Application of Factorial Design In The Optimization of A Procedure For Antimony (Sb) Remediation From Wastewater Employing Mesoporous Array

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Abstract

This study describes the sustainable and eco-friendly synthesis of the silica-based mesoporous structure from the use of alternative amorphous silica extracted from rice husk ash (RHA). The mesoporous material was called MCM-48 (RHA) and its application as adsorbent to the antimony (Sb) remediation in wastewater was tested. The adsorbent was prepared by an efficient and sustainable hydrothermal method, which exhibited an amorphous framework with type IV isotherms and type H1 hysteresis, high surface area ($820.94 \text{ m}^2 \text{ g}^{-1}$) and total pore volume ($0.55 \text{ cm}^3 \text{ g}^{-1}$) with a narrow mesopores distribution, uniform spherical particles, and well-defined architecture. Multivariate optimization using a factorial design (2^4) was employed in the adsorption tests of Sb. The variables evaluated and the conditions selected were: adsorbent mass (45 mg); adsorption time (60 min); pH (ranged from 2 to 10); and concentration of the Sb standard (8 mol L^{-1}). The adsorbent material proposed in this study proved to be efficient for Sb remediation in aqueous media, mainly because it is a material with easy access, low-cost, and eco-friendly.

Highlights

- The sustainable and eco-friendly synthesis of MCM-48 mesoporous arrays.
- Use of RHA as an alternative and inexpensive silicon source.
- The MCM-48 exhibited large surface area and total pore volume.
- The MCM-48 exhibited a high removal efficiency of Sb.

Introduction

Industrial waste, commonly thrown into aquatic environments, contains both inorganic and organic contaminants, representing a global concern for many countries (Akhil et al. 2021). Among the various inorganic contaminants, antimony (Sb) is considered pollutant non-biodegradable and that can cause many environmental damages. Furthermore, carcinogenic contaminants cause health problems, especially for human beings (Viczek et al. 2020). The main industrial activities that can contribute to the discharge Sb in aquatic environments come from the industries of fire retardants, pigments, mining, and ceramics (Aquino et al. 2016; Chu et al. 2019; Meng et al. 2020). Some countries, such as China, Greece, and India, have suffered with problems of contamination in groundwater by Sb, which can cause damage to human health (Antoniadis et al. 2019; Xu et al. 2019). In this sense, the development of methodologies that are efficient for the Sb remediation from wastewater is essential.

Among the various approaches in the literature for the Sb removal (Xiang-Xue et al. 2019; Chen et al. 2020), adsorption technology is most commonly method used, and several adsorbents have been developed (Zhao et al. 2010). Despite the various adsorbent materials already available in the literature, it is still necessary to find an adsorbent material that has the following characteristics: (i) low-cost, eco-

friendly, and sustainable; **(ii)** good physical and chemical stability; **(iii)** excellent textural and structural features; and **(iv)** high selectivity, so on (Costa and Paranhos 2020; Costa et al. 2020b). In this context, the synthesis mesoporous materials has attracted a great deal of interest for the adsorption process and has already been used with success for removal of the organic compounds (Santos et al. 2019; Costa et al. 2020d, c, 2021b, a) and inorganic constituents (de Sá et al. 2020; Costa et al. 2020a).

The mesoporous materials were synthesized for the first time in the early 1990s, and have since been used in the most diverse technological applications. The best known and/or studied mesoporous materials are those of the M41S family, represented by MCM-41 (hexagonal phase), MCM-50 (lamellar phase), and MCM-48 (cubic phase) (Costa et al. 2015, 2017a, b; Santos et al. 2019), which is the focus of this approach.

The mesoporous structures have attractive features, such as good thermal and mechanical stability, and high surface area, which allows the diffusion and/or adsorption process of the organic and inorganic compounds through their uniform pores and high mesoporous arrangement, as well as ease in the synthesis and functionalization process of these ordered structures (Costa et al. 2014, 2015, 2017a, b). The silica-based mesoporous arrays are synthesized via the hydrothermal method from the use of a surfactant (directing agent), a catalyst (acid or basic), and mainly from a silica source, which is responsible for forming the framework of the amorphous material (Costa et al. 2015, 2017b).

