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Production of Portland Cement Loaded with Polyaniline and Evaluation of Sulphidric Gas Sorption Capacity

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Abstract: Cements are materials based on clay and limestone. Its origin was about 4500 years ago and it is believed that they were the basis for the construction of the pyramids in Egypt. As time went by, limestone was calcined, giving origin to the Portland Cement most used today. Its applications are diverse, ranging from the construction industry to the production of sustainable materials. In this sense, this work aims to produce composites of cement loaded with polyaniline and exposure to hydrogen sulfide gas to assess the sorption capacity of this contaminant, present mainly in sewage treatment. The composites were analyzed by resistivity analysis, in order to investigate the influence of PAni in the geopolymer matrix and its ability to conduct electrical energy, after H2S sorption and gravimetry, aiming to observe the increase in mass (g) during the sorption process. All tests were performed in triplicate and the mean, standard deviation and confidence limit were calculated to obtain the reliability of the results.

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Keywords: Cements, Polyaniline, hydrogen sulfide gas, sorption.

Adherence to the BJEDIS' scope: This article presents statistical results by ANOVA and Tukey's method, thus verifying the veracity of the results obtained, as well as the significant differences in the analytical data. This is a fundamental step in chemical analysis.

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1. INTRODUCTION

Historically, the word cement is of origin from the Latin *caementu*, which denotes a kind of natural boulder stone and not squared. Its origin was around 4500 years ago and it is believed that it was already used in the construction of the Pyramids in the ancient Egypt, such an alloy probably consisting of gypsum or lime, i.e. calcined gypsum. In 1824, the englishman Joseph Aspdin burned limestone together with clay, turning it into a fine powder, giving rise to the name Portland Cement. In 2008, P.Kumer Mehta and Paulo Monteiro defined that cement is a dry, finely pulverized material, which by itself is not a binder as a result of hydration. A cement is considered hydraulic when the hydration products become stable in an aqueous environment. The most commonly used hydraulic cement is Portland cement, which consists essentially of reactive calcium silicates (1). Such material is widely used due to its ease of handling, variability of shapes and sizes, and its low cost (2). The preliminary knowledge of the characteristics that the cement should possess is necessary to be able to obtain the desired cement, facing the right proportion of the mixture and the proper use of manufacturing processes (3).

It is essential in the hydration of the cement that the environmental conditions are pleasant and favoring the process, and that it is carried out during a stipulated time. The formation of pores in the structure of the material is due to the evaporation of water in the hydration process, which should be avoided by contributing to the decrease of its mechanical strength. During the cement curing process it is necessary to control the amount of water, in order to avoid its evaporation during the manufacturing process and setting. So that no failures occur in its structure (1).

Polymers are macromolecules composed of many repeating units. Depending on the type of chemical structure, the average number of meros per chain and the type of covalent bond, we can divide polymers into three major groups: Plastics, Rubbers and Fibers. In the technical-scientific area, a polymer is an organic (or inorganic) material of high molar mass (above ten thousand, and can reach ten million), whose structure consists of the repetition of small units (meros)(4)

Currently polyaniline, or PANI, has caught the attention of the scientific society for its high electrical conductivity, despite having been discovered more than 150 years ago.

Before the 1970s, polymers were already used precisely because of their excellent electrical insulation capacity and excellent mechanical properties. In 1977, the high electrical conductivity of trans-polyacetylene (t-Pa) was discovered by H. Shirakawa, A.J. Heeger and A.G. MacDiarmid, who were responsible for changing the concept of polymers (Yang & Heeger, 1994). The electrical conductivity of some polymers, when doped, reaches values typical of semiconductor or even metallic materials. But it was not until the 1970s, with the discovery of doped forms of polymers capable of conducting electric current, that a vast area of research and applications of these materials was established. Polyaniline (PANI), has received prominence due to its good stability, easy obtaining and wide range of applications (5)

Polyaniline, obtained from the polymerization of aniline, is formed by repeating units that contain a reduced form (two benzoid rings) and another oxidized form (a quinoid ring and a benzoid ring) (Figure 1), and the form called emeraldine (y = 0.5), when doped by protonation, is the one that can present the highest values of electrical conductivity.

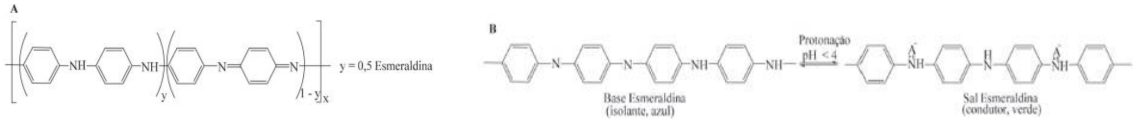

Figure 1. (A) Repeating unit of polyaniline in the form known as emeraldine. (B) Doping reaction via protonation of the basic form (emeraldine base) to the emeraldine salt.

