



## **Synthesis, Characterization and Determination of the Crystallinity Index of the Composite Expanded Vermiculite-Chitosan Beta<sup>1</sup>**

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### **Abstract**

The application of the principles of green chemistry has been going on for more than two decades, mainly with the emergence of nanoscience, when reviewing methods, functionalization, purification, and assembly of nanoparticle blocks. In this work, the natural vermiculite clay was used already expanded as a raw material, having it industrial applications from the mutual interaction with the beta-type chitosan biopolymer in the formation of the final product. The characterization of the raw materials and the composite were performed by infrared Spectroscopy with Fourier Transformed and X-ray Diffractometry. The purpose of the work was based on the following specific objectives: a) the study of the solubility of raw materials, b) the characterization of each raw material and c) the use of the Scherrer method to determine the crystallinity index. The determination of the width value at half height by the Scherrer method from the d200 reflection plane gave the value equal to 0.23 for expanded vermiculite, 1.51 for beta chitosan and 0.93 for the beta chitosan-expanded vermiculite system, fully consistent with the expected crystallinity indexes.

**Keywords:** Hybrid Material. Relative Crystallinity. Waste.

**Síntese, Caracterização e Determinação do índice de Cristalinidade do Compósito Vermiculita Expandida-Quitossana Beta.** A aplicação dos princípios da química verde é feita a mais de duas décadas, principalmente com o surgimento da nanociência, quando se revisa métodos, funcionalização, purificação e montagem de blocos de nanopartículas. Neste trabalho, a argila natural vermiculita foi utilizada já expandida como matéria prima, tendo suas aplicações industriais a partir da interação mútua com o biopolímero quitossana do tipo beta na formação do produto final. A caracterização das matérias primas e do compósito foram realizadas por Espectroscopia de Infravermelho com Transformada de Fourier e Difractometria de Raios-X. A finalidade do trabalho foi buscada a partir dos seguintes objetivos específicos: a) o estudo da solubilidade das matérias primas, b) a caracterização de cada matéria prima e c) uso método Scherrer para a determinação de índice de cristalinidade. A determinação do valor da largura a meia altura pelo método Scherrer a partir do plano de reflexão d200 forneceu o valor igual a 0,23 para a

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vermiculita expandida, 1,51 para a quitosana beta e 0,93 para o sistema quitosana beta-vermiculita expandida, totalmente condizente com os índices de cristalinidade esperado.

**Palavras-Chave:** Material Hybrid. Cristalinidade Relativa. Resíduo.

## 1. Introduction

In the last few years, studies on biocomposites have received the attention of many researchers in different areas of concentration (AGRAWAL *et al*, 2018; HANKEN *et al*, 2019). Likewise, research on vermiculite and other mineral clays has also done considerable progress (YU *et al*, 2010). Vermiculite is a very abundant low-cost clay and has excellent physical and chemical properties such as porous structure, which is flame resistant, inert and has low density (ZHANG *et al*, 2018). In addition to presenting the properties of an adsorbent material, its adsorbent properties are increased when it is expanded, either by surfactant agents or by thermal heating. Also, it can still have its properties enhanced when it becomes hydrophobic. Furthermore, vermiculite can be easily modified with metallic ions and organic agents (ABOLLINO *et al*, 2008). On the other hand, chitosan, which is generally used as a substrate, is a cationic biopolymer, being produced from the deacetylation of chitin, characterized mainly by the Deacetylation Degree (DD) and molecular weight. These parameters strongly affect its physicochemical and biological properties, such as solubility, hydrophobicity and crystallinity (GARCIA *et al*, 2020). Recent research shows the richness of new products when the objective is the mutual interaction among polymers, whether as a conventional composite, intercalated nanocomposite or as an exfoliated nanocomposite. It happens to obtain products that favor

hydrophobic properties, with applications in the pharmaceutical, biomedical and cosmetics fields, as well as in industries and agriculture (ZHANG *et al*, 2009). Hydrophobicity is also important for chitosan, as it has applications in industrial sectors.

So far, the literature describing the preparation of expanded chitosan-vermiculite composite/nanocomposite (e.g., ZHANG *et al*, 2009) does not highlight the use of Scherrer's method for determining the crystallinity index, nor does it mention the use of green chemistry, although some works meet the basic precepts.

