

Master in Bioengineering

Orange II Dye Degradation by Photo Assisted Wet Peroxidation using Gold-Based Catalysts

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by

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Abstract

Nowadays, the textile industry consumes an enormous amount of dyes, which generate massive quantities of effluents with a high degree of coloration, toxicity, and high chemical oxygen demand that cannot be treated by traditional processes. The advanced oxidation processes (AOP's), particularly the Wet Peroxidation (WP), have proved to be an effective alternative to solve this problem.

One way of improving this process is to use gold-based catalysts, which have been reported to have a high efficiency and stability, and most important of all, do not leach. Along with gold, the use of radiation also improves the wet peroxidation, through the formation of more hydroxyl radicals, the main mechanism of the AOP's; moreover, the use of radiation also accelerates the redox cycle for catalyst regeneration.

In this work, the efficiency of the photo assisted wet peroxidation using gold-based catalysts was tested and analyzed by testing different supports. Four metal oxides were used in this work – Alumina (Al_2O_3), Iron Oxide (Fe_2O_3), Titanium Dioxide (TiO_2) and Zinc Oxide (ZnO); catalysts were prepared by the deposition/precipitation method and in every case nanosized Au particles were obtained. An additional catalyst (Fe_2O_3), purchased from the World Gold Council (WGC), was also used for comparison purposes. All materials were characterized by several techniques, namely AAS, TEM and XPS. For each catalyst, several runs were made in order to test the efficiency of the support and catalyst as adsorbents, the use of the oxidant in conjunction with the support and catalyst, and the use of radiation with both oxidant and catalyst/support. These runs were made in a slurry batch reactor in order to treat a solution with a concentration of 0.1 mM of an azo-dye – Orange II (OII). The dye removal was quantified by using a UV-Vis spectrophotometer. Samples were also taken at the end of the runs in order to measure the Total Organic Carbon (TOC), residual hydrogen peroxide and the metal content in the effluent, to assess the leaching of gold. All catalysts have shown negligible Au leaching, putting into evidence their great stability, which was confirmed by consecutive reaction cycles.

An optimization was also carried out after choosing the best catalyst ($\text{Au-Al}_2\text{O}_3$), the one presenting the largest BET surface area, considering the Turnover Frequency

(TOF). The effect of the temperature (ranging from 10 – 70 °C), pH (1.5 – 5.0), hydrogen peroxide concentration (1.5 – 12.0 mM), catalyst concentration (1.0 – 2.5 g/L) and radiation intensity (100-500 W/m²) were analyzed.

Using the best values obtained from the parametric study (T= 50 °C, pH= 3.0, [catalyst]= 2.0 g/L and radiation= 500 W/m²), an outstanding performance was reached: nearly complete Orange II removal, with 90.9±5.7% of mineralization. Employing the same conditions, a simulated acrylic dye effluent was treated, to assess the applicability of this process to industrial wastewater treatment. The amount of oxidant used was 3.52 g/L, since the stoichiometric amount of COD was 796.8±4.0 mgO₂/L. Removals up to 100±1.5%, 72.4±2.2% and 70.0±1.0% for color, TOC and COD, respectively, were obtained; moreover, there was an improvement in the biodegradability of the effluent, and no toxic wastewater was generated. However, the Biochemical Oxygen Demand (BOD₅) concentration was higher than the maximum allowable value, this indicating that the effluent could not be discharged, but could possibly be used in subsequent biological degradation process for reduction of the BOD₅ concentration.

Keywords: Advanced Oxidation Process, Photo assisted Wet Peroxidation, Gold-based Catalysts, Dye-containing Wastewaters

Resumo

Hoje em dia, a indústria têxtil consome uma enorme quantidade de corantes, que geram grandes quantidades de efluentes com um elevado grau de coloração, toxicidade e elevada carência química de oxigénio que não podem ser tratados por processos convencionais. Os processos de oxidação avançados (POAs), em particular o “Wet peroxidation” (WP) (degradação de peróxido de hidrogénio), são uma alternativa eficaz para resolver este problema.

Uma forma de melhorar este processo é através da utilização de catalisadores à base de ouro, os quais têm sido descritos como tendo uma elevada eficiência e estabilidade, e, sobretudo, não lixiviam. Juntamente com ouro, a utilização de radiação também melhora a WP, através da formação de mais radicais hidroxilo, o principal mecanismo dos POAs; além disso, a utilização de radiação também acelera o ciclo redox para a regeneração do catalisador.

Neste trabalho, a eficiência da degradação de peróxido de hidrogénio assistida por radiação, utilizando catalisadores à base de ouro, foi testada e analisada através de testes a diferentes suportes. Quatro óxidos metálicos foram utilizados neste trabalho - alumina (Al_2O_3), óxido de ferro (Fe_2O_3), dióxido de titânio (TiO_2) e óxido de zinco (ZnO); os catalisadores foram preparados pelo método de deposição/precipitação e em todos os casos foram obtidas nano partículas de ouro. Um catalisador adicional (4% Au- Fe_2O_3), obtido a partir do World Gold Council (WGC), também foi utilizado para fins de comparação com os catalisadores preparados em laboratório. Todos os materiais foram caracterizados por várias técnicas, nomeadamente AAS, TEM e XPS. Para cada catalisador, várias corridas foram feitas a fim de testar a eficácia do suporte e catalisador como adsorventes, o uso do oxidante em conjunto com o suporte e o catalisador, e o uso de radiação com ambos oxidante e catalisador/suporte. Estas experiências foram realizadas num reator em descontínuo, de modo a tratar uma solução com concentração de 0,1 mM de um corante azo - Orange II (OII). A remoção do corante foi quantificada utilizando um espectrofotómetro de UV-Vis. No final das experiências, foram retiradas amostras e mediu-se o carbono orgânico total (COT), o peróxido de hidrogénio residual e o teor de ouro no efluente, para quantificar a sua lixiviação. Todos os catalisadores

mostraram uma insignificante lixiviação de ouro, provando a sua grande estabilidade, o que também foi confirmado por ciclos de reação consecutivos.

