Influence of luminous intensity on textile effluent photodegradation

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ABSTRACT. Degradation tests were carried out to determine the luminous intensity influence on textile industry effluent photodegradation. TiO_2, Nb_2O_5, Nb_2O_5-TiO_2 and Nb_2O_5/TiO_2 were used as photocatalysts. FTIR (Fourrier Transform Infrared) and TPR (Temperature Program Reduction) results showed interaction between different forms of the oxides in the Nb_2O_5-TiO_2 and Nb_2O_5/TiO_2 catalysts and the forming of a new phase in Nb_2O_5-TiO_2. The reaction rate was significantly influenced by the luminous intensity. Luminous intensity decrease caused decolourisation increase and COD reduction decrease, suggesting that the concentration of the hydroxyl groups, which are responsible for the chromophores groups degradation, is proportional to the luminous intensity.

Key words: photodegradation, luminous intensity, TiO_2, Nb_2O_5, textile effluent.

RESUMO. Influência da intensidade luminosa na fotodegradação de efluente têxtil. Testes de degradação foram realizados com o objetivo de determinar a influência da intensidade luminosa na fotodegradação de um efluente industrial têxtil. Como fotocatalisadores foram utilizados TiO_2, Nb_2O_5, Nb_2O_5-TiO_2 e Nb_2O_5/TiO_2. Os resultados de FTIR (Infravermelho com Transformada de Fourrier)e RTP (Redução à Temperatura programada) mostraram a existência de interação entre os óxidos de forma diferenciada nos catalisadores Nb_2O_5-TiO_2 e Nb_2O_5/TiO_2 e a formação de uma nova fase no Nb_2O_5-TiO_2. A taxa de reação foi significativamente influenciada pela intensidade luminosa. A redução da intensidade luminosa ocasionou o aumento da descoloração e a diminuição da redução de DQO, sugerindo que a concentração dos grupos hidroxila, que são responsáveis pela degradação dos grupos cromóforos, é proporcional à intensidade luminosa.

Palavras-chave: fotodegradação, intensidade luminosa, TiO_2, Nb_2O_5, efluente têxtil.

Introduction

Among many industrial processes, textile processing is considered the most polluting, because it consumes a great amount of water and dye, producing a large volume of highly complex effluent containing both organic matter and a high content of inorganic salts (Rott and Minke, 1999).

As the effluents are not satisfactorily degraded by conventional treatments, owing to their complexity, new advanced oxidation processes are becoming more popular. Among these processes a promising alternative is heterogeneous photocatalysis (Galindo *et al*., 2000; Kiriakidou *et al*., 1999).

The heterogeneous photocatalysis is based on the irradiation of a photocatalyst with luminous energy equal or higher than its "band gap" energy, which is the distance between the valence band (VB) and the conduction band (CB), causing the excitation of an electron from the valence band to the conduction band, with consequent charge separation (forming an electron-hole pair). The photogenerated electrons from CB and the hole from VB may migrate to the surface and take part in the oxidation-reduction reactions on the interface (Nogueira and Jardim, 1998; Galindo et al., 2000; Gouvêa et al., 2000).

In the heterogeneous photocatalysis using semiconductors, the degradation reaction rate depends on many parameters, including the reactor geometry, semiconductor nature and concentration, oxygen concentration, organic compound concentration, luminous intensity, temperature, pH, presence of interfering species and agitation intensity (Mills and Hunte, 1997).

In this work, the photodegradation of an effluent from a textile industry was studied under the action of illuminated semiconductors, varying the luminous intensity to determine its influence on the degradation reaction.

Materials and methods

Commercial TiO_2 (Quimbrasil) and Nb_2O_5 (CBMM) were used as photocatalysts. They were submitted to washing treatment, vacuum filtration, drying and agglomeration (particle size range, 0.210 to 0.297 mm). They were calcinated at 300°C/6h and at 400°C/4h. Nb_2O_5-TiO_2 was prepared through physical mixture of the dried TiO_2 and Nb_2O_5 in 1:1 weight ratio. This mixture was then agglomerated and calcinated under the same conditions as the TiO_2. Nb_2O_5/TiO_2 catalyst was prepared impregnating TiO_2 with 5wt% Nb_2O_5. Dried Nb_2O_5 was dissolved in oxalic acid (0.5 mol.L^{-1}) under intense stirring at 66°C/8h and this mixture was added to TiO_2 thermally treated. The solvent was evaporated under stirring at 80°C/24h in a thermostatic bath. The material was agglomerated and calcinated under the same conditions as the TiO_2.

