

## Extraction of High Purity Silica from Amazonian Sponges

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### Abstract

Silica has a variety of uses, including functioning as a catalytic support and utility in drug delivery systems. It is traditionally obtained from mineral sources through costly extraction processes, which has led to a search for alternative sources. One of the main features of freshwater sponges is that they contain spicules composed mainly of amorphous silica. The species *Metania reticulata* is found in the Negro river (Amazonas, Brazil) in great abundance, reaching volumes above 3 dm<sup>3</sup>. Different purification processes employing oxidizing solutions and subsequent heat treatment are proposed in order to extract high purity silica from freshwater sponges. With these processes, it was possible to obtain high purity (99.92%) amorphous silicon at a concentration higher than silica commercially used for column chromatography (99.71%) support material while eliminating the other elements present in the sponges (Fe, K, Ca, Ti and S). This study described low-cost techniques for the production and purification of high purity amorphous silica as alternatives to production methods currently in use.

**Keywords:** Silica; Freshwater sponges; X-ray diffraction, X-ray fluorescence; *Metania reticulata*

### Introduction

Several technological processes are used today that employ silica in the production of high performance ceramics [1,2]. Amorphous silica is also used in drug delivery systems [3,4], and as a catalytic support [5-7]. Composed of the two most abundant elements in the Earth's crust, silica (SiO<sub>2</sub>) occurs naturally in amorphous and crystalline forms, as well as in combination with other metals and silicate [2,8].

In the phylum Porifera, ~200 sponge species, all belonging to the class Demospongiae are found in freshwater environments [9]. One of the characteristic of these animals is the spicules, supporting structures composed by amorphous silica [10]. The siliceous spicules from freshwater sponges, in addition to diatoms, clay, grains of sand and organic matter (in variable proportions) form sedimentary lentic deposits which are classed as spongillites whenever spicules are dominant or exclusive. Spongillites have various applications in the ceramic industry, refractory products, chromatography supplies and as support materials for catalysts [11].

Specifically in the Amazon, sponges grow during periods of high water and are easily collected when the rivers are at lower levels [12,13]. Archaeological artefacts and reports show that indigenous Amazonian peoples employed freshwater sponges, known as "cauixi", in the manufacture of ceramic objects [14].

The analysis of sponge spicules from an unidentified species collected from the Negro river, showed that this material is mesoporous amorphous silica [15], which has gained attention due to its various applications [16]. In the Negro river, sponges of Metaniidae family, especially the species *Metania reticulata*, are found in abundance adhering to vegetation subjected to flood pulses [17,18], reaching above 3 dm<sup>3</sup>.

Silica is usually obtained from mineral sources by expensive processes having high energy costs [6]. The search for potential/alternative sources of amorphous silica has grown during the last decade and the potential of various sources, such as rice husk and its ash [19-24], blast furnace waste [25] and shale oil ash [26] have been evaluated.

Studies aimed at obtaining silica from rice husks and husk ash followed two alternate purification strategies: the first is solubilisation of silica by a basic solution followed by selective precipitation and the second is chemical and/or thermal oxidation of organic matter in raw materials [19-24].

By applying these techniques used for the purification of biogenic silica, this study aimed to put forth a method for purifying silica present in the freshwater sponge *Metania reticulata*, and to characterize the purified silica using X-ray techniques.

### Materials and Methods

#### Animal material

Specimens of the freshwater sponge *Metania reticulata* (Bowerbank, 1863) were collected in Parque Nacional de Anavilhanas (authorization SISBIO 21114-1), near the Novo Airão city (Amazonas, Brazil) (2° 32.953' S, 60° 58.825' W) on 10 March 2010. The specimens collected were found adhered to branches and trunks of the flooded vegetation [18]. Voucher specimens were deposited at the Porifera collection of the Museu de Ciências Naturais of Fundação Zoobotânica do Rio Grande do Sul with numbers MCN-POR 8486.

