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Characterization of Mesoporous Silica Sponges (MSS-15) Functionalized with Amino Groups as Adsorbents for Chromium (VI) Removal in Water

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Characterization of mesoporous silica sponges (MSS-15) functionalized with amino groups as adsorbents for chromium (VI) removal in water.

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***Abstract*— Water pollution has been one of the most controversial issues in recent years due to the presence of chemical species, specifically heavy metals. These problems affect not only biodiversity but also human health, since it has the capacity to bioaccumulate and cause health effects. Among these metals is chromium (VI), which is used in the leather and automotive industries that discharge their wastewater without prior treatment. There are alternatives for the reduction of this metal in water, such as the use of adsorbents. This method is one of the most efficient methods to reduce heavy metal ions, as it offers several advantages such as stability, recoverability, flexibility, among others. For the present project, a mesoporous silica sponge type (MSS-15), functionalized with amino groups, was developed and characterized to evaluate if its properties are optimal to reduce the concentration of this metal in water. To explain the adsorption capacity of the materials, textural, structural and morphological properties were determined, as well as the presence of functional groups of the MSS-15 using different characterization techniques, such as X-ray diffraction, thermogravimetric analysis, micro Raman and SEM, from which we can deduce that it has the optimal properties to be a good adsorbent**

Keywords*— *Water pollution; chromium (VI); adsorbents; MSS-15

I. Introduction

In recent years with regard to water pollution with heavy metals has been a matter of concern. There are bodies of water contaminated with this type of metal in which the concentrations exceed the maximum permissible limit according to the Secretary of Health based on the NOM-127-SSA-1994.

Exposure to these metals above permissible limits causes problems for the ecosystem and human health because they have the property of bioaccumulating, chromium (VI) is one of the most toxic metals in existence. It has the property of being soluble, which allows it to be transported and deposited in these bodies of water more easily.

As well as, in the preservation of wood, among others (Çimen, 2015). There are different types of treatment to remove this type of contaminant such as chemical precipitation, electrochemical techniques, ion exchange and removal by adsorption. However, due to their high costs and low effectiveness, more accessible and effective methods have been developed. Such is the case of the use of silica-based mesoporous materials that by their nature have the capacity to adsorb polluting species such as chromium (VI) with greater efficiency than conventional methods (Su et al., 2019; Walaszek et al., 2018).

II. Materials and Methods

2.1. Synthesis of mesoporous materials of type MSS-15

The synthesis of the MSS-15 will be done through the Sol-Gel process following the procedure of Wang et al., 2015 by Sol – Gel process.

2.1.2. Functionalization with amino groups of MSS-15

The functionalization of the mesoporous material MSS-15 will be performed by Ex situ method with the reactive APTES (3-aminopropyltriethoxysilane), the precursor of the NH2 group (Idris et al., 2012; Xing et al., 2017). The different amounts of this precursor (0.1, 0.2 and 0.3 mol), will be for the purpose of varying the surface concentration of amino groups.

2.1.3. Caracterization of materials

Thermogravimetric analysis (TGA)

The thermogravimetric analysis will be performed on a Q500 TGA and Q2000 TA instruments at a temperature range of 25 - 800 °C. The purpose of this analysis is to evaluate the thermal stability of the material and the amino groups with which it was functionalized.

X-ray diffraction (XRD)

The materials will be analyzed in an X-ray diffractometer at low angles (2θ = 0-5°), to analyze mesoporosity in the MSS-15. The diffractometer to use will be Bruker model D8 Advance with a radiation CuKα λ=0.15406 nm (Thiodjio et al., 2018).

Scanning electron microscopy (SEM)

A 20 kV JEOL JSM-6060 LV scanning electron microscope (SEM) shall be used to determine the shape, distribution and particle size of the pure and functionalized material. The samples are prepared on the support with a conductive carbon film with a thickness of 1 - 100 nm, then subjected to an atmosphere of Ar to close the sample under vacuum to be analyzed.

