# Low tungsten content of nanostructured material supported on carbon for the degradation of phenol

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## ABSTRACT

A comparative study using different mass proportions of $WO_3/C$ (1%, 5%, 10% and 15%) for $H_2O_2$ electro-generation and subsequent phenol degradation was performed. To include the influence of the carbon substrate and the preparation methods, all synthesis parameters were evaluated. The $WO_3/C$ materials were prepared by a modified polymeric precursor method (PPM) and the sol–gel method (SGM) on Vulcan XC 72R and Printex L6 carbon supports, verifying the most efficient metal/carbon proportion. The materials were physically characterized by X-ray diffraction (XRD) and by X-ray photoelectron spectroscopy (XPS) techniques. The XRD and the XPS techniques identified just one phase containing $WO_3$ and elevated oxygen concentration on carbon with the presence of $WO_3$. The oxygen reduction reaction (ORR), studied by the rotating ring-disk electrode technique, showed that $WO_3/C$ material with the lowest tungsten content (1% $WO_3/C$), supported on Vulcan XC 72R and prepared by SGM, was the most promising electrocatalyst for $H_2O_2$ electrogeneration. This material was then analyzed using a gas diffusion electrode (GDE) and $585\,mg\,L^{-1}$ of $H_2O_2$ was produced in acid media. This GDE was employed as a working electrode in an electrochemical cell to promote phenol degradation by an advanced oxidative process. The most efficient method applied was the photo-electro-Fenton; this method allowed for 65% degradation and 11% mineralization of phenol during a 2-h period. Following 12 h of exhaustive electrolysis using the photo-electro-Fenton method, the total degradation of phenol was observed after 4 h and the mineralization of phenol approached 75% after 12 h.

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## 1. Introduction

Sewage discharge without sufficient treatment is the main source of organic impurities in surface water [1]. Water contamination by sewage presents great difficulties for conventional water treatment and many additional processes, including coagulation/filtration, softening, membrane processing, ion exchange and granular activated carbon filtration also produce residuals. Therefore, as discharge quality requirements become more stringent, treatment of waste residuals must improve accordingly [1,2].

Aromatic compounds are common pollutants in the waste effluent discharged by many factories and industry processes, including chemical plants, petroleum refineries, phenolic resins, caprolactam textile facilities and some pharmaceutical processes [3,4]. Among the aromatic compounds, the phenolic products are toxic to humans and aquatic organisms and are listed as one of the most common and serious environmental contaminants in water [4]. Due to the toxicity and consequent health hazards of phenolic compounds, these products have been placed on the list of priority pollutants by the U.S. Environmental Protection Agency [5].

Among the existing processes for water treatment are the advanced oxidation processes (AOPs), which are considered to be promising, as "environmentally friendly" processes. Environmentally friendly processes boast a high degradation capacity [6–8], complete mineralization [9,10] or oxidation to very low concentrations [11,12] and the production of environmentally friendly byproducts [7,13,14]. AOPs can be defined as aqueous phase oxidation methods that involve in situ generation of highly reactive species such as hydroxyl radicals, which are the most powerful oxidizing species after fluorine (possessing an oxidation potential of 2.80 V) [7,15]. These reactive species lead to the destruction of the pollutant [15].

Hydroxyl radicals for water and wastewater treatment can be generated by several process including the following: $H_2O_2$/UV,

$O_3$/UV, Fenton's reagent, $O_3$/$H_2O_2$/UV, $TiO_2$ [7,8,16] and more recently, the homogeneous $H_2O_2$/UV and photo-Fenton process. The $H_2O_2$/UV and photo-Fenton process has been used in the treatment of organic pollutants, exhibiting important advantages over processes based on the irradiation of suspended solid photocatalysts [8].

Hydrogen peroxide, used to generate the hydroxyl radical and $H_2O_2$, is considered to be a green chemical when utilized as replacement for chlorine in the treatment of wastewater. Additionally, $H_2O_2$ can be generated *via* two-electron transfer in the oxygen reduction reaction, and carbon electrodes are the reference material for $H_2O_2$ production in alkaline media [17–19]. The use of some metal oxides to enhance the activity of the oxygen reduction reaction to promote the two-electron transfer has already been described [20–22].

The production of electrocatalysts composed of metal oxides and supported on carbon has recently utilized nanostructured transition metal oxide semiconductors because of their large surface area and unique physical properties [23]. Among the various oxides, tungsten trioxide ($WO_3$) is of scientific and technological interest because its optical and electronic properties make it a promising material for use in photocatalysis, electrochromic and sensing device applications [24]. $WO_3$ is an n-type semiconductor and it has relatively high electrical conductivity, such that it may be one of the most promising materials for wastewater treatment [25,26].

To improve the hydrogen peroxide electrogeneration, this work describes a comparative study of four compositions of tungsten oxide nanoparticles supported on carbon (1%, 5%, 10% and 15% $WO_3$/C) as electrocatalysts for ORR. Considering that the preparation methodology [21] and the carbon supports [6] could also influence hydrogen peroxide production, this work also evaluated the effects of the preparation method and the carbon support. Additionally, we identified the best electrocatalyst for $H_2O_2$ electrogeneration using a gas diffusion electrode (GDE). Finally, phenol degradation was studied using several AOPs, and a reaction mechanism for its degradation process was proposed.

