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Effect of Tungsten Anodization Conditions on the Photoelectrical Degradation of Orange II

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Abstract: Orange II degradation was performed on anodized tungsten wire, the effect of the tungsten anodizing conditions on the degradation performance was studied. Significant anodizing variables were considered such as anodizing voltage, anodizing time, electrolyte solution temperature and electrolyte NH_4HF_2/H_2O ratio (% weight). A comprehensive Box-Behnken n factors response surfaces experimental design was proposed. The experimental results indicated that the combined effect of the experimental variables Voltage, NH_4HF_2/H_2O ratio when paired with temperature are the ones with the highest impact on the Orange II degradation reaction, meanwhile the factor with the lowest impact on the Orange II degradation reaction is the anodizing time. In order to have a better understanding of the impact of the factors, statistical semi phenomenological models of the Orange II degradation results were obtained, the mathematical expressions of the models properly described the degradation of Orange II at 20 and 30 ^oC, however failed to adjust the data at 40 ^oC, where the combination of high voltage and high electrolyte NH_4HF_2/H_2O ratio led to the mechanical failure of the anodizes tungsten wires.

Keywords : Orange II degradation, Tungsten anodizing.

Introduction

Effluents from the textile industry often contain recalcitrant components which conventional water treatment processes do not manage to eliminate; in particular azo phenolic dyes exhibit high resistance to degradation[1, 2] and given their chemical configuration (benzene rings, phenolic groups, etc.) pose a danger to the public health [3, 4]. Particularly, in the textile industry one of the most intensively used azo dye is Orange II, which has been reported to be a material with potential carcinogenic effects [5, 6]. Photocatalytic and advanced oxidation technologies (PAOTs) have been reported as an effective, economic and environmentally friendly alternative [7-11]. For any wastewater treatment to be as economical and clean as possible, a sustainable energy source and the reduction in the use of reactive substances is it a requirement. One way to achieve this is by using solar radiation as energy source along with a photoactive material such as titanium dioxide or tungsten oxide. These materials interact with radiation to generate free radicals, very effective in the organic molecules oxidation reaction [12-14].

The reaction is activated by the absorption of a photon (Eg), with energy equal or greater to the photoactive material band gap, on the surface of a semiconductor which generates the jump of an electron from the valence to the conduction band, triggering the formation of a highly reactive electron (e-) and hollow (h +) pairs (Equation 1).

$$WO_3 + h\nu \qquad h^+ + e^- \qquad \longrightarrow \quad (1)$$

If this (e-) and (h+) pair are able to migrate to the surface, they can remain there in metastable conditions and participate in reduction/oxidation reactions causing degradation of contaminants. The interaction of these superficial (e-) and (h+) pairs with aqueous mediums usually generate OH- radicals, which are highly reactive toward most organic molecules and many inorganic species via hydrogen abstraction or chemical attacks to double bonds or to aromatic rings. In this way the organic compounds can be oxidized leading to the formation of carbon dioxide, water and inorganic acids [15].

Metallic tungsten and several of its alloys have numerous applications such as incandescent light bulb filaments, X-ray tubes and electrodes, among others. Its oxide forms have also very interesting infrared adsorbing, high electrical conductivity and catalytic properties Tungsten oxide is also widely used in the synthesis of tailor made nanomaterials [16]. Tungsten oxide band gap has been reported in the range between 2.3 and 2.8 eV and is capable of using solar energy [17-20]. Tungsten oxide or Tungsten is found in nature in the form of hydrates, mainly in the minerals of Tungstita ($WO_3 \cdot H_2O$), meymacite ($WO_3 \cdot 2H_2O$) and hydrotungstite ($H_2WO_4 \cdot H_2O$), this last one is rare to find [21]. WO_3 is a photoactive material of great interest in research due to its low bandgap (2.3-2.8 eV), which grants the material advantageous electrical properties in different areas and applications such solar energy and photoelectrocatalysis [22]. Temperature directly influences the crystalline structure of WO_3; at high temperatures (above 740 ° C) has a tetragonal structure, from 330 to 740 ° C is orthorhombic, while between 17 and 300 ° C is monoclinic.

