

Preliminary study of the ability of Magadiites to remove methanol in aqueous solution monitored by ATR-FTIR

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Abstract

Methanol, present in wastewater, can become an atmospheric pollutant and an environmental liability of effluents. This work proposes the synthesis of layered silicates by hydrothermal route (NaMag and SnMag) and the potential of these materials in removing methanol from water. XRD, ICP OES, UV-Vis, and TPD-NH₃ characterized the adsorbents. The method developed by ATR-FTIR showed an excellent prediction capacity for identifying and quantifying methanol in an aqueous solution. Finally, the data showed 40% efficiency in removing methanol with SnMag in 30 min of reaction.

Keywords: ATR-FTIR, wastewater, methanol adsorption, magadiite.

1. Introduction

Water is a limited resource, making it increasingly challenging to meet the population's needs. Based on the UN World Water Development Report (WWDR), it is estimated that by 2050, 57% of the world's population will live in areas that will experience water scarcity for at least one month per year and that pollution from industrial effluents in water bodies will further limit the amount of water that is safe for human consumption [1]. Residual methanol is a toxic contaminant that, if not treated properly, can cause severe environmental damage, including pollution of water bodies [2]. In addition to water contamination, methanol can evaporate during effluent treatment, causing air pollution. Therefore, efficient removal of methanol from wastewater is a priority to ensure sustainability.

Current wastewater treatment methods, such as distillation and activated carbon adsorption, have been effective in removing methanol from aqueous solutions [3]. However, these methods come with significant limitations, including high operating

costs and substantial energy consumption. In the face of these challenges, it becomes crucial to explore alternative adsorbent materials that can offer higher efficiency, lower cost, and sustainability. Magadiite, a rare silicate mineral, is a promising material that stands out for its exceptional properties and could overcome these limitations.

In this study, we propose to investigate the efficiency of magadiite in methanol adsorption from aqueous solutions, focusing on the optimal operating conditions (adsorbent amount and contact time). Through controlled experiments, we intend to determine the methanol removal efficiency (R%) under different magadiites (NaMag and SnMag) monitored by ATR-FTIR. The results of this study will contribute to the field of catalysis and adsorption, offering valuable insights into the application of magadiite as an innovative and efficient adsorbent material. For this purpose, future tests will be carried out to compare the performance of magadiite with other conventional adsorbents to establish its superiority and potential for industrial

application in methanol adsorption processes in water.

2. Experimental

2.1 Materials

Methanol (Merck, HPLC, $\geq 99.9\%$), Ludox® HS-40 colloidal silica (Aldrich), sodium hydroxide (Aldrich, $\geq 98.0\%$), Sn(IV) chloride pentahydrate (Aldrich, $\geq 98.0\%$) and deionized water. All reagents were used as received.

2.2 Synthesis and characterization of Magadiites

The synthesis strategy was reported in the literature [4]. According to this strategy, the composition of the synthesis gel used for NaMag was 0.1500 Na₂O: 1 SiO₂: 14.2857 H₂O, and for SnMag, it was 0.0075 SnO₂: 0.1640 Na₂O: 1 SiO₂: 14.3 H₂O, corresponding to a Sn/Si ratio = 0.007. Under hydrothermal conditions, pH~12, the synthesis gel was transferred to autoclaves and heated in an oven at 150 °C under autogenous pressure and static conditions for 72 h. After the aging time, the autoclave was cooled to room temperature. After that, the solid product was separated from the supernatant by filtration, washed with distilled water, and dried at 100 °C for eight hours in air with a heating rate of 10 °C min⁻¹. XRD, ICP OES, UV-Vis, and TPD-NH₃ characterized the adsorbents.

2.3 Detection and quantification of methanol by ATR-FTIR

Before obtaining the infrared spectra, in addition to the analysis room environment being fully controlled with temperature and air humidity of approximately 20 °C and 35 %, respectively, the methanol standard solutions were prepared by quantifying 0.3204 g of methanol poured into 50 mL volumetric flasks and completing the volume with deionized water. Ten methanol standard solutions of the same concentration (0.641 % m V⁻¹) were prepared. After arranging the working solutions, the mid-IR spectra by Fourier transform were obtained by a Shimadzu spectrometer, model IRSpirit coupled with a QATR-S single reflection measurement cell, and a diamond prism with a contact diameter of 1.8 mm. The measurements were performed in the spectral range of 1300-900

cm⁻¹, 45 scans in absorbance mode, resolution of 8 cm⁻¹, apodization by the Sqr Triangle function, and 20 µL of each sample input were used. These operating conditions led to 30 s analysis time. The absorbance values were used as the analytical signal for constructing the curve. They were obtained in two steps: baseline subtraction by the peak analysis function and band deconvolution using the Gauss model with Levenberg–Marquardt interaction algorithm. The performance evaluation of the method developed in this work was followed as determined by the document DOQ-CGCRE-008 of INMETRO; more details can be found in [2].