#### Silica extraction

Two different procedures were employed (in triplicate) for the purification of sponge silica. The first one was adapted from Kamath and Proctor [24] (Figure 1). Water (60 mL) was added to 10 g of sponge in an Erlenmeyer flask, the pH adjusted to 1.0 using a 6.0 M HCl

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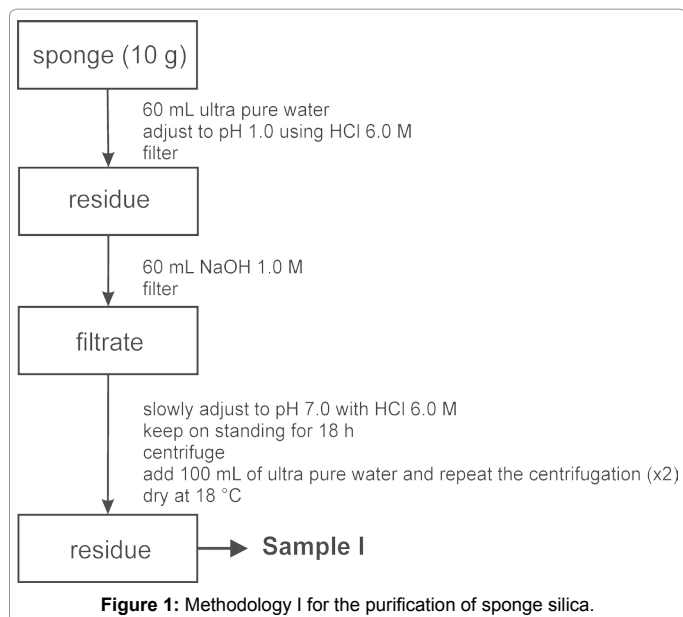


Figure 1: Methodology I for the purification of sponge silica.

solution and kept under constant stirring for 2 h. The resultant material was filtered and the solid was solubilized with 60 mL 1.0M NaOH with heating (80°C) and constant stirring for 1 h. The material was filtered, the solution allowed to cool to room temperature, the pH adjusted to 7.0 using 1.0M HCl solution and left undisturbed for 18 h. Ultrapure water (100 mL) was added, the solution centrifuged at 4000 rpm for 15 minutes, washed with an additional 100 mL of water and centrifuged, the precipitate collected and dried at 80°C (Sample I).

The second method was adapted from da Silva Júnior and colleagues [19] (Figure 2). Sponge material (12 g) and 160 mL of nitric acid were placed in an Erlenmeyer and stirred for 1 h. The solution was filtered and the solid material washed with ultrapure water until it no longer changed colour, and dried at 100°C. To the dried material, 60 mL of H<sub>2</sub>SO<sub>4</sub> - H<sub>2</sub>O<sub>2</sub> (2:1, v:v) solution was added and stirred for 30 minutes at room temperature. The solution was filtered using a sintered glass plate (porosity G3), the residue washed until it no longer changed color and then oven dried at 100°C. The dried material was calcined at 600°C for 4 h in a muffle furnace (Sample II).

### Sample characterization

**X-ray fluorescence:** Energy dispersive X-ray fluorescence (EDXRF) in solid state analyses were used to determine and compare the elemental composition of the sponge material, the silica purified from sponges, as well as commercial silica used for open column chromatography. This technique allows for fast multi-elemental analyses, detecting major and trace elements, and is used in a wide range of studies [27,28].

EDXRF analyses were performed in a Shimadzu EDX 700. Pellets were prepared in a 10,000 Kgf press, using 7.0000 g of high purity H<sub>3</sub>BO<sub>3</sub> for fixing a sample of 1.0000 g. Each sample was analyzed in triplicate, using Rh Kα radiation, a 10 mm collimator and an irradiation time of 200 s for each sample under vacuum.

**Quantification of the detected elements:** For each element found, concentrations were quantified by comparison to salt standards of known purity diluted in boric acid (also of known purity) at six predetermined concentrations, which had been subjected to the same analysis as the samples.

### X-ray diffraction

A Shimadzu XRD 600 was used for X-ray diffraction analysis. The specifications used during data collection were: Cu Kα radiation, 40 kV, 30 mA, 2.0°/min, step angle of 0.020, scanning from 04 to 60°. To calculate the crystallinity of the material, the following equation was employed:

$$x = \frac{1}{1 + K \times \frac{I_a}{I_{cr}}}$$

$I_{cr}$  is the integral of the crystallinity intensity,  $I_a$  is the intensity of the amorphous portion, K is the intensity scatter in function of ratio between the amorphous and its crystalline portion.

### Results and Discussion

Silica solubilisation followed by selective precipitation was used on the spicules of *M. reticulata* in a manner similar to that described by Kamath and Proctor [24] for rice hull ash (Figure 1). This methodology increased the concentration of extracted silica from 97.68 ± 0.19% in the original sample to 99.60 ± 0.07% of the mass of Sample I.