The motivation behind this work is the preparation of a composite of expanded vermiculite clay mineral with chitosan biopolymer respecting the basic aspects of Green Chemistry and the use of Scherrer's method to compare the value of the crystallinity index of the formed product with the index value found in raw materials, from X-ray diffraction for high angles, that is, angulation  $2\theta > 10^\circ\text{C}$ .

This manuscript proposes the synthesis and characterization of the expanded vermiculite nanocomposite in the form of a powder with beta-chitosan in a pseudo-gel state, meeting the basic criteria of green chemistry, aiming at the study of the solubility of raw materials and the characterization by spectroscopy in the region of infrared and X-ray diffraction. The specific objectives were to study the solubility of raw materials, the characterization of the raw material and the product resulting from infrared spectroscopy and X-ray diffractometry,



and the use of the Scherrer's method to determine the crystallinity index.

## 1.2. Basic Principles of Green Chemistry (GC) for Environmental Promotion

Green Chemistry (GC) can be defined as "the creation, development and application of chemical products and processes to reduce or eliminate the use and generation of harmful substances to human health and the environment" (CORREA and ZUIN, 2009).

Chemical processes involving products of fossil origin give rise to problems to human health and the

environment, such as breathing problems and pollution of the ecosystem, respectively. In the search for the development of efficient chemical processes for a safe environment, becoming increasingly sustainable in accordance with the principles of Green Chemistry, a consensus was created over the years on the main points or basic principles of GC (Table 1) which need to be considered when one intends to apply them in an industry or teaching and/or research institution in the area of chemistry or related areas (ANASTAS and WARNER, 1998).

Table 1 - The 12 Basic Principles of Green Chemistry

Basic Principles of Green Chemistry	
P1	<b>Prevention.</b> It is better to prevent the formation of by-products than to treat them later;
P2	<b>Atom economy.</b> Synthetic methods must be developed to maximize the incorporation of reagent atoms into the desired final products;
P3	<b>Less hazardous chemical synthesis.</b> Whenever practicable, high toxicity compounds should be replaced by compounds with lower toxicity in chemical reactions;
P4	<b>Designing safer chemicals.</b> Chemical products must be developed to have the desired function, presenting little or no toxicity;
P5	<b>Safer solvents and auxiliaries.</b> The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be avoided whenever possible or innocuous when used;
P6	<b>Energy efficiency.</b> Synthetic methods should be conducted whenever possible at room temperature and pressure, in order to reduce the energy spent during a chemical process that represents an economic and environmental impact;
P7	<b>Use renewable feedstocks.</b> The products and by-products of chemical processes should be used whenever possible;
P8	<b>Reduce derivatives.</b> Derivatization (use of blocking groups, protection/deprotection, temporary modification) should be minimized or avoided when possible, as these reaction steps require additional reagents and, consequently, can produce undesirable by-products;
P9	<b>Catalysis.</b> The application of catalysts to increase the speed and yield of chemical processes;
P10	<b>Design of products for degradation.</b> Chemicals should be developed for the innocuous degradation of toxic products so that they do not persist in the environment;
P11	<b>Real-time analysis for pollution prevention.</b> Analytical methodologies need to be developed to allow real-time process monitoring to control the formation of hazardous substances;



P12 **Safer chemistry for accident prevention.** Substances used in chemical processes should be chosen to minimize potential accidents such as explosions and fires.

**Source:** adapted from Prado (2003)

Based on these principles, several research groups and companies started studies on the application of Green Chemistry.

In 2007, Dahl and collaborators adapted these principles in the publication "Toward a Greener Nanosynthesis", which dealt primarily with the applications of these principles to the field of nanoscience. They reviewed methods involving Wet Chemical approaches for the production, functionalization, purification and assembly of nanoparticle building blocks. They addressed the development of greener processes for the synthesis of nanomaterials, for example, in the preparation of functionalized metal particles (DAHL *et al.*, 2007).

