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**Efficiency of stone fiber adsorbent as a material
for wastewater depollution**

**Eficiencia de la lana de roca como adsorbente
para descontaminación de aguas residuales**

**Eficiencia da lá de rocha como adsorbente para
descontaminación de augas residuais**

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Summary

Large scale aromatic hydrocarbons (AHs) production and consumption, and their widespread use in various industrial areas makes it important to protect environment against the adverse effects of these substances. Particular attention should be paid to the problem of wastewater pollution by benzene and other small aromatic derivatives.

In this End of Master Degree Thesis we carried out the preparation of aqueous emulsions of benzene and performed the adsorption and extraction processes. As a result we assessed the efficiency of stone - fibrous sorbent as a material for wastewater purification.

To characterize the fibrous material we used the following techniques: Scanning electron microscopy (SEM), Thermogravimetric analysis (TGA), Differential thermal analysis (DTA), Infrared Fourier Transform Spectroscopy (FTIR), X-rays fluorescence (XRF). To determine the adsorption capacity of the fibers we used Spectrofluorimetry.

The stone-fiber showed a good capacity as adsorbents for benzene and related molecules..

Keywords: wastewater, benzene, stone-fyber, adsorbtion, Fluorescence microscopy.

Resumen

La producción y el consumo a gran escala de hidrocarburos aromáticos (AHs) y su uso extensivo en diversas áreas industriales hace que sea importante proteger el medio ambiente contra los efectos adversos de estas sustancias. Debe prestarse particular atención al problema de la contaminación de aguas por benceno y otras moléculas aromáticas de pequeño tamaño.

En esta Tesis de Fin de Máster hemos llevado a cabo la preparación de emulsiones acuosas de benceno y realizado la adsorción y los procesos de extracción. Como resultado, hemos contrastado la eficacia de un adsorbente de lana de roca como material para la purificación de aguas residuales.

Para caracterizar el material fibroso hemos usado las siguientes técnicas: microscopía de barrido electrónico (SEM), análisis termogravimétrico (TGA), análisis térmico diferencial (DTA), espectroscopía infrarroja por transformada de Fourier (FTIR), fluorescencia de rayos X (XRF). Para determinar la capacidad de adsorción de las fibras se empleó la espectrofluorimetría.

La fibra de roca empleada mostró una buena capacidad como adsorbente para benceno y moléculas relacionadas.

Palabras clave: aguas residuales, benceno, fibra de roca, adsorción, fluorescencia y microscopía.

Resumo

A produción e o consumo a gran escala de hidrocarburos aromáticos (AHs) e o seu uso extensivo en diversas áreas industriais fai que sexa importante protexer o medio ambiente contra os efectos adversos destas sustancias. Debe prestarse particular atención ao problema da polución de augas por benceno e outras moléculas aromáticas de pequeno tamaño.

Nesta Teses de Fin de Mestrado temos levado a cabo a preparación de emulsións acuosas de benceno e realizado a adsorción e os procesos de extracción. Como resultado, temos contrastado a eficacia dun adsorbente de lá de rocha como material para a purificación de augas residuais.

Para caracterizar o material fibroso temos usado as seguintes técnicas: microscopía de barrido electrónico (SEM), análise termogravimétrico (TGA), análise térmico diferencial (DTA), espectroscopía infravermella por transformada de Fourier (FTIR), fluorescencia de raios X (XRF). Para determinar a capacidade de adsorción das fibras empregouse a espectrofluorimetría.

A fibra de rocha empregada amosou unha boa capacidade como adsorbente para benceno e moléculas relacionadas.

Palabras clave: augas residuais, benceno, fibra de rocha, adsorción, fluorescencia e microscopía.

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Chapter 1. Introduction

Wastewaters of chemical, petrochemical and non-chemical industries that are consumers of different chemical products are characterized by their complex and variable composition. Usually, these waters are highly toxic, containing both dissolved and suspended contaminants. Particular attention should be paid to the issue of wastewater pollution by aromatic hydrocarbons, including small rings and also aromatic polycyclic hydrocarbons (PAHs).

In this End-of-Masterwork, we discuss the specific issue of wastewater contamination by typical representatives of aromatic hydrocarbons – benzene.

The following wastewater systems may contain benzene: hydrogenation residual waters, purification residual waters, water from oil platforms, water from pyrolysis units, water from catalysis units, units of bitume, lubricants and additives production, ethylbenzene dehydrogenation, gas fractionation units. The amount of these compounds varies in the range 20-5000 mg/L.¹

The toxic effects of benzene on human and biota are known. Benzene or its metabolites cause both structural and numerical chromosome aberrations in humans and laboratory animals. It is known that benzene produces a number of adverse health effects. The most frequently reported health effect of benzene is bone marrow depression leading to aplastic anaemia. At high levels of exposure a high incidence of these diseases is probable. Benzene is a well-established human carcinogen. Epidemiological studies of benzene-exposed workers have demonstrated a relationship between benzene exposure and the production of leukaemia.²

Based on the mentioned above, there is a clear need for restrictions on the content of aromatic hydrocarbons in water, and to find suitable processes for its abatement.

Chapter 2. Objectives

The main objectives of this work are:

- To review the methods used for wastewater purification from AHs.
- Preparation of aqueous emulsions of benzene. Performance of adsorption and extraction processes.
- Determination of the adsorption capacity of a fibrous material with respect to benzene.
- Assessment of efficiency of stone - fibrous sorbent as a material for wastewater purification.

Chapter 3. The state-of-the-art

Wastewater treatment to eliminate / reduce the presence of aromatic hydrocarbons is mandatory both for production processes using / making these compounds and for the use / reuse of water contaminated with these compounds. Choosing an appropriate treatment method of should be taking into account physicochemical properties of aromatic hydrocarbons.

The content of aromatic hydrocarbons in water largely depends on their solubility. The possibility of forming stable emulsions and suspensions, which increases the concentration of aromatic hydrocarbons in water must be taken into account. This phenomenon may be due to the fact that a good solvent such as benzene may dissolve a number of other compounds present in the medium. For example, in sewage plants the concentration of phenol and acetone in benzene may be 3.5 times greater than their corresponding water solubility.³

Aromatic hydrocarbons tend to become very volatile in hot water with stirring, a common process in water treatment plants. This is strongly related to the evaporation of light fractions, which can take place in outdoor treatment pools with surface aeration or water purge forming large air bubbles.⁴

Considering all the facts mentioned above, a complex approach needs to be applied for water purification of water masses containing aromatic hydrocarbons. There are several methods which can be applied for treatment / purification of water containing emulsified, suspended and dissolved aromatic hydrocarbons. These methods can be divided into destructive and regenerative.

- **Destructive methods** of treatment are used in case of technical or economical impossibility of removal of the impurities. These methods, used for purification of water from aromatic hydrocarbons include the firing method, ozonation, liquid-phase oxidation, and biological treatment.
 - **Firing method:** in this kind of treatment, pulverized wastewater is introduced into the high temperature (900-1000 ° C) zone of an organic fuel in

combustion. Thus, water is completely evaporated, the toxic organic substances are thermally oxidized with oxygen in the furnace atmosphere to form non-toxic combustion products. Mineral impurities are trapped into the solid or molten particles in the working chamber and are removed from it in a melt form or mixed with the flue gases.⁵

The disadvantage of this method is the high fuel consumption and overheating of the steam up to 900 - 1000 °C. In this regard, the use of fire sewage disposal method would be appropriate for: i) a small amount of wastewater containing toxic organic contaminants, specially if extraction and neutralization by other methods is not possible or is economically less beneficial; ii) the extraction of dissolved mineral impurities; iii) in the case of combustible industrial waste (e.g.: residual discharge gases) that can be used as fuel.⁶

All the benzene series hydrocarbons are burned during the destruction of waste water free from mineral impurities. This method is efficiently used only at high concentrations of organic substances in waste water solutions (at least 4%).³

- **Ozonation:** ozone has a high oxidizing power ($\text{O}_{3(g)} + \text{H}_2\text{O}_{(l)} + 2 e^- \longrightarrow \text{O}_{2(g)} + 2 \text{OH}^-_{(aq)}$, $E^\circ = 1,24 \text{ V vs. NHE}$) under room temperature and pressure, and is able to oxidize many organic substances contained in water, including benzene, yielding glyoxal, glyoxylic acid, oxalic acid and other small molecules.⁶ Ozonation includes a pretreatment step in which atmospheric air is supplied to the ozone synthesizing equipment. Further, as a result of mixing ozone-air with the water to be treated diffusion of fine bubbles of ozone takes place directly in the water column. As a result, there active oxidizing impurities remain present in the water. The process ends with the disposal of the remaining mixture.⁷

The advantage of this method is its universality. The process of ozonation may simultaneously carry out impurities oxidation, discoloration, deodorization, disinfection of sewage and oxygen saturation. Limitations are due to its cost, complexity of technical implementation, the necessity to use sophisticated equipment and of materials which are resistant to ozone.⁷

- **Liquid-phase oxidation:** this is a process of oxidation of wastewater organic impurities by atmospheric oxygen at high temperature (typically up to 350 °C) and pressure (2 - 28 MPa), while water stays in liquid phase. At high pressures the solubility of oxygen in water is significantly increased, which helps accelerate the oxidation of organic substances. The efficiency of the oxidation process increases with increasing temperature.

Depending on the temperature and contact time, the oxidation of organic impurities occurs completely or partially (to carboxylic and dicarboxylic acids, or other intermediate products). Under the conditions of the process volatiles are oxidized basically in the gas-vapor phase, and non-volatile – in the liquid phase.⁶

Some advantages of this method are: i) the ability to clean a large volume of wastewater without pre-concentration, ii) the lack of harmful oxidation products of organic substances, iii) its ease of combination with other methods, iv) it provides a large level of safety at work. Some disadvantages are: i) the incomplete oxidation of certain chemical substances, ii) the considerable cost of installation equipment, and iii) the high corrosion levels reached in acidic environments.⁵

- **Biological treatment:** this is the most widely used treatment method for destruction of diluted aromatic hydrocarbons. The method is based on the ability of microorganisms to use substrate many organic and inorganic compounds contained in the wastewater as a nutrient. In biological

wastewater treatment processes, part of the oxidizable substances are used by the microorganisms in their biosynthesis processes and the other part is converted to harmless oxidation products: water, CO₂, etc.⁶

For example, biological treatment can be used to neutralize the water of pyrolysis plants containing benzene, toluene, xylenes and naphthalene, for degradation of benzene and its homologues, styrene and α -methyl styrene, naphthalene.³ In this regards, it is important to note that biological oxidation of aromatic hydrocarbons is significantly more complex than that of aliphatic hydrocarbons (they are much more difficult to oxidize).