Raman analysis

For the chemical analysis of the MSS-15, Raman micro spectroscopy was used to observe the presence of the amino groups. This analysis was carried out in a Thermo Scientific DXR2 equipment at a range of 400 - 4000 cm^{-1} using three different sources of excitation (laser) green (He-Ne at 632.9 nm), red (IR semiconductor at 780 nm) and blue (argon at 514.4 nm).

III. RESULTS AND DISCUSSION

3.1. Synthesis and characterization of mesoporous silica sponges (NH2/MSS-15)

After the synthesis of the material, it was characterized to verify if it had the necessary properties to be a good adsorbent.

Thermogravimetric analysis (TGA).

In the next thermogram shown in the figure 1 can see the weight loss in percent with respect to temperature in the range of 30 - 600 °C. In the blue line, we can see a decression in the graph due to the loss of water, since the material, being highly porous, can contain water simply by being in the environment. In the red line you can see the weight derivative, this line provides us with more detailed information of the changes that occur due to the temperature to which the material is submitted. For example, at a temperature of approximately 100°C, water desorption begins, which, as mentioned above, is due to the fact that the material was exposed to the environment, which caused the water to adhere to it. At a temperature of approximately 250 °C another small curve can be seen which represents the dehydroxylation of the surface of the material, remembering that xylanol groups are present in it, at this temperature its thermal decomposition begins as can be seen in the graph.

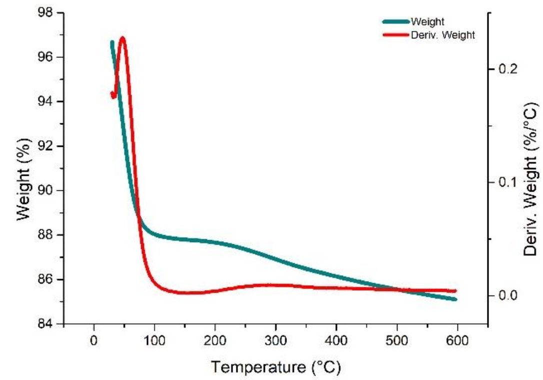

Figure 1. Thermogram MSS-15

In the figure 2 is presented the thermogram of the MSS-15 functionalized with amino groups in which it can be observed as in the previous figure that there is a decression in the brown curve from 70 °C approximately, in this process was lost 15 % of the initial weight of the material. The red line shows the derivative of the weight of the material in which mainly the water desorption from 100 °C. It is observed that the band has an unevenness at approximately 250 °C which according to the literature reported by Gao et al. in 2020 we observe the loss of amino groups with which the material was functionalized, which are found on the surface of the pores, indicating that this functional group is present. Another change can be observed at temperatures higher than 500 °C. This may be due to the de-oxylation of the functional groups added in the functionalization.

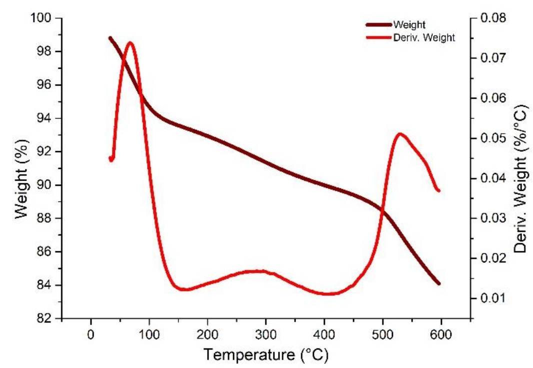

Figure 2. Thermogram $_xNH_2$/MSS-15

X-ray diffraction (low range)

In the diffractogram shown in the figure 3, in a signal at approximately 0. 5° in 2 θ in both materials, which is associated with the type of porosity that presents the material, in this case, it is indeed a mesoporous material, you can see that there are two small reflections which correspond to the textural and structural porden. These results coincide with those of the pore diameter distribution reported by Wang et al, in 2015. In addition, it can also be seen that the graph of the functionalized material moves a little down and the signal is slightly wider than that of the non-functionalized material, this may be due to the amino groups present because the cavities are narrowed by the presence of these functional groups, the same can also be seen in the figure above, that the diagram of the functionalized material is a little out of phase with respect to the other.

