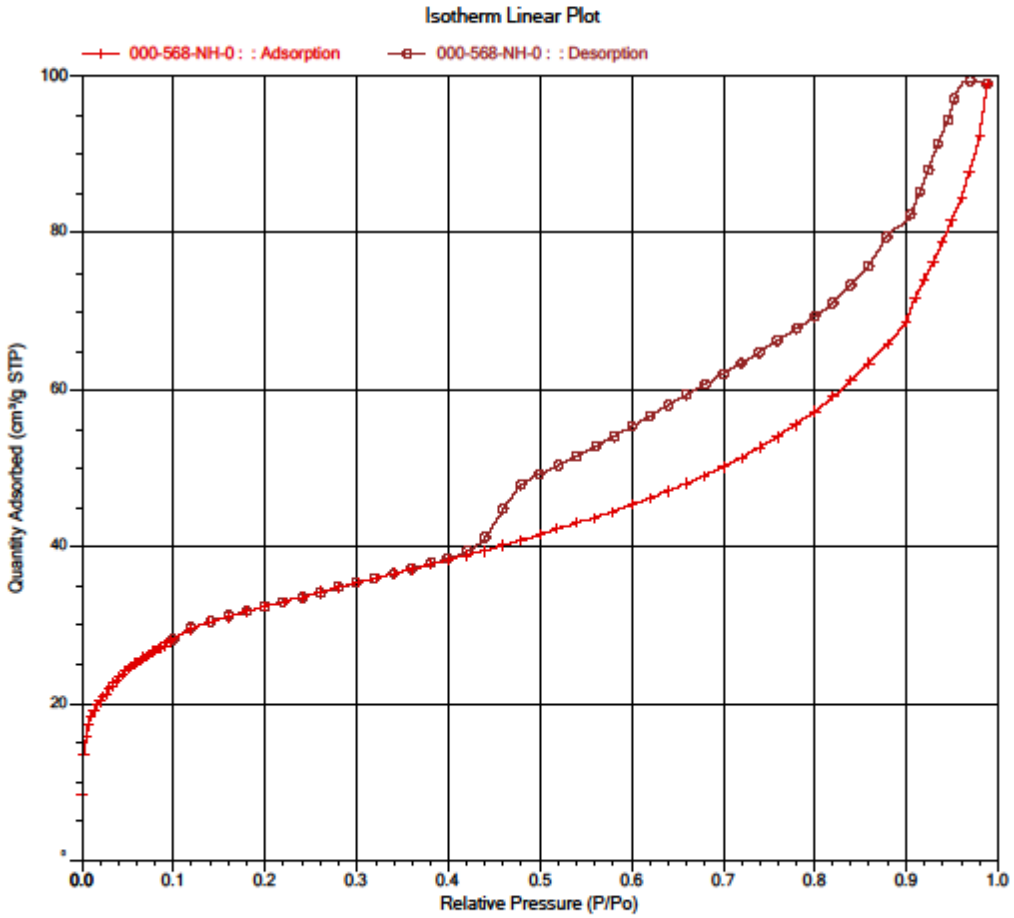
3Flex 4.02 | 3Flex Version 4.02 | Page 6 of 18

Serial # 826 Unit 1 Port 2

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEvelina\Arbona\...\000-568-NH-0.SMP

Started:	1/27/2020 4:42:28 PM	Analysis adsorptive:	N2
Completed:	1/28/2020 2:00:13 AM	Analysis bath temp.:	77.258 K
Report time:	2/4/2020 10:51:08 AM	Thermal correction:	Yes
Sample mass:	0.0379 g	Warm free space:	21.3546 cm³ Measured
Cold free space:	64.0011 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63



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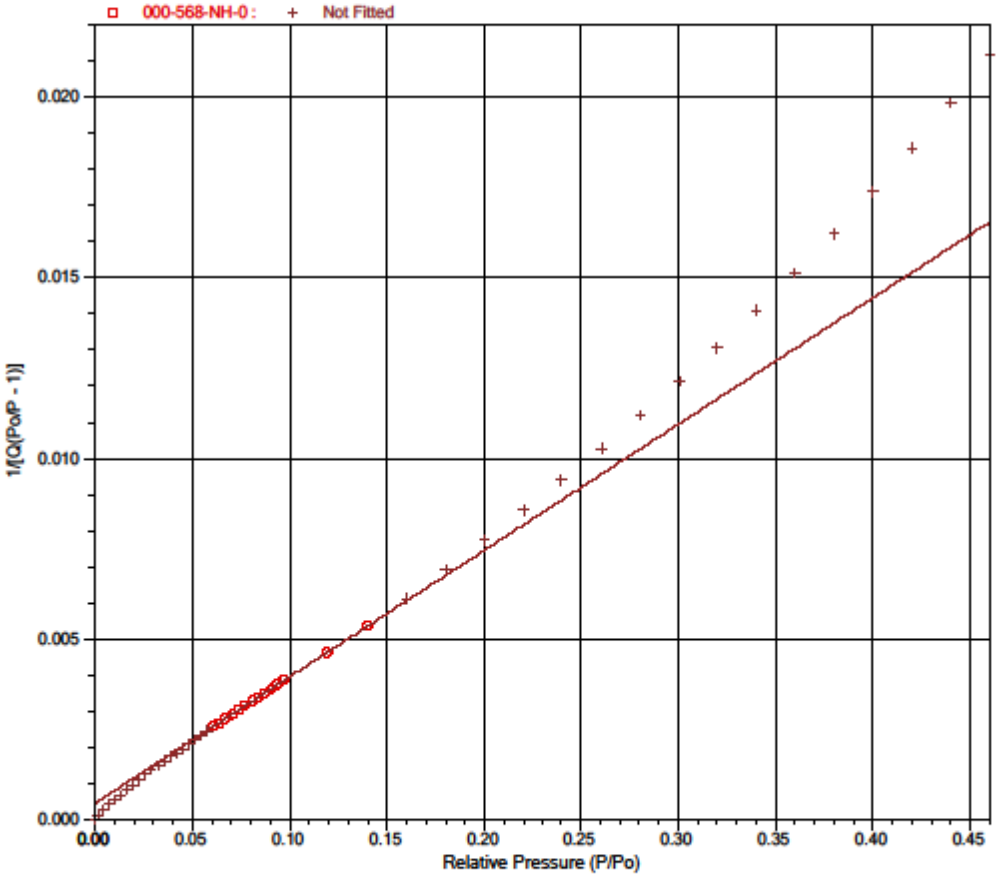
3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 2 | Page 8 of 18