The catalysts were characterized by textural analysis through physical adsorption of N_2 (Quanta chrome Nova 1200); infrared absorption spectroscopy in a BOMEN FTIR equipment, with a KBr pellet with 1% catalyst, and by reduction in a Temperature Programmed Reduction (TPR) equipment built at our laboratory.

A natural textile effluent was collected in an industry, straight from the homogenisation tank and sieving was the only pre-treatment carried out. The freshly collected effluent was composed mainly of green, red and salmon colours, being a mixture of direct, acid and reactive dyes.

The photodegradation tests were carried out in a 2-L glass reactor, adapted with an external water jacket for cooling the reaction environmental, aeration system, magnetic agitation and an internal 1-L glass becker used to separate the luminous source from the solution. The luminous intensity influence was determined with reaction tests using lamps of different powers, namely either a high-pressure 250W mercury vapour lamp, or a compact fluorescent 26W lamp.

Procedure

A 1-g sample of catalyst was suspended in 1 L of natural effluent in the refrigerated (T=33°C), aerated (50 mL.min^{-1}) and magnetically agitated reactor. The mixture was irradiated during 360min with one of the lamps, either 26 W or 250 W. Aliquots of 10 mL were collected in regular intervals of 60 min, centrifuged for 25min at 6500 RPM, filtered through Millipore filter and analysed by UV-VIS spectrophotometry (Shimadzu UV-VIS 1203) to monitor the decolourisation. COD analysis was carried out in the first and last samples to verify the actual extent of the mineralization in the photodegradation process in Hach DR/2010 equipment.

Results and discussion

Characterization of Photocatalysts

After evaluating the textural analysis results (Table 1), it was verified that Nb_2O_5 possesses a specific surface area about four times greater than that of TiO_2, and when these two oxides are combined, the specific surface area of the Nb_2O_5-TiO_2 and Nb_2O_5/TiO_2 showed an intermediate value, which was expected.

The TiO_2 did not show micropores surface area, Nb_2O_5 and Nb_2O_5/TiO_2 showed the same micropores surface area, although Nb_2O_5-TiO_2 was the highest microporous material. The mean pore diameter of the four catalysts was within the mesopores range; however, TiO_2 showed a high value of mean pore diameter when compared to the other catalysts.

Observing the adsorption-desorption isotherms (Figure 1), it was verified that TiO_2 presented few mesopores (small hysteresis), which is to be expected in a mesoporous particle.

The TiO_2 isotherm (Figure 1–A) showed a profile that was very close to the type III isotherm, except for the small hysteresis, indicating the predominance of macropores (Gregg and Sing, 1982). The adsorbed volume was very low, even close to the saturation pressure, where the multilayers formation occurs. The Nb_2O_5 isotherm (Figure 1–B) showed more porous material form (higher adsorbed volume). The greater hysteresis indicates a higher quantity of mesopores. Both Nb_2O_5-TiO_2 and Nb_2O_5/TiO_2 catalysts (Figure 1–C and D) had micropores surface areas larger than their external areas; however, since they show great hysteresis, they also contain many mesopores.

Table 1. Specific superficial area and pore volume.

Catalyst	Specific superficial area (m^2/g)	Total pore volume (cm^3/g)	Mean pore diameter (Å)	External superficial área (m^2/g)	Micropore surface area (m^2/g)	Micropore volume (cm^3/g)
TiO_2	11	0.029	111.50	12	0	0.000
Nb_2O_5	48	0.076	63.29	33	15	0.016
Nb_2O_5-TiO_2	38	0.046	48.35	15	23	0.015
Nb_2O_5/TiO_2	20	0.019	39.68	5	14	0.009

Infrared spectroscopy analysis with Fourier transform (FTIR) was carried out in the catalysts, without any adsorbed material, aiming to compare surface differences between the catalysts. The FTIR spectra were analysed in 400 and 4000 cm^{-1} range, as shown in Figure 2. TiO_2 showed a characteristic vibration region between 400 and 680 cm^{-1} and a peak at 1089 cm^{-1}. Nb_2O_5 presented two characteristic vibration peaks, at 642 and 1650 cm^{-1}, as well as a shoulder at 941 cm^{-1}.

