Preparation of polymer solutions for the obtaining of nanofibers by electrospinning

Preparação de soluções poliméricas para a obtenção de nanofibras por electrospinning

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ABSTRACT
The preference for using nanomaterials is due to properties such as small particle size, diversified shape and large specific surface area. Numerous polymer solutions can be prepared for use in electrospinning, such as: polyvinyl alcohol (PVA), poly-L-lactic acid (PLLA), polyvinylpyrrolidone (PVP), collagen, among others. In this work TiO_2 nanofibers were synthesized by electrospinning, through the preparation of polymer solutions containing polyvinylpyrrolidone. The samples were analyzed by ray diffraction (DRX), by scanning electron microscopy (SEM) for microstructural analysis, and the photocatalytic evaluation, by photodegradation tests of 125 mL of a 20 ppm solution of the methyl orange. The partial results show that TiO_2 nanofibers treated at a temperature of 650 °C showed more efficiency in the degradation of the methyl orange dye. They showed greater photoactivity in the tests, due to the presence of the anatase phase, which is proven to be the most photoactive phase of TiO_2.

Keywords: polyvinylpyrrolidone, titanium dioxide, nanofiber, electrospinning, photocatalysis.

RESUMO
A preferência pela utilização de nanomateriais deve-se a propriedades como o tamanho reduzido das partículas, forma diversificada e grande área de superfície específica. Numerosas soluções de polímeros podem ser preparadas para utilização em electrospinning, tais como: álcool polivinílico (PVA), ácido poli-láctico (PLLA), polivinilpirrolidona (PVP), colagénio, entre outros. Neste trabalho, as nanofibras de TiO_2 foram sintetizadas por electrospinning, através da preparação de soluções poliméricas contendo polivinilpirrolidona. As amostras foram analisadas por difracção de raios (DRX), por microscopia electrónica de varrimento (SEM) para análise microestrutural, e a avaliação fotocatalítica, por testes de fotodegradação de 125 mL de uma solução de 20

ppm do laranja de metilo. Os resultados parciais mostram que as nanofibras de TiO_2 tratadas a uma temperatura de 650 °C mostraram maior eficiência na degradação do corante laranja de metilo. Mostraram maior fotoactividade nos ensaios, devido à presença da fase anatase, que é comprovadamente a fase mais fotoactiva do TiO_2.

Palavras-chave: polivinilpirrolidona, dióxido de titânio, nanofibras, electrospinning, fotocatálise.

1 INTRODUCTION

The decline in material dimensions enables a large surface area/volume connection, and is directly related to electrochromism, since in addition to increasing the number of active sites for the occurrence of redox reactions, it also increases the material's coloring speed. This feature provides greater adhesion of the surface with the electrolyte, determining fast ionic exchange. In this way, whenever the electrochromic material has the structure in the nanometer scale, the response time property is superior to the original material. With the use of nanomaterials it is possible to obtain, in addition to savings in the amount of material used, also a high performance of these devices (in the order of milliseconds) [1].

Electrospinning is an easy to handle and effective method for producing fibers with small diameters, using electric fields of high voltage (5-50KV) and low current (0.5-1μA). In this process, a jet of fluid material is ejected and stretched through an electric field, for the production of fibers/nanofibers [1]. In addition to the aforementioned advantages of using this technique, we can also highlight the variety and type of material (from biopolymers to ceramics) that can be obtained with electrospinning synthesis. Because it produces fibers, fabrics, and non-woven fibers, quickly and continuously, with diameters varying between micrometers, nanometers, and etc [2].

Generally, the process for the continuous production of nanofibers is composed of five operational components, which are: syringe filled with liquid and/or fluid, the formation of the jet in the capillary, the thinning of the constant jet, and the appearance and growth of the jet of instability that are responsible for the beginning of the reduction in the diameter of the fibers [2].

A multitude of polymeric solutions can be prepared for use in electrospinning, such as: polyvinyl alcohol (PVA), poly-L-lactic acid (PLL), collagen, polyvinylpyrrolidone (PVP), etc.