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\ArbonaJ...\000-568-NH-0.SMP

Started:	1/27/2020 4:42:28 PM	Analysis adsorptive:	N2
Completed:	1/28/2020 2:00:13 AM	Analysis bath temp.:	77.258 K
Report time:	2/4/2020 10:51:08 AM	Thermal correction:	Yes
Sample mass:	0.0379 g	Warm free space:	21.3546 cm³ Measured
Cold free space:	64.0011 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63

BET Surface Area Plot



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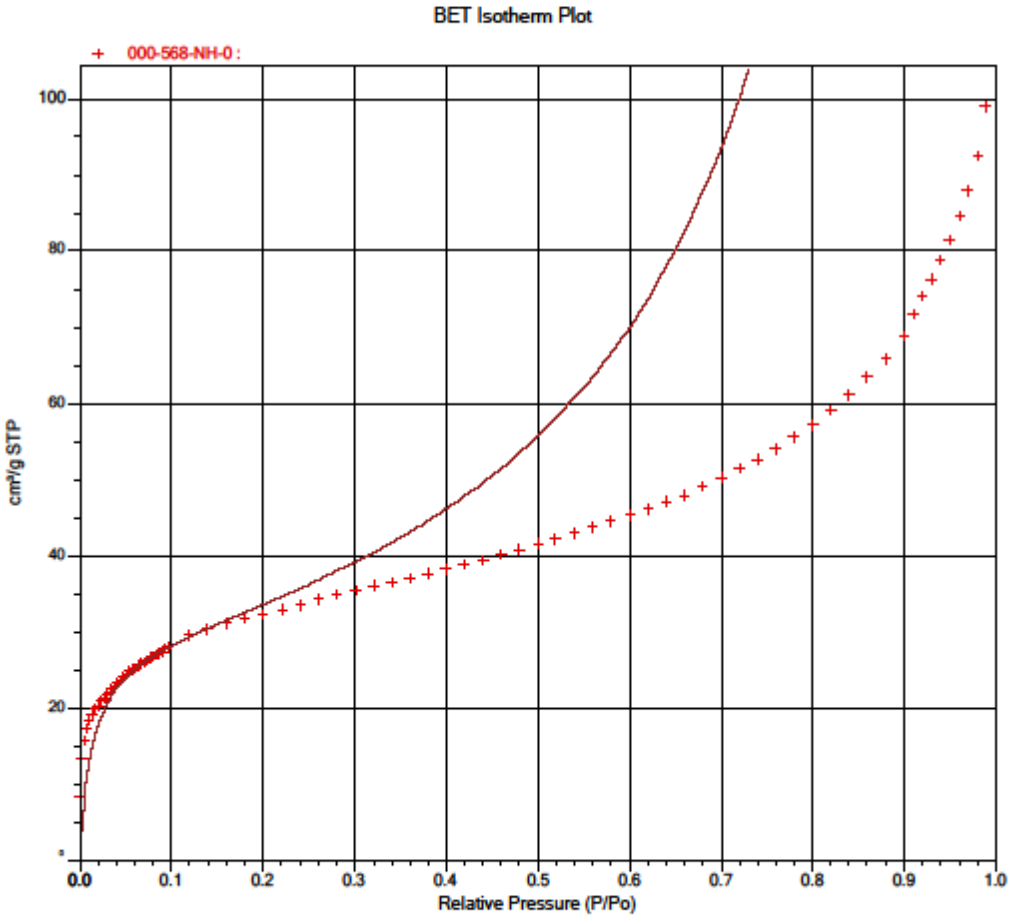
3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 2 | Page 9 of 18

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\ArbonaJ...\000-568-NH-0.SMP

