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## Hydrogen Sulfide Adsorption on Cobalt (II) and Chromium (III) Modified kaolinite

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**Abstract** In this work it is reported the synthesis, characterization and hydrogen sulfide (H<sub>2</sub>S) adsorption of Co (II) and Cr (III) modified kaolinite. The modified matrices were prepared by cation exchange process. The pure and modified matrices were characterized by X-ray diffractometry, X-ray fluorescence, FTIR-spectroscopy and thermogravimetry. Based on X-ray fluorescence data, it was verified that the total amount Co(II) and Cr(III), incorporated to the clay matrix (expressed as oxides) were: CoO (20.1 %) and Cr<sub>2</sub>O<sub>3</sub> (1.3%). The total amount of adsorbed H<sub>2</sub>S (gravimetric data) are: pure kaolinite (2.6 mg/g), K-Co (4.7 mg/g) and K-Cr (2.8 mg/g).

**Keywords** IonExchange, H<sub>2</sub>S, Adsorption, Kaolinite, Clay.

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### Introduction

As it is well known today, Hydrogen sulfide is a major air pollutant entering the atmosphere, and can contaminate water and soil. So, it is very important to develop methodologies able to promote its withdraw from air, water or soil.

Taking into account that they are present all around the world, as well as its non toxic (except from inhalation) nature and cheap prices, clays are very good potential matrices for solid-gas adsorption, as well as for solid-solution compounds as shown for crude oil adsorption on vermiculite [1-2].

In this work it is reported the synthesis, characterization and hydrogen sulfide (H<sub>2</sub>S) adsorption of Co (II) and Cr (III) modified kaolinite.

### Experimental

Cobalt (II) and chromium (III)solutions (0,1mol/L) were prepared by using CoCl<sub>2</sub>.6H<sub>2</sub>O and Cr(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O, respectively. The employed kaolinite was supplied by Santana<sup>®</sup>, and have, as informed by the supplier, the following chemical composition: Si (20.4 %), Fe (13.0 %), Al (7.7 %), Sn (2.6 %), Mg (0.6 %), K (0.2 %), S (0.2 %), Mn (0.06 %), Ni (192 ppm and Ca (170 ppm).

In order to synthesize the Co (II) and Cr(III) modified samples, 10 g of kaolinite were suspended in 100 mL of the prepared solutions and mechanically stirred (300 rpm) for 48 hours. Then, the prepared matrices were filtered off and washed with distilled water and dried under vacuum at room temperature (28 °C). The modified samples will be named, hereafter, as follows: K-Co and K-Cr.

The hydrogen sulfide (H<sub>2</sub>S) employed to adsorption on the modified matrices were prepared by reacting FeS with concentrated HCl. The adsorption processes were performed as follows: about 2.4 cm<sup>3</sup> of the modified matrix was confined in a glass reactor thorough which a H<sub>2</sub>S flux was directed. The total mass of employed modified matrices were measured in a analytical balance before and after the H<sub>2</sub>S adsorption. So, the total amount of adsorbed H<sub>2</sub>S per gram of modified matrix was determined gravimetrically.



The infrared spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) were obtained in KBr pellets, by using a Perkin-Elmer FTIR (model spectrum 65) apparatus. The thermogravimetric curves ( $25\text{--}900\text{ }^{\circ}\text{C}$ ) were obtained in a Shimadzu TGA-50H apparatus ( $\text{N}_2$  atmosphere, heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ ). The X-Ray diffraction patterns were collected in a Rigaku (MiniFlex II) apparatus ( $30\text{KV}$ ,  $15\text{mA}$ ,  $\text{Cu K } \alpha = 0,1542\text{nm}$ ,  $\text{Ni filter} = 0,03\text{mm}$ ), and the X-Ray fluorescence spectra in a Shimadzu apparatus (EDX – 720 Energy Dispersive X-Ray spectrometer).

## Results and Discussion

### Kaolinite

By inspection of the X-Ray diffraction pattern of the clay sample provided by Santana<sup>®</sup>, it is verified that it is a kaolinite-quartz sample (Figure 1). The 001 diffraction plane it is associated with a  $7.2\text{ }^{\circ}$  interlayer distance to the employed sample, in agreement with those reported for kaolinite [3].