As the raw material in the original work was rice husk ash [24], we also used a second method based on a study by da Silva Jr et al. [19] using rice hulls *in natura*. The first step of the original method immersed the samples in aqua-regia (HCl : HNO<sub>3</sub> - 3:1, v:v) for 1 h under constant agitation [19]. In an effort to optimize the extraction from sponges, aqua-regia was substituted for concentrated nitric acid (Figure 2) as is employed in the preparation of materials for taxonomic identification [29] and preparation of spicules used to pack gas chromatography columns [30]. The material (Sample II) had a higher content of silica (99.92 ± 0.01%) exceeding that of commercial silica (99.71 ± 0.03%) (Figure 3) and material uniformity that was reflected in the low deviation. Besides the increased silicon concentration of the product isolated by method II, there was also a gain in yield (62.12 ± 0.02%) when compared to method I (55.89 ± 0.04%).

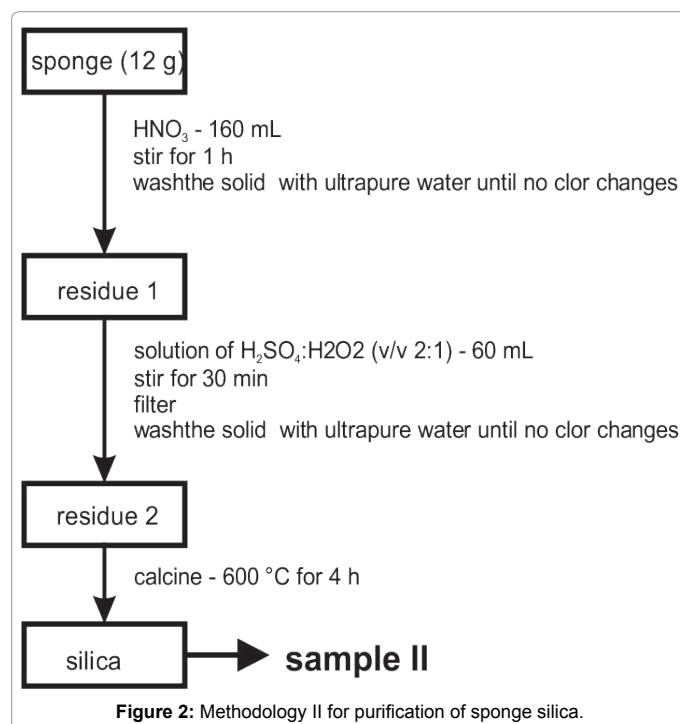
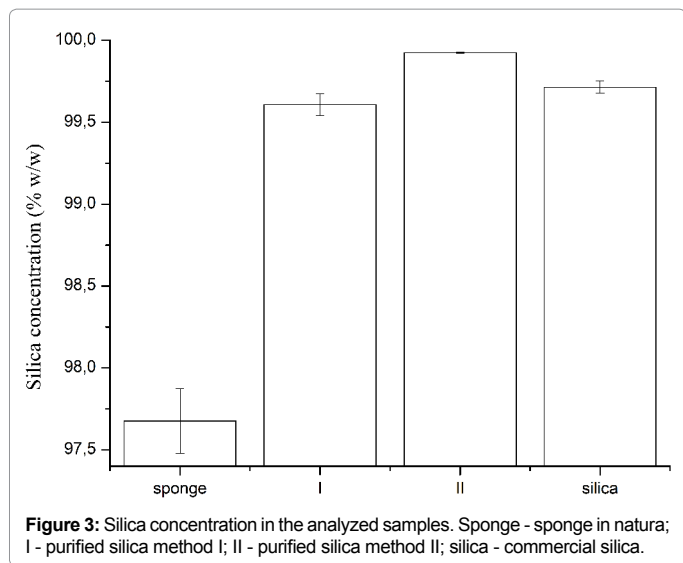


Figure 2: Methodology II for purification of sponge silica.



**Figure 3:** Silica concentration in the analyzed samples. Sponge - sponge in natura; I - purified silica method I; II - purified silica method II; silica - commercial silica.

The efficient removal of certain contaminating elements, such as Ca, Fe and Mn, increases with increasing acidity of the extraction solution [23]. In the starting material (Figure 4), Fe was  $1.09 \pm 0.12\%$  of the mass of the sponge (Figure 4A), while in sample I (subjected to a washing with a hydrochloric acid) Fe was reduced to  $0.25 \pm 0.03$  (Figure 4B). In Sample II (Figure 4C), the iron concentration was that same as that of commercial silica ( $0.02 \pm 0.001$ ) (Figures 4D and 5).