Started:	1/27/2020 4:42:28 PM	Analysis adsorptive:	N2
Completed:	1/28/2020 2:00:13 AM	Analysis bath temp.:	77.258 K
Report time:	2/4/2020 10:51:08 AM	Thermal correction:	Yes
Sample mass:	0.0379 g	Warm free space:	21.3546 cm³ Measured
Cold free space:	64.0011 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63



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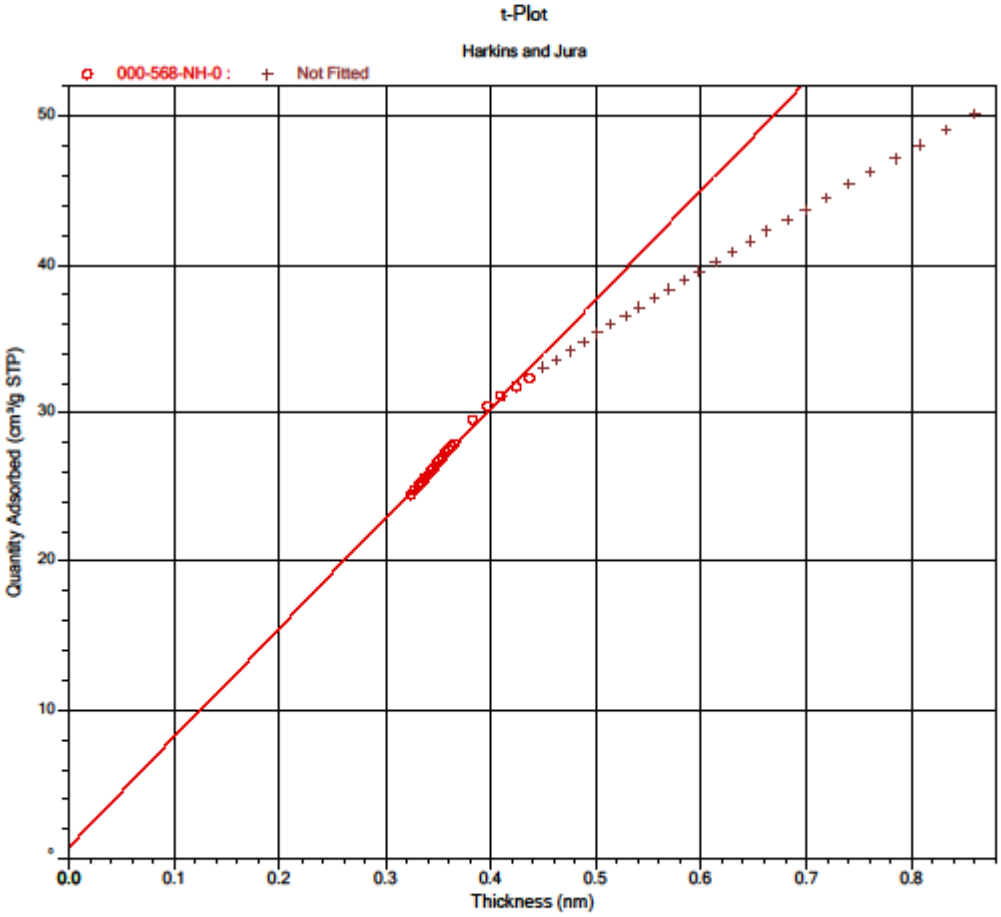
3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 2 | Page 12 of 18

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\ArbonaJ...\000-568-NH-0.SMP

Started:	1/27/2020 4:42:28 PM	Analysis adsorptive:	N2
Completed:	1/28/2020 2:00:13 AM	Analysis bath temp.:	77.258 K
Report time:	2/4/2020 10:51:08 AM	Thermal correction:	Yes
Sample mass:	0.0379 g	Warm free space:	21.3546 cm³ Measured
Cold free space:	64.0011 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63



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3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 2 | Page 15 of 18

