Heterogeneous Catalyzed Oxidative Degradation of Indigo: A Theoretical and Experimental Study

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ABSTRACT

Almost fifteen percent of the total world production of dyes is lost during the dyeing process and is released in the textile effluents. Removal of colour and organics by photocatalytic degradation is emerging as an effective treatment technique.

This work presents evidence of indigo degradation through reaction with OH radicals and ozone. The reaction medium was prepared to mimic an industrial effluent, with an alkaline pH of 12, and another sample of this medium was acidified with nitric acid to pH = 2. After five hours, the first experiment showed 15.5% degradation, while for the second one it was 47%. The residual media was filtered for remove the indigo powder, and then lyophilized. The residuals of the basic medium reaction did not show IR evidence of any organic compound, while in the acid sample isatin was identified as the main product.

We also report DFT computational calculations on the indigo adsorption on TiO_2 surface models, and the subsequent addition reaction with OH radicals and ozone O_3 reaction. Our theoretical and experimental results suggest that TiO_2/UV photocatalysis could be an adequate method for treatment of wastewaters in textile industries.

Keywords: indigo, photocatalysis, textile industries, computational chemistry.

1 INTRODUCTION

Indigo is a blue dye which has been widely used in several civilizations as a pigmenting agent. The current consumption of this dye is enormous due to the popularity of blue jeans, which are dyed with indigo. However, a significant amount of unused dyes remain in textile industry wastewater, the treatment of which presents a challenge, particularly in semi-arid countries where water resources are of great concern.

Natural indigo is present at ambient temperature and normal pressure as dark blue-violet needles or prisms with distinct coppery lustre[1,2]. Indigo is insoluble in water and poorly soluble in most common solvents[3]. The poor solubility is most likely due to the strong inter- and intramolecular hydrogen bonds that are formed in indigo crystals[4].

Advanced oxidation (AO) processes have been defined broadly as those aqueous phase oxidation processes that are driven by highly reactive oxidants, such as H_2O_2, ozone, and most importantly hydroxyl radicals (OH).[5] In practice, AO processes may employ chemical, photochemical, sonochemical, radiolytic, corona discharge techniques, or their various combinations, to generate OH and bring about chemical degradation of pollutants.
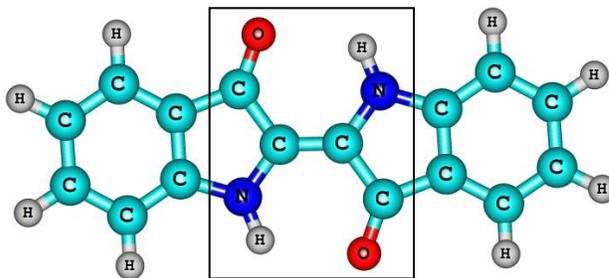

Figure 1: Indigo chromophore group.

The oxidation processes involving hydroxyl radicals have shown their potential to destroy toxic organic compounds in wastewater effluents. The OH radical is the most reactive oxidant that can be applied in water treatment as OH will degrade most organic solutes at rates approaching diffusion controlled limits.[6] The most common ways to generate this radical are the combination of ozone with ultraviolet light, ozone with hydrogen peroxide, hydrogen peroxide with ultraviolet light, hydrogen peroxide with ferrous or ferric ion and by a semiconductor (commonly TiO_2) in combination with visible or UV radiation and molecular oxygen.[7,8,9,10]

The chemical oxygen demand (COD) test is commonly used to indirectly measure the amount of organic compounds in water. Most applications of COD determine the amount of organic pollutants found in surface water (e.g. lakes and rivers), making COD a useful measure of water quality. It is expressed in milligrams per liter (mg/L), which indicates the mass of oxygen consumed per liter of solution. On the other hand, theoretical methods represent valuable tools for the full understanding of chemical systems, predicting reactivity, and elucidating reaction mechanisms. The comparison between experimental and calculated overall data is, in most cases. the only available criterion for that purpose.

