

EVALUATION OF Nb₂O₅ AND Ag/Nb₂O₅ IN THE PHOTOCATALYTIC DEGRADATION OF DYES FROM TEXTILE INDUSTRIES

M.K.Silva, R.G.Marques, N.R.C.F.Machado and O.A.A.Santos*

Universidade Estadual de Maringá, Departamento de Engenharia Química,
Av. Colombo 5790, Bl. D-90-Campus Universitário, CEP 87020-900, Maringá - PR, Brazil
Phone: (55) (044)261-4323, Fax: (55) 44)263-3440,
E-mail: onelia@deq.uem.br

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Abstract - The textile industries are distinguished by the use of dyes that are applied to textiles. Dyes are pollutant materials that are difficult to decompose by microbiological treatment. An alternative way to prevent contamination of the environment by dyes is the oxidation of these materials through photocatalysis, a process by which illumination of an oxide semiconductor produces photoexcited electrons and cations that migrate over the surface of the oxide, effectively participating in the chemical reaction. The purpose of this work is to synthesize catalysts and study their performance in the photocatalytic degradation of dyes. Niobium pentoxide and silver oxide supported on niobium pentoxide (Ag/Nb₂O₅), prepared by the impregnation method, were used as catalysts. Prior to use the catalysts were submitted to thermal treatment for drying and calcination. Drying was carried out at 150°C for 12 hours and then the solids were calcined at 500°C for 5 hours. After that the catalysts were applied in the photocatalytic degradation of different types of dyes from textile industries. Discoloration tests were carried out in a photocatalytic reaction unit during a period of 24 hours under different operational conditions in the presence and absence of ultraviolet light (UV). The results, evaluated by spectrophotometry, show that photodegradation of the dyes occurs, which allows evaluation of the influence of the silver on photocatalytic degradation.

Keywords: dyes, photocatalytic degradation, oxide-metal catalysts.

INTRODUCTION

Currently, the effluent treatment processes used by industry to reduce the level of contaminants need improvement and there is a need to develop new processes. Industrially the most efficient treatments used for destruction of toxic compounds are incineration and microbiological treatment. However, the high cost of incineration and the possibility of incomplete oxidation with formation of furan and dioxin traces discourage adoption of this type of treatment. On the other hand, developments in biological treatment have been considerable due to

advances in the microbiological sector, even considering that it takes a long time to achieve the required standards of quality and that some industrial effluents do not degrade microbiologically (Ollis et al., 1991).

New processes, such as the advanced oxidative processes or POA are appearing and gaining space. These processes are based on the formation of the strongly oxidizing hydroxyl radicals (OH⁻), which can react with a wide variety of compounds, causing their total oxidation and forming innocuous compounds such as water and CO₂ (Byrne et al., 1998).

*To whom correspondence should be addressed

Heterogeneous photocatalysis is one of the POA that has been widely studied, mainly during the two last decades (Rivera et al., 1993; Fernández et al., 1995; Zhang et al., 1998). This process is based on the activation of semiconductor material by solar or artificial light. The semiconductor is characterized by a narrow band of energy in the region between the valence bands (VB) and conduction bands (CB), referred to as the band gap. The absorption of photons with energy higher than that of the band gap results in the excitation of an electron from the valence band to the conduction band with concomitant generation of a gap (h^+) in the valence band (see Figure 1). The potential generated is positive enough to produce radicals ($HO \cdot$) from adsorbed water molecules on the surface of the semiconductor. The efficiency of photocatalysis depends on the competition between the process where the electron is removed from the surface of the semiconductor and the process of recombination of the electron/vacancy pair, which results in liberation of heat.

Recent and more detailed studies show that the degradation mechanism does not occur exclusively by hydroxyl radicals but also by other radical species derived from oxygen, such as $O_2 \cdot^-$ and $HO_2 \cdot$, formed by the capture of photogenerated electrons (Hermann et al., 1997).

One of the interesting features of heterogeneous photocatalysis is the use of solar energy as an activator agent for the semiconductor, making possible the full degradation of contaminants such as phenol, chlorophenol, chlorinated hydrocarbons, insecticides and dyes, among others (Hermann et al., 1997). A wide variety of toxic organic composites may be degraded through heterogeneous photocatalysis. The majority of these compounds is oxidized to CO_2 and H_2O .

Within the industrial sector, the textile industries are major users of dyes, which contaminate the liquid effluents of these industries. The dyes are extremely pollutive and difficult to decompose by microbiological treatment. An alternative path for the oxidation of these dyes is through photocatalysis.

Dyes are organic compounds with a high capacity for selective absorption of light, and intense colors that they impart on matter. In chemistry only those aromatic substances capable of irreversibly coloring a textile support are considered dyes. The dyeing or coloring operation can be done in cold, warm or boiling water baths. When the colorful film is applied with brushes, the dye substance is referred to

as a pigment, which will be always insoluble in water if it is organic.