Uma otimização também foi realizada depois de se ter obtido o melhor catalisador (Au-Al₂O₃), uma vez que apresentou a maior área de superfície BET e Turnover Frequency (TOF). O efeito da temperatura (10-70 °C), pH (1,5-5,0), a concentração de peróxido de hidrogénio (1,5-12,0 mM), a concentração do catalisador (1,0-2,5 g/L) e a intensidade da radiação (100-500 W/m²) foram analisados.

Utilizando os melhores valores obtidos a partir do estudo paramétrico (T = 50 °C, pH = 3,0, [catalisador] = 2,0 g/L e radiação = 500 W/m²), foi alcançado um desempenho notável: remoção quase completa do corante, com 90,9±5.7% de mineralização. Aplicou-se as mesmas condições operatórias no tratamento de um efluente de tingimento de fibras acrílicas simulado de modo a avaliar a aplicabilidade deste processo para tratamento de efluentes industriais. A quantidade de oxidante usado foi de 3,52 g/L, uma vez que a quantidade estequiométrica de CQO era de 796.8±4.0 mgO₂/L. Remoções de 100±1.5%, 72,4±2.2% e 70,01.0% para a cor, COT e CQO, respetivamente, foram obtidos; além disso, houve uma melhoria na biodegradabilidade do efluente e não ocorreu a formação de compostos tóxicos. No entanto, a concentração de Carência Bioquímica de Oxigénio (CBO₅) foi maior do que o valor máximo permitido, impossibilitando a sua descarga, no entanto, a utilização de um processo de tratamento subsequente tal como a degradação biológica poderá ser a alternativa ideal para reduzir a CBO₅.

Palavras-chave: Processo de Oxidação Avançado, Catalisadores à Base de Ouro, Decomposição de Peróxido de Hidrogénio Assistida por Radiação, Efluentes Tingimento

Declaração

Declara, sob compromisso de honra, que este trabalho é original e que todas as contribuições não originais foram devidamente referenciadas com identificação da fonte.

Assinatura:

Data:

Contents

Acknowledgments	i
Abstract	iii
Resumo	v
List of Figures	xi
List of Tables	xv
Nomenclature	xvi
Abbreviations	xvi
1 Introduction	1
1.1 Framework	1
1.2 Dyes	1
1.3 Objectives	2
2 State of Art	4
2.1 Advanced Oxidation Processes	4
2.2 Fenton's Oxidation / Wet Peroxidation	5
2.2.1 Homogeneous Process	6
2.2.2 Heterogeneous Process	7
2.3 Photo assisted Wet Peroxidation	8
2.4 Influence of Reaction Parameters	9
2.4.1 Effect of pH	9
2.4.2 Effect of H ₂ O ₂ Concentration	9
2.4.3 Effect of Catalyst Concentration	10
2.4.4 Effect of Temperature	11
2.4.5 Effect of Radiation	11
2.5 Use of Gold-based Catalysts on Photo Assisted Wet Peroxidation	11
3. Materials and Methods	17
3.1. Dye and dyeing effluent	17
3.2. Catalyst Preparation and Characterization	17
3.3. Analytical Methods	18
3.3.1. Total Organic Carbon (TOC)	18
3.3.2. Hydrogen Peroxide	18
3.3.3. Hydroxyl Radicals	18
3.3.4. Gold Concentration	19
3.3.5. Toxicity	19
3.3.6. Biodegradability	19

3.3.7.	pH	19
3.3.8.	Chemical Oxygen Demand (COD)	20
3.3.9.	Biological Oxygen Demand (BOD ₅)	20
3.3.10.	Color / Dye Concentration.....	20
3.4	Experimental Procedures	21
4.	Results and Discussion	24
4.1.	Materials Characterization	24
4.2.	Orange II dye removal	25
4.2.1.	Adsorption vs. Reaction without Radiation.....	25
4.2.2.	Wet peroxidation vs. Wet peroxidation assisted with Radiation.....	30
4.2.3.	Effect of Radiation Type	34
4.2.4.	Catalysts Stability	37
4.2.5.	Turn Over Frequency (TOF)	39
4.2.6.	Optimization	40
4.3.	Acrylic Dye Treatment.....	45
5.	Conclusions and Suggestions for Future Work	48
6.	References	50
Annex		55