In this work, the indigo degradation process in acqueous solutions was studied by the COD method followed by UV/Vis spectroscopy to identify and quantify reaction products. We also report a quantum chemistry and computational kinetics study on the mechanism and kinetics of the oxidation of indigo by OH and O_3 species.

2 EXPERIMENTAL SECTION

An indigo dispersion was prepared according to the patent by Fono and Patton, 1979: 200 mg of indigo, 2 g of NaOH and 200 mL of water. This solution has a pH of 12: it is blue when indigo is suspended, but it is clear when the dye, which is extremely insoluble (2ppm or less), sediments. Another dispersion was prepared in the same way, but was acidified with nitric acid to pH = 2. This dispersion is blue when the dye is suspended, but reddish after sedimentation.

An ozone generator permits the regulation of the oxygen feed and of the applied voltage to give the corona effect. The oxygen current and the voltage were adjusted to 0.2 liters per minute and 9kV, respectively. In these conditions the rate of ozone production was iodimetrically determined to be 2.39×10^{-5} moles per minute.

Reaction occurred in a 300 mL gas washing flask with three exits: one for oxygen admission, a second one for sampling, and the last one for exhausts. The tube for exhausts was connected to a trap containing 100 mL of 0.2M potassium iodide, 100 mL of 0.2M sulfuric acid and 10 mL of sodium thiosulfate. In this trap, ozone reacts with iodide giving iodine, but thiosulfate returns it to iodide. When the thiosufate is finished, the iodine color appears, indicating it is time for a new addition of the thiosulfate solution.

During experiments, samples of 5 mL aliquots (5mg of indigo, 1.91×10^{-5} moles) were taken every 30 minutes, for several hours.

The indigo was analyzed by means of a modification of the standard chemical oxygen demand (COD) method (1998), designed by Calderon (2001): 10 mL of 0.25 N potassium dichromate (12.259 g/L); 5 mL of indigo dispersion and 15 mL of concentrated sulfuric acid. This mixture was heated to boil during 1.5 hours. The final solution is stable and, after cooling to room temperature, it is transferred to a volumetric flask (100mL) and the volume is completed with distilled/deionized water. The dichromate concentration is determined by its absorbance at 447 nm. A reference solution for absorbance was prepared with 5 mL of electrolyte without indigo and the other components without reflux and diluted to 100 mL with water. This solution gave a UV spectrum with a maximum at 447 nm (Absorbance = 1.533) and a minimum at 410 nm (Absorbance = 1.079). Several dilutions of this sample were prepared for dichromate concentrations from 0 to 1.2259 mg/L, and their absorbance gave a calibration linear curve with the following equation:

[Dichromate] (mg/L) = 0.797 x Absorbance + 0.0489

R^2 = 0.9996

After refluxing with dichromate and weighted samples of pure and dried indigo, the final product was diluted to 100 mL. Figure 3 shows the relationship between the added weight of indigo and the absorbance of the final solution:

Indigo weight = −5.8092 ∗ Absorbance + 8.806

Degradation of indigo with ozone in the pH=12 alkaline medium

200 mL of an indigo dispersion were prepared according to the Fono and Patton recipe. Ozonation was run in the reactor. Samples of 5 mL were taken every half an hour during 5 hours. Samples were analyzed by the dichromate-acid method. Results are shown in Figure 2. The alkaline medium is colorless after the dye sediments. Experiments were repeated three times.
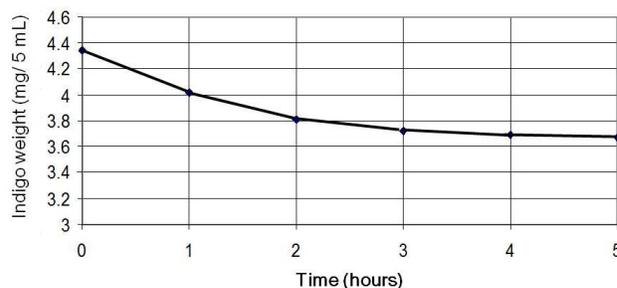

Figure 2. Ozonation of indigo in basic media.