In the literature there are several works showing the synthesis of these mesoporous materials from the use of the commercial silica sources, mainly tetraethylorthosilicate (TEOS) (Costa et al. 2014, 2017b; Ambursa et al. 2017), silica gel (Santos et al. 2019), and sodium silicate (Costa et al. 2017a; Santos et al. 2019). However, there are some works that show the preparation of the mesoporous structures from the use of the alternative, sustainable, and eco-friendly materials as a silica source, such as fly ash (Castillo et al. 2018), rape straw (Li et al. 2019), straw ash (Ma et al. 2016), bamboo leaf ash (Arumugam et al. 2018), rice husk (Sohrabnezhad and Daraie Mooshangaie 2019), sedge ash (Ghorbani et al. 2013), and sugarcane bagasse (Norsuraya et al. 2016), so on. In the present approach, we use the rice husk ash (RHA) as an alternative, inexpensive, eco-friendly, low-cost, abundant, and accessible source of amorphous silica for the synthesis of the mesoporous material with a cubic phase (MCM-48 (RHA)), which was later used as an adsorbent material in the Sb removal in aqueous media.

The most of the approaches found in the literature, which are dedicated to the adsorption studies, are carried out from the univariate optimization of the adsorption tests, which aim at understanding the adsorption mechanism between the adsorbent material and the adsorbate, especially from the correlation of experimental adsorption data with kinetic and isothermal theoretical models (Costa et al. 2014; Costa and Paranhos 2019). However, these approaches are laborious and requires expertise analyst.

Recently, a demand has emerged for the optimization step of the procedures are fast and with reduced number of experiments (Ferreira et al. 2018). In this sense, the multivariate optimization techniques have been shown powerful to evaluation the variables that affect the analytical response in order to obtain the best conditions of optimization to ensure the procedure reliability. Among the multivariate optimization

tools factorial design is more employed and allows a preliminary evaluation of the variables for development of linear models (Costa et al. 2019; Gamela et al. 2020). These tools have numerous advantages, such as: **(i)** possibility of evaluating synergistic and antagonistic interactions between variables; **(ii)** possibility of forecasting the system under study in a condition that has not been tested in practice; and **(iii)** reduces the generation of chemical waste which contributes to the principles of green chemistry (Ferreira et al. 2017; Costa et al. 2018). Factorial designs have been used in several areas, but its use in absorption procedures has not been explored sufficiently.

In this context, the factorial design was employed to optimize a procedure for Sb remediation in wastewater. In addition, the adsorbent material used was obtained from a cleaner, low-cost, and eco-friendly approach from the use of alternative amorphous silica extracted from RHA.

Experimental

2.1. Standards, solvents, and reagents

The rice husk (RH) of agulhinha (Indian origin) variety was received from the Brazilian Agricultural Research Corporation (Embrapa) (São Carlos, São Paulo, Brazil). Details about thermal treatment realized to obtain RHA from RH and characterizations are available in the publication of Costa et al. (2018). Ultrapure water (18.2 M Ω cm resistivity) produced by a Milli-Q® Plus Total Water System (Millipore Corp., Bedford, MA, USA) was used to prepare all the solutions. The Sb analytical standards (Qhemis, São Paulo, SP, Brazil), cetyltrimethylammonium bromide (CTAB) (Neon, Suzano, SP, Brazil), sodium hydroxide (NaOH) (Synth, Diadema, SP, Brazil), and chloric acid (HCl) 37% w/v (Synth, Diadema, SP, Brazil) were used during the procedure. All glassware and polypropylene flasks were washed with soap, soaked in 10% v/v nitric acid (HNO₃) for 24 h, and rinsed with ultrapure water prior to use.