The degradation of benzene by microorganisms is possible, but only after long-term adaptation. Benzene derivatives are generally characterized by a high degree of biodegradability. The presence of different functional groups increases the ease of the compounds to biological degradation in the following sequence: - CH₃, -OOSN₃, - CHO, - CH₂OH, -SNON.SOON, - CN, -NH₂, - OHCOOH, - SO₃H.⁶

The widespread use of biological treatment methods is due to its advantages: i) the ability to remove from the wastewater a variety of organic compounds, including toxic ones; ii) the simple hardware design; iii) the comparatively low operating costs. The disadvantages of the method should include: i) high capital costs, ii) the need for strict observance of technological cleaning regimes, iii) toxic effect on microorganisms of a number of organic and inorganic compounds, iv) the necessity of wastewater dilution in case of a high concentration of impurities.⁶

- **Regenerative methods:** the use of regenerative techniques for wastewater treatment arises not only because of the necessity to treat wastewater, but also to extract from it valuable impurities, which in some cases may be recycled in the production, which makes the cleaning process more cost-effective and

sustainable. These methods include: adsorption, coagulation, flotation, extraction, azeotropic distillation and rectification.

- **Adsorption:** this is one of the most effective methods of wastewater treatment from aromatic compounds, which allows water treatment of harmful substances.⁶ The method is based on the physical or chemical interaction between molecules and solid surfaces (surface phenomena). Coarse-grained, fine and superfine activated carbons are used as adsorbents due to their high ability to adsorb hydrophobic compounds such as aliphatic and aromatic hydrocarbons, their halogen - and other nitro compounds and hydrophilic compounds. Adsorption of soluble organic pollutants by activated carbon is, in general, highly effective.⁶ This kind of treatment can be performed by regenerative (extraction from the adsorbent materials followed by disposal) or destructive ways (extraction of substance from the adsorbent and its destruction with the adsorbent).

Advantages of the method are: i) the ability to do the adsorption of substances from multicomponent mixtures; ii) its high efficiency, especially at low concentration waste water treatment. From a technical - economic point of view, the adsorption is very efficient for the extraction of valuable products for use / reuse in the production cycle.⁶

- **Coagulation:** this method is used for the purification of emulsions and suspensions from wastewater, including colloids of particle size 0.001-0.1 mm. These particles have electric charge which arises due to absorption of ions from the aqueous solution. The charge does not allow the colloidal particles to agglomerate and thus increase the stability of the colloidal solution. Therefore, addition of a coagulant to the colloidal solution (aluminum salts, iron, magnesium), reduce electric charge of colloidal particles, so that they rapidly coalesce into large particles settle to the bottom of cleaning facilities.⁴

Coagulation process is carried out by passing the wastewater through the electrolytic cell with the anode made of aluminum or iron. Under a constant electric current the necessary coagulants (aluminum or iron hydroxides) are formed.

- **Flotation:** this process allows removal of complex mixtures of aromatic hydrocarbons (oil) from wastewater of coke production. Wastewater treatment by flotation is carried out by removing undissolved impurities using air bubbles finely dispersed into the wastewater. The method is based on the formation of "particle - air bubble" aggregates, floating them and removing the formed foam layer from the liquid surface. Formation of "particle-bubble" aggregates is favoured by a decrease of surface energy of the floated particles and air bubbles in the boundary layers. The bubbles are formed by mechanical crushing of the air, due to the vacuum or air pressure from supersaturated solutions in water, or by electroflotation. The formed aggregates of impurities particles and air bubbles have a lower density than the floatable particles, so that they float and accumulate in the upper layer of water, from where they can be removed by means of special devices.⁴

Extraction: this method is widely used for wastewater treatment of organic impurities. The use of the method is conditioned to the case of a significant concentration of organic impurities or to the high cost of the recoverable material. Extraction is based on the distribution of the extracted component is a mixture of two mutually insoluble liquids in accordance to their relative solubility. After the distribution equilibrium is established, which is characterized by the law of the equilibrium distribution, expressed in terms of the distribution ratio $R_d = (C_e / C_w)$, where C_e and C_w are the concentrations of the component in the extractant and in water, respectively.⁵

Wastewater extraction consists of three stages. The first stage is the intensive mixing of waste water with extractant. The development of the contact

surface between the liquid forms two liquid phases. The second step is the separation of the extract. The third step is the regeneration of the extractant.

To reduce the content of dissolved contaminants to concentrations below the limit, it is necessary to choose the appropriate extractant and the waste water feed rate.⁸

This method is used for extraction of styrene, ethylbenzene, naphthalene, and polycyclic aromatic hydrocarbons. As a solvents are used limitedly water-soluble petroleum ether, various fractions of gasoline, as well as the absorption and diesel oil (in the coking industry).³

The advantages of extraction processes include: i) the favourable kinetics of the process, ii) the possibility of use high initial concentrations of the extracted component. The use of this method is restricted by i) high cost of organic extracting agents, ii) the possibility of contamination of already treated wastewater, and iii) inefficiency at low concentrations of impurities.⁵

- **Azeotropic distillation:** based on the ability of some organic compounds to form with each other, or with water, inseparably boiling mixtures, having boiling temperature below the boiling point of water. The ability of benzene and its homologues form with water azeotropic mixtures allows to completely remove these hydrocarbons by water distillation. This type of distillation is conducted in a packed column, in the lower part of which water vapor is supplied. The condensate of the organic substance is separated from of the water condensate, and the water after separation from aromatic hydrocarbon is recycled.³
- **Rectification:** this method is used to separate waste water from many organic impurities (benzene, chlorobenzene, butyl acetate, etc.). The essence of the distillation is the separation of liquid mixtures by repeated mass exchange between the vapor and liquid phases moving counter-current to each

other. The process takes place in a column-type apparatus. Driving down liquid is enriched with high boiling compounds, and vapor moving up is enriched by low-boiling ones.⁵

The specificity of the azeotropic distillation and rectification is related with the relatively small concentrations of impurities and the needing for their almost complete separation from the wastewater.

Chapter 4. Materials and Methods

4.1. Preparation of aqueous emulsions of benzene by dispersing

4.1.1 Reagents

- Benzene, C₆H₆, 99+%, A.C.S., spectrophotometric grade, Sigma-Aldrich[®]
- Distilled water

4.1.2. Equipment and materials

- Magnetic stirrer
- 20 conical flasks with ground glass stopper with a capacity of 100 ml
- Volumetric glass
- Micropipettes with capacity of 10-100 µl, 100-1000 µl, 500-5000µl
- Stone – fiber, TERMOLIFE[®]
- Weigher with an accuracy of 0.01 g
- Time clock

4.1.3. Experimental procedure

The flasks are poured into 100 ml of distilled water (measured by volumetric glass) and the required exact amount of the organic liquid (benzene, toluene or a mixture thereof) using a micropipette. Emulsions have varying aromatic content:

1 series: in each flask respectively add the exact amount of benzene or toluene, 0.2; 0.4; 0.6; 0.8; 1.0 ml.

2 series: in each flask respectively add the exact amount of benzene or toluene, 0.02; 0.04; 0.06; 0.08; 0.1 ml.

3 series: in each flask respectively add the exact amount of benzene or toluene, 2.0; 4.0; 6.0; 8.0; 10.0 ml.

Prepared emulsions are stirred 20 minutes (image 3.1 a). After stirring time 0.50 g of the weighed fiber is placed in each flask and vigorously shaken about 2 minutes. Then allowed to stand about 24 hours to achieve the adsorption equilibrium (image 3.1 b).



(a)



(b)

Picture 4.1. a) Emulsions stirring. b) Prepared emulsions with stone- fiber.

4.2 Extraction of benzene

4.2.1. Reagents

- Prepared series of emulsions
- n-Hexane, C_6H_{14} , Panreac[®]

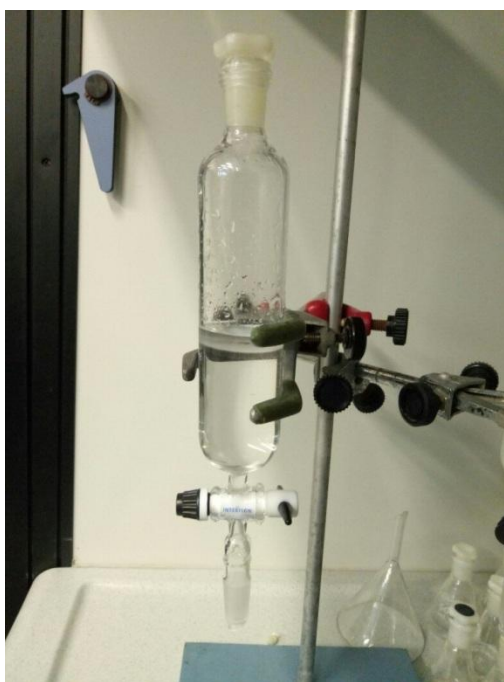
4.2.2 Equipment and materials

- Paper filters
- Tapered funnel for filtering
- Separation funnel 100 - 150 ml
- Micropipette with capacity 500-5000 μ l
- 20 conical flasks with ground glass stopper with a capacity of 50 ml

4.2.3 Experimental procedure

After the adsorption time liquid carefully poured into the conical flask of 100 ml and stoppered. If the fluid contains particles of fiber, it is filtered into a conical flask through a filter paper moistened with water. The first portions of filtrates (5 - 10 ml) are discarded, as the concentration of aromatic hydrocarbons (AH) can be lowered due to the adsorption on filter paper.

By pipette taking exactly 50 ml of the filtrate, transferring to a separatory funnel, hexane is added, stoppered and shaken vigorously for 2 minutes. Extraction of benzene and mixture of benzene and toluene is performed with hexane by 3 operations, adding each time 6 ml of hexane. After each extraction step the mixture in a separating funnel is left to rest until separation of the organic and aqueous phases (picture 3.2). After separation the aqueous mixture (the bottom) layer is decanted into another separatory funnel for the next extraction operation, and the remaining organic layer is carefully transferred through filter paper into a dry flask (50 ml).



Picture 4.2. Separation funnel (the upper layer – hexane, the bottom layer – solution)

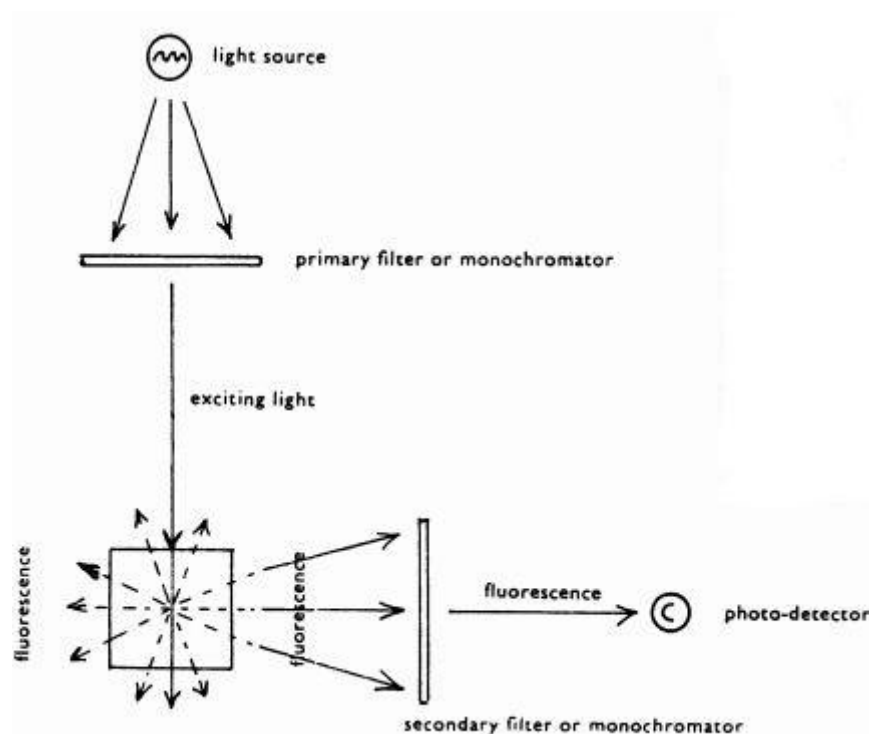
After the last extraction operation the filter paper is washed with 5 ml of pure hexane. The extract in the flask should be transparent, not to contain water. The flask stoppered.