This paper will study the effect of the tungsten anodization conditions in terms of anodizing voltage, anodizing time, electrolyte solution temperature and electrolyte NH_4HF_2/H_2O ratio (% weight), on the photoelectrical degradation of orange II.

Materials and Methods.

Tungsten wires Anodization

For all anodizations, a single titanium cathode in sheet (Ti, Gallium Source, USA) of 3.5 cm high and 1.5 cm wide was used as cathode, the anode consists of eight tungsten wires (1 mm in diameter) cut to 3.5 cm in length. Prior to anodization cathode and anode are washed for ten minutes in 30 mL of methanol (MeOH, El Alquimista Chemicals, Colombia) and air dried; The anodization vessel (145 mL capacity) together with a magnetic stirrer (2 cm) are washed with distilled water and air-dried, then washed in methanol in the same manner as the cathode and anode.

Once the materials for anodization have been prepared, the required amount of ammonium fluoride (NH_4HF_2, Merquimia, Colombia), is directly weighed into the anodization vessel, then 1.4 ml of distilled water and 126 mL of ethylene glycol (EG, Lega Chemicals, Colombia) were added. The mixture is homogenized for ten minutes using a magnetic stirrer (200 rpm). The cathode and anode are connected to the negative and positive terminals respectively to a power supply (BK Precision, XLN15010), and are accommodated so that both are submerged 3 cm into the anodization medium with a distance between them of 2 cm. The required voltage and time are programmed in the power supply. During the anodization the agitation is maintained at 200 rpm. The system was immersed in a temperature controller water bath to keep the experiment temperature regulated.

After the anodization process is completed, the anode is removed from the anodization solution and washed with methanol for 2 minutes. The anodized tungsten wires are then baked (Thermo Scientific, Lindberg Blue M) using a 2 ° C/min ramp from room temperature to 450 °C, this final temperature is maintained for one hour and then material is allow to cool down to room temperature by natural convection and storage in inert atmosphere (Yang et al., 2009).

Experiments developed previously in the anodization of metallic sheets [23-26] and literature review were used to establish the value range to be used in the experimental set up of the main variables involved in the anodization process [14, 27-29] and they effect on the reaction of Orange II degradation, such as anodizing voltage, anodizing time, electrolyte solution temperature and the NH_4HF_2/H_2O ratio (% weight), the high, medium and low values of the independent variables are summarized en Table 1. A Box-Behnken n factors response surfaces experimental design was proposed; the independent variables combinatorial and the response variable (Orange II degradation) values are presented in Table 2.

Table 1. Independent variables values.

Factor	Description	Unit	-1	0	1
A	Voltage	V	20	35	50
B	Temperature	°C	20	30	40
C	NH_4HF_2/H_2O	%W	0,2	0,4	0,6
D	Time	min	30	60	90

Orange II Degradation

Anodized wires are evaluated on their performance in degradation of orange II (OII) in aqueous solution. The reaction was carried out in a photoreactor of the Laboratory of Chemical Engineering (LIQ) of the National University of Colombia, using nine UVA lamps (wavelength 320 to 400 nm). 35 mL of 0.1 mM OII solution is poured into a 40 mL Pyrex vessel. Two 4 cm high and 0.5 cm wide Ti cathodes and the eight tungsten oxide wires generated in the anodization process (1 mm in diameter and 3.5 cm) were submerged, as anode and cathodes, approximately 3 cm in the orange II solution. A bias 2 V was kept applied all along the experiment (DC source, GW, GPS-3030), Orange II degradation experiments are performed for 90 minutes. The concentration of OII is determined via UV spectrophotometry (Genesys 20 UV-VIS spectrophotometer, λ = 486 nm) at the beginning and at the end of the degradation experiment, whereby the percent degradation is determined using equation 2.

$$Degradation\ \% = 100x\,\frac{([OII]initial-[OII]final)}{[OII]initial} \qquad (2)$$