Nb_2O_5-TiO_2 showed the characteristic region of TiO_2 at 400 and 680 cm^{-1} and the 1650-cm^{-1} peak peculiar to Nb_2O_5. However, it was possible to observe the peak disappearance at 1089 cm^{-1}, which is peculiar to TiO_2, and the shoulder referent to Nb_2O_5. The interaction between the two oxides in this catalyst caused the formation of a new phase, represented by an extra peak at 2360 cm^{-1}. The interaction between the oxides in Nb_2O_5/TiO_2 resulted in the displacement of the characteristic Nb_2O_5 peak at 549 cm^{-1}, as well as the disappearance of all characteristic vibration peaks referent to Nb_2O_5 and TiO_2. It can be seen, in Figure 2, that in the low and high-energy regions, the differences between the catalysts were more pronounced, whereas in the intermediate region the spectra were closer, showing their characteristic and extra peaks.

Hydrogen consumption was quantified and the reduction percentage for each catalyst was determined by TPR profile. The results are shown in Table 2 and Figure 3.

It may be observed that the hydrogen consumption was much higher for Nb_2O_5 in relation to TiO_2, whereas the Nb_2O_5-TiO_2 and Nb_2O_5/TiO_2 showed a reduction of 40 and 50%, respectively, in hydrogen consumption related to TiO_2 (Table 2). These catalysts, too, showed a decrease in TiO_2 reduced amount and an increase in Nb_2O_5 reduced amount. This increase was more pronounced in Nb_2O_5/TiO_2 catalyst. The increase in Nb_2O_5 reduced amount in this catalyst can be explained by small crystallites formation on the TiO_2 surface during impregnation, which eases the reduction.

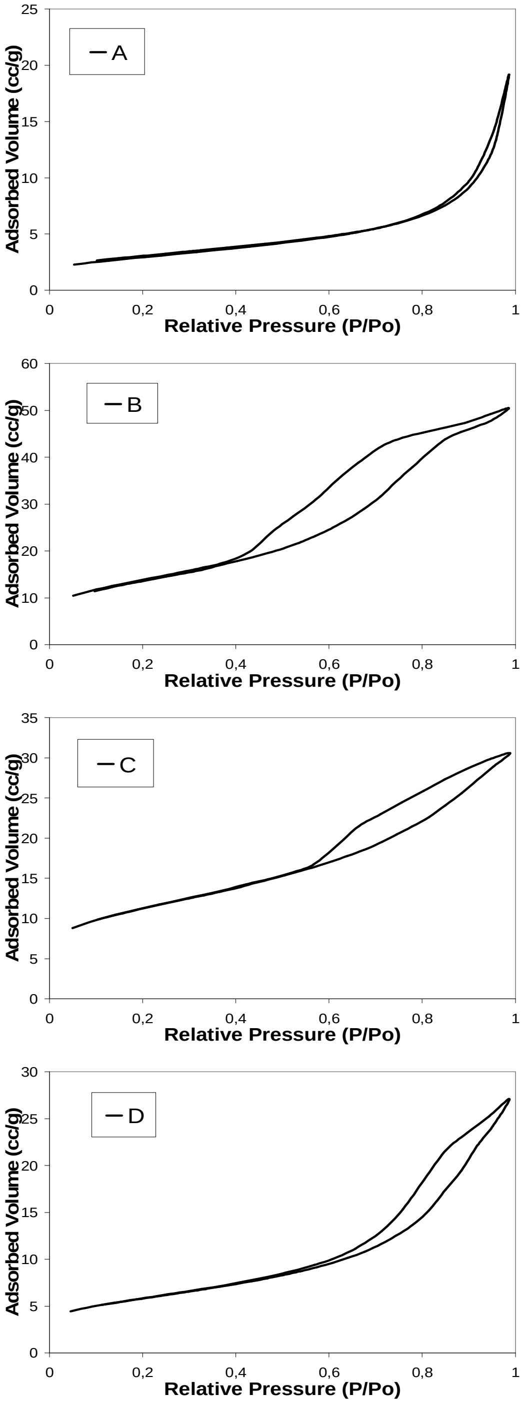

Figure 1. Adsorption-desorption isotherm for TiO_2 (A), Nb_2O_5 (B), Nb_2O_5-TiO_2 (C) and Nb_2O_5/TiO_2 (D).

Table 2. Temperature Programmed Reduction.