The obtained hexane extracts are numbered and transmitted to fluorimetric analysis for determining the number of aromatic hydrocarbons therein.

4.3 Determination of the concentration of aromatic hydrocarbons in the filtrate using fluorimetry analysis

Fluorescence is a highly sensitive analytical tool which can be used to measure concentrations as low as 10^{-8} to 10^{-10} g./ml. (0.01 to 0.0001 $\mu\text{g./ml.}$)¹⁰

Fluorimetry analysis is performed by Luminescence Spectrometer Aminco Bowman®.



Picture 4.3.1 A simplified outline of a fluorimeter¹⁰

When light strikes an organic molecule in the ground state, it absorbs radiation of certain specific wavelengths to jump to an excited state. A part of the absorbed energy is lost on vibration relaxation. Eventually the molecule returns to the ground state while emitting a kind of optical energy, which is called “fluorescence”. Fluorescence continues for a period of 10^{-8} to 10^{-9} sec in most cases.

As mentioned above, a part of the radiation absorbed by a substance is lost as vibration energy, therefore, the fluorescence emitted from the substance has a longer wavelength than the excitation radiation (Stokes’ law).

The ratio of the optical energy absorbed by a substance to the total fluorescence energy emitted from the substance is called “quantum efficiency”. It can generally be said that the larger the quantum efficiency a substance has, the more fluorescence it emits.

Table I - Fluorescence of benzene¹⁰

	Excitation λ_{\max} , mμ	Fluorescence λ_{\max} , mμ	Relative intensity
Benzene	269	291	1

4.4 Characteristics of stone-fiber

4.4.1 Scanning electron microscopy (SEM)

When an electron beam falls on the surface of a solid take place several phenomena: a reissue of the incident radiation, light emission, secondary electrons and Auger, X-rays, etc. All these signals can be used to obtain information on the nature of the sample (morphology, composition, crystal structure, electronic structure, etc.). In fact, the drive equipment permits the analysis of secondary electrons, backscattered electrons and X-rays characteristic.¹¹

The technique consists mainly of sending an electron beam on the sample and by an appropriate detector register the result of this interaction. The beam moves on the show performing a scan in the X and Y directions, so that the position in which the beam is at every moment coincides with the appearance of brightness in proportion to the signal emitted, at a certain point on the screen.¹¹

X-rays are generated in a sample subjected to bombardment address can identify the elements present and establish their concentration. When a sufficiently rapid electron beam falls on the surface of a solid, there is the ionization of atoms present, the loss of internal electrons. In this state of an electron outermost layer jumps immediately to cover deficit, and fill the gap produced. This change involves a release of energy, which is equal to the difference between the energies he had every electron in its orbital correspondent.¹¹

This energy manifests itself in two ways: Auger electrons or X-rays and is unique for each item. When it is the intensity of electromagnetic radiation outside his energy is obtained a spectrum of X-ray-constituted by a series of peaks,

designated as lines of varying intensity, which is called X-ray characteristic - that is superimposed on a continuous background lower intensity (continuous X-rays).¹¹

The SEM was carried out by equipment Microscopia SXAIN.

4.4.2 Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA)

Thermogravimetry (TG) is based on the measurement of the mass change of a sample when the sample is subjected to a temperature program in a controlled atmosphere. This mass variation may be a mass loss or a mass gain.¹²

Thermogravimetry is being used coupled to DTA technique.

Differential thermal analysis (DTA). The stone fiber and an inert reference are undergo identical thermal cycles. Any temperature difference between sample and reference is recorded. In this technique the heat flow to the sample and reference remain the same rather than the temperature.

The results were obtained by Analizador ATG-ATD, TA SDT2960 (N/I 35890), Unidade de Espectroscopia Molecular, SAI.¹³

4.4.3 X-rays fluorescence

Technique: Wave Length Scatter X-Ray Fluorescence Spectrometry (WDXRF)

Equipment: S4 Pioneer (Bruker-AXS)

Measurement conditions: semi-quantitative in helium atmosphere. The samples are introduced into a suitable vessel and an ultra-fine polymer is used as the primary radiation input window. In this case it is a polypropylene polymer "Prolene" (manufacturer: Chemplex Industries, Inc.) with a thickness of 4 μm .

The X-ray fluorescence technique provides an accurate method of determining the chemical composition of materials. The operating principle is to sample a stream of high-energy photons (X-rays) and analyze the spectrum of secondary photon energy emitted by the sample.

The bombardment of atoms with photons of high enough energy causes the electrons in the inner orbits of the atoms to escape to the exterior and the photoelectric effect occurs.

The basis of this FRX technique in the "wavelength dispersion" mode is to use a series of analyzer crystals that allow the separation of different lines that compose an X-ray spectrum according to the wavelength.

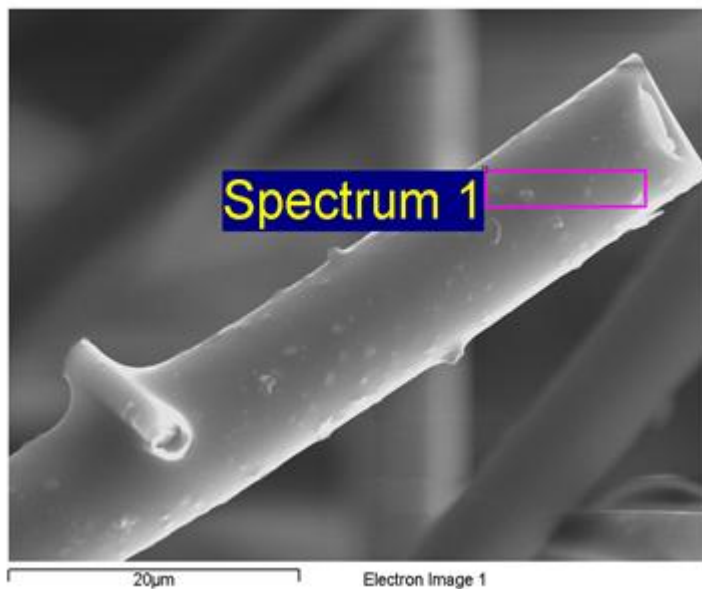
After X-ray diffraction is produced in analyzer crystals, the X-ray detectors (scintillator and proportional fluxes) collect all the photons emitted by sample and analyze the respective intensities for each wavelength.

Thus, since the analyzed radiation is characteristic of the atoms present in the sample, the chemical composition of the test sample can be determined.¹⁴

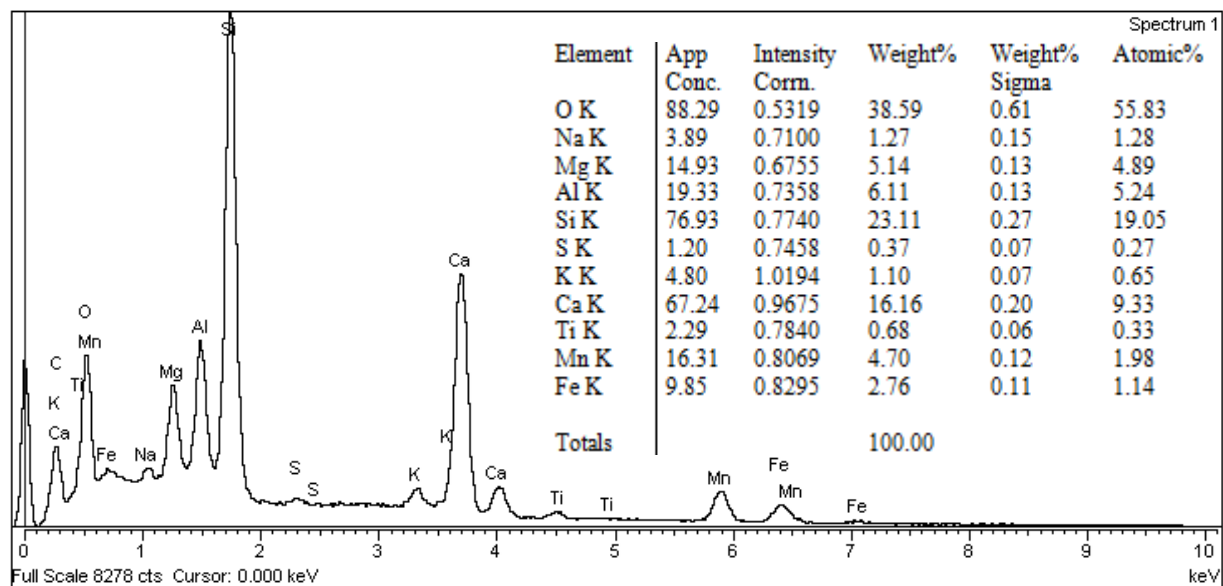
Chapter 5. Results and discussions

5.1. Scanning electron microscopy (SEM)

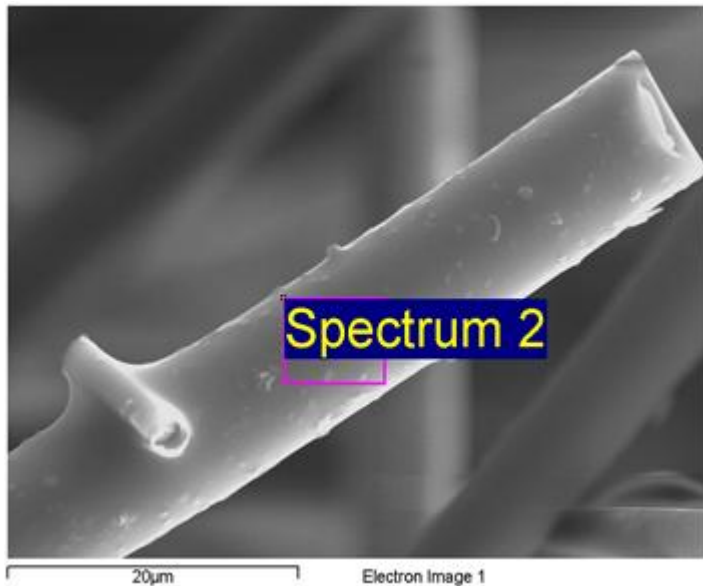
As a result of SEM were obtained 2D images (pic.5.1.1, 5.1.3, 5.1.5, 5.1.7). Also it is represented the UV spectrum of the individual parts of the fiber (pic. 5.1.2, 5.1.4, 5.1.6). From obtained results we can discuss about the size, shape and qualitative composition.