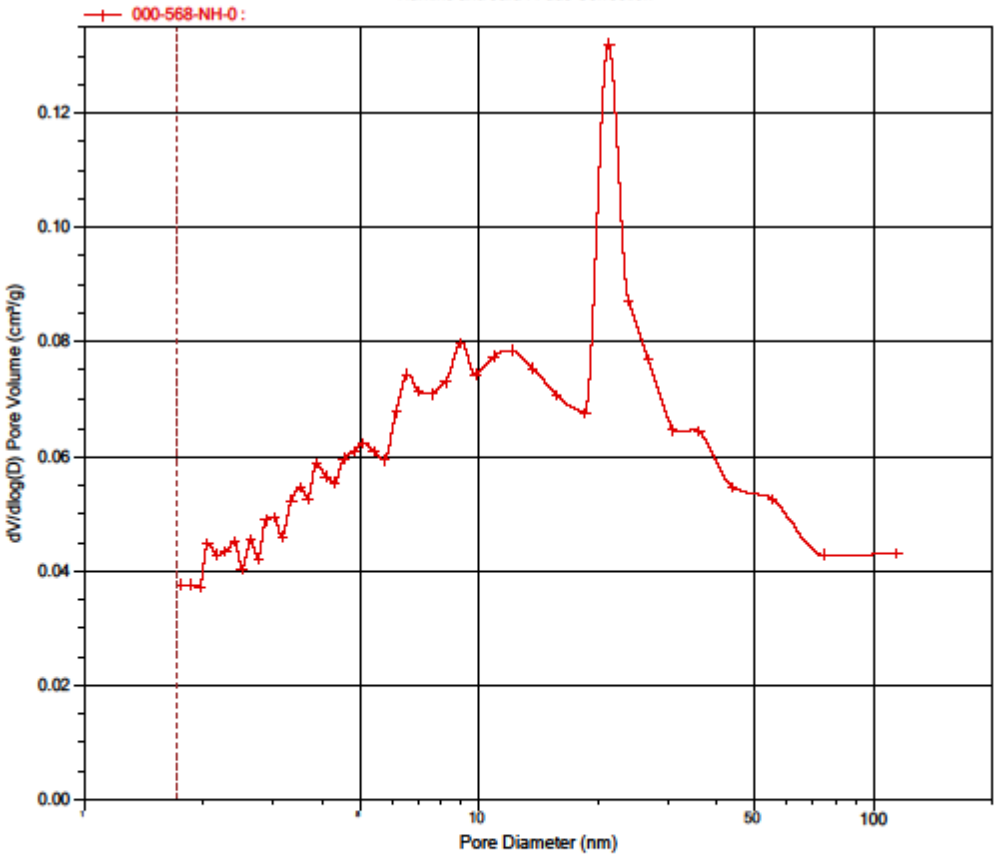
Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\ArbonaJ...\000-568-NH-0.SMP

Started:	1/27/2020 4:42:28 PM	Analysis adsorptive:	N2
Completed:	1/28/2020 2:00:13 AM	Analysis bath temp.:	77.258 K
Report time:	2/4/2020 10:51:08 AM	Thermal correction:	Yes
Sample mass:	0.0379 g	Warm free space:	21.3546 cm³ Measured
Cold free space:	64.0011 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63

BJH Adsorption dV/dlog(D) Pore Volume

Harkins and Jura : Faas Correction



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3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 2 | Page 18 of 18

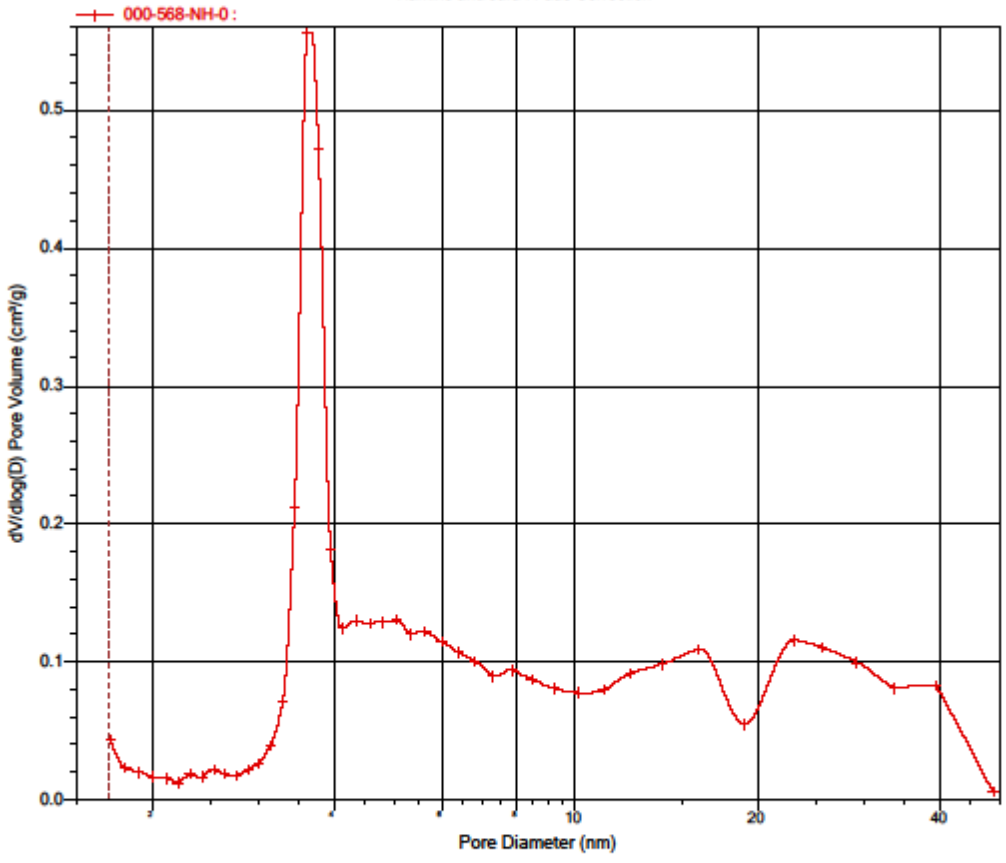
Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\ArbonaJ...\000-568-NH-0.SMP

Started:	1/27/2020 4:42:28 PM	Analysis adsorptive:	N2
Completed:	1/28/2020 2:00:13 AM	Analysis bath temp.:	77.258 K
Report time:	2/4/2020 10:51:08 AM	Thermal correction:	Yes
Sample mass:	0.0379 g	Warm free space:	21.3546 cm³ Measured
Cold free space:	64.0011 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63