Other relevant publications, such as the ones carried out by Professor Yi Tang and collaborators at UCLA (University of California at Los Angeles) developed a new synthetic route for the production of simvastatin, which a drug used to treat bad cholesterol, by using enzymes and low-cost materials. Codexis (Biocatalysis Company) later optimized this chemical process, resulting in a reduction of risks and waste compared to traditional synthesis (hazardous reagents and numerous steps) (XIE and TANG, 2007).

### 1.3. The Scherrer Method: measuring the width at half maximum

Scherrer equation is a widely used tool to obtain the crystallite size (D) of polycrystalline samples in an X-ray diffraction experiment. It describes a simple relationship between the diffraction peak width at half maximum (Full Width at Half Maximum – FWHM),

the Bragg angle ( $\theta_B$ ) and the X-ray wavelength ( $\lambda$ ). This equation is widely used in the characterization of materials because some of their physical properties depend on the crystallite size (CULLITY, 2001). Equation 1 is most commonly written as:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad \text{Equation 1}$$

Where D is the size of the crystallite in the direction perpendicular to the lattice planes,  $\beta$  is the width at half height of the diffraction peak,  $\theta$  is the Bragg angle for highlighted reflection,  $\lambda$  is the X-ray wavelength and k is a numerical factor often treated as a form factor of the crystallites that make up the sample (CULLITY, 2001).

The width at half maximum of the diffraction peaks is the measure of the peak width at half maximum intensity, as shown in Figure 1.

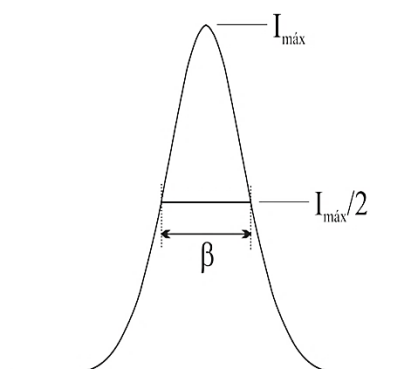


Figure 1 - Width at half maximum of a diffraction peak. **Source:** Cullity (2001)

According to literature (e.g., FOCHER *et al.*, 1990) the Scherrer method by width half maximum was successfully used for semi quantitative determination of the crystallinity index of the cellulose systems. In the literature, the Scherrer method is widely used to



determine the apparent crystal size of crystals.

### 3. Results and Discussion

#### 3.1. Materials, Glassware and Reagents

Table 1 lists the raw materials and types of solvents/reagents available for **the proposed synthesis. Selection of the best carrier agent will be based on solubility and GC principles**

#### 3.2. Glassware

A 250 mL Becker, glass rod, volumetric flask, Buchner funnel, kitassate, 125 mL reaction flask, graduated pipette, 10 and 5 mL

volumetric pipette, desiccator cabinet and 50 mL beaker were used.

#### 3.3. Equipments and accessories

The equipments and accessories used for the development of the studies were: Air compressor; Greenhouse / Quimis brand; Rotary evaporator; Magnetic stirrers: brand fisaton, model 752A; Universal iron support; Semi-analytical scale / Brand: Celta; Vacuum filtration system.

Table 1 - Specifications of reagents and raw materials

Substance Name	Molecular Formula	Degree of purity	Brand
Acetic Acid	CH <sub>3</sub> COOH	99,70 %	CHEMCO
Nitric acid	HNO <sub>3</sub>	65,00 %	NEON
Methyl alcohol	CH <sub>3</sub> OH	99,99 %	NEON
Deionized water	H <sub>2</sub> O	-	-
Calcium chloride	CaCl <sub>2</sub>	96,00 %	DINÂMICA
Chloroform	CHCl <sub>3</sub>	99,80 %	FMAIA
Ethyl Ether	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	99,99 %	VETEC
Carbon tetrachloride	CCl <sub>4</sub>	99,50 %	DINÂMICA
Triethylamine	C <sub>6</sub> H <sub>15</sub> N	99,00 %	VETEC
Expanded vermiculite	Provided by <i>Usina de Beneficiamento da Mina (UBM)</i> in the city of Santa Luzia-PB.		
Chitosan beta	Provided by <i>Primex</i> ( <a href="http://www.primex.is/chtininni.htm">www.primex.is/chtininni.htm</a> )		

#### 3.4. Specialized Instruments

The X-ray diffractograms were obtained in an X-Ray Diffractometer, model D5000 SIEMENS-BRUKER, with a CuK $\alpha$  radiation source ( $\lambda = 1.5406$ ). Scans were performed at the interval of  $2\theta = 5-80^\circ$ , step  $0.02^\circ \text{ s}^{-1}$  and speed of  $0.5^\circ \text{ min}^{-1}$ .