Where $[OII]_{initial}$ and $[OII]_{final}$ represent the Orange II concentration at time reaction equal 0 and 90 minutes, respectivily

Results and Discussion

The summarized results are presented in Table 2 show that the maximum Orange II degradation value obtained were for the anodizing conditions corresponding to 20 V, 30 ^oC, 0,2 of NH_4HF_2/H_2O ratio and 30 minutes of anodization (39.72 %), on the other hand the anodization conditions corresponding to 35 V, 30 ^oC, 0,4 of NH_4HF_2/H_2O ratio and 60 minutes of anodization yielded the lowest Orange II degradation (5,23 %). Some of the anodization experiments led an intensive corrosion of the tungsten wire, breaking them apart, those wire were considered not suitable to be use in the Orange II degradation experiments and this is the reason why some of the experiments in Table II have not Orange II degradation value reported; this phenomenon was mainly observed in experiments such as 8, 13, 22 and 26 were the anodization conditions seems to be critical, ie they had the highest voltage, the highest temperature or the highest NH_4HF_2/H_2O ratio.

Table 2. A Box-Behnken n factors response surfaces experimental design and Orange II degradation experiments.

	Factor						Factor				
Experiment	A	B	C	D	Degradation (%)	Experiment	A	B	C	D	Degradation (%)
1	-1	-1	0	0	32,80	15	0	1	-1	0	29,74
2	1	-1	0	0	7,29	16	0	-1	1	0	9,00
3	-1	1	0	0	21,10	17	0	1	1	0	-
4	1	1	0	0	28,57	18	0	0	0	0	5,23
5	0	0	-1	-1	14,16	19	0	-1	0	-1	13,18
6	0	0	1	-1	29,71	20	0	1	0	-1	9,80
7	0	0	-1	1	16,01	21	0	-1	0	1	16,59
8	0	0	1	1	-	22	0	1	0	1	-
9	0	0	0	0	5,75	23	-1	0	-1	0	15,73
10	-1	0	0	-1	39,72	24	1	0	-1	0	21,18
11	1	0	0	-1	26,16	25	-1	0	1	0	9,30
12	-1	0	0	1	18,85	26	1	0	1	0	-
13	1	0	0	1	-	27	0	0	0	0	12,04
14	0	-1	-1	0	22,06						

Table 2 showed that the combined effect of the experimental variables Voltage, NH_4HF_2/H_2O ratio when paired with temperature are the ones with the highest impact on the Orange II degradation reaction, meanwhile the factor with the lowest impact on the Orange II degradation reaction is the anodizing time. In order to have a better understanding of the impact of the factors, statistical semi phenomenological models of the Orange II degradation results were obtained, the mathematical expressions of the models are described in equation 3 and 4

$$Z = a + bY + cY^2 + dX + eX^2 \qquad (3)$$

Where Z is the percent degradation, Y is the NH_4HF_2/H_2O ratio and X is the anodizing voltage.

$$Z_1 = a + bY_1 + cY_1^2 + dX + eX_1^2 + gX_1Y_1 \qquad (4)$$

Conversely, in equation 4, Z_1 is the percent degradation, Y_1 is the NH_4HF_2/H_2O ratio and X_1 is the anodizing voltage.

Surface response for the data sets at 20 ° C and 30 ° C and their respective equations were obtained using Matlab 7.14. To determine the coefficients of the equations, the mathematical models of the program were taken into account and the one that best fitted the data series was chosen. The parameters a, b, c, d, e, and g of each equation are shown in Table 3.

Table 3. Mathematical model parameters for equations 3 and 4.