The aim of the present work is to verify the influence of silver in the presence of niobium pentoxide on the photocatalytic degradation of dyes from textile industries as well as to analyze the behavior of these dyes in contact with catalysts prepared and excited by ultraviolet light (UV light). Thus, the work aims to study the photocatalytic degradation of dyes in the presence of Nb_2O_5 and Ag/Nb_2O_5 catalysts.

METHODOLOGY

Catalyst Preparation

To verify the influence of silver on the photocatalytic degradation of dyes, Nb_2O_5 and Ag/Nb_2O_5 catalysts with 2 wt% silver were prepared. The methodology used to prepare the Nb_2O_5 was thermal treatment and for Ag/Nb_2O_5 it was wet impregnation.

Prior to use, the $Nb_2O_5 \cdot nH_2O$ was washed with deionized water with the objective to remove possible impurities from the manufacturing process. After that, the solution was vacuum-filtered by concomitant washings with cold water and finally with warm water ($70^\circ C$). The resultant material was dried at $150^\circ C$ for approximately 24 hours. Then, the niobium pentoxide was ground with a mortar and pestle and calcined in an oven at $500^\circ C$ for 5 hours.

To prepare the Ag/Nb_2O_5 catalysts, the Ag_2SO_4 precursor was calcined in the oven at $500^\circ C$ for approximately 2 hours and then dissolved in deionized water under shaking. The resultant solution was added to the thermally treated niobium pentoxide and placed in a bath under shaking at $80^\circ C$ for 24 hours. After that, the material obtained was dried at $150^\circ C$ for 12 hours and calcined in the oven at $500^\circ C$ for 5 hours.

Photocatalytic Tests

For the catalytic tests, the following dyes were used: yellow neutracyl, dark blue neutracyl, blue dispersatyl, orange dispersatyl, black dispersatyl, black neutracyl.

Solutions of 10 ppm were prepared with the several dyes, and then the solutions were submitted to spectrophotometry scanning tests to measure their absorbance. The wavelengths found for yellow neutracyl, dark blue neutracyl, blue dispersatyl,

orange dispersatyl, black dispersatyl and black neutracyl were 410 nm, 568 nm, 560 nm, 430 nm, 535 nm and 565 nm, respectively.

Then, a calibration curve was constructed for each dye to be analyzed by varying its concentration from 10 ppm to 0 ppm in 1 ppm steps through the addition of deionized water, followed by readings in the spectrophotometer. After construction of the calibration curve, the catalytic tests were initiated.

The dye degradation tests were carried out in a photocatalytic reaction unit (see Figure 2), where air was fed in by a hose. While conducting the tests, the unit was isolated to prevent contact of the reaction

mixture with light from the environment as well as the leakage of ultraviolet light, which is harmful to health.

The photocatalytic tests were carried out with Nb₂O₅ and Ag/Nb₂O₅ catalysts in the presence of UV light bulb. The reaction mixture was 200mL of 10ppm dye solution containing 1g of catalyst in suspension.

The dye solution was introduced into the reaction unit, after which the catalyst was added and then the system was isolated and turned on. The tests were carried out during a period of 24 hours. After that a sample of the resultant solution was analyzed in the spectrophotometer to verify the discoloration of the dyes.

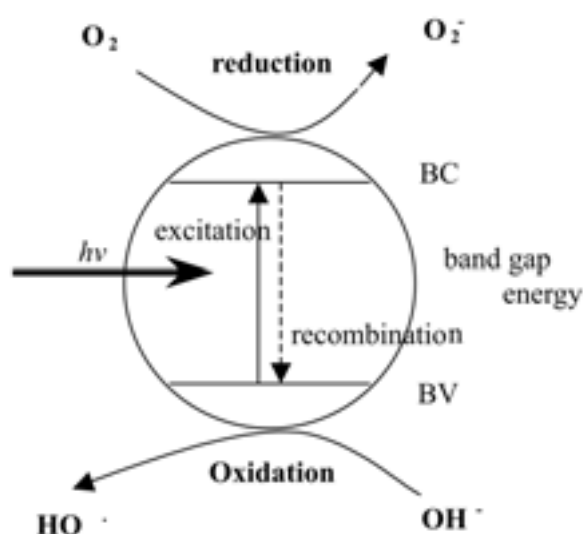


Figure 1: Schematic representation of the semiconductor materials.
VB: valence bands and CB: conduction bands.