List of Figures

Figure 1.1 - Orange II azo dye structure.....	2
Figure 2.1 - Advanced Oxidation Processes.....	5
Figure 2.2 - Proposed scheme for the photochemical improvement in the Fenton-like catalysis Catalysis.....	12
Figure 2.3 - Influence of the laser intensity on the catalytic activity of Au/HO-npD for the Fenton reaction of phenol degradation (left) and H ₂ O ₂ decomposition (right). Reaction conditions for phenol degradation using increasing laser powers. (a) 0 mJ pulse-1, (b) 20 mJ pulse-1, (c) 38 mJ pulse-1, and (d) 70 mJ pulse-1. Reaction conditions: 100 mg L ⁻¹ (1.06 mM) of phenol and 200 mg L ⁻¹ (5.88 mM) of H ₂ O ₂ and Au/HO-npD 1.0% 160 mg L ⁻¹ (0.0056 mM) at pH = 4.....	13
Figure 2.4 – Effect of irradiation and H ₂ O ₂ /phenol molar ratio on phenol decomposition and H ₂ O ₂ decomposition; H ₂ O ₂ /phenol molar ratio: ●1.0;△2.0;◆3.0; □ 4.0;▲5.5 ; ○ 7.0;■7.0 (dark). Reaction conditions:1 g L ⁻¹ phenol (10.64 mM), pH 4, 400 mg L ⁻¹ catalyst (0.02 mM of gold)	14
Figure 2.5 - Fenton-like degradation of AO7 aqueous solution with (a) bare CeO ₂ , (b) 0.5 at.% Au-CeO ₂ , (c) 1.0 at.% Au-CeO ₂ , and (d) 2.0 at.% Au-CeO ₂ in the pre-adsorbed mode (A) in dark and (B) under the visible irradiation, and in the pre-mixed mode (C) in dark and (D) under the visible irradiation. [CeO ₂] = 0.5 g/L, [H ₂ O ₂] = 20 mM, [AO7] = 35 mg/L.....	15
Figure 2.6 - Four consecutive cycles of phenol decomposition catalyzed by Au/DNPs. Open/closed symbols refer to fresh or reused catalyst, respectively. Reaction conditions: 1 g L ⁻¹ phenol (10.64 mm), 2 g L ⁻¹ (58.8 mm), pH as indicated, 400 mg L ⁻¹ catalyst (0.02 mm of gold).....	16
Figure 3.1 - Diagram (a) and photo (b) of the radiation assisted wet peroxidation set-up.....	22
Figure 3.2 - Variation of the radiation intensity as a function of the dye concentration.....	23
Figure 4.1 - Dye removal as a function of time for Al ₂ O ₃ and 0.8% Au-Al ₂ O ₃ (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM, when used).....	26
Figure 4.2 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for Al ₂ O ₃ and Au-Al ₂ O ₃ (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM in a) and [OII] = 0 in b)).....	27
Figure 4.3 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for Fe ₂ O ₃ and 4% Au-Fe ₂ O ₃ (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM in a) and [OII] = 0 in b)).....	28
Figure 4.4 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for Fe ₂ O ₃ and 0.8% Au-Fe ₂ O ₃ (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM in a) and [OII] = 0 in b)).....	28
Figure 4.5 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for TiO ₂ and Au-TiO ₂ (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM in a) and [OII] = 0 in b)).....	29

Figure 4.6 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for ZnO and Au-ZnO. (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM in a) and [OII] = 0 in b)).....	29
Figure 4.7 - Dye removal as a function of time for the Al ₂ O ₃ and Au-Al ₂ O ₃ system (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m ² , when used).....	30
Figure 4.8 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for Al ₂ O ₃ and Au-Al ₂ O ₃ . (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m ² , when used).....	31
Figure 4.9 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for Fe ₂ O ₃ and 4% Au/Fe ₂ O ₃ (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation = 500 W/m ² , when used).....	32
Figure 4.10 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for Fe ₂ O ₃ and 0.8% Au-Fe ₂ O ₃ (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m ² , when used).....	32
Figure 4.11 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for TiO ₂ and Au-TiO ₂ (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m ² , when used).....	33
Figure 4.12 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for ZnO and Au-ZnO (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m ² , when used).....	33
Figure 4.13 - Dye removal as a function of time for Au-Al ₂ O ₃ (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [catalyst] = 2.0 g/L, [OII] = 0.1 mM and visible radiation= 500 W/m ² , when used).....	35
Figure 4.14 - Dye and TOC removals after 2 h for 0.8% Au-Fe ₂ O ₃ (a), 4.0% Au-Fe ₂ O ₃ (b), Au-ZnO (c), Au-TiO ₂ (d) and Au-Al ₂ O ₃ (e) (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and visible radiation= 500 W/m ² , when used).....	36
Figure 4.15 - Dye removal along time in 3 consecutive reaction cycles for Au-Al ₂ O ₃ (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m ²).....	37
Figure 4.16 - TOC and dye removal, hydrogen peroxide consumption and its efficiency of use after 2 h of reaction in 3 consecutive reaction cycles for Au-Al ₂ O ₃ (a), Au-Fe ₂ O ₃ (b), Au-TiO ₂ (c) and Au-ZnO (d) (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m ²).....	38
Figure 4.17 – TOFs for dye and TOC removals for all gold catalysts prepared.....	39

