Development and application of multi-walled carbon nanotubes decorated with niobium pentoxide in the removal of sacubitril/valsartan

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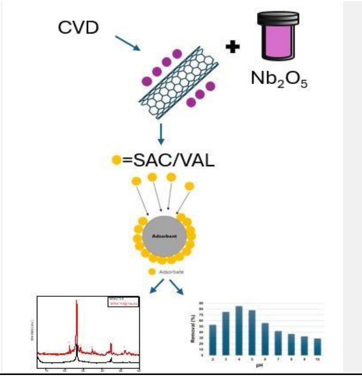

The use of medications grows exponentially around the world and, sometimes, due to their incomplete metabolism, these substances such as Sacubitril/Valsartan (SAC/VAL) are excreted in their unchanged form. The present work aims to synthesize and characterize a developed material to be used mainly in the removal of aquatic contaminants for adsorption. The characterization indicated that the niobium pentoxide was fixed onto the surface of the multi-walled carbon nanotubes. The adsorption test indicated that the maximum removal was obtained at pH 4, corresponding to 85 % removal and adsorption capacity of 97.0 mg g^{-1}.

Introduction

The emerging pollutants are a major problem to society since they can cause several environmental problems also are difficult to remove through traditional water treatment methods [1]. One way, to remove the traces of pollutants is through adsorption technology, which is efficient and reliable [2,3]. Furthermore, the adsorption field is always aiming for the development of new materials which increases the removal of potential.

One solution is the application of multi-walled carbon nanotubes (MWCNTs), which can be employed as the basis for the latter decoration of the surface with oxides [4]. The niobium pentoxide (Nb_2O_5) is a semiconductor metal oxide, presenting low toxicity in cells, chemical and thermal stability, and strong corrosion resistance [5].

Taking into consideration the MWCNTs and the Nb_2O_5 decoration potential, a new adsorbent was developed. The material was characterized through x-ray diffraction analysis, scanning electron microscopy, and pH point of zero charge (pH_{pzc}). Later the material was employed in the removal of SAC/VAL to be evaluated as adsorbent.

Material and Methods

1) Synthesis: MWCNTs were synthesized by Chemical Vapor Deposition [6]. The production of MWCNTs@Nb_2O_5 composite was carried out in two stages: MWCNTs functionalization and Nb_2O_5 decoration. In this way, the functionalization utilized acid nitric 3 mol L^{-1}, and posteriorly, the decoration used nickel ferrite with the citrate-based by the sol-gel method [7].

2) Characterization: The crystalline structure of the MWCNTs@Nb_2O_5 composite was characterized in an X-ray diffractometer (XRD, Philips, X'pert MPD), settled at 40 kV, 40 mA, and Cu (λ = 1.54056 Å) anode at 0.05° s^{-1} ranging from 5 – 60 º. The morphology was characterized by scanning electron microscopy (SEM) in a JEOL microscope (JSM 6060) with a maximum operational tension of 30 kV and a nominal resolution of 3.5 nm with magnifications up to 200.000x. The applied tension was 10–20 kV. The pH point zero charge was determined through the salt titration method [8].

3) Adsorption test: Experimental adsorption with MWCNTs@Nb_2O_5 was performed by batch mode in ambient temperature with SAC/VAL as a contaminant. Adsorption was studied with 50 mg MWCNTs@Nb_2O_5 in 100 mL of SAC/VAL solution (50 mg L^{-1}) at pH (2 - 10). The adsorbate solubilized with 2 % ethyl alcohol (95 %). The solution was then incubated for 24 hours on a rotary shaker at 120 rpm. The SAC/VAL residual concentration was measured using a UV-vis spectrophotometer (Shimadzu) at λ=226 and 254.