BJH Desorption dV/dlog(D) Pore Volume

Harkins and Jura : Faas Correction



Appendix 4: BET result. Filters with MOFs. Amina group modification

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3Flex 4.02 — 3Flex Version 4.02 — Page 1 of 17
Serial # 826 Unit 1 Port 3

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\Arbo...\000-567-COOCl-0.SMP

Started:	2/3/2020 3:24:01 PM	Analysis adsorptive:	N2
Completed:	2/3/2020 11:20:19 PM	Analysis bath temp.:	77.080 K
Report time:	2/4/2020 10:51:06 AM	Thermal correction:	Yes
Sample mass:	0.0694 g	Warm free space:	21.2723 cm³ Measured
Cold free space:	64.4103 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63

Summary Report

Surface Area

Single point surface area at P/Po = 0.139670484:	89.6595 m²/g
BET Surface Area:	94.3015 m²/g
t-Plot Micropore Area:	11.0202 m²/g
t-Plot external surface area:	83.2813 m²/g
BJH Adsorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter:	49.1415 m²/g
BJH Desorption cumulative surface area of pores between 1.7000 nm and 300.0000 nm diameter:	66.1151 m²/g

Pore Volume

Single point adsorption total pore volume of pores less than 168.4635 nm diameter at P/Po = 0.988492540:	0.123878 cm³/g
Single point desorption total pore volume of pores less than 168.4635 nm diameter at P/Po = 0.988492540:	0.123878 cm³/g
t-Plot micropore volume:	0.003811 cm³/g
BJH Adsorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter:	0.102406 cm³/g
BJH Desorption cumulative volume of pores between 1.7000 nm and 300.0000 nm diameter:	0.109798 cm³/g

Pore Size

Adsorption average pore diameter (4V/A by BET):	5.2545 nm
Desorption average pore diameter (4V/A by BET):	5.2545 nm
BJH Adsorption average pore diameter (4V/A):	8.3356 nm
BJH Desorption average pore diameter (4V/A):	6.6429 nm

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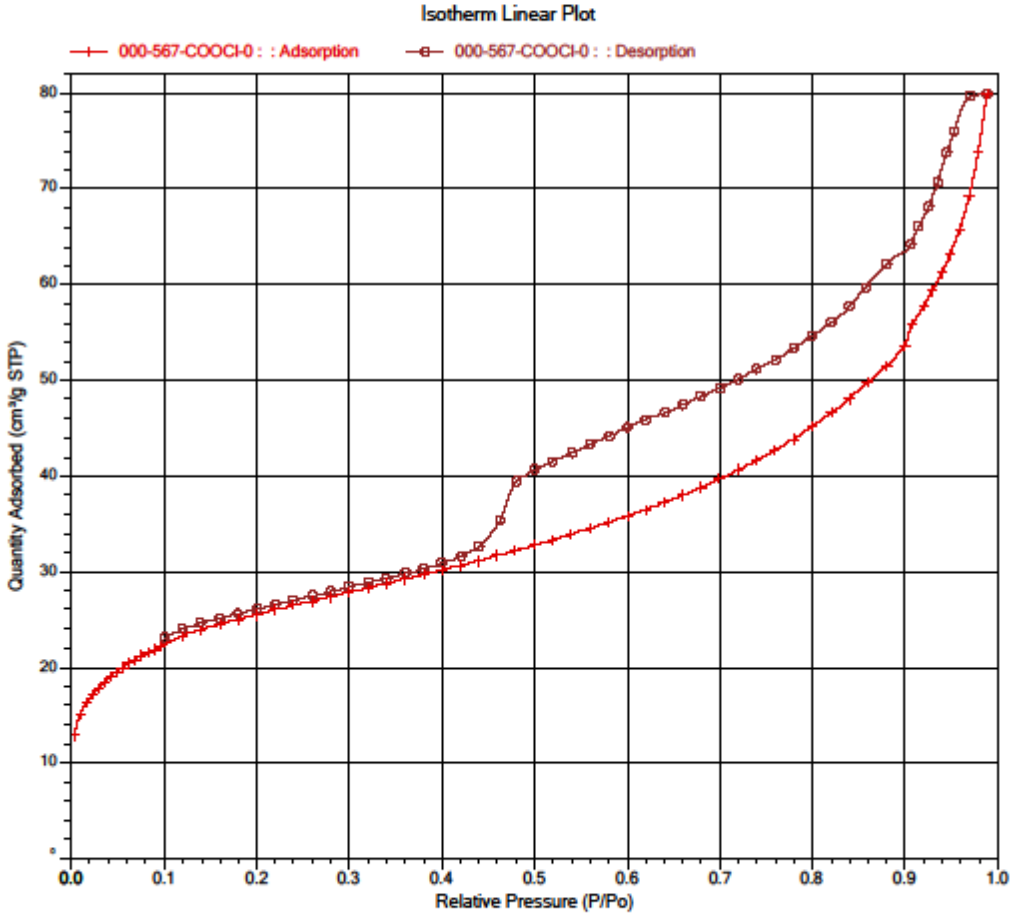
3Flex 4.02 | 3Flex Version 4.02 | Page 5 of 17