Parameter	T 20°C	T 30°C
a	8,84E+01	7,12E+01
b	-4,55E+01	-1,93E+02
c	1,61E+01	1,55E+02
d	-2,46E+00	-2,00E+00
e	2,29E-02	2,13E-02
g	0,00E+00	2,76E+00

In Figure 1, the response surface for the 20 °C temperature set of experiments is presented, the highest degradation values are located on the lowest values of anodizing voltage and Orange II degradation is inversely proportional to the anodizing voltage. As can be seen, the percentage of degradation increases in low and medium voltage, and a NH_4HF_2/H_2O ratio of about 0.4 wt., This may be due to the fact that this value approaches an optimum in terms of concentration, if the concentration of electrolyte in the anodizing solution is not high enough the conductivity of the medium will be low affecting electrons transfer necessary for the anodizing reaction to take place, but also if the concentration of ion fluorine in the anodizing is too high, it will favor the formation of fluorine complexes with the tungsten, which will compete with the oxidation reaction of tungsten. This response surface has a correlation factor (R2) of 0,987 which indicates that the data are closely correlated with the generated model and is a good option to calculate degradation estimates as a function of the anodizing conditions and thus to reduce costs in reagents and energy consumption.

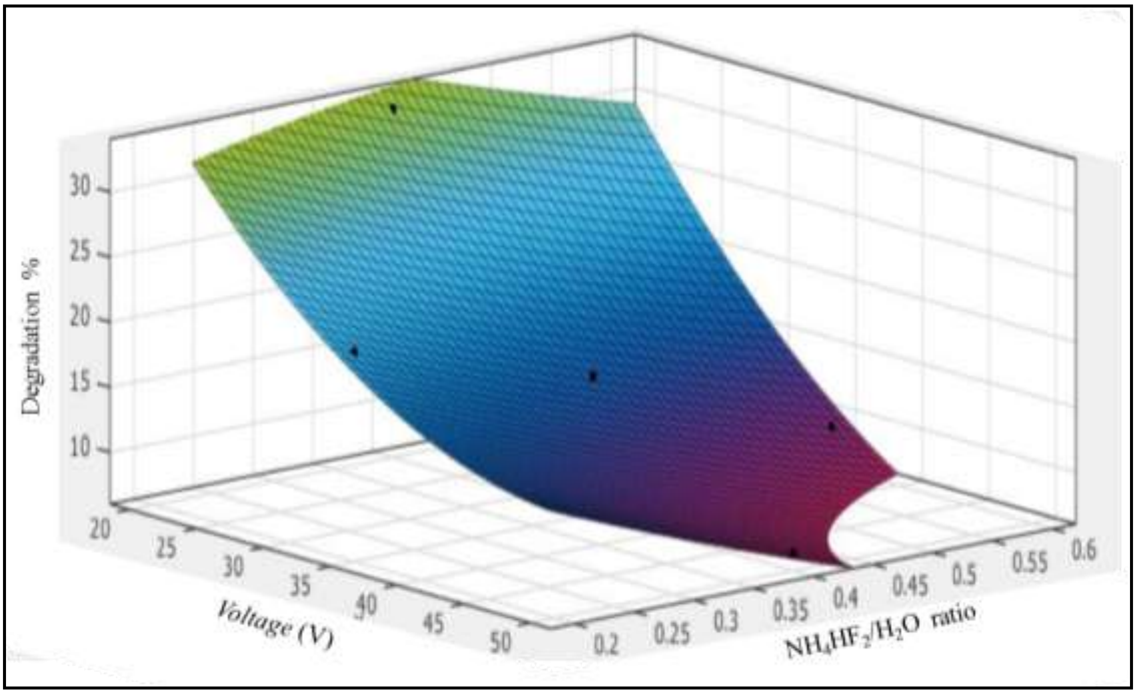

Figure 1. Response surface Degradation vs Voltage, NH_4HF_2/H_2O ratio at T = 20 ° C

Figure 2 shows the response surface when the temperature is 30 °C, it should be noted that this surface encompasses most of the experimental data given that they are the average conditions of the experimental plan. In this case, it is possible to observe a response surface with marked differences with the previous one (Figure 1), the main feature is that now the best degradations are obtained to average voltages and not to the low ones, and in a wider range of the available NH_4HF_2/H_2O ratios evaluated. Although the 30 ^{o}C surface has a correlation factor (R2) of 0,812, it is still a good approximation and it is valid for first hand estimations.