Figure 4.18 – Effect of hydrogen peroxide concentration in dye removal as a function of reaction time (a), and in TOC and dye removal, in overall hydrogen peroxide consumption and in its efficiency of use after 2 h of reaction (b) (pH=3.0, T= 30 °C, [catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m ²).....	41
Figure 4.19 - Influence of catalyst dose in dye removal as a function of reaction time (a), and in TOC and dye removal, in overall hydrogen peroxide consumption and its efficiency of use after 2 h of reaction (b) (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [OII] = 0.1 mM and radiation= 500 W/m ²).....	42
Figure 4.20 - Influence of initial pH in the Orange II dye removal as a function of reaction time (a), in TOC and dye removal, overall hydrogen peroxide consumption and its efficiency of use after 2 h of reaction (b) (T= 30 °C, [H ₂ O ₂] = 6 mM, [catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m ²).....	43
Figure 4.21 - Influence of the radiation intensity in the dye removal as a function of reaction time (a), in TOC and dye removal, overall hydrogen peroxide consumption and its efficiency of use after 2 h of reaction (b) (pH= 3.0, [H ₂ O ₂] = 6 mM, T= 30 °C, [catalyst] = 2.0 g/L and [OII] = 0.1 mM).....	44
Figure 4.22 - Influence of reaction temperature in the dye removal as a function of reaction time (a), in TOC and dye removal, overall hydrogen peroxide consumption and its efficiency of use after 2 h of reaction (b) (pH= 3.0, [H ₂ O ₂] = 6 mM, [catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m ²).....	45
Figure 4.23 – Dye an TOC removal (a) and specific oxygen uptake rate (k') (b) as a function of reaction time during degradation of the industrial acrylic effluent (T= 50 °C, pH= 3.0, [H ₂ O ₂] = 3.52 g/L, [catalyst] = 2.0 g/L and radiation= 500 W/m ²).....	46
Figure C.1 – Emission spectrum of Heraeus TQ 150 mercury lamp.....	57
Figure C.2 – Transmittance from quartz and Duran 50 reactors.....	57
Figure D.1 - HRTEM images of Au-Al ₂ O ₃ (a), Au-Fe ₂ O ₃ WGC (c), of Au-Fe ₂ O ₃ (e), Au/TiO ₂ (g) and Au/ZnO (i) along with the corresponding gold nanoparticle size distribution histograms (b,d,f,h,j).....	58
Figure D.2 - Au 4f XPS spectra of Au supported on Al ₂ O ₃ , Fe ₂ O ₃ , TiO ₂ and ZnO (a) and Au 4d XPS spectra of Au-ZnO (b).....	59
Figure E.1 - Dye removal as a function of time for Fe ₂ O ₃ and 0.8% Au-Fe ₂ O ₃ (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM, when used).....	60
Figure E.2 - Dye removal as a function of time for Fe ₂ O ₃ and 4.0% Au-Fe ₂ O ₃ (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM, when used).....	60
Figure E.3 - Dye removal as a function of time for TiO ₂ and Au-TiO ₂ (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM, when used).....	61
Figure E.4 - Dye removal as a function of time for ZnO and Au-ZnO (pH=3.0, T= 30 °C, [H ₂ O ₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM, when used).....	61

Figure F.1 - Dye removal as a function of time for Fe_2O_3 and 0.8% $\text{Au-Fe}_2\text{O}_3$ ($\text{pH}=3.0$, $T=30\text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2]=6\text{ mM}$, $[\text{Support or catalyst}]=2.0\text{ g/L}$, $[\text{OII}]=0.1\text{ mM}$ and radiation= 500 W/m^2 , when used).....	62
Figure F.2 - Dye removal as a function of time for Fe_2O_3 and 4.0% $\text{Au-Fe}_2\text{O}_3$ ($\text{pH}=3.0$, $T=30\text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2]=6\text{ mM}$, $[\text{Support or catalyst}]=2.0\text{ g/L}$, $[\text{OII}]=0.1\text{ mM}$ and radiation= 500 W/m^2 , when used).....	62
Figure F.3 - Dye removal as a function of time for TiO_2 and Au-TiO_2 ($\text{pH}=3.0$, $T=30\text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2]=6\text{ mM}$, $[\text{Support or catalyst}]=2.0\text{ g/L}$, $[\text{OII}]=0.1\text{ mM}$ and radiation= 500 W/m^2 , when used).....	63
Figure F.4 - Dye removal as a function of time for ZnO and Au-ZnO ($\text{pH}=3.0$, $T=30\text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2]=6\text{ mM}$, $[\text{Support or catalyst}]=2.0\text{ g/L}$, $[\text{OII}]=0.1\text{ mM}$ and radiation= 500 W/m^2 , when used).....	63
Figure G.1 - Dye removal as a function of time for Fe_2O_3 and 0.8% $\text{Au-Fe}_2\text{O}_3$ with visible radiation ($\text{pH}=3.0$, $T=30\text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2]=6\text{ mM}$, $[\text{Support or catalyst}]=2.0\text{ g/L}$, $[\text{OII}]=0.1\text{ mM}$ and radiation= 500 W/m^2 , when used).....	64
Figure G.2 - Dye removal as a function of time for Fe_2O_3 and 4.0% $\text{Au-Fe}_2\text{O}_3$ with visible radiation ($\text{pH}=3.0$, $T=30\text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2]=6\text{ mM}$, $[\text{Support or catalyst}]=2.0\text{ g/L}$, $[\text{OII}]=0.1\text{ mM}$ and radiation= 500 W/m^2 , when used).....	64
Figure G.3 - Dye removal as a function of time for TiO_2 and Au-TiO_2 assisted with visible radiation ($\text{pH}=3.0$, $T=30\text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2]=6\text{ mM}$, $[\text{Support or catalyst}]=2.0\text{ g/L}$, $[\text{OII}]=0.1\text{ mM}$ and radiation= 500 W/m^2 , when used).....	65
Figure G.4 - Dye removal as a function of time for ZnO and Au-ZnO assisted with visible radiation ($\text{pH}=3.0$, $T=30\text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2]=6\text{ mM}$, $[\text{Support or catalyst}]=2.0\text{ g/L}$, $[\text{OII}]=0.1\text{ mM}$ and radiation= 500 W/m^2 , when used).....	65
Figure H.1 - Dye removal along time in 3 consecutive reaction cycles for $\text{Au-Fe}_2\text{O}_3$ ($\text{pH}=3.0$, $T=30\text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2]=6\text{ mM}$, $[\text{catalyst}]=2.0\text{ g/L}$, $[\text{OII}]=0.1\text{ mM}$ and radiation= 500 W/m^2).....	66
Figure H.2 - Dye removal along time in 3 consecutive reaction cycles for Au-TiO_2 ($\text{pH}=3.0$, $T=30\text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2]=6\text{ mM}$, $[\text{catalyst}]=2.0\text{ g/L}$, $[\text{OII}]=0.1\text{ mM}$ and radiation= 500 W/m^2).....	66
Figure H.3 - Dye removal along time in 3 consecutive reaction cycles for Au-ZnO ($\text{pH}=3.0$, $T=30\text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2]=6\text{ mM}$, $[\text{catalyst}]=2.0\text{ g/L}$, $[\text{OII}]=0.1\text{ mM}$ and radiation= 500 W/m^2).....	67

