



## Synthesis of Polymethylmethacrylate spheres covered with vanadyl phosphate, vanadium pentoxide and rhodamine-B for hydrogen sulfide capture

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**Abstract** In this article it is reported the use of Polymethylmethacrylate (PMMA) spheres covered with vanadyl phosphate (PMMA-VP), vanadium pentoxide (PMMA-VO) and rhodamine-B (PMMA-RB) for hydrogen sulfide capture. The vanadyl phosphate, vanadium pentoxide and rhodamine The PMMA itself to not exhibits affinity towards hydrogen sulfide under the experimental conditions employed in the present work. The hydrogen sulfide maximum capture capacity of the hybrid matrices were measure as 2.06, 9.54 and 3.33 mg/g for PMMA-VP, PMMA-VO and PMMA-RB, respectively.

**Keywords** Polymethylmethacrylate, Hydrogen sulfide, Adsorption, rhodamine-B

### Introduction

Hydrogen sulfide is an important air and water pollutant, and large amounts of it are produced as a by-product of industry. Been soluble in water and organic solvents, H<sub>2</sub>S actuates as a strong corrosive agent towards metals. Hence, there is a lot of interest in obtaining chemical or physical routs and procedures able to capture, form air or water, this compound.

In this article it is reported the use of Polymethylmethacrylate spheres covered with vanadyl phosphate, vanadium pentoxide and rhodamine-B for hydrogen sulfide capture.

### Experimental Work

Vanadyl phosphate (VOPO<sub>4</sub>·2H<sub>2</sub>O) was prepared according to the methodology described elsewhere [1-7]: 12.5 g of vanadium pentoxide, V<sub>2</sub>O<sub>5</sub> (Aldrich), 111g of H<sub>3</sub>PO<sub>4</sub> 85% (Vetec), 288 mL of distilled water and 1.5 mL of HNO<sub>3</sub> 65 % (Vetec) were mixed under reflux for 16 hours. After this period, a yellow solid was obtained and filtered off, washed with acetone and dried under vacuum at room temperature.

Polymethylmetacrylate, PMMA (Dental Vipi), whose structural formula is shown in Figure 1, Vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) and rhodamine-B (Aldrich) were employed was supplied.

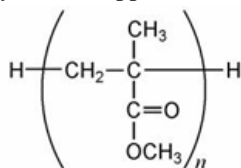


Figure 1: Structural formula for PMMA



In order to cover the polymer spheres, aqueous solutions of  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{V}_2\text{O}_5$  and rhodamine-B with concentrations of  $2,5 \times 10^{-2} \text{ mol L}^{-1}$ ,  $2,0 \text{ mol L}^{-1}$  and  $2,0 \text{ mol L}^{-1}$ , respectively, were prepared.

In each recovering experiment, 20 g of polymer was suspended in 25 mL (vanadyl phosphate and rhodamine-B) or 50 mL (vanadium pentoxide) solution and then mechanically stirred (30 rpm) for 48 h. After this, the prepared matrices were filter off and dried at room temperature in a desiccator for 4 days.

The hydrogen sulfide ( $\text{H}_2\text{S}$ ) employed to adsorption on the modified matrices were prepared by reacting FeS with concentrated HCl. The adsorption processes were performed as follows: about  $2.4 \text{ cm}^3$  of the modified matrix was confined in a glass reactor thorough which a  $\text{H}_2\text{S}$  flux ( $10 \text{ cm}^3/\text{min}$ ) was passed by 30 minutes. The total mass of employed modified matrices were measured in a analytical balance before and after the  $\text{H}_2\text{S}$ . So, the total amount of adsorbed  $\text{H}_2\text{S}$  per gram of modified matrix was determined gravimetrically.

The X-ray diffraction patterns were obtained in a Rigaku diffractometer model MiniflexII, with a scan rate of  $5^\circ/\text{min}$ , applied voltage of 15kV and current 15 mA, using Cu  $K_\alpha$  radiation and a Ni filter.

Thermogravimetric analysis were performed in a Shimadzu DTG-60 H apparatus, with a heating rate of  $10^\circ \text{C min}^{-1}$  under  $\text{N}_2$  atmosphere ( $50 \text{ mL min}^{-1}$ ).

The SEM images were obtained using a microscope Phillips model XL30-ESEM.

The FT-IR spectra were obtained in a PerkinElmer apparatus, model Spectrum 65 in KBr discs ( $4000$  to  $400 \text{ cm}^{-1}$ ).

## Results and Discussion

The vanadyl phosphate, vanadium pentoxide and rhodamine B polymethylmetacrylate recovered matrices will be named here as PMMA-VP, PMMA-VO and PMMA-RB, respectively. The PMMA itself to not exhibits affinity towards hydrogen sulfide under the experimental conditions employed in the present work. The hydrogen sulfide maximum capture capacity of the hybrid matrices were measured as 2.06, 9.54 and 3.33 mg/g for PMMA-VP, PMMA-VO and PMMA-RB, respectively. It is worth noting that such adsorption capacities are well above those verified for 13X and 5A zeolites [8] and for pillarized montmorillonite [9]. It is worth noting that the rhodamine B recovered sample exhibits a lower hydrogen sulfide capture capacity when compared with kaolinite recovered sample [10].

