Boosting sulfonamides electrodegradation efficiency with Ruthenium-modified $BiVO_4$ catalysts

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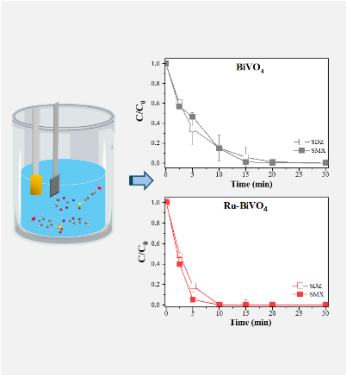

This research investigates the characteristics of BiVO4 when adding 1% ruthenium and its influence on physical and electrochemical properties. The material was applied to the degradation of sulfadiazine (SDZ) and sulfamethoxazole (SMX) through electrochemical treatment. Physical and electrochemical characterizations demonstrated that there was an improvement in the material's properties when adding ruthenium. Furthermore, the antibiotics SDZ and SMX were completely degraded after just 10 min of application of the process under neutral conditions and using low current density (1 mA cm^{-2}) and supporting electrolyte concentration (0.063 mol L^{-1}).

Introduction

The release of recalcitrant compounds, originating from industries, into water bodies is a major global challenge, since failure to treat these compounds causes damage to the ecosystem[1]. Advanced oxidative electrochemical processes are based on the electrogeneration of oxidizing species for mineralization of pollutants. The choice of material is crucial, as depending on the material and the process, different species will be formed. Ruthenium is widely studied for having excellent electrocatalytic properties, however it has a high value, which is why it is important to study new alternative materials. Therefore, the proposed work aims to study the electrocatalytic properties of a promising and cheap semiconductor, bismuth vanadate ($BiVO_4$), and dopping it with ruthenium. Finally, the photoanode eficiency was applied to sulfadiazine (SDZ) and sulfamethoxazole (SMX) degradation by electrocatalysis.

Material and Methods

The synthesis of the materials consisted of electrodeposition of 10 layers of bismuth (III) nitrate solution in ethylene glycol, applying a potential of up to -1.8 V vs Ag/AgCl (KCl sat), subsequently adding the acetylacetonate solution of vanadyl in dimethyl sulfoxide followed by calcination to complete formation of the material. In the materials doped with ruthenium, 1% $RuCl_3$ was added to the bismuth nitrate solution. The materials produced were characterized physically and electrochemically.

The phase composition of the samples were characterized by X-Ray diffraction (XRD, Shimadzu 6000 X-ray Diffraction Protocol) and the morphology of the films was characterized by field emission scanning electron microscopy (FE–SEM, JEOL®, JSM-IT300 model), operating at 15 kV.

The electrochemical characterizations (EC) and degradation experiments were performed in a three-electrode cell filled with 0.063 mol L-1 NaCl solution (pH 6.8) using BiVO4 and Ru-BiVO4 as working electrode, platinum as counter electrode and Ag/AgCl as reference. The EC were carried out using a potentiostat/galvanostat (PGSTAT302N, Autolab, Methrom®).

The antibiotics concentration during the degradation process was monitored using ultra-high performance liquid chromatography (UHPLC), using a Shimadzu Nexera X3instrument equipped with a diode array detector (SPD-M40).

Results and Discussion

The SEM-EDS images demonstrate a greater roughness of Ru-$BiVO_4$ films (Fig. 1b) on the surface of the film, when compared to the film without ruthenium films (Fig. 1a). The XRD patterns of the $BiVO_4$ and Ru-$BiVO_4$ films (Fig. 1c) demonstrate a monoclinic structure (JCPDS 14-0688) without influence of the addition of ruthenium in the monoclinic phase of $BiVO_4$, which may indicate efficient doping.