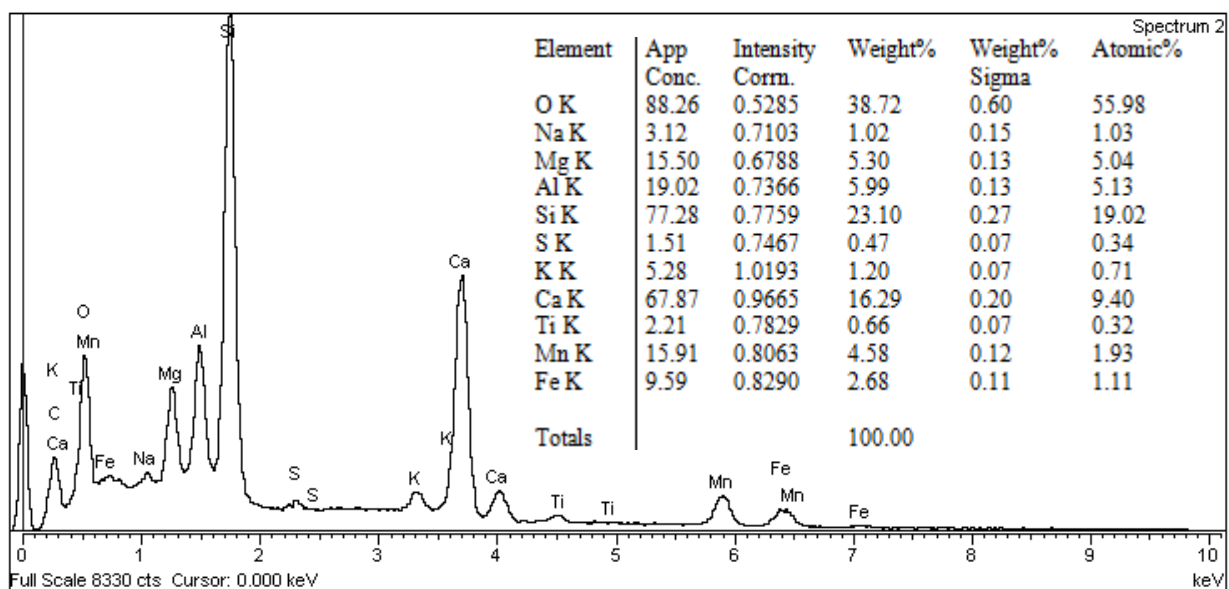
Picture 5.1.1 – Electron scanning microscopy image 1



Picture 5.1.2 - UV spectrum 1



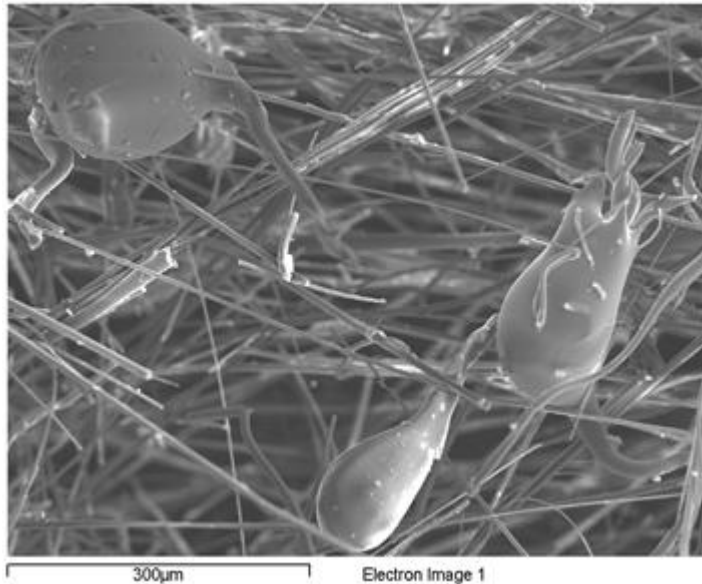
Picture 5.1.3 – Electron scanning microscopy image 2



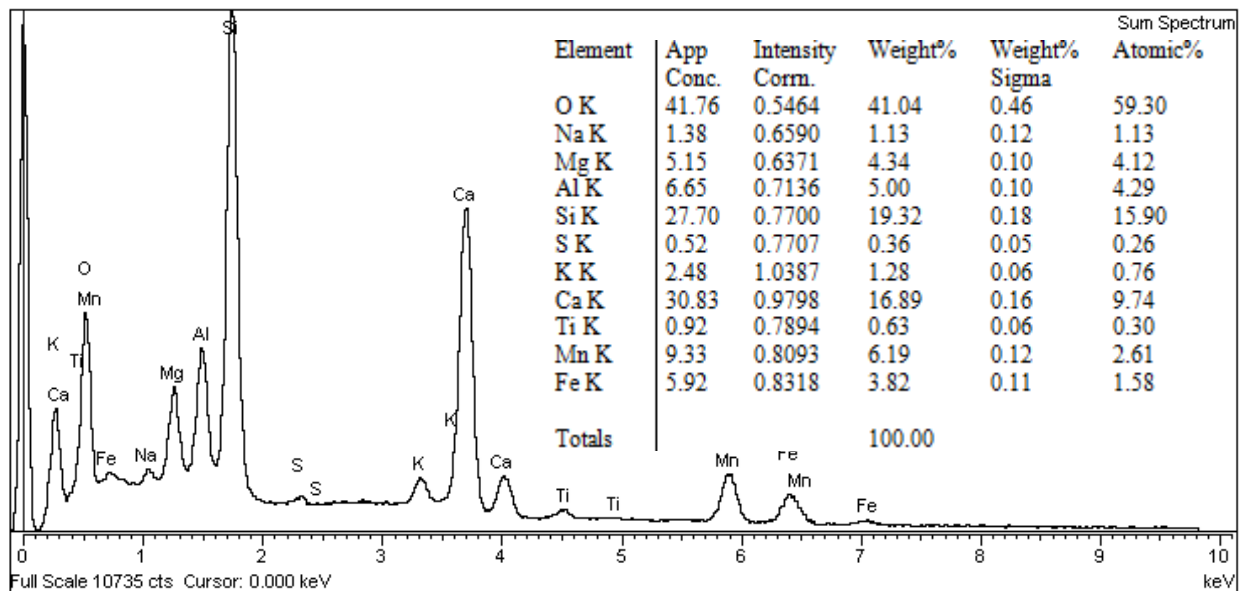
Picture 5.1.4 - UV spectrum 2

At pic. 5.1.1 and 4.1.2 we can observe that the surface of material is mostly homogeneous. The diameter of the fibers that compose the adsorbent material used in this work is about 11 μm . Considering the edge it can be assumed that the fiber is hollow. Therefore the surface area increases a lot, which can considerably affect the absorption capacity of the fiber.

UV spectrums (pic. 4.1.2, 4.1.4) show that the dominant components of fiber are: O $\approx 38,72\%$; Si $\approx 23,11\%$; Ca $\approx 16,29\%$.



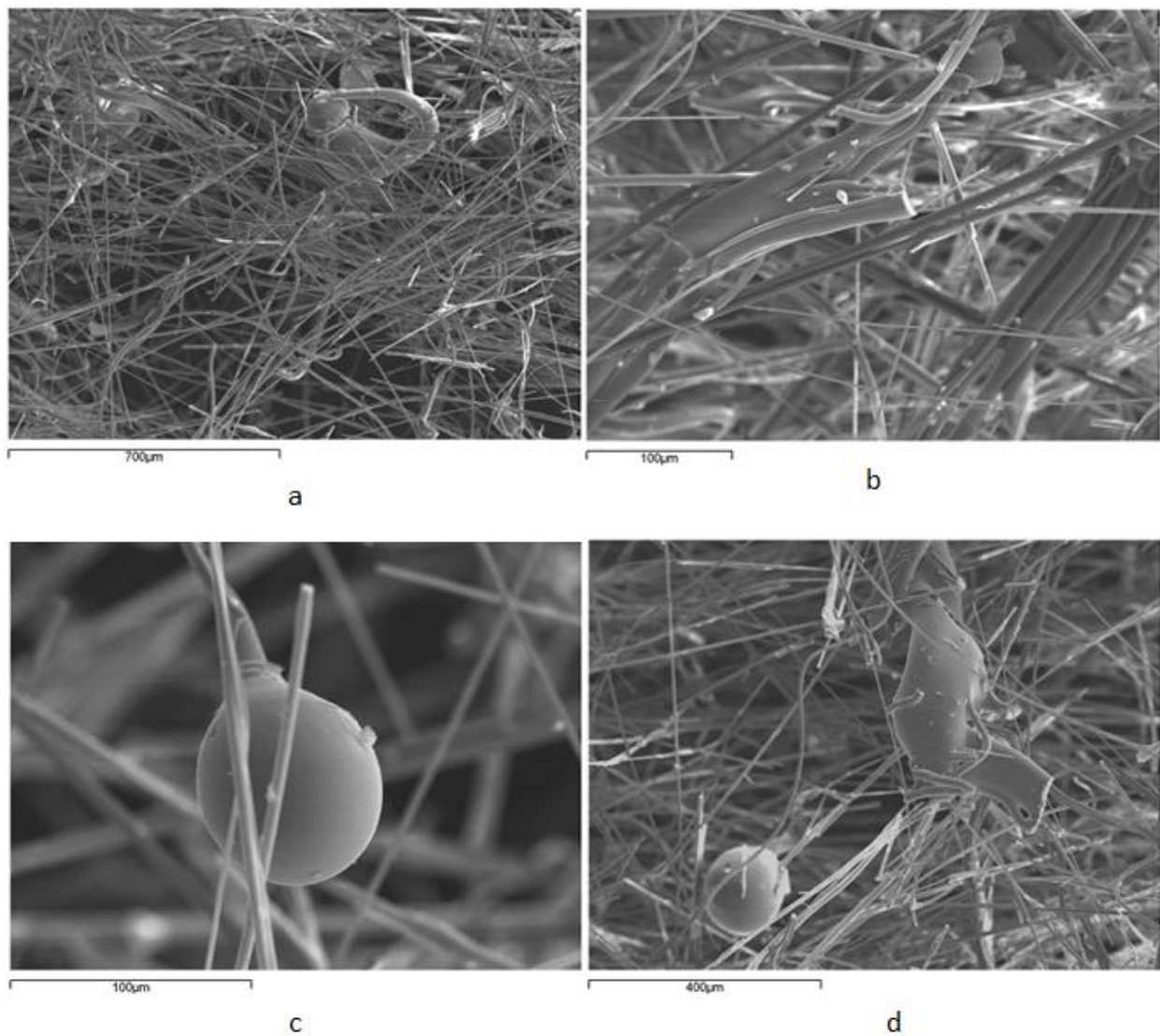
Picture 5.1.5 – Electron scanning image 3



Picture 5.1.6 - UV spectrum 3

Picture 5.1.5 shows the material presents conglomerates of different sizes and shapes, probably produced during cooling after synthesis. The length varies within 200-250µm, width varies within 80-160µm.