2.2. Preparation of MCM-48 (RHA) mesoporous array

The mesoporous array (named MCM-48 (RHA)) was synthesized from RHA of the agulhinha variety. Thus, amorphous silica was extracted from the RHA by leaching with sodium hydroxide solution and the MCM-48 (RHA) was synthesized by a hydrothermal route. The extraction of the sodium silicate solution was performed according to our methodology developed recently (Costa and Paranhos 2018), and the MCM-48 (RHA) was synthesized as follows: **(i)** 10 g of CTAB was dissolved in 70 mL of NaOH (0.75 mol L⁻¹) under constant stirring at room temperature for 1 h; **(ii)** after this time, 50 mL of the sodium silicate solution from RHA were added slowly into the solution; **(iii)** therefore, this mixture was stirred at room temperature for 2 h and then transferred to a Teflon-lined stainless steel autoclave, which was placed in a vacuum oven and heated at 100 °C for 48 h; **(iv)** after this time, the solution pH was adjusted to ~ 10 with HCl (1 mol L⁻¹) and the reactor was left in the oven for another 24 h at 100 °C; **(v)** the solid product obtained was filtered, washed with deionized water, and dried in a vacuum oven at 100 °C for 12 h; **(vi)** finally, CTAB removal was performed by calcination at 550 °C for 6 h at a rate of 1 °C min⁻¹.

2.3. Characterization of MCM-48 (RHA) adsorbent

The characterization of the RH and RHA was complemented using Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM/EDS). The prepared MCM-48 (RHA) was characterized using Fourier transform infrared spectroscopy (FTIR) spectra for powder samples in the form of KBr pastilles achieved in the region of 4000 to 400 cm^{-1} using a Varian 3100 equipment (at room temperature, 32 scans, and a resolution of 4 cm^{-1}). Powder X-ray diffractometry (XRD) analysis was required on a LabX XDR-6000 (Shimadzu) equipment using Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$) at a voltage/current display of 30 kV/30 mA. The data were collected with a diffraction angle (2θ) ranging from 5 to 80° and scanning rate of 2° min $^{-1}$. SEM analysis was achieved in a FEG-XL30 (Philips) equipment with an EDS accessory, operating with the help of a secondary electron (SE) detector and an accelerator power of at 3 kV. Nitrogen adsorption and desorption isotherms of MCM-48 (RHA) (evacuated for 2 h at 150°C) was acquired using a NOVA 1200 apparatus in the at liquid nitrogen temperature (– 196.15°C). Additionally, the surface area (S_{BET}) and the pore size distribution (D_{BJH}) values were calculated from the adsorption data, using the Brunauer-Emmentt-Teller and the Barrett-Joyner-Halenda methods, respectively.

2.4. Determination of the Sb

The Sb concentrations were measured using an inductively coupled plasma optical emission spectrometry (ICP OES) (iCAP 7000, Thermo Scientific, Waltham, MA, USA). Argon gas (99.996%, White Martins-Praxair, Sertãozinho, SP, Brazil) was used to generate the plasma in all ICP OES measurements. The instrumental conditions were established as the manufacturer recommendations, as being: power (1.2 kW), plasma gas flow (15.0 L min $^{-1}$), auxiliary gas flow (1.5 L min $^{-1}$), nebulizer gas flow (0.7 L min $^{-1}$), and sample introduction flow rate (2.1 mL min $^{-1}$). The emission lines monitored were Sb 206.8 and 231.1 nm.

2.5. Multivariate optimization of adsorption procedure

A full factorial design (2^4) was used in order optimize experimental conditions of adsorption procedure for Sb removal from wastewater. In this study, the variables were evaluated in three levels including the central point: **(i)** pH solution (2, 6, and 10), **(ii)** adsorption time (5, 60, and 115 min), **(iii)** concentration of the Sb standard (2.0, 5.0, and 8.0 mg L $^{-1}$), and **(iv)** adsorbent mass (5, 25, and 45 mg). A total of 19 experiments were carried including triplicate in the central point, that was used to estimate the pure error. As response to full factorial design (2^4) was calculated (%) removal of Sb, obtained from Eq. (1):

$$\% \text{ removal of Sb} = \frac{(\text{Concentration}_{\text{added}} - \text{Concentration}_{\text{found}})}{\text{Concentration}_{\text{added}}} \times 100$$

where $\text{Concentration}_{\text{added}}$ and $\text{Concentration}_{\text{found}}$ (mg L $^{-1}$) are the initial and equilibrium concentrations of Sb, respectively.