Serial # 826 Unit 1 Port 3

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEvelina\Arbo...\000-567-COOCl-0.SMP

Started:	2/3/2020 3:24:01 PM	Analysis adsorptive:	N2
Completed:	2/3/2020 11:20:19 PM	Analysis bath temp.:	77.080 K
Report time:	2/4/2020 10:51:06 AM	Thermal correction:	Yes
Sample mass:	0.0694 g	Warm free space:	21.2723 cm³ Measured
Cold free space:	64.4103 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63



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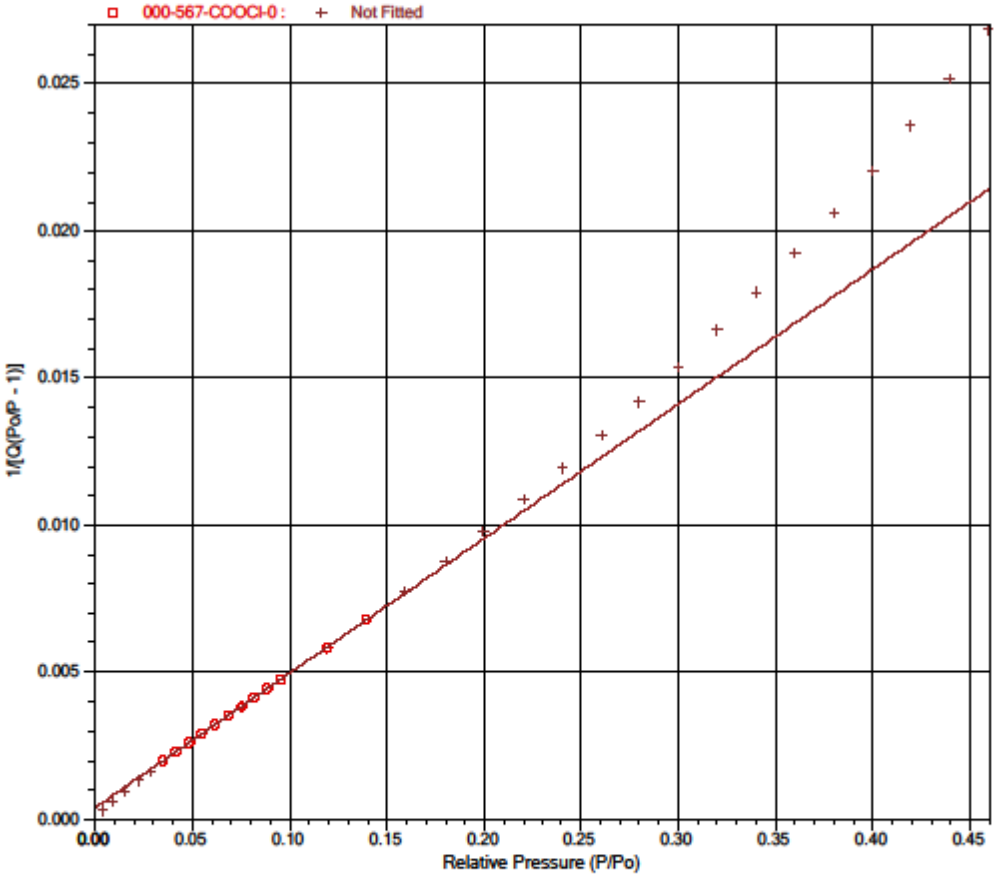
3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 3 | Page 7 of 17

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\Arbo...\000-567-COOCl-0.SMP

Started:	2/3/2020 3:24:01 PM	Analysis adsorptive:	N2
Completed:	2/3/2020 11:20:19 PM	Analysis bath temp.:	77.080 K
Report time:	2/4/2020 10:51:06 AM	Thermal correction:	Yes
Sample mass:	0.0694 g	Warm free space:	21.2723 cm³ Measured
Cold free space:	64.4103 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63