## 2. Materials and methods

### 2.1. $WO_3$ preparation

Various concentrations (1%, 5%, 10% and 15%, w/w) of tungsten trioxide electrocatalysts were first prepared using the polymeric precursor method (PPM), as described in our previous studies [21,22]. Tungsten chloride (Aldrich) and Vulcan XC 72 R (Cabot Corporation) were used in order to find the best composition for $H_2O_2$ electrogeneration. Once we determined the best proportion of tungsten using the Vulcan XC 72R carbon as a support and the PPM, the best tungsten proportion was then prepared using the sol–gel method (SGM) as previously described [21,27] and the Printex L6 (Evonik) was used as the carbon support. These tungsten materials were used to evaluate the effects of preparation method and carbon support on $H_2O_2$ electrogeneration.

### 2.2. Characterization of $WO_3$ materials

#### 2.2.1. X-ray diffraction and X-ray photoelectron spectroscopy analysis

The tungsten-based materials were physically characterized by X-ray diffraction (XRD) using a D8 Focus diffractometer (Bruker AXS) with a CuKα radiation source operating in the continuous scan mode ($2° min^{-1}$) from 20 to 60°. The XPS analysis was conducted at a pressure of less than $10^{-6}$ Pa using a commercial spectrometer (UNI-SPECS UHV). The Mg Kα line was used ($h\nu$ = 1253.6 eV) and the analyzer pass energy for the high-resolution spectra was set

to 10 eV. The inelastic background of the W 4f, O 1s e C 1s electron core-level spectra was subtracted using Shirley's method. The composition of the near surface region was determined with an accuracy of $\pm10\%$ from the ratio of the relative peak areas, which were corrected by Scofield's sensitivity factors for the corresponding elements. The spectra were fitted using multiple Voigt profiles without placing constraints. The width at half maximum (FWHM) varied between 1.0 and 2.0 eV and the precision of the peak positions was $\pm0.1$ eV.

#### 2.2.2. Electrochemical characterization

The oxygen reduction reaction was analyzed by the rotating ring-disk technique using a commercial ring-disk electrode (Pine Instruments) consisting of a central glassy carbon disk (area = $0.25 cm^2$) and an Au ring (area = $0.19 cm^2$) with a collection efficiency of $N$ = 0.37 as support for the working electrode. A platinum wire and a Hg/HgO were used as the counter electrode and the reference electrode, respectively. A $1 mol L^{-1}$ NaOH solution was used as the supporting electrolyte, and it was prepared from a supra-pure grade reagent purchased from Merck. All electrochemical measurements were conducted with an Autolab PGSTAT 302 N potentiostat/galvanostat and the working electrodes were constructed using the configuration proposed by Assumpção et al. [6,21]. For all of the electrochemical analyses, the electrolyte was first saturated with oxygen and oxygen flow was maintained over the electrolyte during the measurements. Measurements were performed at a fixed scan rate of $5 mV s^{-1}$ at room temperature. An EDI101 rotator and a CTV101 speed control unit were also used. The electrode rotation rate was varied from 100 to 3600 rpm and the experiments were controlled with General Purpose Electrochemical System (GPES) software.

### 2.3. $H_2O_2$ quantification using gas diffusion electrodes

Once the best electrocatalyst for $H_2O_2$ electrogeneration was identified, a GDE was configured with a diameter of 2.5 cm and used as working electrode in an electrochemical cell to determine the true quantity of $H_2O_2$ produced by exhaustive electrolysis at different potentials as proposed by Forti et al. [14]. As reference electrode and counter electrode the Ag/AgCl (Analyser) and a Pt electrode were employed, respectively and as electrolyte a $0.1 mol L^{-1}$ $H_2SO_4$ and $0.1 mol L^{-1}$ $K_2SO_4$ solution was used. An oxygen stream at 0.2 Bar was also maintained for all experiments and the $H_2O_2$ was quantified by reacting 500 μL of the electrolyte containing $H_2O_2$ with 4 mL of a solution containing $2.4 \times 10^{-3}$ $mol L^{-1}$ $(NH_4)_6 Mo_7O_{24}$ and $0.5 mol L^{-1}$ $H_2SO_4$. The reaction produces a yellow product, which can be detected by UV–vis at 350 nm [28,29]. The $H_2O_2$ concentration was determined from a previously constructed analytical curve using a Varian Cary 50 instrument.

### 2.4. Phenol degradation by AOPs

Once the highest production of $H_2O_2$ using a GDE composed of tungsten oxide nanoparticles was determined, the best potential for $H_2O_2$ electrogeneration was selected for the degradation of 350 mL of $100 mg L^{-1}$ phenol (Sigma–Aldrich) in a solution containing $0.1 mol L^{-1}$ $H_2SO_4$ and $0.1 mol L^{-1}$ $K_2SO_4$. For these experiments the same electrochemical cell used for the $H_2O_2$ production was employed at the same conditions. For phenol degradation, several methods were employed: photodegradation, electrodegradation, photo-electrodegradation, electro-Fenton and photo-electro-Fenton processes. In all photo-processes, we used an UV radiation source from a 9 W mercury lamp (Pen Ray Power Supply, model PS-1 from UVP). For the Fenton-process, we added $3 \times 10^{-3}$ $mol L^{-1}$ iron (II) sulfate ($Fe^{2+}$) to the $100 mg L^{-1}$ phenol solution, which was subject to degradation. All of the