TiO_2 is the most used semiconductor in heterogeneous photocatalysis, as it has the following characteristics: non-toxicity, insolubility in water, photostability, possibility of immobilization on solids and chemical stability over a wide pH range [3-4]. Its application dates back to the 70s, when Fujishima and Honda [5] reported the photodecomposition of water in a TiO_2 electrode irradiated in a photoelectrochemical cell, generating hydrogen and oxygen. It was from these studies that photocatalysis became a very efficient option in the destruction of pollutants.

Within this context, this work synthesized TiO_2 nanofibers by electrospinning to function as semiconductors in heterogeneous photocatalysis. Where the photocatalytic activity of nanofibers was evaluated by photodegradation tests of 125 mL of a 20 ppm solution of methyl orange dye.

2 EXPERIMENTAL

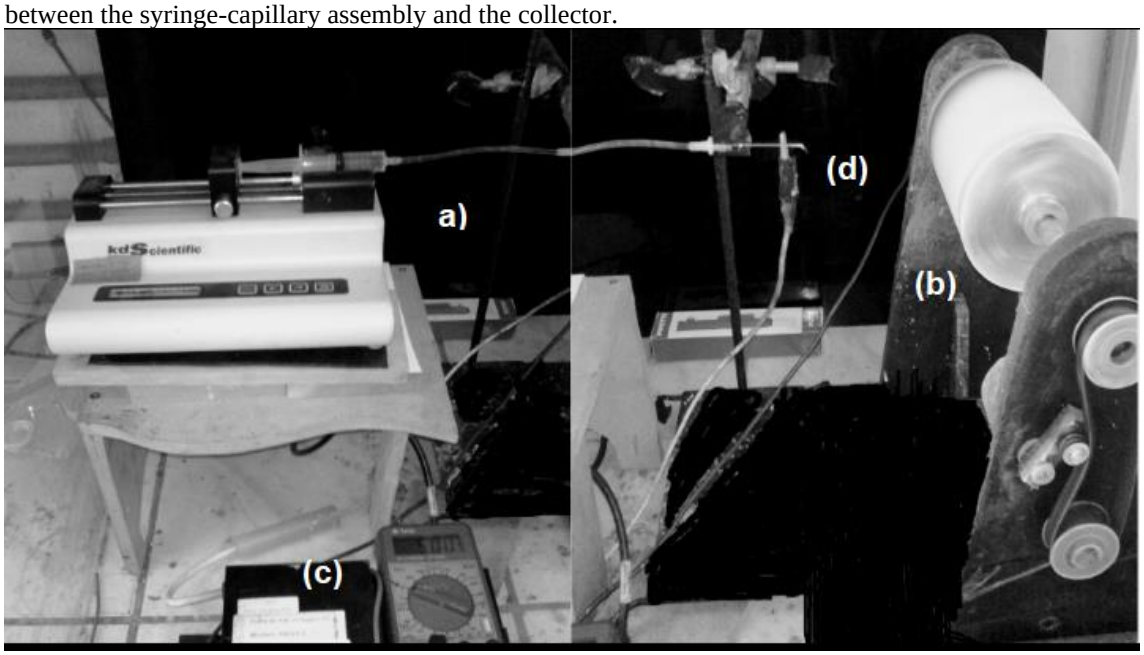
For the electrospinning synthesis, it was initially necessary to prepare a precursor solution containing:

i) TiO_2 solution – 2.5 mL of titanium propoxide (TiP) were mixed; 2 mL of glacial acetic acid and 5 mL of an alcoholic solution containing 10% by weight of polyvinylpyrrolidone (PVP). This solution was obtained by mixing 10 g of the polymer polyvinylpyrrolidone (PVP) in a beaker containing 100 mL of ethyl alcohol, without heating and, under constant magnetic stirring, until all the polymer was completely dissolved. The Figure 1 is a photographic image of the TiO_2 solution for the synthesis of nanofibers by electrospinning.

Figure 1. TiO_2 solutions for the synthesis of nanofibers, by electrospinning.

ii) Electrospinning - The nanofibers were obtained by the electrospinning process (Figure 2), in which a 5 mL plastic syringe connected to a stainless steel hypodermic needle with an internal diameter of 1 mm was filled with the precursor solution. The needle was connected to the high voltage source. The distance between the tip of the needle and the rotating cylindrical collector that is covered with a sheet of aluminum foil was 12 cm. A voltage of 13.5 kV was applied between the needle and the collector. An infusion pump (KD Scientific) controlled the flow of the precursor solution (1.8 mL/h). Nanofibers were collected every 30 minutes for a period of 4 hours.