In comparison with the previous UV spectrum, conglomerates (pic.5.1.6) show insignificantly higher values of O and Ca (41.04 and 16.89 %), but lower values of Si (19.32%).



Picture 5.1.7 – Electron scanning microscopy images with different resolution

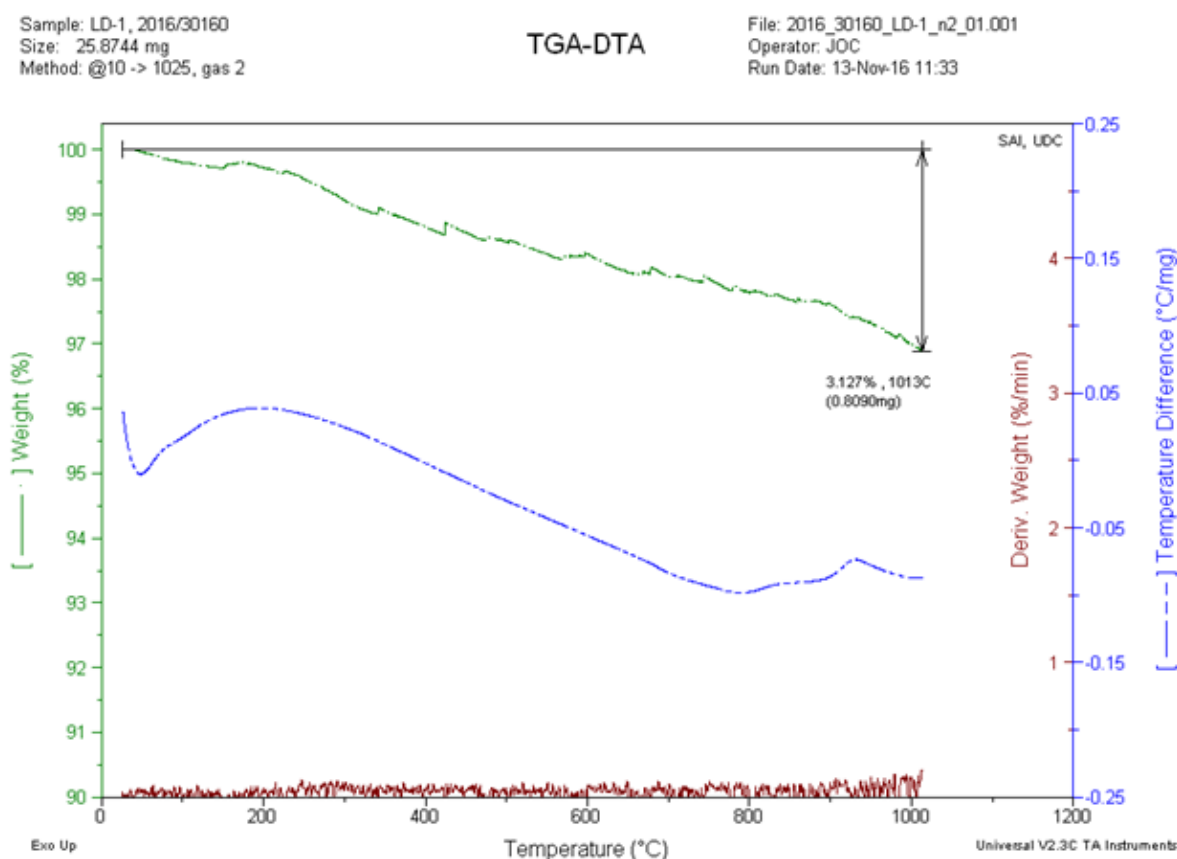
Image (a) allows to observe the mutual positions and the length of the fibers. Fibers are arranged randomly. The length is about 700 μm, but there is a presence of much shorter fragments, which is an indication of the fragility of the material. Small fragments are probably the result of breakage of longer fibers, and not of the synthesis itself.

Image (b) shows that the different fibers differ in their diameter. The widest fibers are as 2-5 or even bigger.

Images (c) and (d) give comparative view of fibers and conglomerations. The lasts have rounded and elongated shape.

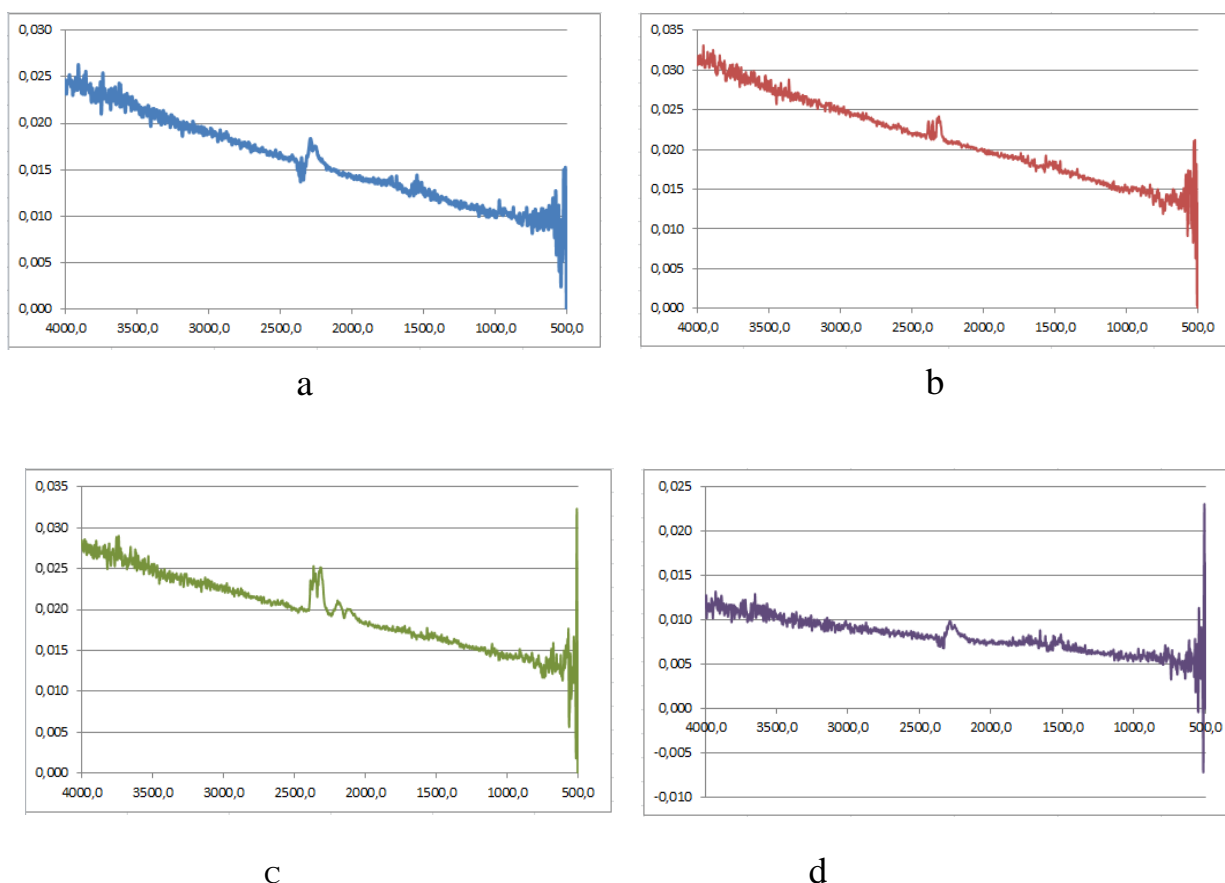
4.2 Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA)

TGA and DTA results represent how fiber acts under the influence of different temperatures in N₂ and air atmosphere.



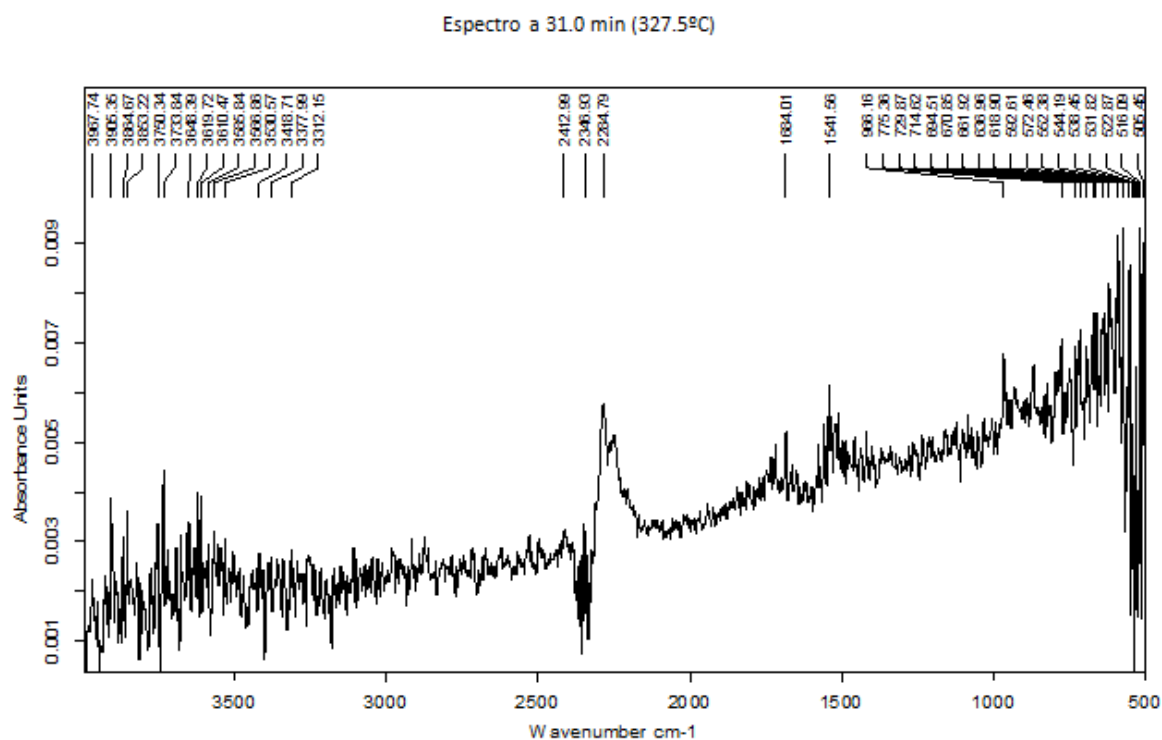
Picture 5.2.1 – Weight loss changes under N₂ atmosphere.

