#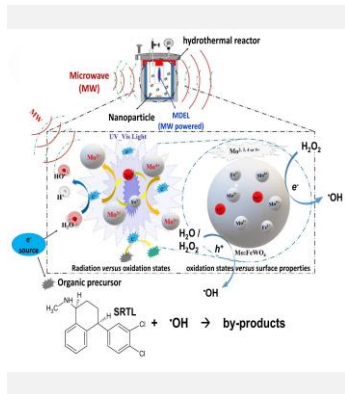 Photocatalysts obtained by the synergistic effect of microwave, ultraviolet, and visible radiation aiming the sertraline degradation

V. Marques[1]. R. Nogueira[1], A. Moreira[1]. (1) São Paulo State University (UNESP), Av. Prof. Francisco Degni, 55 – J. Quitandinha, Araraquara - SP, Brazill. marques.ferreira@unesp.br

Nanomaterials based on Mo:FeWO$_4$ have been produced by a new synthetic route that uses the synergistic effect of microwave (MW), ultraviolet (UV), and visible (Vis) radiation during the nanomaterial crystallization. The microwave power, presence of the UV-Vis light source, synthesis time, and dopant were shown to influence the physicochemical properties of the materials. These materials were applied in the degradation of the sertraline (SRTL) emerging pollutant under visible light or UV-A (365 nm) in the absence or presence of hydrogen peroxide (H$_2$O$_2$). SRTL removal was up to 49% and 80% under Vis and UV-A light, respectively. However, the degradation performance increased to 99% when 10 mmol L^{-1} of H$_2$O$_2$ was used. Therefore, in addition to being a direct photocatalyst, the materials were efficient in the H$_2$O$_2$ activation to produce hydroxyl radicals responsible for optimizing the degradation of the SRTL contaminant.

Introduction

Different synthetic routes have been investigated to obtain photocatalytic materials with optimized photoactivity for the degradation of priority environmental pollutants [1]. Recently, a new synthesis route that synergistically applies microwave (MW), ultraviolet (UV), and visible (Vis) radiation to grow nanostructures has proved effective in producing samarium-modified TiO$_2$ as a photocatalyst for atrazine degradation [2]. The different radiations used synergistically during the synthesis of the nanomaterial can influence its morphological, crystalline nature, optical properties, and, especially, its photoactivity. When nanostructures are based on metals with variable oxidation states, such as iron (2+ or 3+) and molybdenum (2- to 6+), photoactivity can be optimized due to shallow or deep defects in the crystal structure. In addition to being a direct photocatalyst, these materials can also be used as hydrogen peroxide photo(activators) which is an excellent electron acceptor. Thus, when excited for the conduction band of a semiconductor, reactive oxygen species (ROS) are producing from the reduced of H$_2$O$_2$ in CB [3]. Therefore, molybdenum-modified iron tungstate catalysts (Mo:FeWO$_4$) were obtained and applied to the degradation of the antidepressant Sertraline (SRTL).

Material and Methods

Synthesis of nanomaterials: In a 50 mL beaker, 10 mL of the (115 mg L^{-1}) Na$_2$WO$_4$ solution followed by 5 mL of the (7.58 mg L^{-1}) FeCl$_3$ solution were added under constant stirring and kept for 5 min. Afterwards, 0.133 g of H$_2$MoO$_4$ was added to the mixture and kept stirring for a further 5 min. The whole mixture was then transferred to a Teflon vessel, added to a microwave discharge electrodeless lamp (MDEL) when necessary, and subjected to microwave treatment. The synthesis variables investigated were microwave power, pure or doped material, synthesis time, MDEL, and heat treatment. The notation FeW_1 to FeW_16 is the summary identification of the samples, while the values (X_Y_Z_M) represent X = Synthesis time (min), Y = Microwave power (W), Z = Dopant, M = MDEL). In the photodegradation studies, 5 mg of each catalyst was dispersed in 10 mL of a 10 mg L^{-1} sertraline solution. The mixture was kept stirring in the dark for up to 2 hours to achieve the equilibrium and were then irradiated with visible light or UV-A (365 nm) for 2 hours. The four best catalysts were then selected for 2-hour photodegradation studies in the presence of 10 or 50 mmol L^{-1} H$_2$O$_2$. Degradation was monitored by HPLC-UV using a calibration curve with R^2 = 0.996, LOD = 4.98 µg L^{-1} and LOQ = 16.60 µg L^{-1}.

Results and Discussion

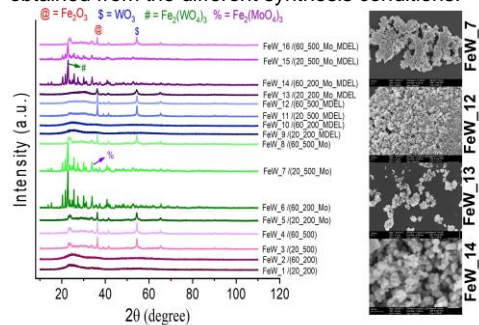Fig. 1 shows the X-ray pattern of the samples obtained from the different synthesis conditions.

Fig. 1 - X-ray pattern of the samples treated at 500 °C and SEM_FEG images.