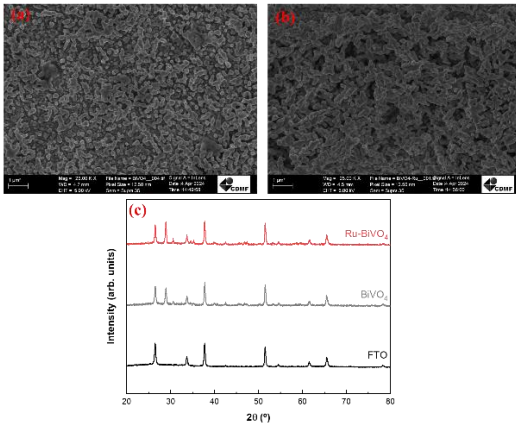

Fig.1. SEM-EDS spectra analysis conducted **a)** BiVO4 and **b)** Ru-BiVO4; **c)** XDR patterns of $BiVO_4$, Ru-$BiVO_4$ and FTO samples

In the in linear voltammetry, observed onset potential for OER as shown in Fig. 2a. This was done by extrapolating the lines of the capacitive and faradaic regions, and finding the intersection between them. This parameter is regarded crucial because when the overpotential of OER is higher, there is a greater probability that the process leads to hydroxyl radical generation. Thus, the electrode will be more effective in degrading organic compounds. Furthermore, in Fig.2b we have the Nyquist diagrams, where it is known that the size of the arc corresponds to the resistance to charge transfer, where the smaller arc indicates a better charge transfer efficiency on the electrode surface [3].

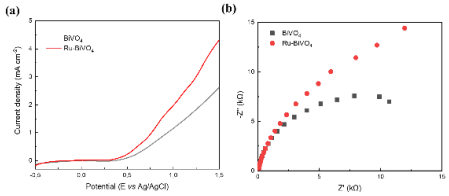

Fig 2. (a) Linear and (b) Ru-BiVO4; **a)** Linear voltammetry curves conducted at 5 mV s^{-1}**b)**; Nyquist diagrams recorded anodes.

It can be observed that doping with 1% Ruthenium reduces the on set, indicating that it may be more efficient in the treatment of effluents contaminated with organic compounds. Corroborating the linear scan, it is observed that the arc of the nyquist diagram is smaller for electrodes containing ruthenium, indicating that reactions can occur more quickly.

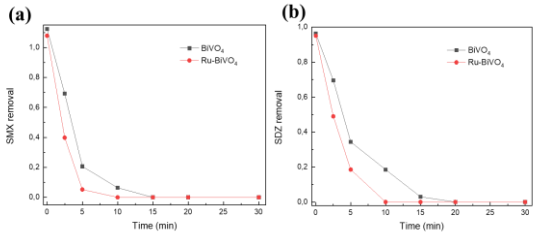

Fig.3. a) SMX and **b)** SDZ degradation by electrocatalysis using Ru-$BiVO_4$ or $BiVO_4$ as anode; SDZ= SMX = 1.0 mg L^{-1}; [NaCl] = 0.063 mol L^{-1}

The degradation of SDZ and SMX was investigated by electrocatalysis applying current density of 1 mA cm2 and 0.063 mol L-1 NaCl as supporting electrolyte (Fig. 3). The use of the developed anodes as a catalyst resulted in a removal for SDZ and SMX. However, when using Ru-doped electrodes, SMX was completely removed in just 5 min and SDZ was completely removed after 10 min of application of the process. These results can be related to the generation of oxidizing species generated in the solution followed by the degradation of organics. These results highlight the relevance of Ru doping in $BiVO_4$ to improve the efficiency of the anode applied to the degradation of antibiotics.

Conclusions

In this work $BiVO_4$-based anodes were developed and applied to study the degradation of SDZ and SMX antibiotics through electrochemical treatment. It was observed that when doping with 1% Ru there was a significant improvement in the electrochemical characteristics and in the removal efficiency of two antibiotics. Therefore, it is possible to state that the Ru-$BiVO_4$ electrode is an excellent alternative for treating water contaminated with organic pollutants.

Acknowledgments

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