BET Surface Area Plot



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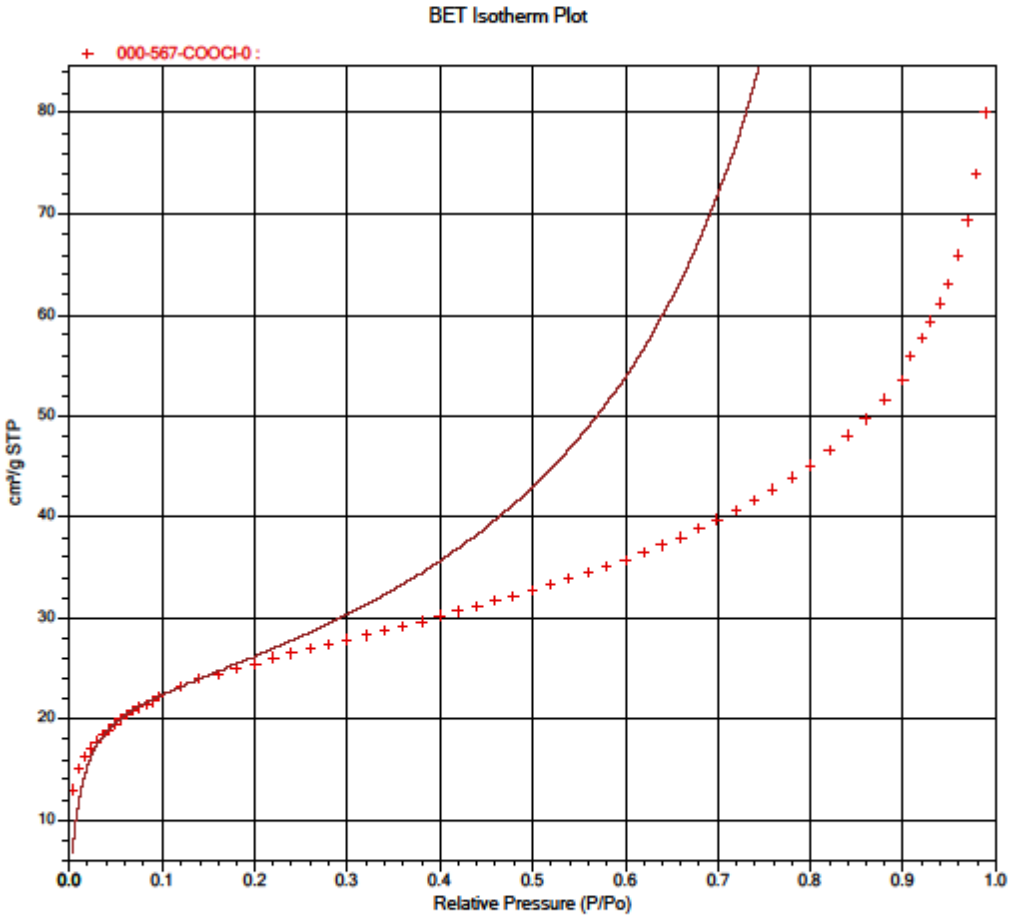
3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 3 | Page 8 of 17

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\Arbo...\000-567-COOCl-0.SMP

Started:	2/3/2020 3:24:01 PM	Analysis adsorptive:	N2
Completed:	2/3/2020 11:20:19 PM	Analysis bath temp.:	77.080 K
Report time:	2/4/2020 10:51:06 AM	Thermal correction:	Yes
Sample mass:	0.0694 g	Warm free space:	21.2723 cm³ Measured
Cold free space:	64.4103 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63



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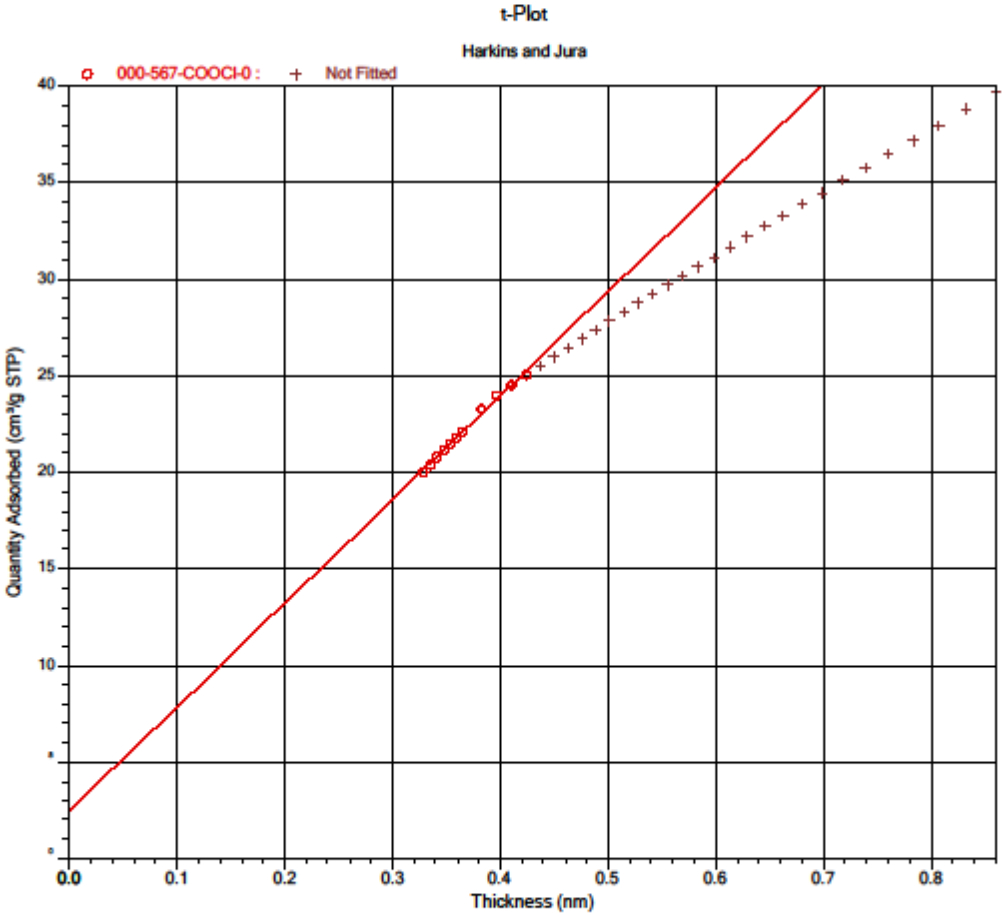
3Flex 4.02 | 3Flex Version 4.02 Serial # 826 Unit 1 Port 3 | Page 11 of 17