In order to use spicules as a support for catalysts, the removal of contaminants found in sponge (Fe, K, Ca, Ti, P, and S) is of great importance, as these can influence the kinetics of various reactions, may act as inhibitors or catalyze secondary reactions [31-35]. Potassium, normally found in sponge material, was reduced to undetectable levels by the purification process, even though it was present in commercial silica. The same was observed for calcium and titanium, while copper was found in the same concentration in all samples, including raw material and commercial silica ( $0.003 \pm 0.001\%$ ) (Figure 6). Phosphorus and bromine were present only in untreated samples and were not detected in purified samples or the commercial silica used for comparison. Sulphur, which corresponded to  $0.03\%$  of the starting material, was not detected in the purified samples or commercial silica (Figure 7).

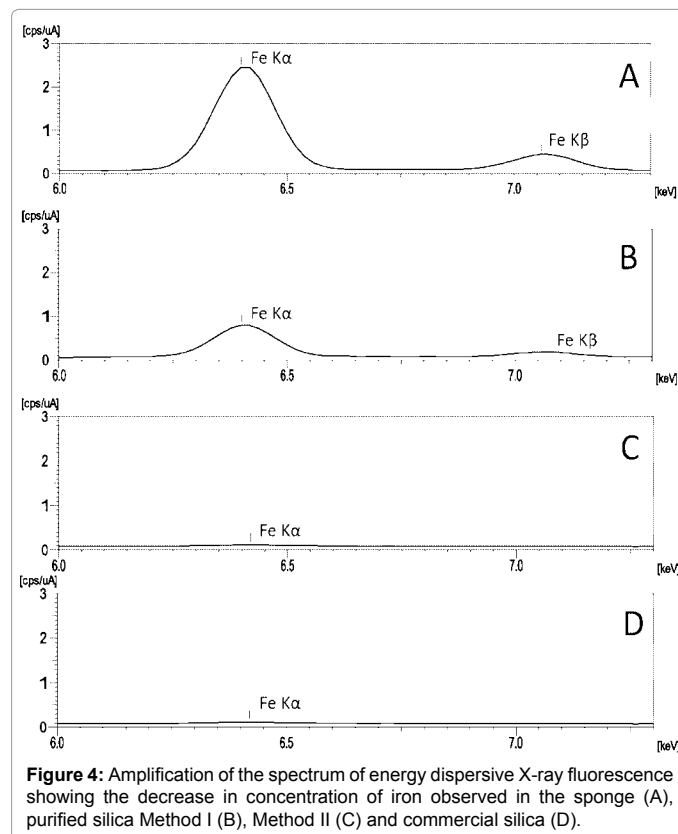
Spicules *in natura*, when evaluated in X-ray diffraction, showed 57.42% crystallinity, indicating the presence of crystalline contaminants, as the silica present in sponges was amorphous. After purification, no crystallinity was observed in either sample.

Both methodologies extracted amorphous silicon, but the second method, adapted from da Silva Junior et al. [19] resulted in higher purity. Another factor that favours this methodology was the ease of execution that in that it employed simple techniques such as filtration, pH adjustment (for precipitation) and centrifugation compared to the method of Kamath and Proctor [24]. All amorphous silicas are not identical, having different catalytic activities, even though they are identical when analyzed by  $^{29}\text{Si}$  magnetic resonance and X-ray diffraction [36].

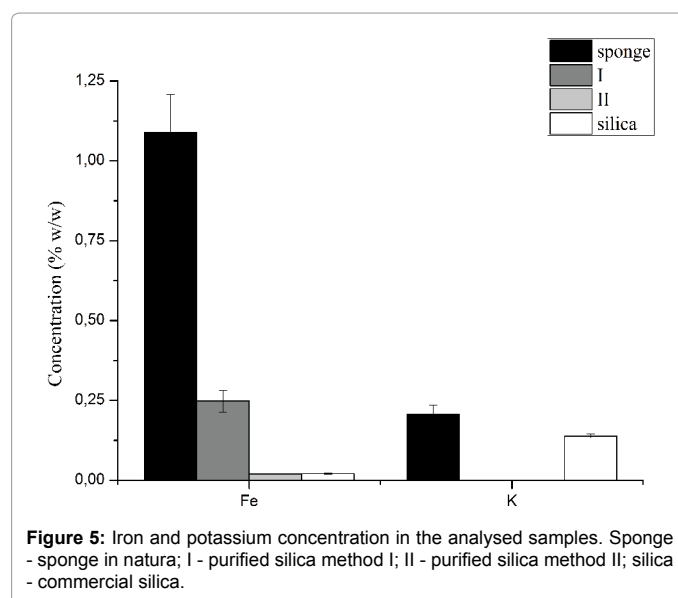
Spongiculture is an alternative to the sponge harvesting from the wild. In marine environments, it has already shown good results, while in fresh water, hydroelectric reservoir lakes are potential environments for cultivation of sponges [37].