List of Tables

Table 2.1 - Studies found regarding the photo assisted wet peroxidation using gold based catalysts.....	12
Table 4.1 - Characterisation of the gold supported materials: BET surface areas, gold loading, average gold nanoparticle sizes, gold oxidation state and gold dispersion.....	25
Table 4.2 Characterization of the synthetic acrylic dyeing effluent before and after photo-assisted wet peroxidation and removal efficiencies.....	47
Table A.1 – Components of the simulated acrylic dyeing effluent.....	55

Nomenclature

BOD₅ - Biochemical Oxygen Demand after 5 days [mg O₂/L]

COD - Chemical Oxygen Demand [mg O₂/L]

D_p – particles diameter (mm)

E°– Oxidation Potential (V)

I - Radiation Intensity [W/m²]

k – Kinetic Constant (mol/s.L)

S_{BET} – Superficial area obtained through the equation Brunauer-Emmett-Teller (BET)
(m²/g)

SOUR or k' - Specific Oxygen Uptake Rate [mg O₂/(g_{vss}.h)]

T - Temperature [°C]

TOC - Total Organic Carbon [mg C/L]

Abbreviatures

AAS – Atomic Absorption Spectrometry

AOP – Advanced Oxidation Process

HR-TEM – High Resolution Transmission Electron Microscopy

hν - Radiation

M.A.V. - Maximum Allowable Value

OII – Orange II Dye

UV - Ultra-violet

UV/Vis. – Ultra-violet/Visible

V. fischeri - *Vibrio fischeri*

Vis. - Visible

WP – Wet Peroxidation

XPS – X-ray Photoelectron Spectroscopy

1 Introduction

1.1 Framework

Environmental issues have been gaining importance in modern society and the discharge of wastewaters into the environment, without prior treatment, is one of the most important problems.

The textile business is an example of the industrial sectors where large quantities of water are used, usually as a solvent, and dyeing is a fundamental operation during fabric processing. High volumes of colored effluents are produced in such industrial activities, typically with low dye concentrations (about 0.1 mM). In addition to the negative visual effects, decreased absorption of light by the existing vegetation occurs, which leads to disturbances in photosynthesis and changes in the biological cycle of microorganisms. At the same time, increased chemical oxygen demand (COD) decreases the amount of dissolved oxygen.

Some of the common ways of wastewater treatment include adsorption, sedimentation, chemical coagulation and biological degradation. However, these treatment processes proved to be inefficient. The biological approaches, for example, take too much time and cannot degrade toxic dyes (Can *et al.* 2006) and the other technologies only transfer the pollutant to another phase rather than destroying it.

1.2 Dyes

Dyes are used in a wide range of activities, from textile to food industries, and are sold in different physical forms, such as powders, granular, liquid solutions and pastes. These molecules comprise two key groups: the chromophore, responsible for the dye colour, and the functional group, auxochrome, which bonds the dye to the fibre (Waring *et al.*, 1990). The main chromophores are azo ($-N=N-$), carbonyl ($-C=O$), methine ($-CH=$), nitro ($-NO_2$) and quinoid groups, and the most common auxochromes are amine ($-NH_2$), carboxyl ($-COOH$), sulfonate ($-SO_3H$) and hydroxyl ($-OH$) groups (dos Santos *et al.* 2007).

Dyes are often grouped in classes related with the chemical structure and application process. The most common are the azo and anthraquinones, but also aldotriaryl-methanes, diphenyl-methanes, sulfurs, among others, exist. Azo dyes represent the largest amount of dye production, although they constitute a serious risk to the environment and human health, due to their high toxicity and possible carcinogenic properties (Teli *et al.* 2000).

Orange II (OII) (Figure 1.1), also called acid orange 7, is widely used in the dyeing of textiles (Paz *et al.*, 2005). Since OII is the most studied compound among the azo dyes, its degradation pathways and formation of by-products are fully described (Chen *et al.*, 2001). Thus, it can be used as a model compound for oxidative degradation studies of azo dyes, particularly when new processes / catalysts are to be developed.

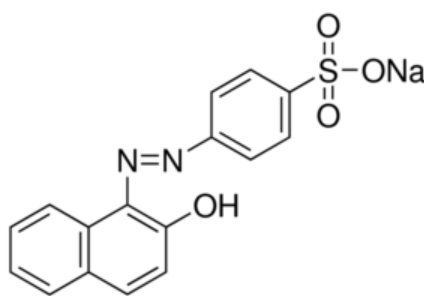


Figure 1.1 - Orange II azo dye structure (García *et al.* 2014).

1.3 Objectives

In order to face the problems mentioned above, in this study, the efficiency of an advanced oxidation process, namely photo assisted wet peroxidation, to remove an azo dye, was investigated.

Given the recent studies, it was decided to utilize gold based catalysts, known by their high stability, particularly negligible metal leaching, and efficiency. Different supports were tested in order to determine the most suitable to the process and to disperse the nano sized Au particles.

The analysis and comprehension of the effects of parameters like pH, temperature, catalyst support and hydrogen peroxide concentration are the main objectives of this study, in order to fully optimize the reaction.

Since one of the main challenges of the heterogeneous catalysis is the stability and leaching of the metal catalyst from the support, an investigation regarding these aspects is crucial.