Figure 2. Electrospinning apparatus for the synthesis of TiO_2 nanofibers. (a) The injection pump connected to the hypodermic syringe, (b) rotating cylindrical collector, (c) high voltage power supply, and (d) distance between the syringe-capillary assembly and the collector.



iii) Heat Treatment - The nanofibers obtained were subjected to a heat treatment in an electric oven (Sanchis) at temperatures of 650 ºC, 700 ºC, 750 ºC and 800 °C, with a 1hour plateau and a heating rate of 1.4 °C/min, in order to remove polymeric material and form crystalline phases.

Characterization of nanofibers

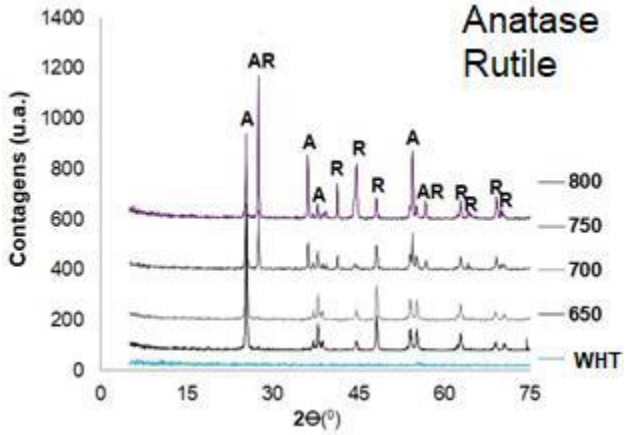
A PHILIPS diffractometer with CuKα radiation, with a voltage of 40 kV and 40 mA, equipped with the X'PERT HightScore® software, was used to identify the phases present in the nanofibers. A scanning electron microscope (SEM, JEOL 6060) was used to assess the morphology. The photocatalytic performance of TiO_2 nanofibers was analyzed by changing the concentration of the methyl orange dye, under UVA irradiation.

The photocatalysis process was carried out in a photocatalytic reactor, made of pyrex glass, where radiation was provided by 12 black UVA lamps, of 8 W each, model Fluor BLB T5 and brand Sadokin. The lamps are arranged in two semi-cylinders, which have a reflecting internal surface. The other components of the photocatalytic reactor include; a magnetic stirrer, a compressed air aeration system and a thermostatic bath. To carry out the photocatalytic assays, the TiO_2 nanofibers were mixed with 125 mL of a solution containing 20 ppm of the methyl orange dye. The mixture was placed in an ultrasound (Cole-Parmer CP-750) for 15 minutes. The solution was then transferred to the photocatalytic reactor, under constant agitation, at a temperature of 30 °C. Air was bubbled during the period of exposure to UVA light. Before the start of each test, a 4 mL sample of this solution was collected and defined as the initial sample. During the test, with a UVA light system turned on, 4 mL aliquots of the solution were removed with a plastic syringe, at 15 minutes intervals, filtered through 0.2 μm filters and placed in polymethylmethacrylate (PMMA) cuvettes to then be analyzed by spectrophotometry.