There is an obvious weight loss in going from 0 to 1000°C (pic.5.2.1). It represents (green line) ca. 3 % from the total mass or 0,8090 mg. The differential plot ($d(\% \text{weight})/d(T)$, red line) does not show any significant peak, which indicates a progressive loss of mass – 0.1-0.3 % for all the temperature interval. The temperature difference (blue line) shows evidence of water loss below 100 °C.

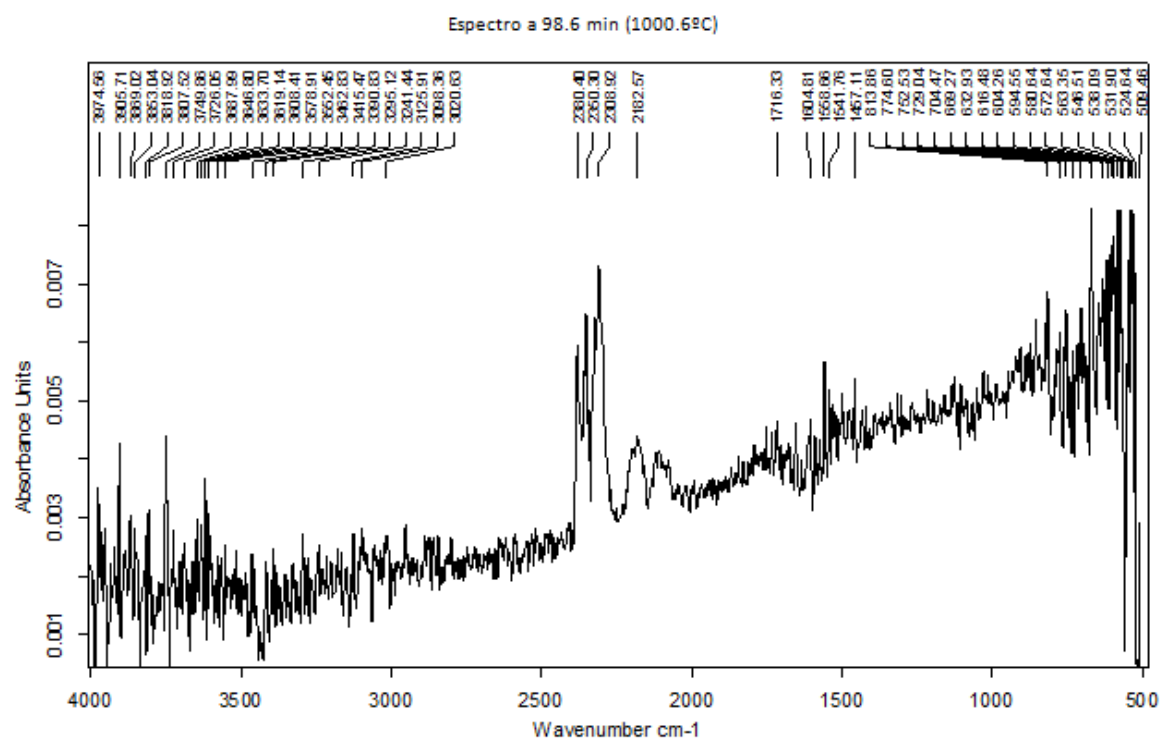


Picture 5.2.2. FTIR spectra: a - 31.0 min, 327.5°C; b - 84.2 min, 856.1°C; c - 98.6 min, 1000.6°C; d - 33.2 min, 394.4°C .

Pictures 5.2 (a, b, c, d) represent FTIR (Fourier Transform IR Spectroscopy) spectra of the fibrous material at different times moments and temperature values. For all four spectrums the characteristic temperatures peaks are observed at ca. 2500-2180 cm^{-1} , assigned to Si-H stretching vibrations. Around cm^{-1} and below appears the skeleton vibrations, without any relevant changes.

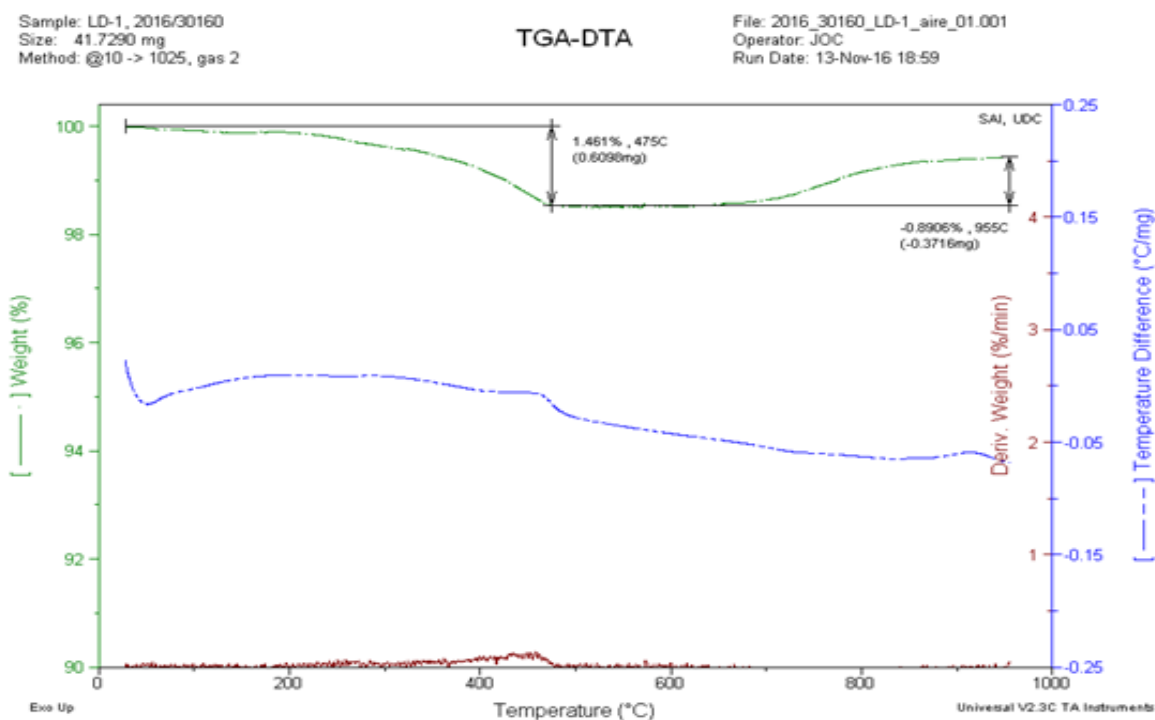


Picture 5.2.3 - Spectrum A



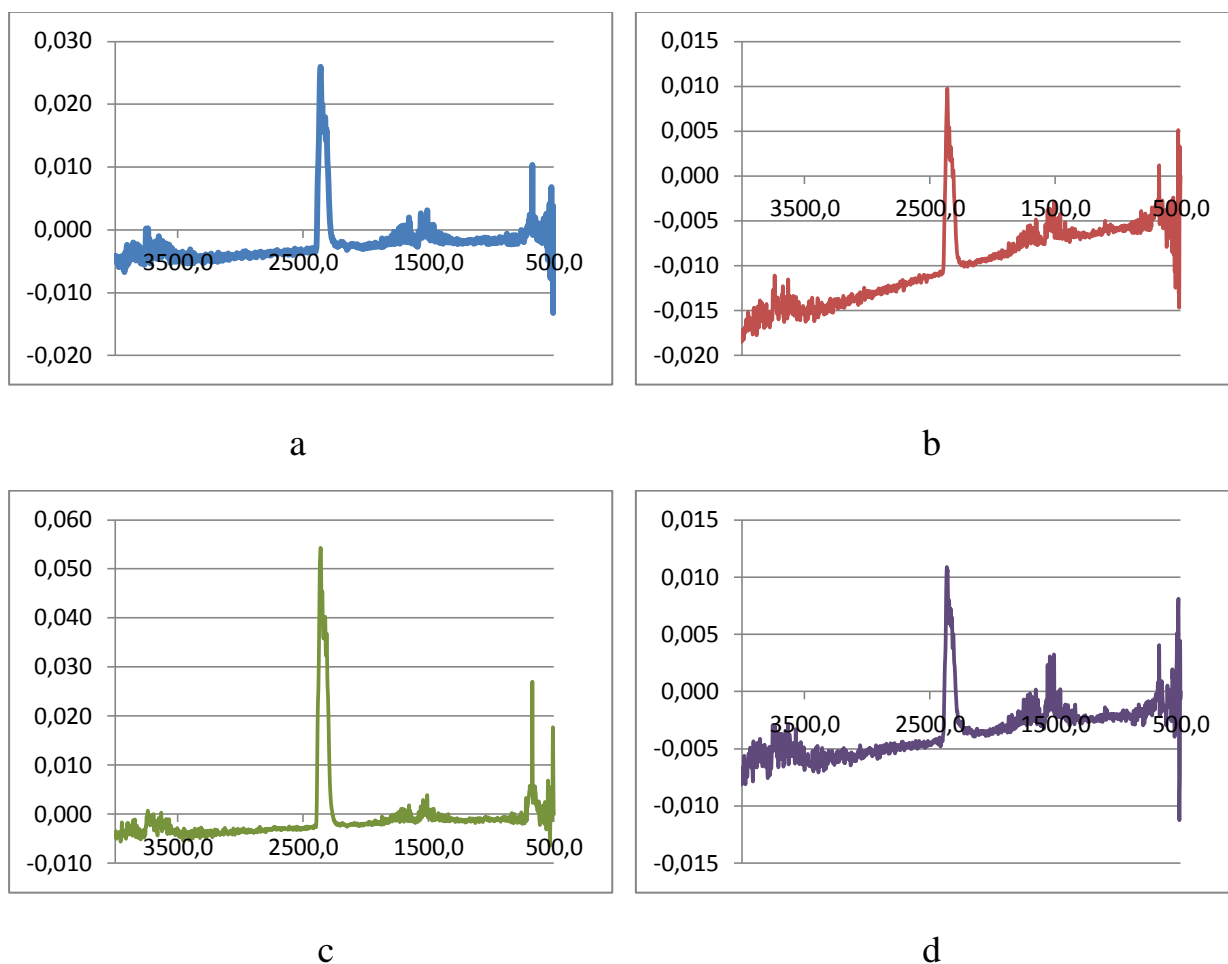
Picture 5.2.4 - Spectrum D

Pictures 5.2.3 and 5.2.4 show the most outstanding pics.