2 State of Art

2.1 Advanced Oxidation Processes

Usually, oxidative processes use oxygen, ozone, chlorite, sodium hypochlorite, chlorine dioxide, potassium permanganate or hydrogen peroxide as oxidative agents, however, some substances/pollutants are resistant to oxidation. Therefore, the use of Advanced Oxidation Processes (AOPs) is required. The basis of these processes is, generally, the generation of hydroxyl radicals which have a high oxidative potential (2.8 eV vs. NHE - normal hydrogen electrode) and are able to react with almost every type of organic compounds (Haber and Weiss 1934).

Strong oxidants such as ozone (O_3) or hydrogen peroxide (H_2O_2) in presence of metals, semiconductors, such as titanium dioxide (TiO_2) and zinc oxide (ZnO), in presence of ultraviolet radiation (UV), are responsible for the generation of the hydroxyl group. While processes that contain solid catalysts are designated as heterogeneous (due to the existence of more than one phase), others with the catalyst dissolved in the effluent are called homogeneous.

The primary benefits of AOPs are related to the possibility of degrading pollutants in low concentrations, and the easiness in combining with other processes such as biological and activated carbon adsorption, and also the fact that these processes are conducted in some cases at ambient pressure and temperature (Ikehata *et al.* 2006).

Several of these processes operate with hydrogen peroxide, since it is one of the most versatile oxidants, exceeding chloride, chloride dioxide and potassium permanganate. The formation of hydroxyl radicals ($HO\bullet$) is enhanced through the use of catalytic agents, such as iron minerals, ozone and/or ultraviolet light.

The formed radicals attack the organic compounds and may lead to their complete oxidation, producing CO_2 and H_2O . However, in some situations, partial oxidation can be the main route, usually producing more biodegradable by-products (Lange *et al.* 2006).

Figure 2.1 shows the main Advanced Oxidation Processes. Fenton's reaction is one of the most promising advanced methods for effluents degradation and will be further detailed below.

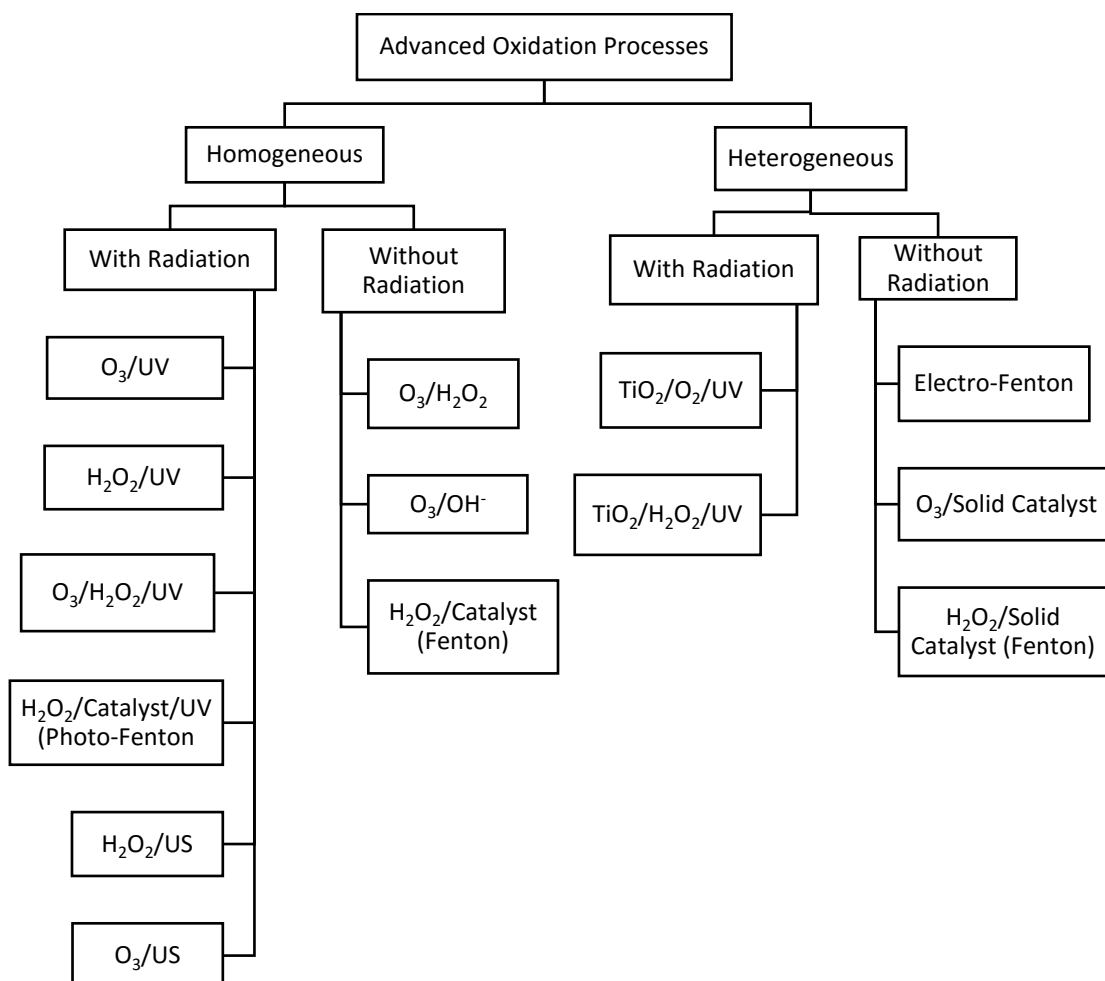


Figure 2.1 - Advanced Oxidation Processes, adapted from Poyatos et al. (2010)

2.2 Fenton's Oxidation / Wet Peroxidation

H.J.H Fenton described the highly oxidative properties of a hydrogen peroxide and Fe^{2+} ion solution for the first time in the end of the 19th century (Fenton 1894). Currently, the Fenton reaction is described as a catalytic generation of hydroxyl radicals by a chain reaction between iron ions and hydrogen peroxide, in an acid environment, producing CO_2 , H_2O and inorganic material as final products (Esplugas *et al.* 2002); if oxidation is not complete, oxidation by-products will be obtained. This type of reaction can also

occur between other metal ions, and in that case, the reaction is usually called Wet Peroxidation (WP).