Degradation of indigo with ozone in the pH=2 acidic medium

In the same way, 200 mL of an indigo dispersion were prepared according to the Fono and Patton recipe, and then acidified with nitric acid to pH = 2. Ozonation was run in the reactor. Samples of 5 mL were taken every half an hour during 5.5 hours. Samples were analyzed by the dichromate-acid method and results are shown in Figures 3 and 4. The acid media is reddish-amber after the dye sediments. Experiments were repeated three times.
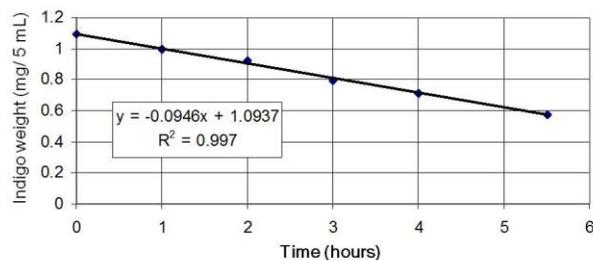

Figure 3. Ozonation of indigo in acidic media.

During the reaction, the concentration of dissolved ozone remains constant, and depends on the partial pressure reached in the generator, and on the temperature. The ozone concentration in the stream of enriched oxygen exiting from the generator is large enough for sustain saturation of the reacting medium, as determined in the $KI/Na_2S_2O_3/H_2SO_4$ trap. Intervals of 1.5 hours are needed to activate the trap during the reaction. In the same way, the concentration of indigo remains constant owing to its very low solubility. Thus, a reaction order equal to zero is expected. In the acidic medium, this order is found. Yet, in the basic medium, the graph corresponds neither to zero nor to first order. In the basic medium, the kinetic analysis shows two

periods: at the beginning, during two hours or more, the reaction exhibits zeroth order, giving a straight line with a regression coefficient $R^2 = 0.9845$. With the other points a straight line is also obtained with $R^2 = 0.9796$.

The conversion obtained in the acidic medium is about 47%, while in the basic medium it is only approximately 15.5%. The red–amber color obtained during ozonation of acidic dispersion was identified as the same color obtained by Grosjean et al.[11] in samples of paints containing indigo, degraded in atmospheres of nitric vapors.

3 THEORETICAL SECTION

Electronic calculations were performed with the Gaussian 09 system of programs.[12] Geometry optimizations and frequency calculations were carried out using the M05-2X functional[13] in conjunction with several basis sets. No symmetry constraints were imposed in the geometry optimizations. Thermodynamic corrections at 298 K were included in the calculation of relative energies. All the stable structures were characterized as minima on the potential energy surface (PES) by using analytical second derivatives. Unrestricted calculations were used for open shell systems.

The remarkable stability of indigo has been attributed to intramolecular hydrogen bonding between the two adjacent carbonyl and N-H groups (see Figure 1), which keeps the molecule in a trans planar configuration, preventing the photochemical cis-trans isomerization.[14,15]

Photodegradation processes occur when indigo reacts with activated oxygen species, such as hydroxyl and super oxide radicals, generated on a TiO_2 surface. We have calculated the binding relative energy and Gibbs free energy between indigo and a TiO_2 cluster model surface. The complexation energies are calculated as:

$$\Delta E = E_{complex} - (E_{indigo} + E_{surface}) + \Delta(ZPE)$$

$$\Delta G = G_{complex} - (G_{indigo} + G_{surface})$$

The fully optimized structure of the adsorption complex is shown in Figure 5.
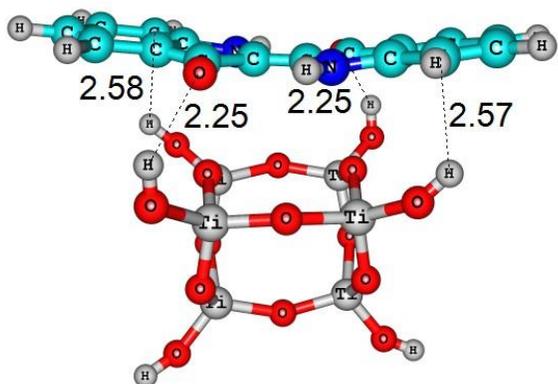

Figure 4: Indigo adsorbed on a TiO_2 surface model.