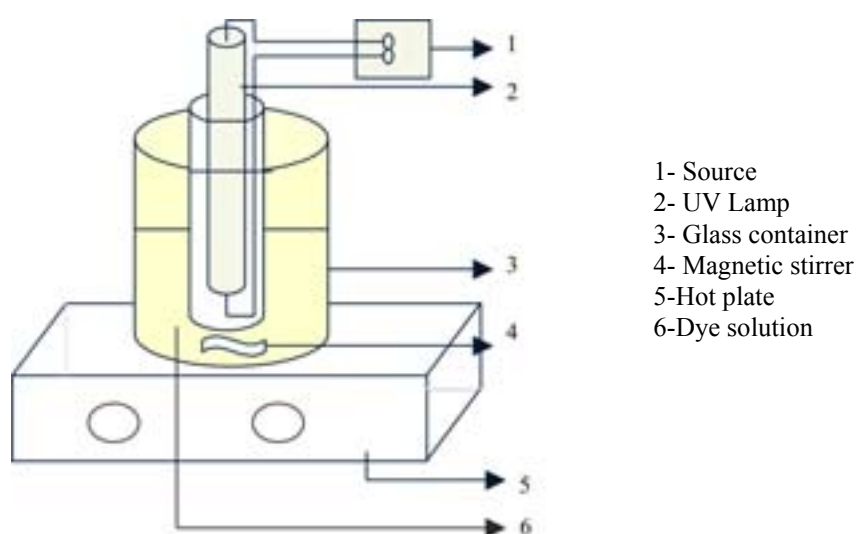


Figure 2: Experimental apparatus

RESULTS AND DISCUSSION

BET Surface Area

Table 1 shows the BET surface areas of calcined Nb₂O₅ and Ag/Nb₂O₅. The silver-supported catalyst has a very low value for surface area (23 m²/g), similar to that obtained for niobium pentoxide (24 m²/g). These results are in agreement with those of other authors.

Photocatalytic Reaction

After the degradation tests it was possible to determine the residual concentration for each dye present in the solution through spectrophotometry with the aid of the calibration curve. The results are shown in Tables 2 and 3.

In Tables 2 and 3 one can see that the photocatalytic degradation of all dyes studied occurred regardless of

the type of catalyst used. However, the addition of silver to the niobium pentoxide catalysts resulted in a sharp reduction in the residual concentration of the dye in the reaction solution after the photocatalytic discoloration test (Table 3).

The tests carried out with pure niobium oxide showed that the best degradation, 38.14% discoloration, was achieved with black dispersatyl, while the worst degradation, 9.89% discoloration, was obtained with black neutracyl. The presence of silver in the catalyst, Ag/Nb₂O₅, resulted in a better performance of the catalysts, showing over 90% degradation for all dyes. In this case, the best results, 99.45% degradation, were obtained with dark blue neutracyl, while the worst discoloration, 90% degradation, was obtained with black neutracyl. These results show that the addition of silver results in a better performance of the process, making more efficient the photocatalytic degradation of the dyes present in effluents from textile industries.

Table 1: Catalysts and their BET surface areas

Catalyst ¹	BET surface area (m ² /g)
Nb ₂ O ₅	24
Ag/Nb ₂ O ₅	23

¹ Calcined materials: 500°C for 5 hours.

Table 2: Degradation tests with Nb₂O₅ catalyst.

Dyes	Final Concentration (ppm)	Degradation (%)
Yellow neutracyl	8.50	14.96
Dark blue neutracyl	6.62	33.77
Blue dispersatyl	7.76	22.39
Orange dispersatyl	6.78	32.24
Black dispersatyl	6.19	38.14
Black neutracyl	9.04	9.89

Table 3: Degradation tests with Ag/Nb₂O₅ catalyst.

Dyes	Final Concentration (ppm)	Degradation (%)
Yellow neutracyl	0.420	95.79
Dark blue neutracyl	0.055	99.45
Blue dispersatyl	0.165	98.35
Orange dispersatyl	0.184	98.16
Black dispersatyl	0.376	96.24
Black neutracyl	1.000	90.00

CONCLUSIONS

The photocatalytic degradation tests suggest the efficiency of the photocatalysis method, since the discoloration of all the dyes under study occurred independently of the type of catalyst used. The addition of silver to the niobium pentoxide catalyst, Ag/Nb₂O₅, resulted in a sharp reduction in the residual concentration of the dye in the reaction mixture after the photocatalytic discoloration tests for all the dyes studied.

Degradation of the dark blue neutracyl dye reached a maximum of 99.45%; the solution started with a concentration of 10ppm and reached a residual concentration of 0.055ppm. This value is below the concentration allowed for the effluents of textile industries, which varies between 1 and 5ppm. The worst discoloration obtained on the niobium-supported silver catalysts, Ag/Nb₂O₅, was 90% degradation for the black neutracyl dye, while the best degradation on the catalysts of pure niobium oxide was 38.14% discoloration for the black dispersatyl dye, evidence of the importance of the presence of silver in the catalysts. The results show the importance of the study of oxides and metallic solid catalysts, in contrast to the biological methods, in the catalytic photodegradation of dyes, as an alternative process for the treatment of effluents from textile industries.

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