Catalyst	Mass of catalyst (g)	Hydrogen Consumption		Reduction (%)	
		TiO_2 (µgH_2/gTiO_2)	Nb_2O_5 (µgH_2/gNb_2O_5)	$TiO_2 \rightarrow Ti_2O_3$	$Nb_2O_5 \rightarrow NbO_2$
TiO_2	0.2520	56.67	-	0.22	-
Nb_2O_5	0.0509	-	283.10	-	3.76
Nb_2O_5-TiO_2	0.2516	34.13	926.91	0.13	12.33
Nb_2O_5/TiO_2	0.2506	28.56	5952.81	0.11	79.25

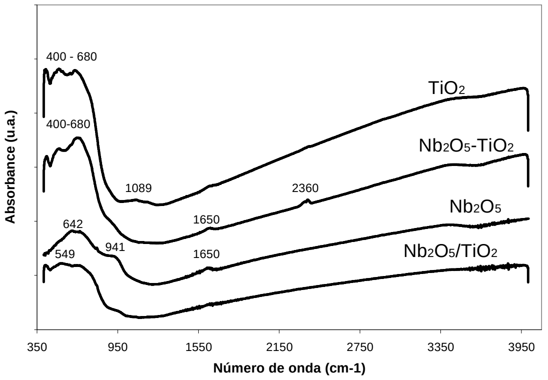

Figure 2. FTIR spectra for the four catalysts.

The reduction peak referent to TiO_2 in the Nb_2O_5-TiO_2 and Nb_2O_5/TiO_2 catalysts was displaced towards lower temperatures. This displacement was more pronounced in the Nb_2O_5/TiO_2 (Figure 3).

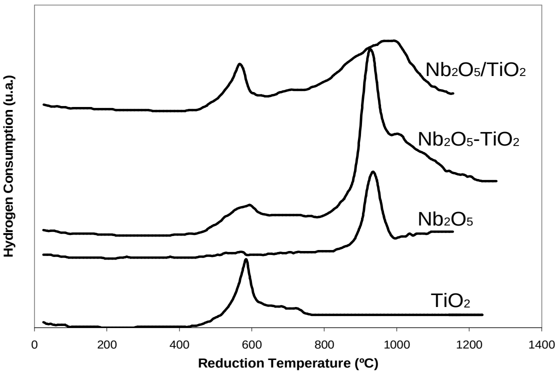

Figure 3. Profile of the Temperature Programmed Reduction.

The reduction profile for the Nb_2O_5-TiO_2 showed that TiO_2 reduction was easy to achieve; however, there was a decrease in the reduced amount. This result showed that the synergic effect between the oxides generated an extra phase.

The reduction peak referent to Nb_2O_5 in the Nb_2O_5-TiO_2 and Nb_2O_5/TiO_2 catalysts was displaced towards higher temperatures. This result showed easiness in the Nb_2O_5 reduction, confirmed by the high reduction percentage.

These results confirm that there are different forms of interaction between the oxides in the Nb_2O_5-TiO_2 and Nb_2O_5/TiO_2.

Photocatalytic degradation of the natural textile effluent

The UV-VIS absorption spectrum of the effluent showed three maximum absorption peaks (at 310; 620 and 670 nm). The peak at 670 nm was chosen to evaluate the degradation process, since it was located in the visible region and showed higher absorbance when compared to the peak at 620 nm.

Degradation tests were carried out, using two different luminous sources to verify the influence of the luminous intensity in the natural effluent photodegradation. The degradation profiles using different luminous sources are showed on the Figures 4 and 5.

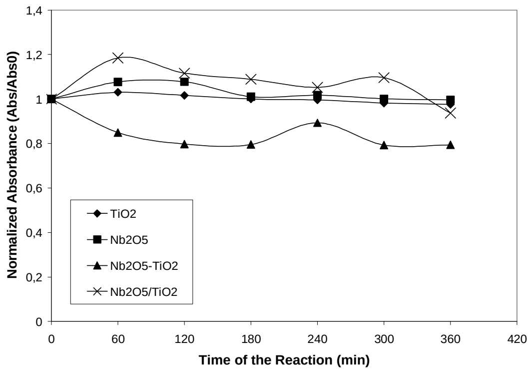

Figure 4. Degradation profile using 26 W lamp.