The vibrational spectroscopy analyzes in the mid-infrared region by Fourier transform were performed using

a Shimadzu IR Prestige-21 spectrophotometer, with attenuated total reflectance accessory (ATR) coupled with the following analysis conditions: Region  $4000 - 500 \text{ cm}^{-1}$ ; Resolution:  $4 \text{ cm}^{-1}$ ; Number of accumulations: 20; Mode: transmittance.

Analysis of X-Ray Diffraction and Analysis of vibrational spectroscopy in the mid-infrared region by Fourier



transform (FTIR) were performed at the Laboratory of Fuels and Materials (LACOM) of the João Pessoa Campus of the Federal University of Paraíba (UFPB).

### 3.5. Solubility tests

For the solubility tests, the following reagents were used as shown in figure 10, and the results are shown in Table 2.

Table 2 - Solubility of expanded vermiculite with some solvents

Solvents /Clay	H <sub>2</sub> O	Ethyl ether	Triethylamine	Nitric acid	Methyl alcohol	Chloroform	Carbon tetrachloride
Expanded vermiculite	Slightly soluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble

The solubility tests were carried out in test tubes without heating, where 1 mg of expanded vermiculite sample was placed in 2 ml of the solvents listed in Table 2.

Most solvents are not recommended, however, the literature always uses a dilute solution of acetic acid or nitric acid for chitosan due to its chemical properties. Thus, in accordance with the principles of green chemistry, the interaction should be made between the chitosan gel, when the powder is dissolved in a dilute solution of nitric acid, and the agglomeration vermiculite.

### 3.6. Synthesis

After the solubility and synthesis tests of all products, the residues obtained were stored in containers for later and appropriate disposal.

#### 3.6.1. Preparation of Chitosan beta ( $\beta$ ) pseudo gel

Initially, 0.50 g of powdered  $\beta$ -type chitosan was added to 20.0 mL of a 10% HNO<sub>3</sub> solution, which remained under mechanical stirring, rotating at 6 rpm for a period of 2 hours (figure 1). The product was called CHITGEL.

#### 3.6.2. Interaction of $\beta$ chitosan pseudo gel by expanded vermiculite

In a 250 mL Becker, 1.00 g of expanded vermiculite was added to the  $\beta$  chitosan pseudo gel, which remained under mechanical agitation, rotating at 6 rpm for 2 hours. After the process, the product was washed with ethyl ether in a vacuum filtration system (Figure 4) and dried in a rotary evaporator at a temperature of 343.15 K for a period of 2 hours, as shown in Figure 5. The final product was called CHIVIREX.



Figure 1 - System for obtaining the chitosan gel

## 3. Results and discussion

### 3.1. Solubility Tests

Solubility tests showed that there was incompatibility in the interaction of expanded vermiculite and chitosan,

relative to the use of a single solvent in the synthesis. Vermiculite was partially soluble in water, but in the others it was insoluble. Chitosan presents solubility in water, however, it must not be solubilized in this solvent for not forming a polyelectrolyte. This must be transformed into a pseudo gel using a 10% aqueous solution of nitric acid. With

the use of chitosan in the pseudo-gel state, the formation of an exfoliated nanostructure was possible for these two components, according to diffractograms of the resulting products.



Figure 3 - Previous Washing System for the formed compounds



Figure 4 – Rotovaporator drying system

Source: author's image, 2020

### 3.2. Infrared Spectroscopy

From the analysis of the spectra obtained by Infrared (Figure 5) it was possible to identify the following raw

materials: beta chitosan and expanded vermiculite and the exfoliated nanocomposite obtained after synthesis.