We have also studied the addition of an OH radical and of ozone to the free indigo molecule. The fully optimized structures of the adducts are presented in Figures 5 and 6. Relative energies are calculated with respect to the sum of the separated reactants at 0 K, and they are reported in Table 1. $\Delta E_{(TS)}$ is the effective activation energy ($\Delta E_{TS} = E^{TS} - E^R$), and ΔE is the reaction energy ($\Delta E = E^P - E^R$).
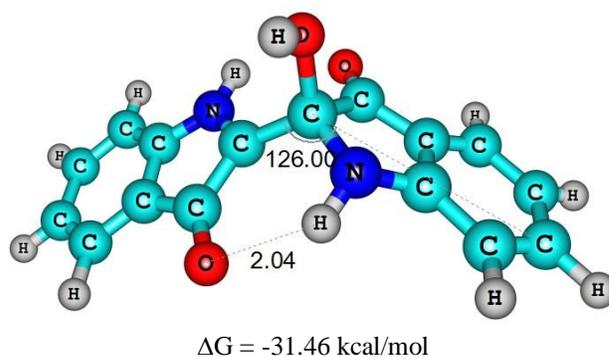

$\Delta G = -31.46$ kcal/mol

Figure 5: Optimized structure of the indigo-OH adduct.
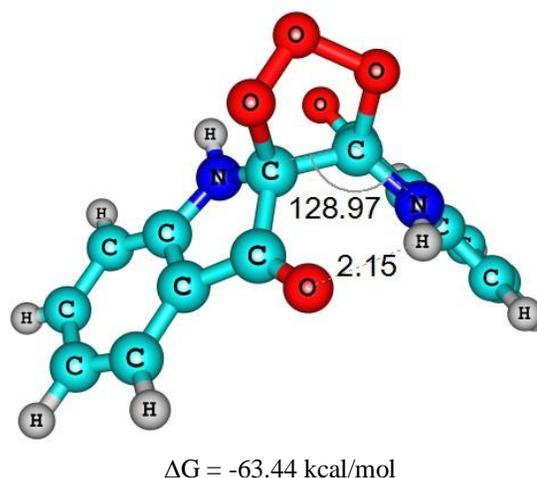

$\Delta G = -63.44$ kcal/mol

Figure 6: Optimized structure of the indigo-O_3 adduct.

The most relevant OH-addition channel corresponds to the C_1-$C_{1'}$ central double bond. Ozone O_3 also bind to the central double bond, and break the planarity of the molecule. In both cases, the reaction energy, ΔE, is negative and very large, indicating that these reactions are irreversible and energetically favored, yielding an adduct that is stabilized by delocalization of the unpaired electron over the whole molecule.

Pathway	ΔE(TS)	ΔE	ΔG(TS)	ΔG
OH addition	-7.52	-40.42	1.76	-31.46
O_3 addition		-77.04		-63.44

Table 1: Relative Energies and Gibbs free energies, in kcal/mol, in the indigo + OH and indigo + O_3 reactions

When indigo molecule is adsorbed on TiO_2 surface, is expected a higher reactivity towards free radicals and oxygen species. In the case of O_3 addition, it can be observed (figure 7) that the O atom of indigo molecule bind to a Ti atom on the surface, and the formation of isatin is favored.
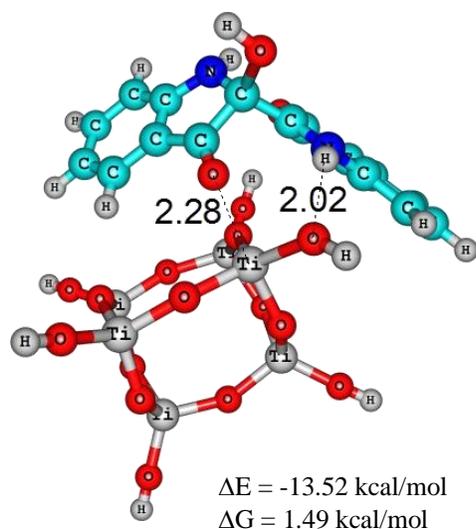