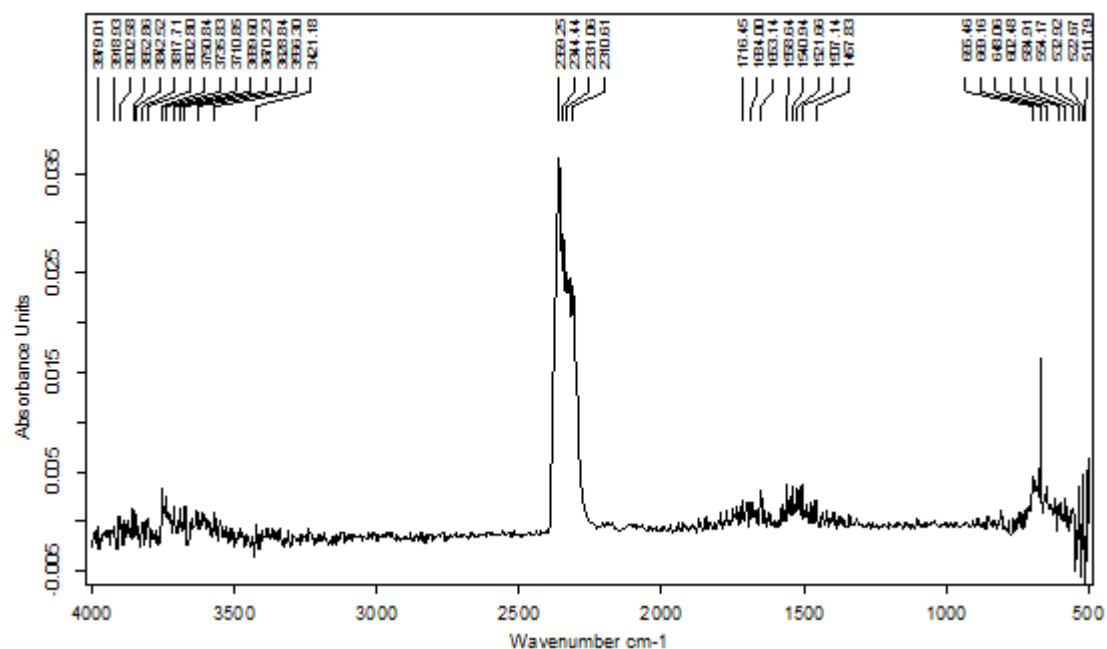
Picture 5.2.5 - Weight changes as a function of temperature (air atmosphere).

There is a weight loss from 200°C to 475°C. It represents ca. 1.451% of a total mass or 0.6098 mg. There is no mass changes in between 475°C - 680°C. The differential curve shows a peak in between 680°C to 955°C, that represents ca. 0.9 mg. Also there is a minor peak in the interval 350°C to 480°C ($\approx 0.2\%$). These peaks do not represent any significant mass loss. Again the data show a loss of water below 100 °C.

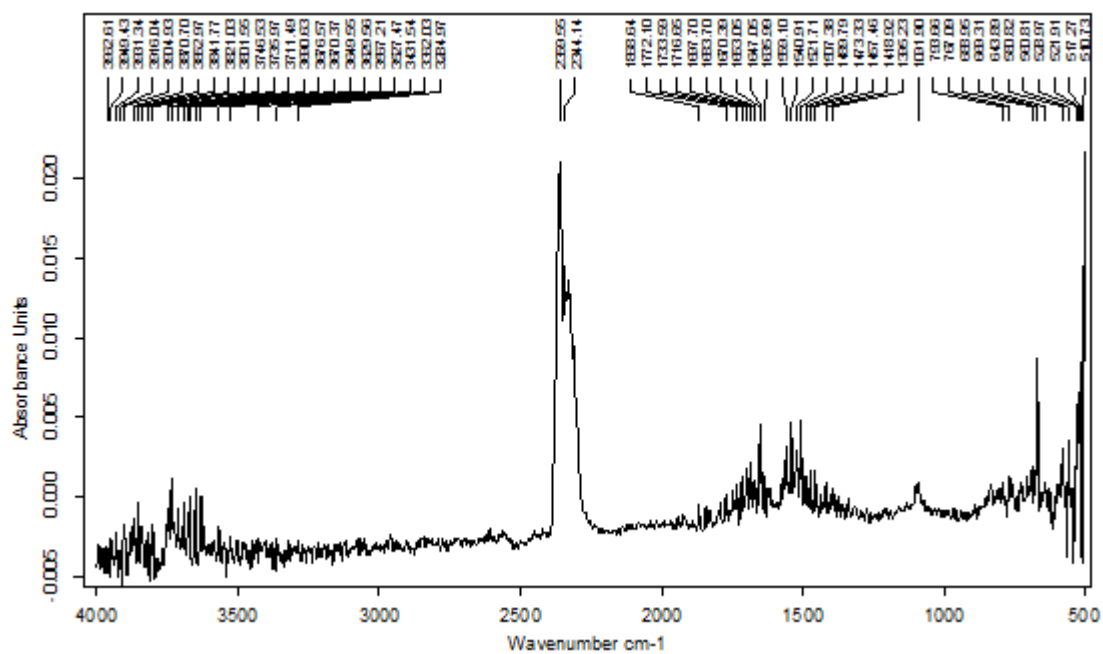


Picture 5.2.6 FTIR spectra: a - 40,9 min 427.7 °C; b - 64.2min 658.4 °C;
c - 96,4 min 954.9 °C; d - 33.1 min 350,4 °C.

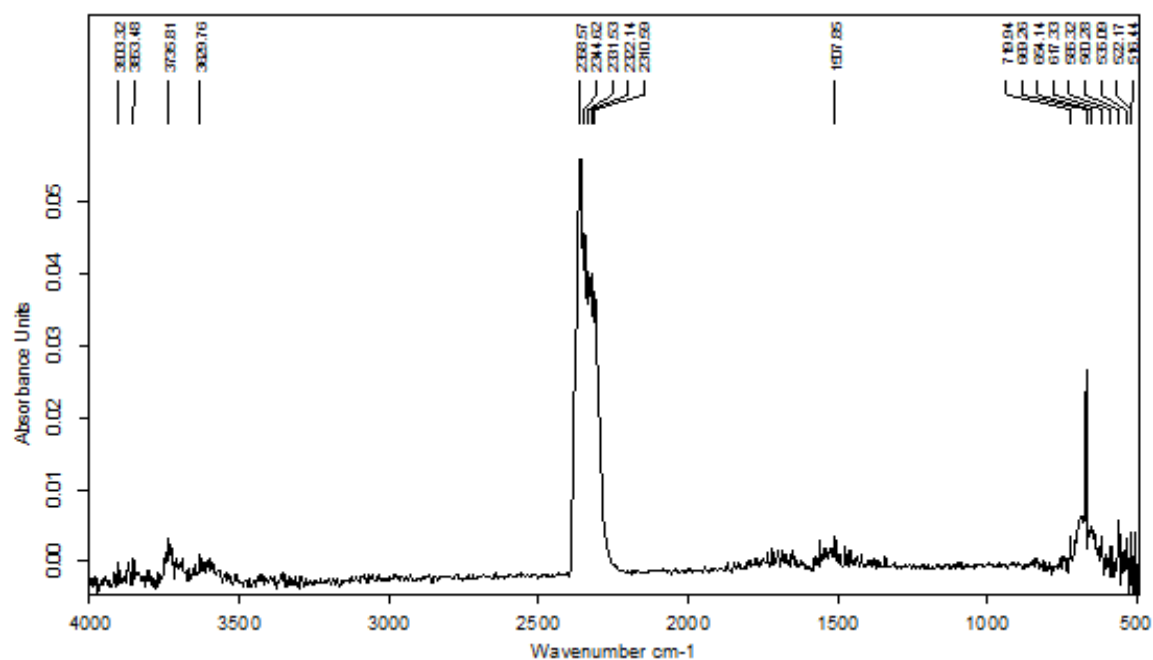
Pictures 5.2 (a, b, c, d) represent FTIR (Fourier Transform IR Spectroscopy) spectra of the fibrous material at different times moments and temperature values. For all four spectra the characteristic temperatures peaks are observed at ca. 2500-2180 cm^{-1} , assigned to Si-H stretching vibrations. No sign of Si-OH stretchings is observed around 3500 cm^{-1} . Below 1000 cm^{-1} the skeleton vibrations are observed, without any relevant changes. The observed lack of changes with temperature is an evidence for a strong stability of the fibrous material in the interval of temperatures studied.



Picture 5.2.8 - Spectrum 40.9 min (427.7°C)



Picture 5.2.9 - Spectrum 64.2 min (658.4°C)



Picture 5.2.10 - Spectrum 96.4 min (954.9°C)

5.3 X-rays fluorescence

Results from X-rays fluorescence are shown in table 5.3.

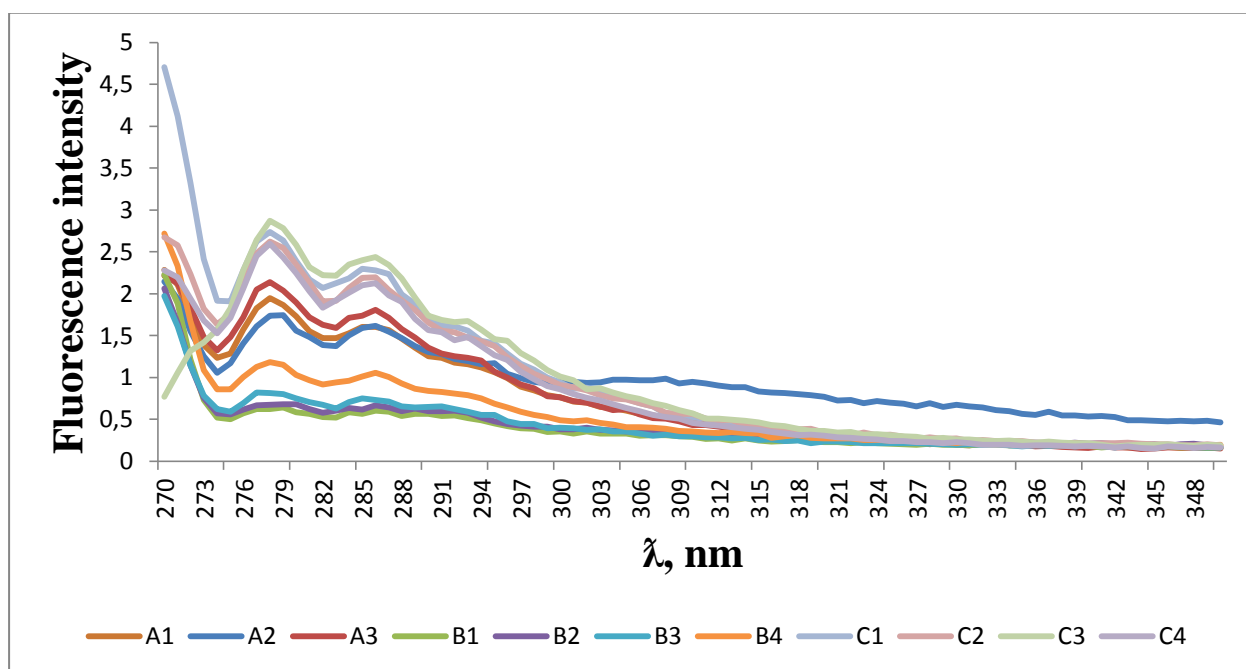
Table 5.3 – Composition of the adsorbent fibers. Results expressed as oxides.