Results and Discussion

Figure 1(A) shows the XRD diffractograms corresponding to MWCNTs (black) and MWCNTs@Nb_2O_5 (red), where it was possible to observe that the crystalline peaks characteristic of CNTs were identified according to JCPDS (No. 01-0646). Furthermore, the decorated sample showed all peaks corresponding to Nb_2O_5 (JCPDS No. 27-1313). This result is an indication that the MWCNTs were coated with Nb_2O_5. The SEM micrography (Figure 1B) showed that the CNTs were decorated with Nb_2O_5 nanoparticles [2]. It was found that the MWCNTs@Nb_2O_5 possess a pH_{ZCP} equivalent to 7.2. This indicates that the surface of the material will be positively charged when the pH is below the pH_{ZCP} and negatively charged when the pH values are above the pH_{Zcp}.

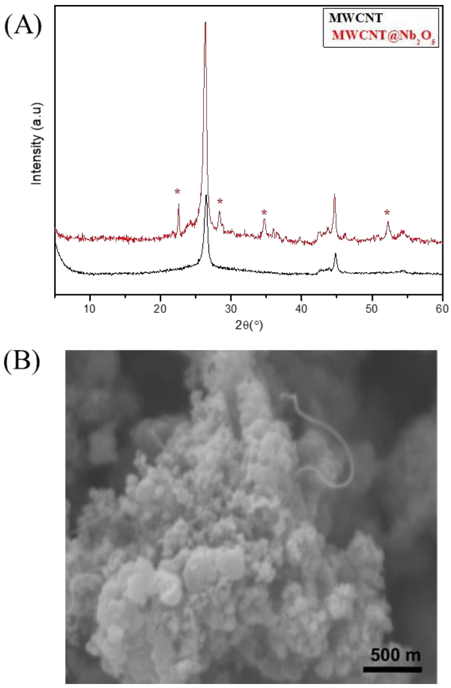

Figure 1. (A) XRD diffractograms of the MWCNTs and MWCNTs@Nb_2O_5, and (B) SEM micrography of the MWCNTs@Nb_2O_5.

In acid conditions, SAC/VAL presents an anionic character (pKa = 4.73). Above this pH (4.73) the drug is partially ionized, affecting electrostatic interactions between the adsorbent and the pollutant [9]. Similarly, electrostatic interactions are also affected at pH values below the pH_{ZCP}.

The adsorption phenomenon can occur through various mechanisms, depending on the affinity between absorbent and adsorbate molecules. In this study, some hypotheses about the removal of SAC/VAL on MWCNTs@Nb_2O_5 are suggested, such as π-π stacking, dipole-dipole interactions through hydrogen bonding, Yoshida hydrogen bonding, cation-π, and n-π interactions. The presence of aromatic rings in both the adsorbate and the adsorbent allows for the occurrence of Yoshida hydrogen bonding, n-π interactions, and π-π stacking, regulating the adsorption mechanisms of SAC/VAL on MWCNT@Nb [6].

Last the pH effect on the removal (R) is given in Figure 2. It was found that the pH strongly affected the adsorption where the values go from 52.45 % at pH 2 to reaching maximum value at pH 4, which corresponds to 85 %. After that, the percentage of removal started to decline reaching 28.63% removal. The maximum removal value corresponds to 97.0 mg g^{-1}.

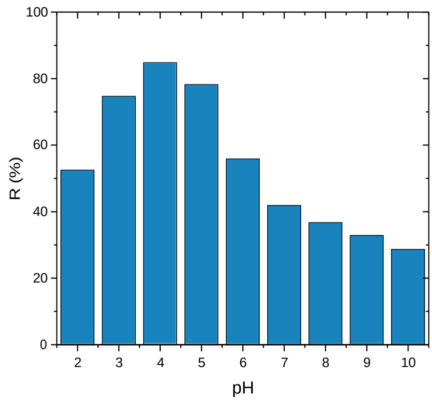

Figure 2. pH influence on the adsorption of SAC/VAL onto MWCNTs@Nb_2O_5

Conclusions

A potential carbon-based nano adsorbent decorated with niobium was synthesized for adsorption tests. Therefore, MWCNTs@Nb_2O_5 showed good adsorption capacity, indicating that it will be a promising material for future tests in photocatalysis.

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