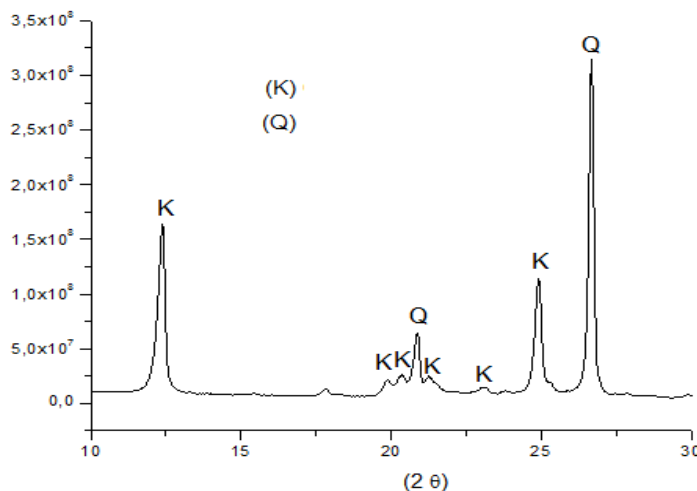


Figure 1: X-Ray diffraction pattern for the employed clay sample, exhibiting diffraction peaks characteristics of kaolinite (K) and quartz (Q).

The obtained infrared spectrum for the unmodified clay sample is in agreement with the literature data for kaolinite, been observed peaks at  $1110\text{ cm}^{-1}$ ,  $1034\text{ cm}^{-1}$  and  $1007\text{ cm}^{-1}$ , associated the Si-O-Si stretching [4],  $940$  and  $913\text{ cm}^{-1}$  associated with the superficial OH groups and Al-Al-OH groups [1]. The other main bands/groups are:  $795\text{ cm}^{-1}$  (Si-O),  $754\text{ cm}^{-1}$  (Si-O-Al),  $698\text{ cm}^{-1}$  (OH), out of plane Si-O-Al ( $540\text{ cm}^{-1}$ ), in plane Si-O ( $471\text{ cm}^{-1}$ ) and Si-O inflexion ( $430\text{ cm}^{-1}$ ) [3]. In figure 2 is shown a section of the obtained infrared spectrum, focusing the bands associates with OH groups. By X-Ray fluorescence, the following chemical composition (expressed as oxide percentages) was obtained:  $\text{SiO}_2$  (32.1 %),  $\text{Fe}_2\text{O}_3$  (18.7 %),  $\text{Al}_2\text{O}_3$  (16.4 %),  $\text{TiO}_2$  (10.5 %),  $\text{ZrO}_2$  (8.1 %),  $\text{K}_2\text{O}$  (3.4 %),  $\text{BaO}$  (3.1 %),  $\text{SrO}$  (1.9 %) and  $\text{Cr}_2\text{O}_3$  (0.2 %).

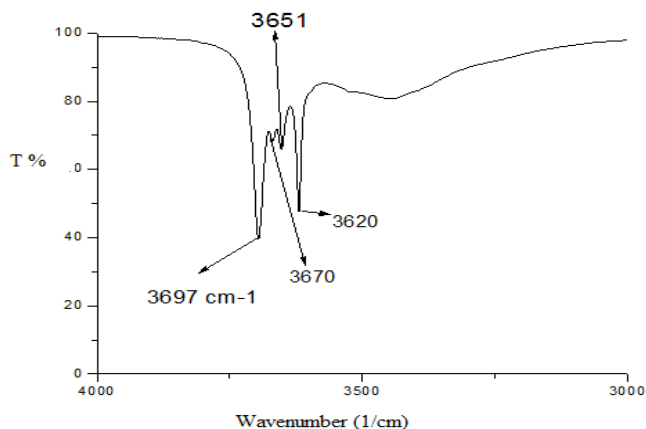


Figure 2: FT-IR Spectrum for employed kaolinite, with special attention to superficial OH stretching ( $3697$ ,  $3670$  and  $3651\text{ cm}^{-1}$ ) and internal (between octahedral and tetrahedral sheets) OH groups ( $3620\text{ cm}^{-1}$ ).