Oxide	%
SiO ₂	34.5
CaO	22.6
Na ₂ O	10.7
Al ₂ O ₃	10.2
MgO	7.7
MnO	6.0
Fe ₂ O ₃	4.0
K ₂ O	1.5
TiO ₂	0.86
SO ₃	0.73
BaO	0.34
SrO	0.11
CuO	0.036

From the results, it becomes evident that the dominant compounds are SiO_2 , CaO , Na_2O and Al_2O_3 . The amounts of oxides that may show a semiconductor behavior are minimal, so the material is not expected to have photocatalyst properties.

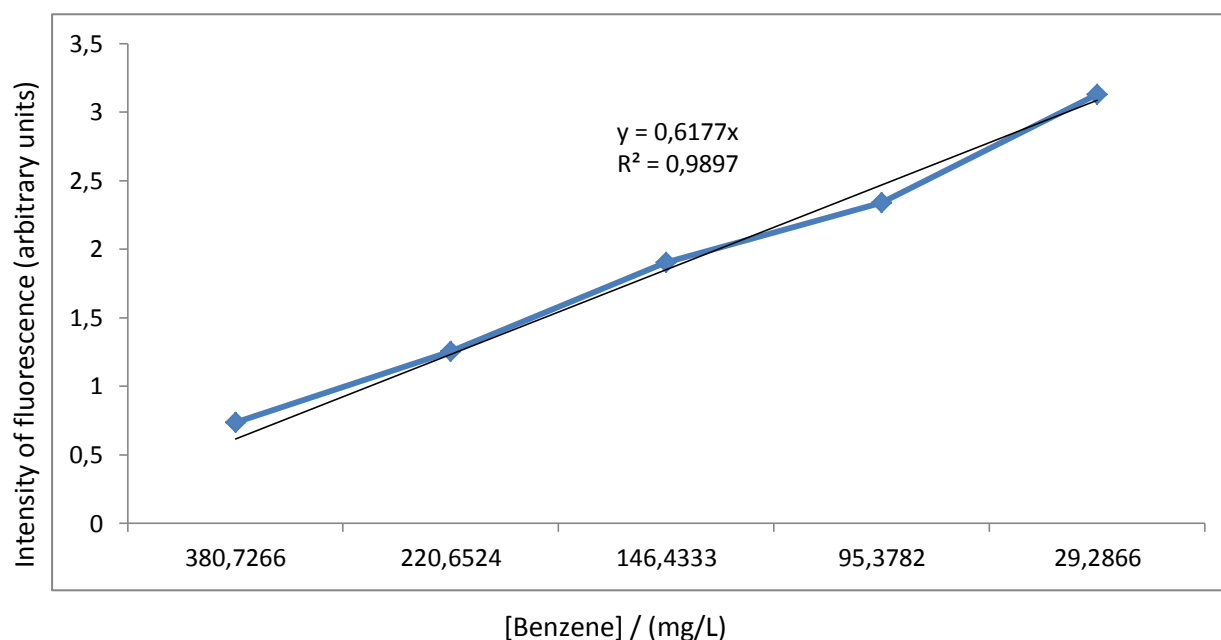
5.4 Fluorimetric analysis

As described previously in the experimental part, the benzene emulsions were extracted with hexane. Once this was done, though most of the extract was hexane, a small amount of benzene phase was observed. Possibly this may be due to the differential solubility of water in benzene and hexane, that induces phase separation. To overcome this difficulty, the heterogeneous mixture was emulsified for a fixed time by sonication and the fluorescence measured immediately after the process was finished. These emulsions of wet benzene into wet hexane lasted enough before coalescing, so there was no problem to measure the fluorescence spectra, that are shown in Fig. 5.4.1.



Picture 5.4.1 – Intensity of fluorescence emission of the benzene extracts.

Using a calibration done with samples of known concentration of benzene in n-hexane (Fig. 5.4.2), we could estimate the concentration of each of the extracts in Fig. 5.4.1. The obtained results are shown in Table 5.4.



Picture 5.4.2 – Calibration of intensity of fluorescence emission for samples of different concentration of benzene in n-hexane. Correlation: $I.F.=0.6177 \cdot [Benzene]$

Table 5.4: Concentrations of aromatic compound extracted from emulsions.

Sample name	[Benzene] ₀ / (g/L)	Fluorimetric intensity	[Benzene] / (g/L)	Absorption % (recovery)
A1	3,5144	1,6042	2,5970	26,11
A2	5,2716	1,5936	2,5798	51,06
A3	7,0288	1,7379	2,8135	59,97
B1	0,9125	2,2965	0,1757	80,74
B2	0,9935	2,1887	0,3514	64,63
B3	1,2128	2,3975	0,5271	56,54
B4	1,6373	2,1011	0,8786	46,34
C1	17,572	0,5637	3,7178	78,84
C2	35,144	0,6137	3,5433	89,92
C3	70,288	0,7492	3,8813	94,79
C4	87,86	1,0114	3,4014	96,13

The results of fluorimetric analysis show that stone-fiber has reasonable adsorption capacity. The recovery is higher than 50 % in all cases. Series A and C show an increasing recovery with increasing concentration, while series B is the opposite. We do not have a reasonable hypothesis to explain this at the moment. More experiments would be needed to check whether this behavior corresponds to a real trend or just to experimental errors.

In any case, with the observed recoveries, a short series of consecutive adsorption processes would be extremely effective to eliminate pollution by benzene or benzene-like derivatives.

Chapter 6. Conclusions

Conclusions.

This End of Master Degree Thesis attempted to characterize a stone-fiber material as potential adsorbent for aromatic organic compounds pollution, and investigated its adsorption capacity in relation to benzene. From the results obtained by using different techniques we derive the following conclusions:

- SEM analysis shows that the surface of material is mostly homogeneous with an average diameter of the fibers *ca.* 11 μm . Observations show the fiber is hollow, which considerably affects its absorption capacity. The material forms conglomerates of different sizes and shapes, probably during cooling after synthesis. The length varies within 200-250 μm , while width varies within 80-160 μm .
- TGA and DTA analysis showed that there is a slow and progressive loss of mass in going from 100 to 1000 $^{\circ}\text{C}$ (3 % from the total mass, *ca.* 0,81 mg) under N_2 atmosphere. In air atmosphere there is a weight loss on going from 200 $^{\circ}\text{C}$ to 475 $^{\circ}\text{C}$ (1 % of a total mass or 0.61 mg). In both cases the data show a loss of water below 100 $^{\circ}\text{C}$. FTIR analysis showed evidence for a strong stability of the fibrous material in the interval of temperatures from 350 $^{\circ}\text{C}$ to 955 $^{\circ}\text{C}$.
- X-rays fluorescence showed that the dominant compounds of stone fiber are SiO_2 , CaO , Na_2O and Al_2O_3 . The amounts of oxides that may show a semiconductor behavior are minimal, so the material is not expected to have photocatalyst properties.
- The results of fluorimetric analysis show that stone-fiber has a good adsorption capacity. The quantity of adsorbed benzene varies from 26% to 96%. More research would be needed to get deeper knowledge into the potential applicability of this fibers for waste- or residual water purification processes.

Conclusiones.

En este Trabajo de Fin de Máster se ha pretendido caracterizar un material compuesto de lana de roca como potencial adsorbente para polución por compuestos orgánicos aromáticos, así como investigar su capacidad de adsorción en relación con el benceno. De los resultados obtenidos empleando distintas técnicas, se pueden extraer las siguientes conclusiones:

- El análisis SEM muestra que la superficie del material es muy homogénea desde el punto de vista morfológico, con un diámetro promedio de las fibras de *ca.* 11 μm . Las observaciones muestran que las fibras son huecas, lo que afecta considerablemente a su capacidad de adsorción. El material forma conglomerados de distintos tamaños y formas, probablemente durante el proceso de enfriado tras la síntesis. La longitud de la fibras oscila entre 200-250 μm , y su ancho entre 80-160 μm .
- Los análisis TGA y DTA han mostrado una pérdida lenta y progresiva de masa durante el calentamiento de 100 to 1000 $^{\circ}\text{C}$ (3 % de la masa total, *ca.* 0,81 mg) en atmósfera de N_2 . En atmósfera de aire se observa una pérdida de masa durante el calentamiento de 200 $^{\circ}\text{C}$ a 475 $^{\circ}\text{C}$ (1 % de una masa total de 0.61 mg). En ambos casos los datos muestran una pérdida de agua por debajo de 100 $^{\circ}\text{C}$. El análisis FTIR ha mostrado evidencia de una fuerte estabilidad del material fibroso en el intervalo de temperatura de 350 a 955 $^{\circ}\text{C}$.
- La fluorescencia de RX ha mostrado que los compuestos dominantes en el material empleado son SiO_2 , CaO , Na_2O y Al_2O_3 . Las cantidades de óxidos que podrían mostrar un comportamiento como semiconductores son mínimas, por lo que no se espera que el material presente propiedades como fotocatalizador.
- Los resultados del análisis fluorimétrico muestran que el material empleado tiene una buena capacidad adsorbente. La cantidad de benceno adsorbido varía entre el 26% y el 96%. Se requiere más investigación para comprender mejor la posible aplicabilidad de este material en procesos de purificación de aguas residuales o contaminadas.

Conclusións.

Neste Traballo de Fin de Mestrado tentamos caracterizar un material composto de lá de rocha como potencial adsorbente para polución por compostos orgánicos aromáticos, así como investigar a súa capacidade de adsorción en relación co benceno. Dos resultados obtidos empregando distintas técnicas, pódense extraer as seguintes conclusións:

- O análise SEM amosa que a superficie do material é moi homoxénea dende o punto de vista morfolóxico, cun diámetro promedio das fibras de *ca.* 11 μm . As observacións amosan que as fibras son ocas, o que afecta considerablemente a súa capacidade de adsorción. O material forma conglomerados de distintos tamaños e formas, probablemente durante o proceso de enfriado tras a síntese. A lonxitude das fibras oscila entre 200-250 μm , e o seu ancho entre 80-160 μm .
- Os análises TGA e DTA amosaron unha perda lenta e progresiva de masa durante o quencemento de 100 a 1000 $^{\circ}\text{C}$ (3 % da masa total, *ca.* 0,81 mg) en atmósfera de N_2 . En atmósfera de aire obsérvase unha perda de masa durante o quencemento de 200 $^{\circ}\text{C}$ a 475 $^{\circ}\text{C}$ (1 % dunha masa total de 0.61 mg). En ambos casos os datos amosan unha perda de auga por debaixo de 100 $^{\circ}\text{C}$. A análise FTIR amosou evidencia dunha forte estabilidade do material fibroso no intervalo de temperatura de 350 a 955 $^{\circ}\text{C}$.
- A fluorescencia de RX amosou que os compostos dominantes no material empregado son SiO_2 , CaO , Na_2O e Al_2O_3 . As cantidades de óxidos que poderían amosar un comportamento como semicondutores son mínimas, polo que non se espera que o material presente propiedades como fotocatalizador.
- Os resultados da análise fluorimétrica amosan que o material empregado ten unha boa capacidade adsorbente. A cantidade de benceno adsorbido varía entre o 26% e o 96%. Requírese máis investigación para comprender mellor a posible aplicabilidade deste material en procesos de purificación de augas residuais ou contaminadas.

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