Adsorption experiments were conducted in amber flasks (25°C, 400 rpm) in 5 mL of Sb solution. After adsorption process, the samples were centrifuged (3500 rpm, 5 min), and then the supernatant concentration was performed using an ICP OES.

Results And Discussion

As mentioned before, all characterizations of the RH and RHA were performed in our recently published article in the literature (Costa and Paranhos 2018), however this characterization was complemented by SEM/EDS analysis.

3.1. Characterization of MCM-48 (RHA) adsorbent

Figure 1(a) illustrates the FTIR spectra obtained for the MCM-48 (RHA) mesoporous array before and after the CTAB removal. The MCM-48 (RHA) with CTAB presents the narrow bands centered around at 2921, 2852, and 1485 cm^{-1} referents to the C – H stretch of the CH_2 and CH_3 groups of the CTAB groups. However these bands are absent in the calcined MCM-48 (RHA) (Santos et al. 2019). It is also possible to observe for both samples, a broad band around at 3443 cm^{-1} , which can be attributed to the vibration of the O – H bond of the Si – OH groups, as well as the vibration related to the stretching of the O – H bond of H – O–H molecules adsorbed on the surface of the MCM-48 (RHA) (Jang et al. 2009), and also a narrow band around at 1634 cm^{-1} that is assigned to the flexion vibration of H_2O molecules trapped within the mesoporous matrix of the MCM-48 (RHA). Finally, it is possible to observe the main bands associated with the cubic structure of the MCM-48 (RHA), confirmed by the bands located around at 1089 cm^{-1} (ν_{as} , Si – O–Si); 965 cm^{-1} (ν_s , Si – OH); 806 cm^{-1} (ν_s , Si – O), and at 465 cm^{-1} (δ , Si – O–Si) (Endud and Wong 2007; Jang et al. 2009).

Although the MCM-48 (RHA) mesoporous matrix presents a high degree of ordering from the small angle XRD analysis, it is typical that mesoporous materials also have an amorphous diffraction pattern, as seen from the high angle XRD analysis (Fig. 1(b), which can be attributed to the amorphous condensed silica framework of MCM-48 (RHA) array from the silica source used in its hydrothermal synthesis (Costa et al. 2020d).

Figure 1(c) shows the results of the liquid N_2 adsorption/desorption analysis for MCM-48 (RHA). It is possible to observe that the N_2 adsorption/desorption isotherms present a characteristic profile of type IV isotherm and type H1 hysteresis with high adsorption of liquid N_2 , according to the IUPAC classification for nanostructured materials of the M41S family of mesoporous materials (Santos et al. 2019; Costa et al. 2020d, c). Furthermore, these results are confirmed by the narrow mesopores distribution shown by MCM-48 (RHA), which is a characteristic profile of mesoporous matrixes with well-defined regular arrays of mesopores and high N_2 adsorption values. The textural and structural features of MCM-48 (RHA) mesoporous array were calculated from the N_2 adsorption and desorption isotherms, which were summarized in Table 1. In summary, the MCM-48 (RHA) mesoporous material showed: **(i)** high surface area (S_{BET}) value, calculated from BET method; **(ii)** high pore volume (V) and total pore volume (V_T) values; and **(iii)** average pore diameter and pore diameter (D_{BJH}) values between the range of mesoporous materials, which were defined between 2 and 50 nm. The high degree of ordering of the cubic mesoporous structure of MCM-48 has been demonstrated previously (Santos et al. 2019) from the small

angle XRD analysis, which presented the main diffraction planes (211 and 220) of *la3d* space-group symmetry.

Table 1
Textural and structural properties of MCM-48 (RHA) mesoporous material

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V ($\text{cm}^3 \text{g}^{-1}$)	V_{T} ($\text{cm}^3 \text{g}^{-1}$)	D_{BJH} (nm)	Average pore Diameter
MCM-48 (RHA)	820.94	0.18	0.55	3.66	2.69
S_{BET} : BET surface area; V : pore volume; V_{T} : total pore volume; D_{BJH} : pore diameter.					