The thermogravimetric curve obtained for kaolinite is shown in Figure 3. The mass loss (0.4 %) from 200 °C to 450 °C is associated with the release of physisorbed water molecules. The main mass loss (5.7 %), in the 450-650 °C range is due to the condensation of OH (superficial and internal) groups, releasing water molecules, as follows:  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow \text{Al}_2\text{O}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O}$ .

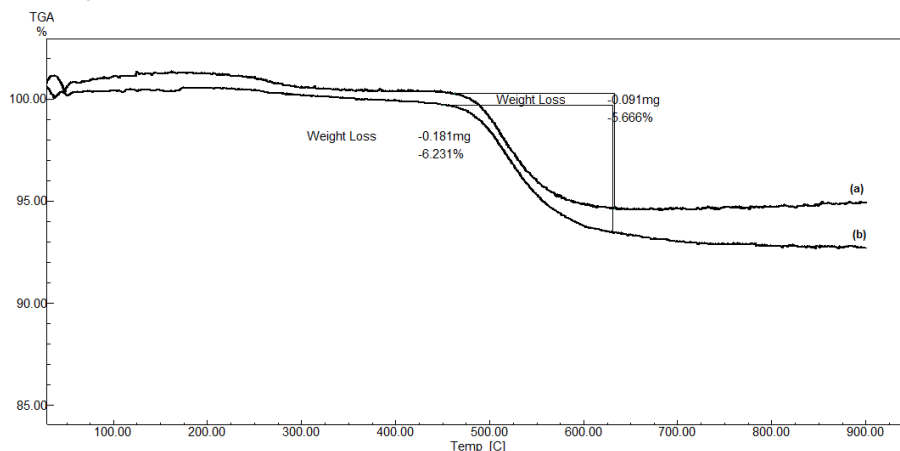


Figure 3: Thermogravimetric curves for kaolinite (a) and  $\text{H}_2\text{S}$  adsorbed kaolinite matrix (b).

#### Modified and modified- $\text{H}_2\text{S}$ adsorbed kaolinite

It is worth noting that the cation exchange performed to prepare the modified kaolinite samples, and the subsequent  $\text{H}_2\text{S}$  adsorption have not exerted any modification on the nanostructure of kaolinite, as verified by inspection of the modified/adsorbed samples, which exhibits the same diffraction peaks exhibited by the pure kaolinite sample.

In the FT-IR spectra of the  $\text{H}_2\text{S}$  adsorbed samples, the bands associates with S-H vibrational modes are not observed. This fact can be explained considering that the S-H bands are superimposed with the clay bands, as well as that such S-H bands are week, in comparison with the intensity of kaolinite bands.

Based on X-Ray florescence data, the total amount of Co(II) and Cr(III), incorporated to the clay matrix (expressed as oxides) can be pointed out: CoO (20.1 %) and  $\text{Cr}_2\text{O}_3$  (1.3%).

The total amount of adsorbed  $\text{H}_2\text{S}$  (gravimetric data) are: pure kaolinite (2.6 mg/g), K-Co (4.7 mg/g) and K-Cr (2.8 mg/g). The total amount of adsorbed  $\text{H}_2\text{S}$  for K-Co and K-Cr matrices are well above the values observed for clinopitilite, 13X zeolite and 5 Azeolite [5] and well below those observed for Cu(II), Zn(II) and Fe(III) pillared montmorillonite [6]. On the other hand, the very simple and cheap experimental procedure employed in the present work, makes, from an economical point of view, the prepared K-Cr and K-Co matrices, specially the first one, more attractive than any other. The Co-Ni matrix exhibits an adsorption capacity about lower than the Rhodamine-B modified kaolinite (10.1 mg/g) [7].

Cobalt generally forms octahedral compounds. This fact probably affect that coordination of Co(II) inside the kaolinite skeleton, leaving coordination sites available (to coordinate with sulfur). The very low adsorption capacity of the Cr(III) matrix can be explained by the hard and soft acids and bases theory:  $\text{S}^{2-}$  it is a soft base, and so, have a lower affinity for a hard acid such as Cr(III).