The most crystalline samples (FeW_6, 7, 14 and 15) have a mixture of Fe_2O_3, WO_3, $Fe_2(WO_4)_3$ and $Fe_2(MoO_4)_3$ phases, while other samples have a higher percentage of Fe_2O_3 and WO_3 (FeW_3, 4, 5, 8, 11, 12, 13 and 16) or a totally amorphous characteristic (FeW_1, 2, 9 and 10). The amorphous nature is a consequence of the low microwave power, while the greater crystallinity is associated with higher power or longer synthesis time. SEM-FEG images showed that the samples are made up of agglomerates of spherical particles with a diameter of a few nanometers. Fig. 2 shows the bandgap values calculated for the different samples, which vary from 2.43 to 3.21 eV.
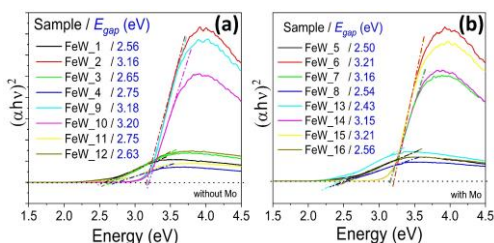

Fig. 2 - TAUC plot showing the bandgap energies of the unmodified (a) and Mo-modified samples.

The response to light absorption does not indicate the influence of Mo or the crystallinity of the material. As this property correlates with structural defects, techniques such as photoluminescence will be used to investigate this behavior in depth. Considering that light absorption varies from the visible to the ultraviolet region, SRTL photodegradation assays were carried out under visible or UV-A light. Under visible light, the best performance was a total SRTL removal of 49%, 45%, 40% and 38% in 2h for FeW_13, 12, 4 and 7, respectively (Fig. 3).
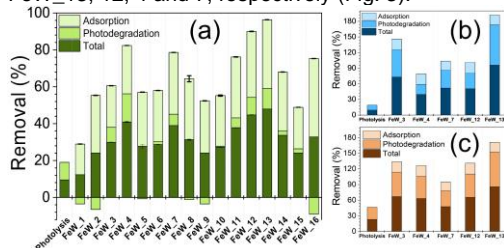

Fig. 3. Photocatalysis assays of SRTL (10 mg L^{-1}) under visible light (a) and in the presence of 10 mmol L^{-1} (b) or 50 mmol L^{-1}(c) of H_2O_2 in 2h.

Thus, degradation in the presence of 10 mmol L^{-1} (a) or 50 mmol L^{-1} (b) of H_2O_2 increased total removal to >95% or >82%, respectively, in the presence of FeW_13.

These results show that the materials improved the SRTL degradation in presence of H_2O_2. Repeated assays under UV-A light show an improvement in the performance of other catalysts to degrade SRTL in the absence of H_2O_2 (Fig. 4). However, the performance of the FeW_13 sample is still superior and is improved in the presence of H_2O_2 under UV-A light.
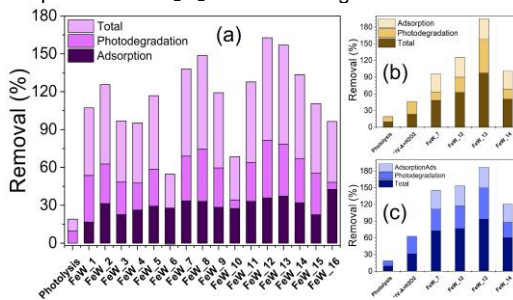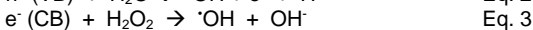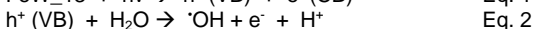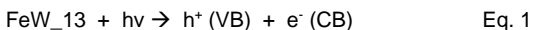

Fig. 4. Photocatalysis assays of SRTL (10 mg L^{-1}) under UV-A light (a) and in the presence of 10 mmol L^{-1} (b) or 50 mmol L^{-1}(c) of H_2O_2 in 2h.

The mechanisms involved in the degradation of SRTL in the presence or absence of H_2O_2 are summarized by equations 1 to 4. The hydroxyl radicals formed from the oxidation of water or the reduction of H_2O_2 are responsible for improving the SRTL degradation under visible or UV-A light.

$$FeW\_13 + hv \rightarrow h^+ (VB) + e^- (CB) \qquad \text{Eq. 1}$$
$$h^+ (VB) + H_2O \rightarrow \ ^{\cdot}OH + e^- + H^+ \qquad \text{Eq. 2}$$
$$e^- (CB) + H_2O_2 \rightarrow \ ^{\cdot}OH + OH^- \qquad \text{Eq. 3}$$
$$SRTL + \ ^{\cdot}OH \rightarrow \text{by-products} \qquad \text{Eq. 4}$$

Conclusions
The photocatalysts obtained in this study using a new synthesis route showed that the crystal structure is greatly influenced by the different synthetic conditions investigated. The bandgap varied between energies in the visible and ultraviolet regions, making it possible to apply for different spectra of electromagnetic radiation. Among the materials obtained, FeW_13, a material modified with Mo, added of the MDEL and produced in 20 min using a microwave power of 200W showed good performance for the SRTL degradation. Using visible or UV-A light, the materials were efficient in direct degradation and in activating H_2O_2 to produce hydroxyl radicals.

References
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