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\Arbo...\000-567-COOCl-0.SMP

Started:	2/3/2020 3:24:01 PM	Analysis adsorptive:	N2
Completed:	2/3/2020 11:20:19 PM	Analysis bath temp.:	77.080 K
Report time:	2/4/2020 10:51:06 AM	Thermal correction:	Yes
Sample mass:	0.0694 g	Warm free space:	21.2723 cm³ Measured
Cold free space:	64.4103 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63



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3Flex 4.02 | 3Flex Version 4.02 | Page 14 of 17

Serial # 826 Unit 1 Port 3

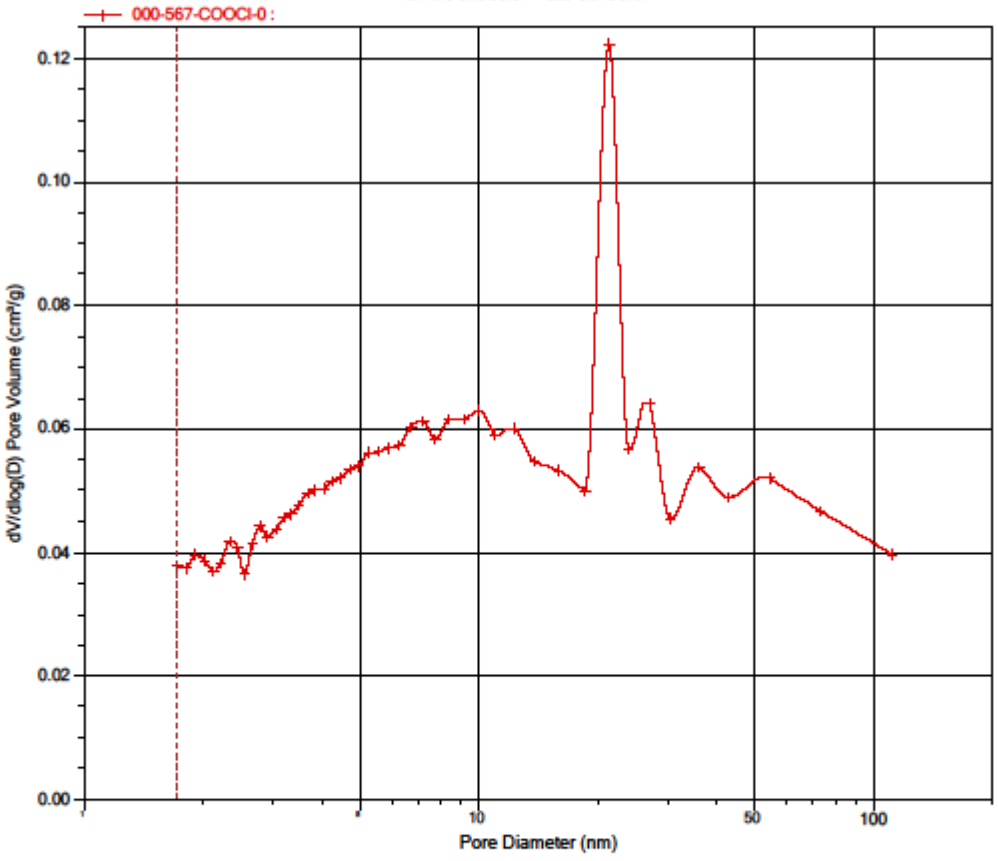
Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\Arbo...\000-567-COOCl-0.SMP

Started:	2/3/2020 3:24:01 PM	Analysis adsorptive:	N2
Completed:	2/3/2020 11:20:19 PM	Analysis bath temp.:	77.080 K
Report time:	2/4/2020 10:51:06 AM	Thermal correction:	Yes
Sample mass:	0.0694 g	Warm free space:	21.2723 cm³ Measured
Cold free space:	64.4103 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63

BJH Adsorption dV/dlog(D) Pore Volume

Harkins and Jura : Faas Correction



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3Flex 4.02 | 3Flex Version 4.02 | Page 17 of 17

Serial # 826 Unit 1 Port 3

Sample:
Operator:
Submitter:
File: C:\3Flex\data\RepoEveliina\Arbo...\000-567-COOCl-0.SMP

Started:	2/3/2020 3:24:01 PM	Analysis adsorptive:	N2
Completed:	2/3/2020 11:20:19 PM	Analysis bath temp.:	77.080 K
Report time:	2/4/2020 10:51:06 AM	Thermal correction:	Yes
Sample mass:	0.0694 g	Warm free space:	21.2723 cm³ Measured
Cold free space:	64.4103 cm³	Equilibration interval:	5 to 20 s
Low pressure dose:	10.0000 cm³/g STP	Sample density:	1.000 g/cm³
Automatic degas:	No		

Comments: SiAl LOT: A-501-63

BJH Desorption dV/dlog(D) Pore Volume

Harkins and Jura : Faas Correction