## Conclusions

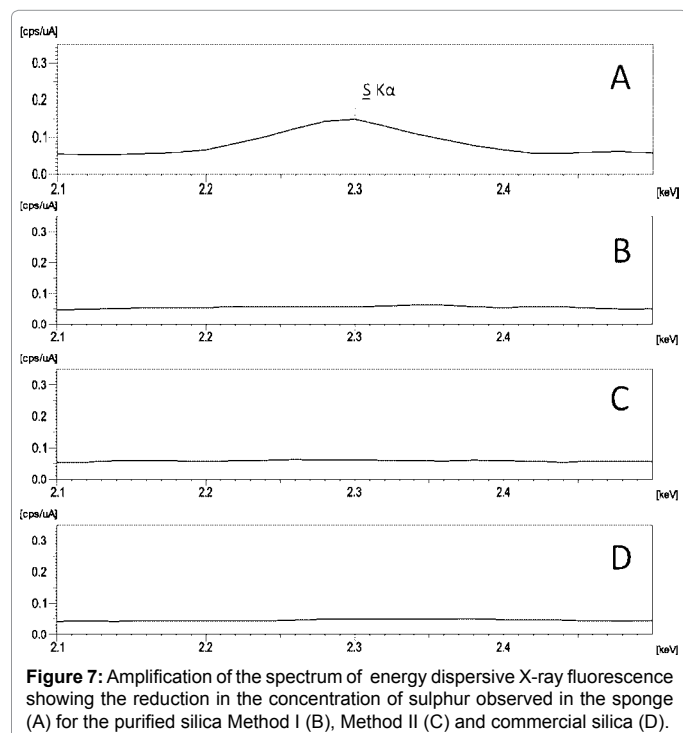
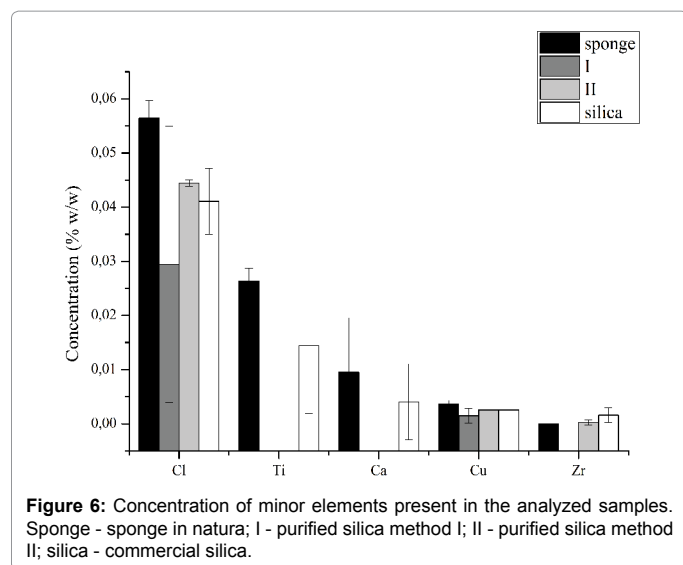
Purification of the silica from the skeleton of the freshwater sponge *M. reticulata* resulted in the removal of several contaminants, yielding a product with purity superior to commercially available silica currently used as chromatography support materials. These processes had few steps and relatively low cost reagents. In light of the data presented, "cauxi" may a potential natural resource that could be exploited in a sustainable way and farmed in the Amazonian floodplains as well as in the man-made lakes in the region.



**Figure 4:** Amplification of the spectrum of energy dispersive X-ray fluorescence showing the decrease in concentration of iron observed in the sponge (A), purified silica Method I (B), Method II (C) and commercial silica (D).



**Figure 5:** Iron and potassium concentration in the analysed samples. Sponge - sponge in natura; I - purified silica method I; II - purified silica method II; silica - commercial silica.



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