2.4 Methanol adsorption tests in water

The tests presented in this work consist of a reaction mixture of aqueous methanol solutions at 0.641% m V⁻¹ with the adsorbents NaMag and SnMag, varying the adsorbents' mass quantity and contact time. In the adsorbent quantity tests, NaMag was chosen, varying the mass ratio of NaMag: methanol in 0.125:1, 0.25:1, 0.5:1, 1:1, 1.5:1 and 2:1. Obtaining values of ideal adsorbent quantity, the tests continued to verify the feasibility of using SnMag for the removal of methanol as a function of the contact time that varied from 30-300 min. At the determined times, aliquots were generally removed, filtered, and analyzed by FTIR-ATR.

3. Results

3.1 Characterization of Magadiites

A range of physicochemical analysis techniques were used to characterize the different NaMag and SnMag adsorbents; a more detailed discussion of these results can be found in [4]. Some of these techniques are presented in this work. Table 1 shows data from X-ray diffractograms (XRD) and the Sn determination performed on an inductively coupled plasma atomic emission spectrometer (ICP OES) of NaMag and SnMag. In Fig. 1, it is possible to observe an excellent structural ordering of all samples, especially the one modified with Sn, indicating that the insertion of this metal preserved its lamellar organization without significant displacement of the 2θ indices and similar values of basal spacing, presenting practically the exact distance between the lamellae, compared to the NaMag sample, which may suggest that the

replacement of Si atoms by Sn was adequate. In addition, the theoretical and experimental amounts of Sn in SnMag correlated well (Table 1).

Table 1. Results of XRD and ICP OES analyses.

Sample	BS ^a (nm)	C ^b (%)	Theoretical Sn ^c (%)	Experimental Sn ^d (%)
NaMag	1.55	100	-	-
SnMag	1.57	62	1.45	1.56

^a Basal spacing calculated by Bragg's Law.

^b Crystallinity calculated in the 2 θ range of 23-30°.

^c Based on the composition of the synthesis gel.

^d Determined by ICP OES.

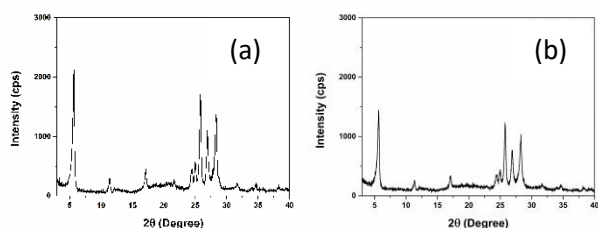


Fig. 1. X-ray diffractograms of (a) NaMag and (b) SnMag samples, synthesized at 150 °C for 72 h.

The UV-Vis spectra in Fig. 2 (a-b) showed only absorption bands in the ultraviolet region (200-380 nm), smaller than 350 nm, intense, and related to the allowed transitions, called charge transfer (CT) bands. In particular, the SnMag material presented an E_{bg} of 4.46 eV (Table 2). The lower value compared to NaMag suggests that Sn strongly influences the crystal field splitting, consequently leading to a more excellent breaking of the degeneracy and a possible overlap of orbitals [5].

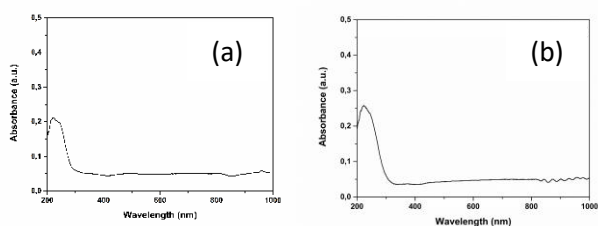


Fig. 2. Diffuse reflectance spectra in the UV-Vis region (200-800 nm): (a) NaMag and (b) SnMag.

Table 2. Results of UV-Vis and TPD-NH₃ analyses.

Sample	E_{bg} ^a (eV)	Acid strength ^b ($\mu\text{mol g}^{-1}$ de NH ₃)
NaMag	4.51	5
SnMag	4.46	35

^a Band gap energies (E_{bg}) calculated by the Tauc method.

^b Acid strength values estimated by isotherms in the region between 150 and 300 °C.