Comparing the TG curves for kaolinite, K-Co and K-Cr matrices before and after  $\text{H}_2\text{S}$  adsorption, can be verified that the mass loss in the 450-650 °C range is higher for the  $\text{H}_2\text{S}$  adsorbed matrices, as expected. However, it is verified that the difference (before and after hydrogen sulfide adsorption) it is lower than that could be expected based on the  $\text{H}_2\text{S}$  adsorption ability of those matrices. This fact can be explained considering that the process of metal cation incorporation in kaolinite occurs with release of  $\text{H}^+$  from the OH groups of kaolinite, making the mass loss due to water condensation lower in the  $\text{H}_2\text{S}$  adsorbed matrices than in the pure kaolinite. The obtained TG curves for free and  $\text{H}_2\text{S}$  adsorbed matrices are shown in Figures 4 and 5. As can be verified by inspection of the TG curves, the thermal desorption of  $\text{H}_2\text{S}$  occurs at higher temperatures (~500 °C) for all cation-modified kaolinite samples, in comparison with pure kaolinite (~450 °C). So, a stronger Lewis acid-Lewis base interaction (covalent bonding, in this case) can be inferred for K-Co and K-Cr samples.



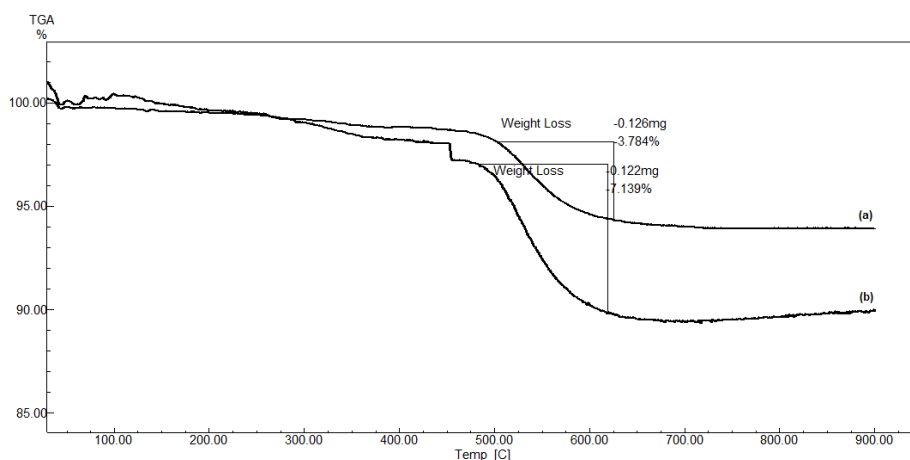


Figure 4: Thermogravimetric curves for K-Co (a) and H<sub>2</sub>S adsorbed K-Co matrix (b)

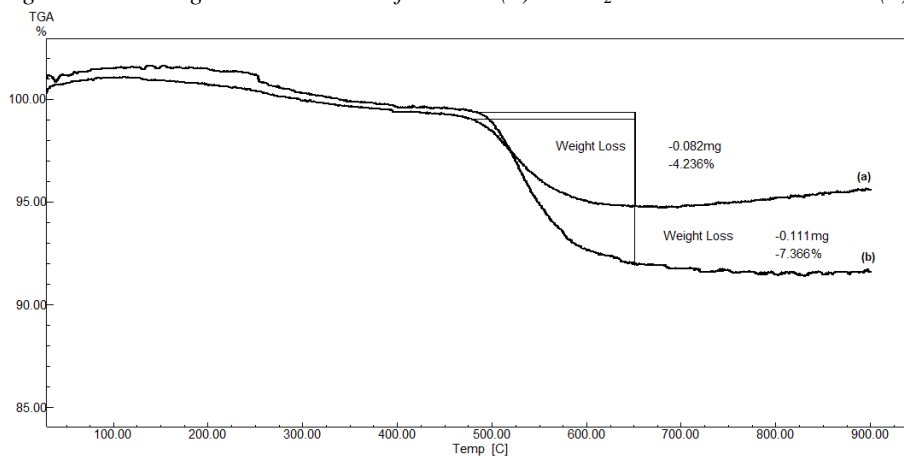


Figure 5: Thermogravimetric curves for K-Cr (a) and H<sub>2</sub>S adsorbed K-Cr matrix (b)

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