3 RESULTS AND DISCUSSION

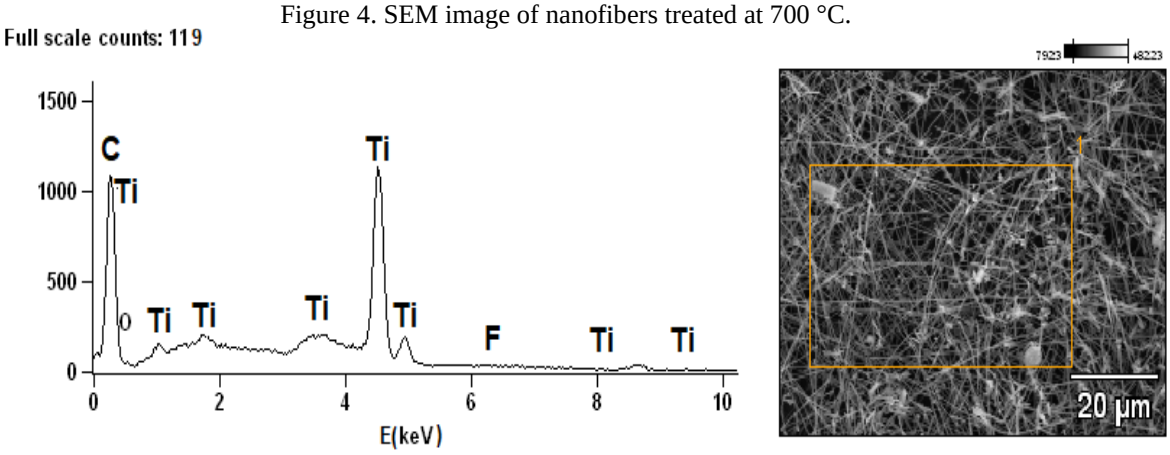
Figure 3 shows the diffractogram of nanofibers synthesized by electrospinning. The samples before heat treatment were amorphous. TiO2 nanofibers treated up to a temperature of 700 °C showed only the presence of the anatase crystalline phase (JCPDS 010782486), with the first characteristic peak at approximately 2Θ = 25.271 °. The nanofibers treated from 750 °C presented, in addition to the anatase phase, the rutile phase (JCPDS 01-077-0442), with the first characteristic peak at approximately 2Θ = 27.294 °, resulting from the occurrence of a TiO2 phase transition. predicted after increasing the heat treatment temperature [1,6].

Figure 3. Diffractograms of WHT nanofibers and after heat treatment at 650 ºC, 700 ºC, 750 ºC and 800 ºC.



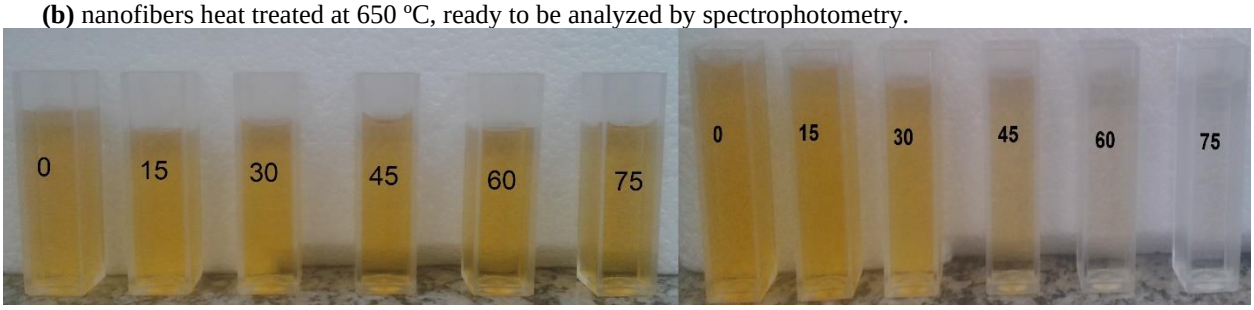
The Figure 4 shows SEM images of the nanofibers. It is possible to observe that the nanofibers are randomly dispersed, without a preferential orientation, originating an agglomerate of nanofibers with a porous structure. EDS (Energy Dispersive X-ray Spectroscopy) confirmed the presence of titanium atoms in different regions of the TiO_2 sample.

Figure 4. SEM image of nanofibers treated at 700 °C.



Figures 5 (a and b) are the cuvettes containing the TiO_2 samples, heat treated at 800 ºC and 650 ºC, respectively, after the end of the photocatalytic tests, to be analyzed by spectrophotometry. The Figure shows the relative concentration of the methyl orange solution during the photocatalytic assay, based on a solution initially containing 125 mL (20 ppm) of the methyl orange dye plus 0.05 g of TiO_2 fibers heat treated at 800 °C and 650 ºC. It can be seen from the coloring of the cuvettes that the TiO_2 samples treated at a temperature of 650 ºC (Figure 5b) degraded practically all the methyl orange dye in just 75 minutes of exposure to UVA radiation. This confirms the photocatalytic efficiency of these samples.