Of all the families of conducting polymers, polyaniline is the only one with the dexterity to synthesize and the chemical stability under environmental conditions. And because of this chemical richness that polyaniline contains, it has become one of the most studied polymers for 2 decades.

In this sense, this work comes with the objective of producing cement composites loaded with polyaniline and exposure to hydrogen sulfide gas to evaluate the sorption capacity of this contaminant, present mainly, in sewage treatment. The production of this work is through data analysis and statistics, as well as the proposal of BJEDIS, in which the objective is performed in an experimental way to obtain results for the area of environmental chemistry and risk assessment, for example. In addition, the topic comes with a more critical approach, being able to understand the confidence limit through laboratory analysis.

2. MATERIALS AND METHOD

2.1. Polyaniline production

The production of polyaniline was made from the preparation of a 1M HCl solution, using 1080 mL of distilled water and 20 mL HCl. From this total amount of 1100, 100 mL was collected and used to dissolves 30 g of ammonium persulfate. In the remaining acid solution was dissolves 10 ml of aniline. After this, the ammonium persulfate was added to the previous solution and left stirring at 300 rpm for 2 hours. Finally, the samples were vacuum filtered and washed with 100 mL distilled water 3 times and then 4 times with 200 mL alcohol. The samples was dry at room temperature for 2 days.

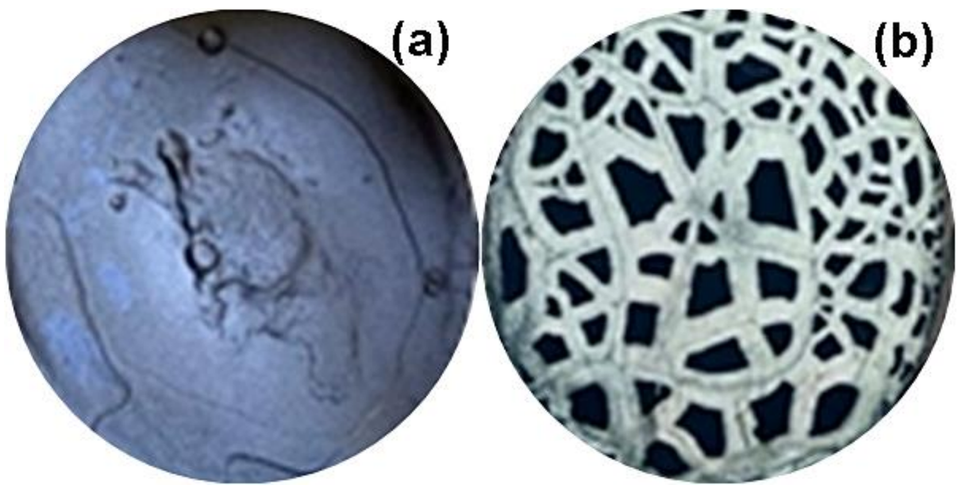

Figure 2. Polyaniline after filtration (a) and polyaniline after 2 days of drying (b).

2.2. Deprotonation of Polyaniline

This step was done using with 17.89 g of Polyaniline dispersed in 1 Molar Sodium Hydroxide solution.

First, the 1M NaOH solution was prepared using a mechanical stirrer. After cooling the 1M NaOH solution, 17.89 g of PANI was added, and this system was stirred for another 30 minutes until the appearance of blue coloration was evident. The resulting material was washed with alcohol and dried at 30°C. This process was important so that when performing the sorption of the composite, the color of the resulting material would give the answer. As in the deprotonation process the initial color of the composite was green becoming blue, in the sorption the result of the color would be inverse for the veracity, that is, the acid would return to its initial green color.

2.3. Production of the Composite

In performing the calculations, 10 mL of distilled water for 4g of cement was used in the mixture concentration.

Then, 0.12 g of PAni (emeraldine base), corresponding to 3% in mass of paste, was weighed and mixed with the cement paste (composite K7) in order to verify the sorption capacity of the sulfidric gas.

2.4. Characterizations

2.4.1. Resistance (Ω):

A Keithley 6517-B electrometer with a homemade sample holder attached was used for this analysis. The voltage applied to the samples was 100V and the current 20 mA. The average diameter of the samples was 0.2 mm and the electrification time was 120 s. The tests were performed in triplicate.

2.4.2. Resistivity ($\Omega.cm^{-1}$):

Resistivity was calculated using the resistance data obtained, using the following formula:

$$\rho = \frac{(R * \pi * r)^2}{e}$$

ρ = Resistivity ($\Omega.cm^{-1}$)

R= Resistance (Ω)

r= radius (cm)

e= Thickness of the sample (cm)

2.4.3. Statistical analysis.

The means of the variables obtained in the treatments were compared using Tukey's test at 5% probability using the SigmaPlot 12.5 program (6, 7).