2.2.1 Homogeneous Process

In the Fenton reaction, a homogeneous reaction occurs in the presence of ferrous ions with hydrogen peroxide, from which $\text{HO}^\bullet$ radicals are formed (Equation 2.1); subsequently, several chain reactions involving the radicals might exist.



The formed hydroxyl radicals can oxidize the Fe^{2+} ion leading to Fe^{3+} through a parallel undesired reaction



The ferrous ions can further dissociate H_2O_2 , as can be seen in the following equations;



As shown in Equation 2.7, hydrogen peroxide also acts as a scavenger of the hydroxyl radical ($\text{OH}^\bullet$), forming hydroperoxyl radical ($\text{HO}_2^\bullet$), which has a smaller oxidation potential than the first, which is detrimental to the reaction. This occurs when there is an excess of hydrogen peroxide (Nogueira *et al.* 2007).

An important advantage in this process is the easiness through which it can be applied to the treatment of effluents, since the reaction occurs at ambient temperature and pressure, involves safe and easy to handle reactants, and does not require any special equipment (Maciel *et al.* 2004).

2.2.2 Heterogeneous Process

The main limitation of this process (Fenton or wet peroxidation) is the narrow pH range (3 to 4) in which the degradation efficiency is maximum. However, this can be solved by adding organic iron complexes that stabilize iron (or the appropriate metal catalyst) in a wider pH interval (Nogueira *et al.* 2007). However, this brings other limitations, namely the fact of requiring adding other species to the medium. Moreover, it is hard to separate and recover the catalyst.

Although the Fenton (or wet peroxidation in general) process shows a proved efficiency, there are some disadvantages, namely the need to remove the metal from solution. Although it is possible to remove it, the procedure implies creating a more complex and expensive process (Maciel *et al.* 2004). In order to overcome this challenge, several studies have been made in order to fix the metal ions onto a solid porous matrix, usually called support. By doing so, the metal is fixed onto the support and is (hopefully) not found in solution but rather present in a solid form (heterogeneous process), being easily recovered in the end of the process.

The principles of the heterogeneous process are very similar to the homogeneous one, however, it becomes considerably complex due to the bonding phenomena between the metal and the solid matrix support. It is widely accepted that hydrogen peroxide is adsorbed on the matrix pores, however that is not completely proved (Feng *et al.* 2006).

The following equation represents the main reaction in the heterogeneous Fenton process, being the same as the homogeneous process, but with the addition of the support (X),



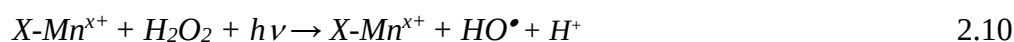
A similar reaction would apply for the wet peroxidation, but of course using another metal rather than iron.

2.3 Photo assisted Wet Peroxidation

The process that combines hydrogen peroxide with ultraviolet radiation is more efficient than each of them separately. That happens due to high hydroxyl radicals production, that are extremely oxidative. According to Huang *et al.* (1993) and Legrini *et al.* (1993), the most commonly accepted mechanism for photolysis of H_2O_2 with UV is the molecule breakdown into hydroxyl radicals with an income of two $HO^\bullet$ for each H_2O_2 molecule (Equation 2.9).



This method differs from the normal wet peroxidation, since it combines the use of UV / visible light, increasing the rate of the process, since the following mechanism for the formation of free radicals also takes place: - decomposition of hydrogen peroxide by incidence of radiation (Equation 2.9); - Regeneration of the metal (catalyst) (Equation 2.10); - Photolysis of the metal hydroxide (Equation 2.11 - photolysis of the compounds formed between metal and organic compounds (Equation 2.12).



where X = support; Mn^{x+} = metal ion.

2.4 Influence of Reaction Parameters

The wet peroxidation process is influenced by many variables, such as pH, hydrogen peroxide concentration, catalyst concentration and temperature, and also be radiation intensity and source, the latter in the case of the photo assisted wet peroxidation. The effect of such operating conditions will be described in the following sections.

2.4.1 Effect of pH

The compound with greater ability to generate hydroxyl radicals by absorbing UV/visible radiation is the $Mn(OH)^{x+}$ ion, which is predominant under acidic conditions (pH 2-3). Contrarily, the photolysis of hydrogen peroxide has a low absorptivity ($19.6 M^{-1} cm^{-1}$ at 254 nm), which makes this pathway an unimportant way to form radicals.

In very acidic pH values, the complex $Mn(OH)^{x+}$ is present in a reduced amount, which represents small formation of radicals and limited catalyst regeneration. Furthermore, the pH <2.5 value allows the scavenging reaction between the hydroxyl radical and H^+ to take place (Equation 2.13) (Spinks and Woods 1990).



On the other hand, at neutral to basic conditions hydrogen peroxide self-decomposition into water and oxygen is promoted, decreasing the amount of available hydroxyl radicals to promote organics degradation. Several researchers referred an optimum pH range between 2-3 for the heterogeneous wet peroxidation process (Parida and Pradhan 2010, Zhao *et al.* 2010, Soon and Hameed 2013, Li *et al.* 2015).