The SEM images obtained for untreated and treated RH and RHA, as well as for the MCM-48 (RHA) are shown in Fig. 2a(i-iii). The untreated RH showed an external epidermis, which is well-organized and has a rippled surface with an elongated and contorted shape, as well as the appearance of a corn cob. However, after the acid treatment carried out therein (Fig. 2a(ii)), it is possible to observe that the surface of the RH has become more rough, due to the dilution or destruction of the amorphous region of the fibers present in the rice husk (Johara et al. 2012; Costa and Paranhos 2018). Thus, the external epidermis of the RHA, presents the same characteristic of the raw RH, however, in the external epidermis it concentrates the greater percentage of silica (Della et al. 2002, 2005). Therefore, Fig. 2a(iii) shows the internal epidermis of the RHA, which shows the porous structure known as the silica skeleton, from the burning of the organic matter of the RH fibers, and this region also contains a considerable amount of silica (Liou 2004; Ahmed and Adam 2007).

The morphology of the MCM-48 (RHA) mesoporous material was evaluated by SEM, as shown in the image presented in Fig. 2a(iv). Thus, it is possible to observe that the MCM-48 (RHA) presented an agglomerate of uniform spherical particles from the amorphous silica matrix, which is characteristic of the nanostructured mesoporous architecture of the M41S family (Costa et al. 2015). From the SEM-EDS analysis it was possible to determine the chemical composition of the MCM-48 (RHA) (Fig. 2b). The MCM-48 (RHA) presented a high content of Si and O, as these are the main constituents of the framework of the amorphous material responsible for the formation of the MCM-48 (RHA) mesoporous material.

3.2. Multivariate optimization of adsorption procedure

Usually, the adsorption procedures are carried using univariate methodology, which requires a high number of experiments, and consequently greater waste generation and higher cost. To get around these problems, a factorial design was used to optimize the variables involved in adsorption procedures. Table 2 shows a matrix experimental for the full factorial design (2^4) containing 19 experiments with real and coded values and the response in function of the % removal of Sb. Before of evaluating the best conditions for the % removal of Sb, it was necessary to evaluate the quality of the linear model obtained from the factorial design. To evaluate check the quality of the linear model, an analysis of variance (ANOVA) was performed, and the results are available in Table 3.

Table 2

Matrix of the full factorial design (2^4) with real and coded values and the response in function of the % removal of Sb

Variables					
Experiment	pH	Adsorption time (min)	Concentration of Sb standard (mol L ⁻¹)	Adsorbent mass (mg)	% Sb removal
1	2 (-1)	5 (-1)	2 (-1)	5 (-1)	24
2	10 (1)	5 (-1)	2 (-1)	5 (-1)	60
3	2 (-1)	115 (1)	2 (-1)	5 (-1)	74
4	10 (1)	115 (1)	2 (-1)	5 (-1)	85
5	2 (-1)	5 (-1)	8 (1)	5 (-1)	55
6	10 (1)	5 (-1)	8 (1)	5 (-1)	76
7	2 (-1)	115 (1)	8 (1)	5 (-1)	74
8	10 (1)	115 (1)	8 (1)	5 (-1)	82
9	2 (-1)	5 (-1)	2 (-1)	45 (1)	80
10	10 (1)	5 (-1)	2 (-1)	45 (1)	84
11	2 (-1)	115 (1)	2 (-1)	45 (1)	89
12	10 (1)	115 (1)	2 (-1)	45 (1)	89
13	2 (-1)	5 (-1)	8 (1)	45 (1)	92
14	10 (1)	5 (-1)	8 (1)	45 (1)	94
15	2 (-1)	115 (1)	8 (1)	45 (1)	95

Variables					
16	10 (1)	115 (1)	8 (1)	45 (1)	94
17 (CP)	6 (0)	60 (0)	5 (0)	25 (0)	93
18 (CP)	6 (0)	60 (0)	5 (0)	25 (0)	93
19 (CP)	6 (0)	60 (0)	5 (0)	25 (0)	93

CP: central point.