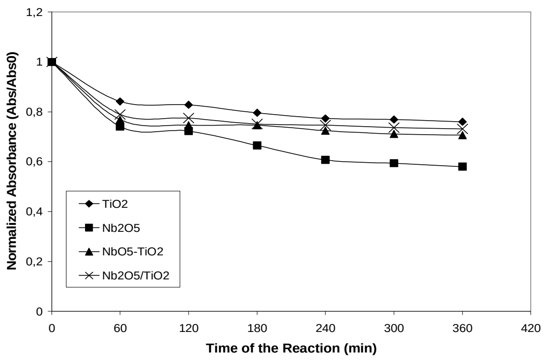

Figure 5. Degradation profile using 250 W lamp.

A linear degradation profile was observed in the tests using 250 W lamp and, as the 26 W lamp was used in the tests, a random profile was observed. The colour reduction occurred during the first hour of irradiation to the four catalysts.

As decolourisation study can be correlated only with the modification of the chromophores group, and not with the effluent real mineralization, determining the COD reduction is absolutely essential, since COD values reflect the organic substances amount in the bulk solution or in the dispersion and the degree to which effluent mineralization has taken place during the irradiation period. The decolourisation and COD reduction results obtained in the experiments carried out with the 26W and 250W lamps are shown in Table 3.

Table 3. Decolourisation and the COD reduction for the four catalysts.

Catalyst	26W lamp		250W lamp	
	Decolourisation (%)	COD reduction (%)	Decolourisation (%)	COD reduction (%)
TiO_2	2.5	53.0	24.0	12.0
Nb_2O_5	0.3	51.0	42.0	8.0
Nb_2O_5-TiO_2	21.6	26.0	29.0	3.0
Nb_2O_5/TiO_2	6.3	46.0	27.0	5.0

It was observed in the tests using 26 W lamp an organic matter reduction much higher than the colour reduction, showing that, for these experimental conditions, the organic matter degradation happened more easily. Organic matter does not constitute chromophores groups that are responsible for effluent colouring.

According to Stafford et al. (1997), the improvement in the mineralization rate in relation to colour reduction, under low luminous intensity, suggests that surface reactions occur at relatively higher degree in these conditions. This occurs because a lower rate of vacancy production allows other species present in the solution to be in adsorption equilibrium with the catalyst surface, and more surface sites are then taken by these other species, in detriment of the hydroxyl groups.

In terms of colour reduction, Nb_2O_5-TiO_2 has shown the most satisfactory result (22%), whereas the other catalysts were not efficient in the experimental conditions studied. Concerning COD reduction, pure catalysts had the best results: TiO_2 (53%) and Nb_2O_5 (51%).

The Nb_2O_5-TiO_2 catalyst has shown higher decolourisation and lower COD reduction; however, it was the only one that showed practically the same performance for both mineralization and decolourisation.

The results obtained using the 250 W lamp showed that, for these conditions, the decolourisation was higher than the organic matter reduction, possibly due to colourless fragments formation, deriving from chromophores groups degradation that contribute to the solution COD. According to Liu et al. (1999), the greater decolourisation in relation to mineralization is due to the fact that only those organic species excited by visible light may be degraded with the help of catalyst particles.

The catalyst that showed higher decolourisation was Nb_2O_5 (42%), whereas for the other catalysts, the colour removal was around 27%. In terms of COD reduction, the TiO_2 was more efficient, with 12% reduction.

The results showed that the reaction rate was significantly influenced by the luminous intensity and, while the decolourisation increased with the luminous intensity, the COD reduction decreased, independently of the photocatalyst used. This statement was contrary to the conclusions of Reutergård and Iangphasuk (1997), who state that the influence of luminous intensity on degradation rate is directly related to the photocatalyst used, and this relation can be either linear or non-linear.

Conclusion

The FTIR and TPR results showed the existence of different interaction forms between the oxides in Nb_2O_5-TiO_2 and Nb_2O_5/TiO_2 catalysts. Nb_2O_5-TiO_2 showed an extra phase, resulting of their interaction, which was responsible for its high photocatalytic activity.

As to the luminous intensity influence, it was verified that the use of a low-intensity lamp (26W) caused COD reduction higher than decolourisation, being easier for the catalysts to degrade organic matter, which does not constitute the chromophores groups responsible for the effluent colour.

The use of a high-intensity lamp (250W) made the decolourisation process more efficient than the COD reduction, possibly due to colourless fragments formation during degradation, which contributed for the solution COD. Therefore, the decolourisation process increased and the COD reduction decreased with the luminous intensity, suggesting that the luminous intensity is directly proportional to the concentration of the hydroxyl groups responsible for the chromophores group degradation.

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