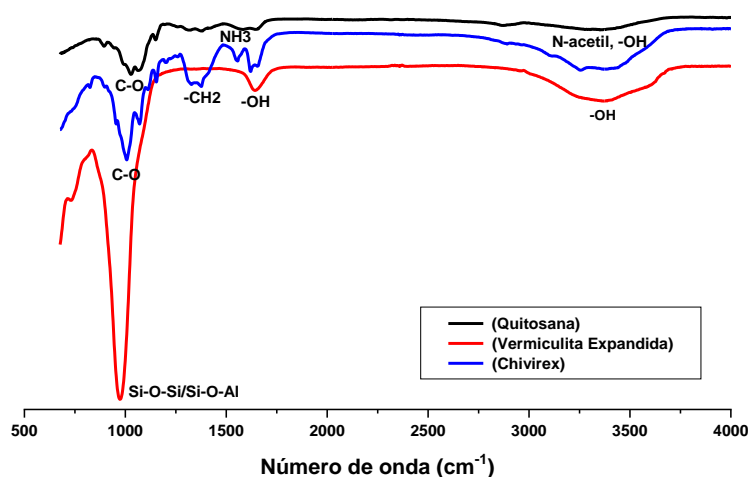


Figure 5 – Vibrational Spectroscopy of chitosan, expanded vermiculite and chivirex composite

In the spectrum of chitosan with 80% deacetylation degree, used as starting material, the bands called amide I, in the range of 1650 and 1670  $\text{cm}^{-1}$  and amide II, which between 1550 and 1600  $\text{cm}^{-1}$  are characteristic bands of chitosan. The amide II absorption bands tend to shift to longer wavelengths for chitosan with a high degree of deacetylation. In the spectrum of chitosan used in the synthesis, the amide I and amide II bands are close to 1385 and 1584  $\text{cm}^{-1}$ , respectively. The band that occurs close to 3370  $\text{cm}^{-1}$  encompasses the OH and N-H groups of the acetylated group. Thus, the absorptions at 1584  $\text{cm}^{-1}$  and 3370  $\text{cm}^{-1}$  are associated with the carbonyl of the N-acetyl and hydroxyl groups, respectively, to calculate the degree of deacetylation. On the other hand, expanded vermiculite presents an intense peak at 988  $\text{cm}^{-1}$  relative to

the Si-O-Si/Si-O-Al asymmetric stretch (DA FONSECA, Maria et al, 2006; TURIANICOVÁ, E. et al, 2014), still showing OH stretch at 3356  $\text{cm}^{-1}$ , OH strain band at 1649  $\text{cm}^{-1}$ , in addition to an important stretch at 665  $\text{cm}^{-1}$ , relative to Al-O or Mg-O. Whereas, in the expanded vermiculite-chitosan composite, the vibrations in the 1377  $\text{cm}^{-1}$  region relative to the C-H of the  $\text{CH}_2$  and  $\text{CH}_3$  group, the vibrational stretch bands of the C-O group are found in the 1005  $\text{cm}^{-1}$  region.

### 3.3. X-Ray Diffractometry

The X-ray diffraction technique was used to characterize the materials in order to examine possible changes in crystallinity and basal spacing both in the raw material and in the resulting product.

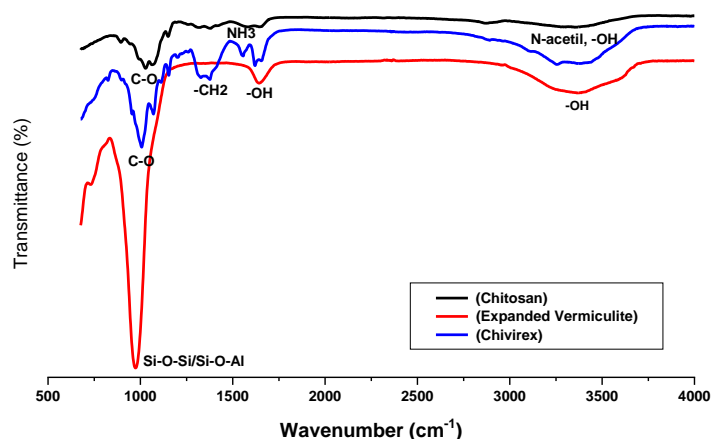


Figure 6 - Diffractogram of chitosan, expanded vermiculite and chivirex composite

X-Ray Diffractometry shows the presence of mica (M), illite (I) and hydrobiotite (HB) (DUMAN et al, 2015) and exposes the incompatibility of the expanded vermiculite and beta chitosan system, regarding the

interaction if the crystallographic pattern is considered. However, chitosan pseudo-gel confers a greater degree of hydrophobicity to the phyllosilicate, that is, the product CHIVIREX (beta chitosan + expanded



vermiculite) is a product made amorphous or with biopolymer molecules dispersed among lamellae, edges and basal space, indistinctly.