Table 3. ANOVA table in function in function of the % removal of Sb with a 95% confidence level

Parameters	<i>SS</i>	<i>d.f</i>	<i>MS</i>	<i>F_{calculated}</i>	<i>F_{tabulated}</i>
Regression	5102	4	1275	51.80	3.111
Residual	57.25	14	4.089		
Lack of fit	49.25	2	24.62	6.156	19.00
Pure error	8.000	2	4.000		
Total	5159	18			

SS: sum of square; **d.f.** degree of freedom; **MS:** mean of square.

To evaluate a model the first step and check the significance of regression. For that it must be a comparison between the ratio of *Mean Square of Regression* (MS_R) and *Mean Square of Residue* (MS_R) was performed. In this case, the $F_{calculated}$ (51.80) was 17-fold higher than the $F_{tabulated}$ (3.111) at the 95% confidence level. These data demonstrate that the regression of the model is highly significant, which gives credibility to the linear model. The second step for the evaluation of model and check if there is lack of fit. In the case, a comparison between the ratio of *Mean square of lack of fit* (MS_{lof}) and *Mean Square of pure error* (MS_{pe}) was performed. It was observed that the model does not presented lack of fit because the $F_{calculated}$ (6.156) was lower than the value of $F_{tabulated}$ (19.00) at the 95% confidence level. In addition, the quality of the linear model also was evaluated by analyzing the graphic of predicted values *versus* observed, as shown in Fig. 3. Thus, it is possible to observe that the model is well adjusted with 99% regression percentage. This observation confirms the good fit of the model that was verified in the Table 3.

After data processing, the evaluation of best conditions for adsorption procedure for the % Sb removal was performed by analysis of Pareto graphic (Fig. 4), evaluating the significance of the variables and their interactions, at a confidence level of 95% (Ferreira et al. 2018). According to the results presented in Fig. 4 (Pareto graphic), the first order variables are all significant. In addition, some second and third order interactions are also significant. The discussion of the influence of variables on the % removal of Sb will

follow the order of significance presented in the Pareto graphic, according to the following sequence: **(i)** adsorbent mass; **(ii)** adsorption time; **(iii)** pH solution; and **(iv)** concentration of the Sb standard.

The adsorbent mass is the most important variable, and the adsorption efficiency increases with the increase in the mass of the MCM-48 (RHA) adsorbent material. Removal efficiency of Sb can be related to the increased surface area of mesoporous array, well as the availability of more adsorption sites for Sb within the framework of architected matrix of MCM-48 (RHA) (Costa and Paranhos 2020; Costa et al. 2020b). Thus, to ensure a high removal percentage of Sb, we choose to use a mass of 45 mg.

The adsorption time is an important variable, especially when new adsorbents are tested (Costa and Paranhos 2019; Costa et al. 2020a, c). In this study, the adsorption time showed a positive effect on the removal efficiency of Sb by MCM-48 (RHA) adsorbent. We verified from Table 2, that the adsorption times evaluated showed excellent results, especially when combined with the condition of greater mass of adsorbent was used. This behavior can be seen between experiments 9 to 19 as shown in Table 2. Figure 4 also shows that the interaction between adsorbent mass and adsorption time is significant with a negative effect, that is, one of the variables must be tested at the maximum level and the other at the lower level. As the adsorbent mass has been fixed at the maximum level (45 mg), the adsorption time can be fixed using the condition of the central point (60 min).

The pH solution is an important factor affecting the removal of the metal species in aqueous solution. The dependence on metal adsorption in function of the pH solution is related to the type of metal that is in the solution, and to the state of ionization of the adsorbent functional group, which affects the availability of the binding sites. Under the established conditions, the experiments were carried at pH solution ranging from 2 to 10, as shown in Table 2. Under the established conditions, the experiments were carried at pH ranging from 2 to 10. It is possible to observe in Table 2 that the removal percentage was adequate in the pH range evaluated, except in experiments 1, 2, 3, 5, 6 and 7, which showed removal efficiency below 80%. However, it is possible to verify that in the mentioned experiments, the adsorbent mass tested was 5 mg, which seems to interfere in the Sb removal in function of the tested pH range. In the experiments that were used mass of 25 and 45 mg, the removal percentage stayed above 85%. These observations show that the studied material has a good adsorption capacity in the Sb remediation in solutions with pH (2 to 10) using the mass greater than 25 mg. As the purpose of the applying MCM-48-based mesoporous array is to remove Sb from different water samples, we understand that there is no need to establish an optimal pH condition. In this case, we can establish a pH range between 2 and 10 using an adsorbent mass of 45 mg. The no need of pH adjustment is interesting and increases the frequency of the analytical method proposed. In this study, the variable concentration of the Sb standard showed a positive effect. This behavior is very interesting because it shows that adsorbent has the capacity to remove concentrations of Sb considered high.