$\Delta E = -13.52$ kcal/mol
$\Delta G = 1.49$ kcal/mol

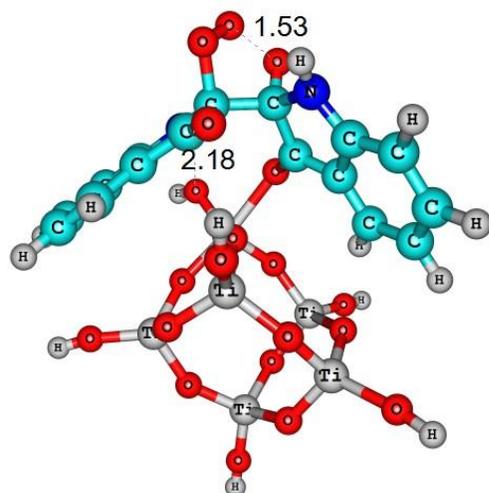Figure 7: OH addition to indigo on a TiO_2 surface model.

Figure 8: O_3 addition to indigo on a TiO_2 surface model.

4 CONCLUSIONS

In this work, the COD method was employed to quantify the the mass of residual indigo after its degradation process in acqueous solutions by reaction with OH radicals and ozone. UV/Vis spectroscopy was used to identify and quantify the color produced during the reaction. Weight loss of indigo and the absorbance increase of residual solutions indicate the amount of degradation. Reaction is slow, as expected from the stability of the dye.

Irradiation of titania with visible light produces a photoinduced decoloration of the dye, due to the breaking of the double-bond conjugation system of the chromophoric group. Observation of the decoloration and of the degradation of solid indigo constitutes an encouraging result for the development of self-cleaning titania-coated surfaces.

The theoretical work is in process, aiming to calculate reaction rate constants for OH and O_3 addition to indigo. In this preliminary study we have obtained large reaction energies and Gibbs free energies, indicating very fast reaction rate constants. In future work, we will extend this approach to more complex systems.

REFERENCES

[1] M. Božič, V. Kokol, Dyes Pigm., 76, 299-309, 2008.
[2] A. Roessler, New electrochemical methods for the reduction of vat dyes, Diss ETH No 15120. Zurich, 2003.
[3] R. J. H. Clark, C. J. Cooksey, M. A. M. Daniels, R. Withnall, Indigo, woad, and Tyrian Purple: important vat dyes from antiquity to present Endeavour, 17, 191-199, 1993.
[4] S. J. Holt, P. W. Sadler, Proc. Royal Soc. London Ser. B Biol. Sci. 149, 495-505, 1958.
[5] D. Ollis, ACS Symposium Series 518, Washington, DC, pp. 18–34, 1993.
[6] J. Hoigné, Water Sci. Technol. 35(4):1–8, 1997.
[7] R. W. Legan, Chem.Engng. 89, 95-100, 1982.
[8] W. H. Glaze, J. W. Kang, D. H. Chapin, Ozone Sci. .Engng. 9, 353-352, 1987.
[9] O. Legrini, E. Oliveros, A. M. Braun, Chem. Rev. 93, 671-698, 1993.
[10] A. Mokrini, D. Oussi, S. Esplugas, Water. Sci. Techno. 35 (9), 95-102, 1997.
[11] Grosjean D., Salmon L. G., Cass A. R., Environ. Sci. Technol 26, 952-959, 1992.
[12] Gaussian 09, Revision A.02, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, 2009.
[13] Y. Zhao, N. E. Schultz, D. G. Truhlar, J. Chem. Theory Comput., 2, 364, 2006..
[14] T. Kobayashi, P. M. Rentzepis, J. Chem. Phys., 70, 886, 1979.
[15] C. Miliani, A. Romani, G. Favaro, Spectrochim. Acta, Part A, 581, 1998.