### 3.4. X-Ray Diffractometry: Scherrer method

The X-Ray Diffractometry showed the characteristic peaks of the expanded vermiculite that were identifiable after the resulting product. This fact was identified by the method of measuring the width

at the average height (FOCHER *et al.*, 1990).

Vermiculite that has two main reflection planes:  $d_{110}$ , referring to the tetrahedral part and  $d_{200}$ , which identifies the octahedral portion of the phyllosilicate, has a crystallinity pattern equal to 0.23, calculated by the full-width at half-maximum method (Scherrer method), differing from the value found at 1.51 for beta chitosan, characteristic of the polymorphism of this type of polymer.

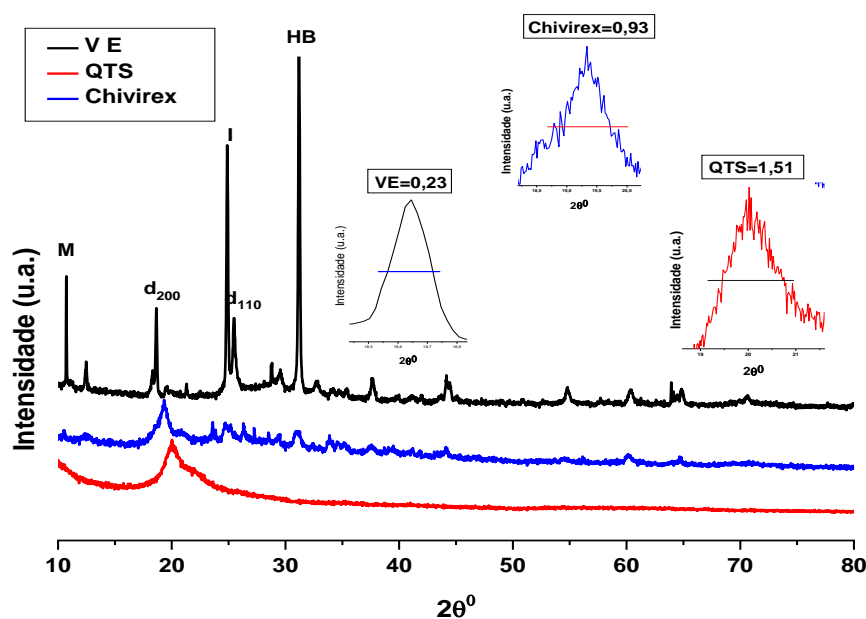


Figure 7 – The diffractograms of Chitosan (DC), Expanded Vermiculite (EV) and the product Chivirex with the determination of the value of full-width at half-maximum method.

The crystallinity index is obtained from the interaction between the two polymers, whose value is 0.93, determined by the Scherrer method, as shown in Figure 7.

### 4. Conclusion

The realization of expanded beta-vermiculite chitosan synthesis is possible only with the use of a lower amount of chitosan and in its pseudo-gel state, as well as the judicious choice of solvent

such as water from the solubility tests. The result of the final product characterization complied with some principles of green chemistry, such as: absence of by-products, less toxic solvents, non-toxic raw materials, non-toxic products and washing with solvents that were kept for treatment and later disposal.

In vibrational spectroscopy in the infrared region, the main absorptions of the two polymers were identified, and



for chitosan, for presenting a degree of deacetylation (DD) 80% has the bands referring to amide II shifted to higher values, characteristic of chitosan with high DD. In vermiculite, stretches are identified at  $988\text{ cm}^{-1}$ ,  $3356\text{ cm}^{-1}$  and  $665\text{ cm}^{-1}$  relative to Si-O-Si or Si-O-Al, OH and Al-O or Mg-O, respectively, in addition to OH strain band at  $1649\text{ cm}^{-1}$ . In the X-Ray Diffractometry, the two main reflection planes were characterized in vermiculite:  $d_{110}$ , referring to the tetrahedral part and  $d_{200}$ , which identifies the octahedral portion of the phyllosilicate. Finally, the two instrumental techniques allowed us to characterize the final product, although they were not taken to the vacuum drying line, but to a rotaevaporator with adequate rotation and heating.