Figure 5 shows the graph of the desirability to the variables evaluated with the most appropriate condition marked with a red line. Thus, the established conditions were: adsorbent mass (45 mg); adsorption time (60 min); pH (ranged from 2 to 10); and concentration of the Sb standard (8 mol L^{-1}).

3.4. Application using real samples

The proposed method of adsorption was applied for the Sb removal in samples of environmental interest, in the case of this study in water samples. Commonly, the concentration of Sb in water samples is at a trace level (ppb), in this sense the samples analyzed were enriched with known concentrations of Sb. A total of five samples were analyzed and Sb concentrations on the order of 8 ppm were added. These samples were submitted to the adsorption procedure with the optimized conditions, and subsequently the final aqueous solution was subjected to analysis by ICP OES. From Eq. 1 it was possible to calculate the % removal of Sb which varied from 88 to 96%. The adsorbent proposed had not matrix effect in the adsorption process, and thus confirming that can be used in the remediation of Sb in water samples.

Conclusions

In this present approach, we carry out the synthesis of MCM-48-based mesoporous array via an inexpensive, sustainable, and eco-friendly hydrothermal method using an alternative silica source extracted from the rice husk ash. The prepared mesoporous material was subsequently tested as an adsorbent material in the Sb remediation, which was completely useful in the adsorption of this metal. The prepared MCM-48 (RHA) array exhibited an amorphous framework with the N₂ adsorption/desorption isotherms of type IV and type H1 hysteresis, due to the high nitrogen adsorption, surface area, and pore volume, and average pore diameter between the range of mesoporous materials. In addition, the mesoporous matrix presents a narrow mesopores distribution and uniform spherical particles, typical the architectures with well-defined regular channels. In addition, the variables of adsorption procedure were optimized using a full factorial design (2⁴). In this case, the factorial design was useful to find the optimized conditions using a smaller number of experiments. We also highlight the effectiveness of the MCM-48, which does not need to adjust the pH of aqueous solutions, this increases the analytical frequency method proposed.

Declarations

Compliance with ethical standards

Ethics approval

Not applicable.

Consent to participate

Not applicable.

Consent for publication

The Authors transfer to Springer the publication rights.

Availability of data and materials

The authors declare that data supporting the findings of this study are available within the article.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Authors' contributions

José Arnaldo Santana Costa: Conceptualization, Methodology, Validation, Investigation, Formal analysis, Resources, Writing – Original Draft. **Vinicius Câmara Costa:** Conceptualization, Methodology, Validation, Investigation, Formal analysis, Resources, Writing – Original Draft. **Matheus Lima de Mello:** Methodology, Validation, Formal analysis. **Caio Marcio Paranhos:** Conceptualization, Methodology, Validation, Investigation, Formal analysis, Resources, Writing – Original Draft, Supervision.

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Figures

Figure 1

FTIR spectra of MCM-48 (RHA) mesoporous array before and after CTAB removal (a), XRD profile (b), and N_2 adsorption/desorption isotherms and BJH pore size distribution of MCM-48 (RHA) mesoporous material without CTAB surfactant (c).

Figure 2

MEV of (i) untreated and (ii) treated RH, (iii) treated RHA, and (iv) MCM-48 (RHA) mesoporous array (a) and EDS spectrograph and elemental mapping of MCM-48 (RHA) mesoporous material (b).

Figure 3

Observed values versus predicted values, for linear model in function of the % Sb removal.

Figure 4

Pareto graphic of effects for full factorial design, in function of the % Sb removal.

Figure 5

Graphic of profiles of predicted values and desirability in function of the % Sb removal.