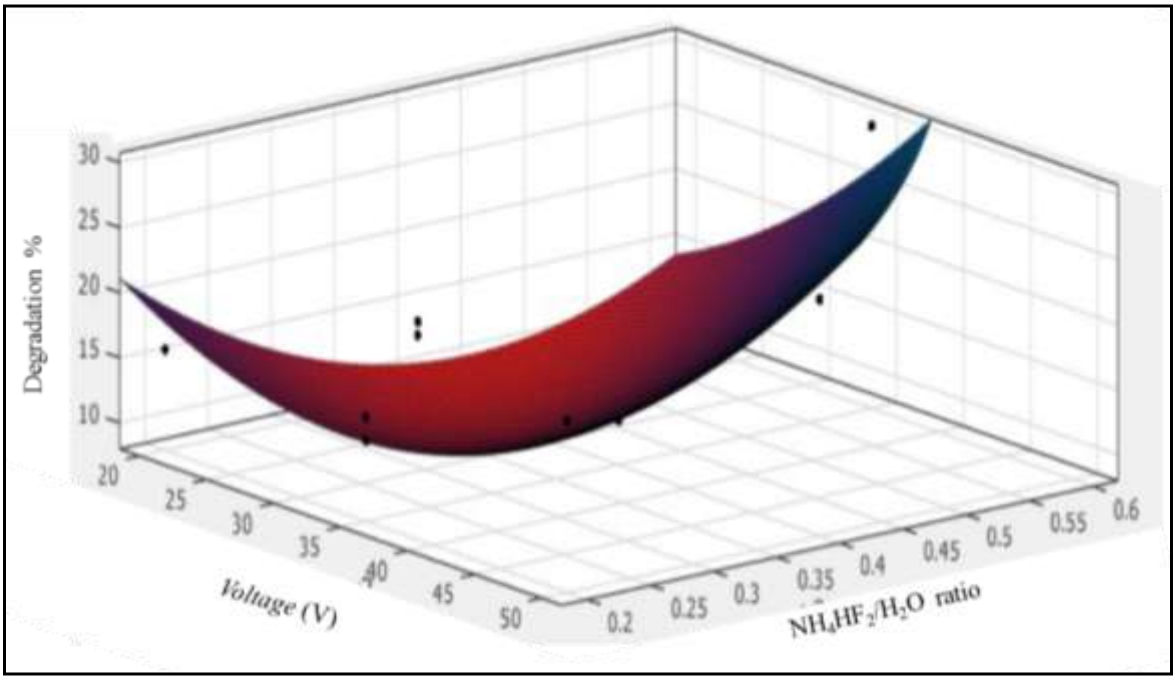

Figure 2. Response surface Degradation vs Voltage, NH_4HF_2/H_2O ratio at T = 30 ° C

Due to the fact that of the experiments performed at 40 °C presented the phenomena of intensive corrosion of the tungsten wire leading to their mechanical failure, the data collected in this case were not sufficient to generate a mathematical model and response surface with a suitable statistical significance.

Conclusions

Anodization is a plausible procedure to generate photoactive WO_3 wire to be use in the photoelectrical degradation of aqueous solutions of Orange II. The best degradation conditions were given at relatively low voltages (20V) and a medium NH_4HF_2/H_2O ratio (0.4), although depending on the anodizing temperature, good degradations can also be achieved at high fluoride ratios and average voltages.

The Box-Behnken n factors response surfaces experimental design allowed to concluded that the combined effect of the experimental variables Voltage, NH_4HF_2/H_2O ratio when paired with temperature are the ones with the highest impact on the Orange II degradation reaction, meanwhile the factor with the lowest impact on the Orange II degradation reaction is the anodizing time

Unsuitable conditions for production of WO_3 wire were observed at critical anodizing conditions such as highest voltage, the highest temperature or the highest NH_4HF_2/H_2O ratio of the Box-Behnken experiments proposed. These anodizing conditions led an intensive corrosion of the tungsten wire causing mechanical failure on them.

Mathematical models with good data correlation coefficients were obtained for the operating conditions considered, at different anodizing temperatures, and it is now possible to use them to design future anodizing experiments in a safe and efficient way.

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