2.4.4. H_2S Sorption Test:

The sorption tests were performed using an erlenmeyer flask, where the gas was produced with 10 mL of HCl and 0.05g of Iron Sulfide II. A kipp pipette was attached to the erlenmeyer flask, a hose at the outlet of the kipp pipette and a glass tube where 0.2g of composite was placed. Sorption was performed for 1h 30 min and the composites were analyzed. All tests were performed in triplicate.

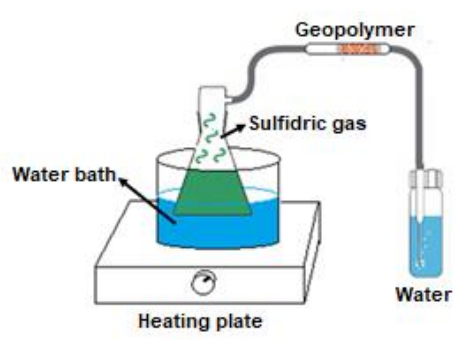

Figure 4. Sorption Test.

3. RESULTS AND DISCUSSION

The samples were submitted to the resistivity test to evaluate the influence of polyaniline in the cement matrix, as well as to verify the influence of the presence of hydrogen sulfide gas in the matrix. The cementitious matrix showed a classic resistive behavior. In contrast, Polyaniline (PAni) showed a behavior with inductive characteristics, meaning that PAni is a material able to store energy in a magnetic field. This behavior is possible due to the intrinsic magnetic characteristics of Polyaniline (8). Inside the K7 composite, PAni is dedoped due to the alkali nature of the cement matrix. So, the conducting filler again behaves like an electric resistive material, and the composite's general behavior is resistive. Finally, the post-sorption K7 composite showed a behavior with capacitive characteristics, meaning that this material can store energy in an electric field, which is possible due to the doping gradient of the PAni trapped into the composite produced by the sorption of the acid (9, 10, 11)

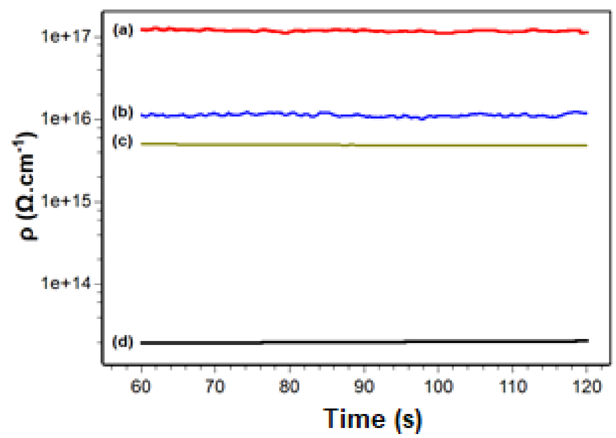

Figure 5. Resistivity of (a) K7 composite, (b) Cement; (c) polyaniline (emeraldine base); (d) K7 composite after hydrogen sulfide gas sorption.

The Table 1 shows the mean resistivity of cement, Pani (EB), and composites before and after sorption. Additionally, significant differences were observed in the different values of resistivity of these materials. Therefore, this indicates the increase of resistivity k7 composite and proves that after sorption the composites decreased the resistivity, showing the Figure 5. By checking the data provided by the mean and Tukey's method, it was possible to identify that the materials are different from each other, Table 1 (letters a, b, c and d), and that after the sorption test the resistivity of the composite decreased, showing the presence of gas by the protonation of polyaniline.

Table 1. Mean resistivity values of cement, Pani (EB) and composites.

Samples	ρ ($\Omega.cm^{-1}$)	CI 95%
Cement	$1,20x10^{16}$ a	± $1,55x10^{5}$
Pani(EB)	$4,85x10^{15}$ b	± $6,85x10^{7}$
K7	$1,15x10^{17}$ c	± $3,46x10^{4}$
K7S	$1,33x10^{13}$ d	± $1,95x10^{6}$

Means followed by the same lowercase letter in the collumm do not differ statistically from each other by the Tukey's test at 5% probability.

4. CONCLUSION

From the experimental procedures and analysis of data obtained in the laboratory, it was possible to conclude that it is plausible to mix the cement with polyaniline. This cement/PANI composition showed to be more resistive due to the characteristics of the components of the formulation (cement and polyaniline (EB)). The resistivity analysis performed after sorption showed that there was a decrease in the electrical resistance of the composite, thus presenting the conductivity of the material. Even though the sorption of the gas was low, it was an extremely important factor in influencing the conductivity of the composites. The ANOVA and Tukey test proves the values are different, this indicates that had the decreased resistivity in composites, after sorption. The data obtained were satisfactory as they allowed the evaluation of the potentiality of the composite to be used in the sorption of a toxic gas, but some structural modifications, such as increasing the porosity, can be made later to have a greater sorption capacity by the composite.

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