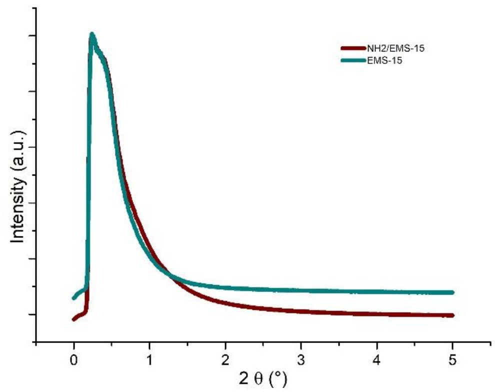

Figure 3. Difractogram of the functionalized and non – functionalized materials (low ranges)

Scanning electron microscopy (SEM)

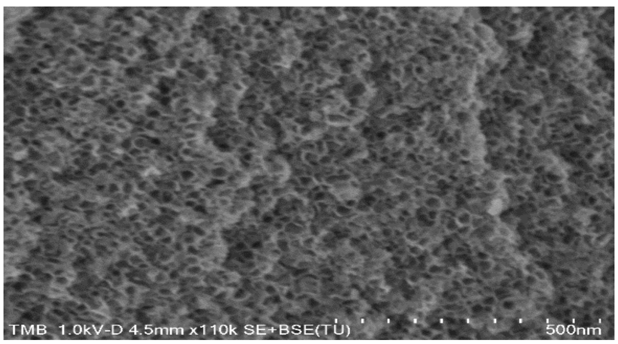

Figure 4. SEM image from MSS-15

Figure 4 shows a highly porous material, i. e. with a high number of cavities, with a diameter between 20-30 nm and a wall thickness of approximately 18 nm which rectifies that the material is a mesoporous silica sponge, which makes the material can function as a good support depending on the intended applications, even with greater capacity to be functionalized unlike the SBA-15 and SBA-16.

Raman analysis

The figure 5 shows the Raman spectrum in which characteristic signals of the functional groups present in the material can be observed. In the blue color spectrum corresponding to pure material, a signal is observed in the range of 430 – 560 cm^{-1} which belongs to the union of Si - OH (silanol groups) which according to the methodology tells us that it is the functional group present on the surface of the material. In the range 703 – 708 cm^{-1} a band is observed which belongs to the Si - O - Si junction (siloxane group) which is the main constituent of our material. In the case of the brown color spectrum corresponding to the functionalized material with amino groups. A signal can be observed in the range of 2950 – 2970 cm^{-1} which confirms that this functional group is present in the material since the signal tells us that there is a bond between N - H (amino).

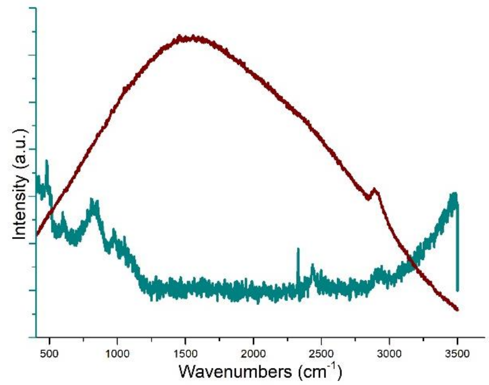

Figure 5. Displacement raman spectrum

IV. CONCLUSIONS

According to the analyzes carried out for these materials, we can verify that we actually obtained a highly porous material which can be functionalized with different species as functional groups with the shape of a sponge, which can be used in heavy metal removal processes in contaminated water.

V. ACKNOWLEDGEMENTS

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