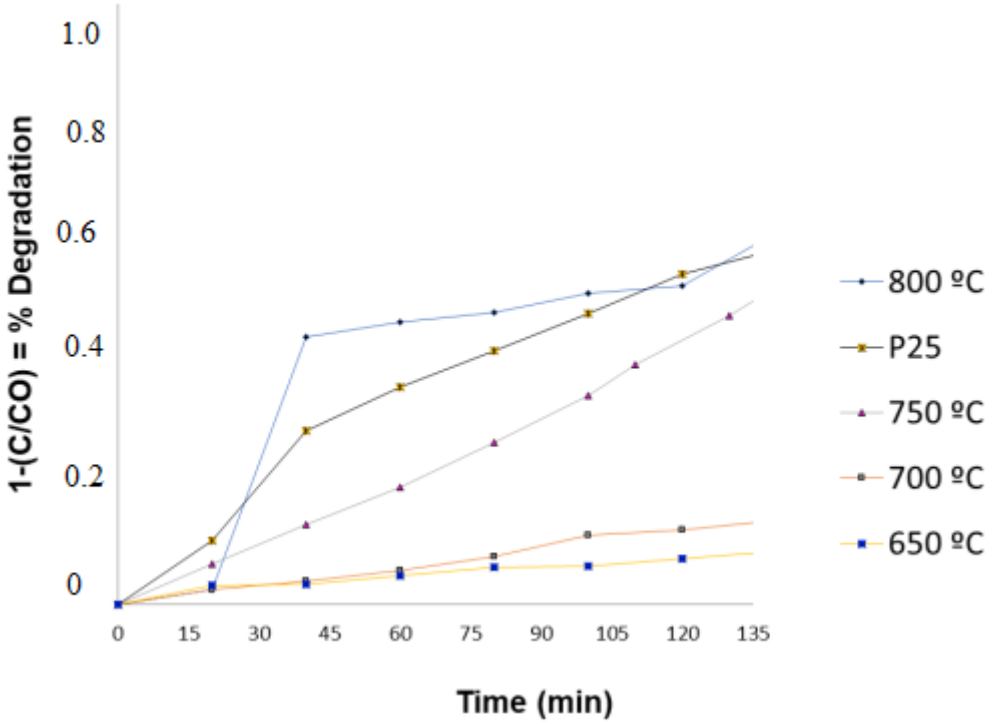
Figure 5. TiO_2 samples after the ends of the photocatalytic tests **(a)** nanofibers heat treated at 800 ºC and **(b)** nanofibers heat treated at 650 ºC, ready to be analyzed by spectrophotometry.



(a) (b)

Figure 6 shows the graphs plotted based on the spectrophotometric analysis of the cuvettes containing the relative concentration of 125 mL of a 20 ppm solution of methyl orange dye, plus 0.05 g of TiO_2 nanofibers, in question, heat treated at 650 ºC, 700 ºC, 750 ºC, 800 °C and the P25 standard, obtained during the heterogeneous photocatalysis test. The most photoactive nanofibers were heat treated at 650 ºC and 700 ºC, degraded 94.91% and 92.08%, respectively, of the methyl orange dye, due to the majority presence of the anatase phase, which is proven to be the most photoactive phase of TiO_2. The other samples heat treated at 750 ºC, 800 ºC and standard P25 degraded 70.21%, 65.09% and 66.73%, respectively, of the dye. This gradual reduction in photocatalytic efficiency occurs as a consequence of the formation of the rutile phase, which forms with the increase in the heat treatment temperature. Rutile is the TiO_2 phase with the lowest photocatalytic activity in the degradation of organic compounds [7].

Figure 6. Relative dye concentration during photocatalytic assay in the presence of P25 standard and TiO_2 nanofibers treated between temperature of 650 ºC and 800 ºC.



4 CONCLUSIONS

It was possible to synthesize TiO_2 nanofibers using the electrospinning technique. Photocatalytic tests showed that TiO_2 nanofibers are effective in the degradation of methyl orange dye and can be applied as semiconductors in heterogeneous photocatalysis. It is noted, in general, that the concentration of the methyl orange solution decreases as the test time increases, especially when TiO_2 nanofibers, heat treated at 650 ºC, were used in the photodegradation test. Because these showed 94.91% effectiveness, a consequence of the majority formation of the anatase phase. The latter is proven to be the most photoactive phase of TiO_2.

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