The obtained thermogravimetric curve for PMMA is shown in Figure 2. A complete mass loss is observed in the  $250$ - $400^\circ \text{C}$ . The mass losses (%) in the  $200$ - $400^\circ \text{C}$  in Figure 2 is associate with the chain-end-initiated unzipping mechanism for PMMA degradation [11-12], with the thermal degradation under nitrogen occurring in two steps, as observed previously [13].

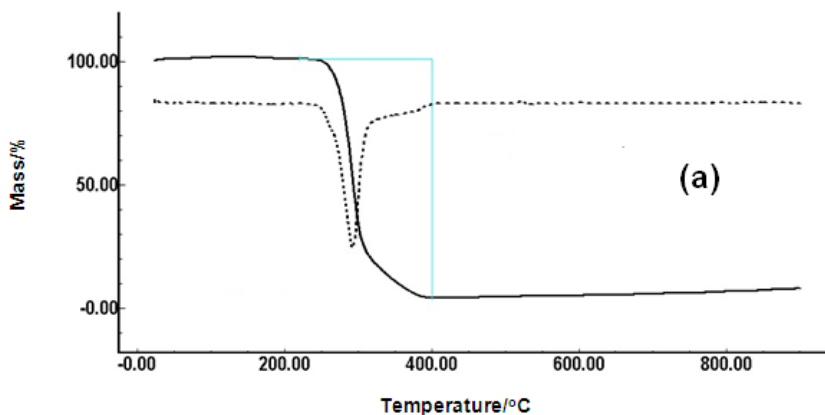


Figure 2: Thermogravimetric curve for PMMA

The TG curves for hybrid and hydrogen sulfide captured samples (not shown) exhibits very similar thermal degradation profiles (almost juxtaposable curves). So, from TG data it is not possible to calculate the total amount of adsorbed  $\text{H}_2\text{S}$ . However, it is worth noting that, whereas for PMMA-VP and PMMA-VO samples, the  $\text{H}_2\text{S}$  desorption starts at  $\sim 250^\circ \text{C}$ , for PMMA-Rb sample, such thermal induced desorption starts at  $\sim 300^\circ \text{C}$ . Such fact is



probably due to a stronger interaction between rhodamine B and H<sub>2</sub>S molecules, associated with protonation of rhodamine B, as previously proposed [10].

The SEM micrograph for PMM spheres are shown in Figure 3. It was verified that the recovering processes dot not changed the spheroid morphology of the polymer particles.

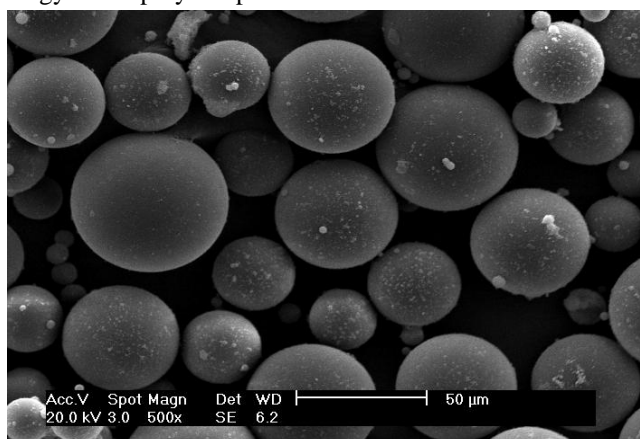


Figure 3: SEM micrography for PMMA

The FTIR spectra for PMM and hybrid matrices are shown in Figure 4. The FTIR spectra for all matrices. To PMMA, are observed main bands at 3438, 2956, 1729 and 1450 cm<sup>-1</sup>, associated with the stretching modes of the OH, CH, CO and OCH<sub>3</sub>, respectively. It is worth noting that for PMMA-RB matrix the characteristic OH band it is not observed, suggesting that for such matrix the water adsorption process is not favorable.