3.2 Detection and quantification of methanol by ATR-FTIR

The present study used FTIR coupled to an ATR cell in absorbance mode to validate the analytical curve prepared at different concentrations considering the protocol determined by INMETRO [6]. Thus, the band related to the vibrations of the C—O bond at 1016 cm⁻¹ was analyzed (Fig. 3 (a-b)). To construct the analytical curve, 9 points corresponding to 70 dilutions of the standard solutions were prepared, alternating between 10 and 5 repetitions per point. However, as the ATR-FTIR was unable to read the samples with lower concentrations (0.008, 0.016, and 0.032 % m V⁻¹), the analytical curve was constructed with 5 points corresponding to 40 dilutions of concentrations ranging from 0.128 to 0.641 % m V⁻¹. Given this limitation, the lowest concentration of methanol reliably quantified was 0.064 % m V⁻¹, considered the detection limit, and 0.128 % m V⁻¹, the quantification limit.

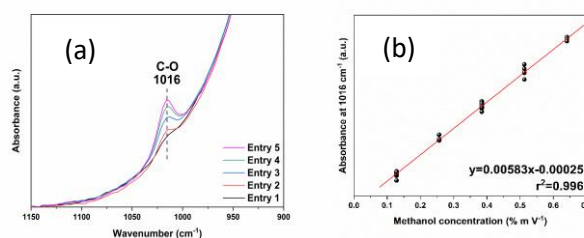


Fig. 3. (a) Spectra obtained by ATR-FTIR of methanol solutions at different concentrations 0.128, 0.256, 0.384, 0.512 and 0.641 % m V⁻¹ from inputs 1-5, respectively. (b) Analytical absorbance curve as a function of concentration with $r^2 > 0.99$.

3.3 Analysis of methanol removal from water

The methanol adsorption results on NaMag and SnMag adsorbents presented here are preliminary and refer specifically to the analysis of the amount

of adsorbent and the contact time. For this, the calculation of the methanol removal efficiency (R given in %) was taken into account, as shown in equation (1), and the concentration values were estimated considering the equation of the straight line (Fig. 3 (b))

$$R_{(\%) } = ((C_i - C_t) / C_i) \times 100 \quad (1)$$

Fig. 4 (a-b) shows the graph of the amount of adsorbent as a function of R (%). Considering the values of adsorbent masses used in the tests, an efficiency increase was expected with the mass of NaMag. 43% was achieved with the 2:1 adsorbent:methanol ratio (0.6416 g:0.3204 g). For the analysis of the contact time (Fig. 4 (c-d)), the 1:1 adsorbent: methanol ratio was considered, 0.3204 g of NaMag was used with 0.3204 g of methanol and 0.3204 g of SnMag and 0.3204 g of methanol in water reacting at different times (30, 60, 120, 180, 240 and 300 min). With NaMag, there is an exponential growth in methanol removal (from 5-23%) with increasing contact time (from 30-300 min). With SnMag, greater efficiency of methanol removal is evident, reaching 40% in the first 30 minutes of the reaction.

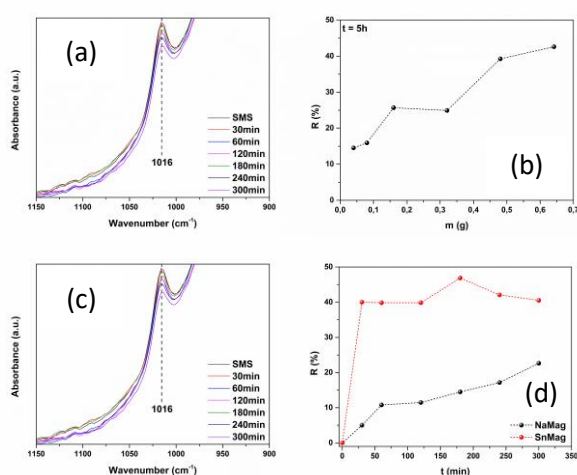


Fig. 4. (a) ATR-FTIR spectra of the standard methanol solution (SMS) at a concentration of 0.641 % m V⁻¹ and of the solutions at different adsorbent:methanol ratios. (b) Data on the efficiency of methanol removal with different mass amounts of NaMag in water for 5 h. (c) ATR-FTIR spectra of the standard methanol solution (SMS) at

a concentration of 0.641 % m V⁻¹ and at different contact times with the NaMag and SnMag adsorbents. (d) Data on the efficiency of methanol removal with the NaMag and SnMag adsorbents as a function of contact time.

It is concluded that Magadiites were successfully obtained. The mid-FTIR region spectroscopy method developed here offers advantages such as direct analysis, without sample preparation, without solvents, economically viable, and performed in a maximum of 30 seconds per sample. Finally, Magadiites proved to be excellent adsorbents in methanol removal processes in water.

Acknowledgements

The authors thank UFMA, IFMT, UFMT, FAPEMAT and CAPES.

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