The determination of the value of full-width at half-maximum by the Scherrer method from the  $d_{200}$  reflection plane provided a value equal to 0.23 for the expanded vermiculite 1.51 for the beta chitosan and 0.93 for the expanded beta-vermiculite chitosan system, which is fully consistent with the expected crystallinity indices. And probably the chitosan substrate must have been inserted in the vermiculite lamellae, as well as in the basal spaces and edges, due to the homogeneity of the material obtained.

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### References

- ABOLLINO, Ornella et al. Interaction of metal ions with montmorillonite and vermiculite. **Applied Clay Science**, v. 38, n. 3-4, p. 227-236, 2008.
- AGRAWAL, Pankaj et al. Effect of ethylene-methyl acrylate compatibilizer on the thermo-mechanical, rheological, and morphological properties of poly (Lactic acid)/biopolyethylene/clay biocomposites. **Polymer Composites**, v. 39, p. E164-E173, 2018.
- ANASTAS, P.T.; WARNER, J. **Green Chemistry: Theory and Practice**; Oxford University Press: Oxford, 1998.
- CULLITY, B. D. Elements of X-ray diffraction. 3<sup>a</sup> ed. Canadá: Addison-Wesley Publishing Company, 2001.
- CORRÊA, Arlene G.; ZUIN, Vânia G. Química Verde: fundamentos e aplicações. **São Carlos: EdUFSCar**, 2009.
- DA FONSECA, Maria G. et al. Interaction of aliphatic diamines with vermiculite in aqueous solution. **Applied clay science**, v. 32, n. 1-2, p. 94-98, 2006.
- DAHL, Jennifer A.; MADDUX, Bettye L. S.; HUTCHISON, James E. Toward greener nanosynthesis. **Chemical reviews**, v. 107, n. 6, p. 2228-2269, 2007.
- DUMAN, Osman; TUNÇ, Sibel; POLAT, Tülin Gürkan. Determination of adsorptive properties of expanded vermiculite for the removal of Cl Basic



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Revista on-line <http://www.scientia-amazonia.org>  
ISSN:2238.1910

Red 9 from aqueous solution: kinetic, isotherm and thermodynamic studies. **Applied Clay Science**, v. 109, p. 22-32, 2015.

FOCHER, B. et al. Alkaline N-deacetylation of chitin enhanced by flash treatments. Reaction kinetics and structure modifications. **Carbohydrate Polymers**, v. 12, n. 4, p. 405-418, 1990.

GARCIA, Isadora Atrib et al. Avaliação de métodos titulométricos para determinação do grau de desacetilação em quitosana/Evaluation of titulometric methods for determination of deacetylation's degree in chitosan. **Brazilian Journal of Development**, v. 6, n. 1, p. 4066-4084, 2020.

HANKEN, Ruth BL et al. Effect of natural and expanded vermiculite clays on the properties of eco-friendly biopolyethylene-vermiculite clay biocomposites. **Composites Part B: Engineering**, v. 175, p. 107184, 2019.

PRADO, Alexandre G. S. Química verde, os desafios da química do novo milênio. **Química Nova**, v. 26, n. 5, p. 738-744, 2003.

TURIANICOVÁ, E. et al. Interaction of natural and thermally processed vermiculites with gaseous carbon dioxide during mechanical activation. **Applied clay science**, v. 88, p. 86-91, 2014.

XIE, Xinkai; TANG, Yi. Efficient synthesis of simvastatin by use of whole-cell biocatalysis. **Applied and environmental microbiology**, v. 73, n. 7, p. 2054-2060, 2007.

ZHANG, Weiyi et al. Preparation and characterization of capric-palmitic-stearic acid ternary eutectic mixture/expanded vermiculite composites as form-stabilized thermal energy storage materials. **Journal of Materials Science & Technology**, v. 34, n. 2, p. 379-386, 2018.