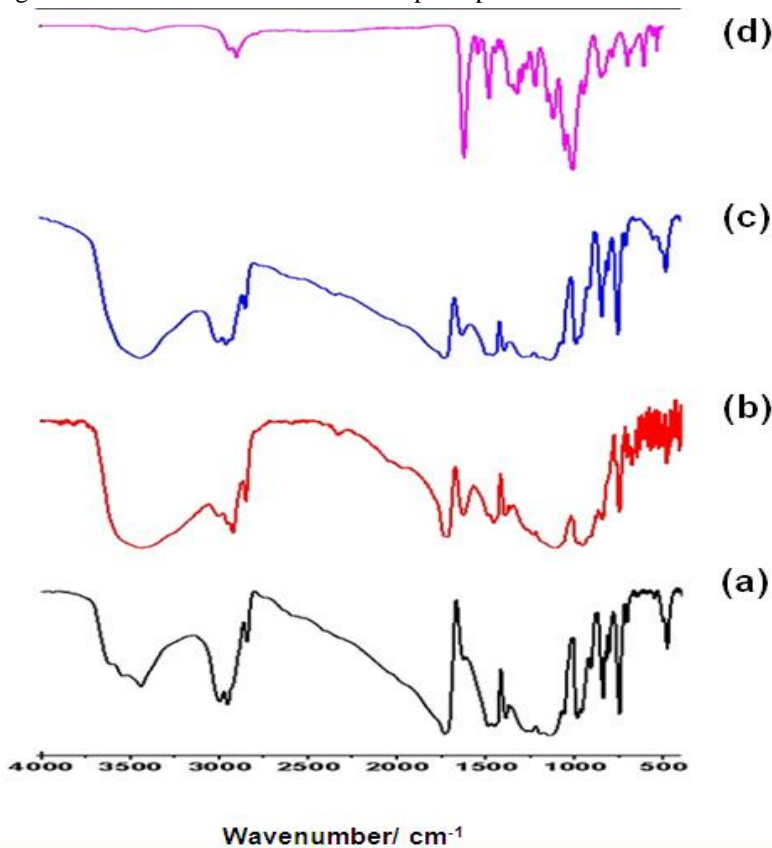


Figure 4: FTIR spectra for (a) PMMA, (b) PMMA-VP, (c) PMMA-VO and (d) PMMA-RB



In the FTIR spectra of the H<sub>2</sub>S reacted matrices is shown in Figure 5. It is worth noting that a broad band around 3600 cm<sup>-1</sup> absent in the H<sub>2</sub>S unexposed matrix is present, for PMMA-RB sample. Such band it is associated with H<sub>2</sub>S spectrum [14]. For PMMA-VP and PMMA-Vo samples, the characteristic OH band was replaced, after reaction, by the SH band. In agreement with the gravimetric data, the PMMA pure sample do not exhibits such band.

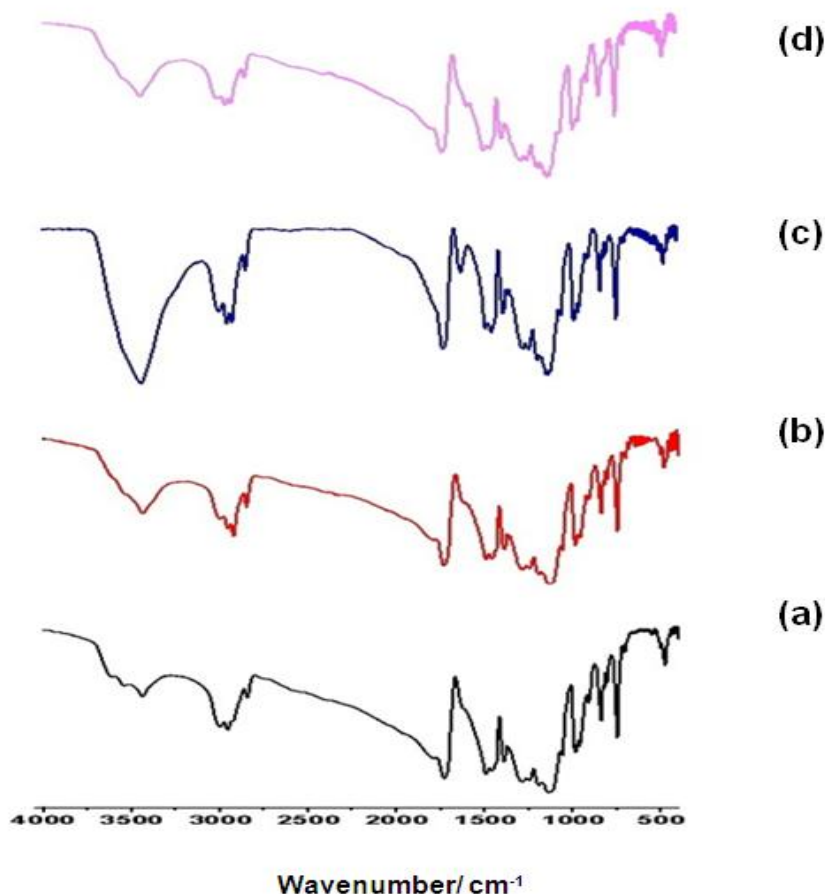


Figure 5: FT-IR spectra for samples after hydrogen sulfide exposure:  
(a) PMMA, (b) PMMA-VP, (c) PMMA-VO and (d) PMMA-RB

The X-ray diffraction patterns for PMMA, hybrid and hydrogen sulfide captured samples (not shown) exhibits only three diffraction peaks of very low intensity, indicating that before and after reactions, the PMMA matrix is, for any practical purpose, amorphous.

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