2.4.2 Effect of H_2O_2 Concentration

The initial concentration of H_2O_2 plays a very important role in the oxidation of organic compounds in WP processes and in the operatory costs of such treatment processes, thus it is necessary to determine the optimum dose of reagent.

The improvement of the process by the addition of H_2O_2 is mostly due to the increased production of hydroxyl radicals by these processes described in Equations 2.8, 2.9 and 2.10. However, some other reactions benefit wet peroxidation (Equation 2.14 and Equation 2.15)(Selvam *et al.* 2005):



However, at high concentrations, the reaction between excess H_2O_2 and the strong oxidant $^\bullet OH$ species becomes more relevant and, as a consequence, no subsequent improvement on the heterogeneous WP rate can be noticed, because the produced $HO_2^\bullet$ radicals are less reactive than the $HO^\bullet$ radicals (Equations 2.7) (Galindo *et al.* 2001).

Contrarily, if the concentration is low, the oxidation degree is small and there is possible formation of unwanted intermediate complexes. Inherently, it is common to observe the existence of an optimum oxidant (hydrogen peroxide) dose in either wet peroxidation or radiation-assisted wet peroxidation processes.

2.4.3 Effect of Catalyst Concentration

Since Mn^{x+} ions can act as coagulants, the wet peroxidation reagent can have both functions: oxidization and coagulation in the treatment processes, being the latest only possible on homogeneous systems. The efficiency of the process increases with the catalyst concentration up to a point where the excess of metal ion reacts with the hydroxyl radical occurs (Equation 2.16).

The ideal concentration of catalyst depends on the type of effluent to be treated, however ratios from 1:10 to 1:50 for the Mn^{x+} :substrate ratio (w:w) are usually used (Morais 2005).



2.4.4 Effect of Temperature

The possibility of increasing the operating temperature, as a way of improving the efficiency of the process, has been scarcely investigated, because the idea of thermal decomposition of H_2O_2 into O_2 and H_2O seems to be widely accepted as a serious drawback (Gogate and Pandit 2004). However, according to the Arrhenius law, increased temperatures (often up to ca. 50 °C) can lead to a more efficient use of H_2O_2 upon enhanced generation of $\text{HO}\cdot$ radicals at low Mn^{x+} concentrations. A decrease of the metal dose is important since it improves the efficiency of H_2O_2 use by minimizing competitive scavenging reactions (Zazo *et al.* 2011). Therefore, increasing the temperature can be considered as a way to intensify the conventional WP process.

2.4.5 Effect of Radiation

The use of radiation, increases the rate of WP since there are additional mechanisms for the formation of free radicals, as explained previously (Equations 2.9 to 2.12).

2.5 Use of Gold-based Catalysts on Photo Assisted Wet Peroxidation

The photochemistry of gold nanoparticles, either in colloidal solutions or supported on a solid, has been a topic of much attention (Subramanian *et al.* 2001). Now there is a renewed interest on the photochemistry of supported gold nanoparticles in systems and supports with low gold loading that are relevant to heterogeneous gold catalysis.

Currently, there are several Fenton processes with different iron-based catalysts that proved to be very effective in waste water treatment, with high degradation rates of the organics and interesting mineralization performances. However, leaching is a drawback of these procedures. The solution to this problem might be the use of noble metals (which do not leach) in the catalytic degradation of organic components (Bistan *et al.* 2012).

Recently, the addition of UV/visible light to the process of wet peroxidation with gold catalysts was studied (Navalon, de Miguel et al. 2011; Navalon, Martin et al. 2011; Ge, Chen et al. 2014), and no leaching was observed. In such reports, it was also shown that the addition of radiation greatly improved the efficiency of the process, which mechanism is summarized in Figure 2.2.

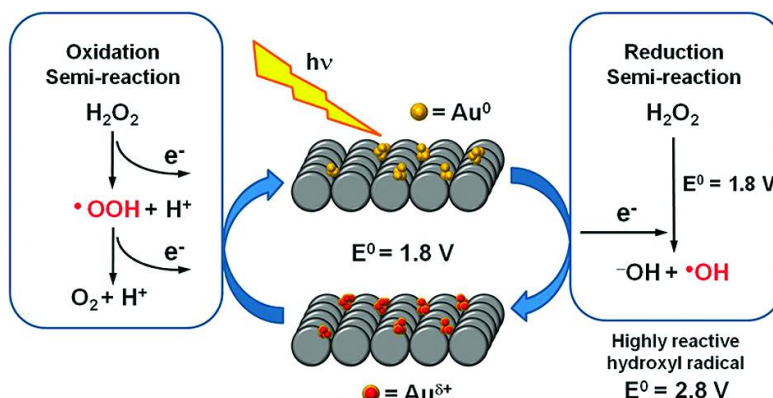


Figure 2.2 - Proposed scheme for the photochemical improvement in the Fenton-like catalysis Catalysis (Navalon et al. 2011).

Table 2.2 - Studies found regarding the photo assisted wet peroxidation using gold based catalysts

Pollutant	Operation Conditions	Efficiency	Catalyst-Support	Reference
Phenol	pH=4 t=3 h Catalyst= 160mg/L [H ₂ O ₂]=200mg/L [Phenol]=100mg/L radiation: Laser Flash (70mJ/Pulse)	~100%	Au-Diamond (1%)	(Navalon <i>et al.</i> 2011)
Phenol	pH=4 T=30°C Catalyst= 1g/L [H ₂ O ₂]=100mg/L Phenol=100mg/L radiation: Sunlight	~100%	Au-Diamond	(Navalon <i>et al.</i> 2011)
Orange 7 dye (O7)	pH=3 t=6 h T=30°C Catalyst=0.5g/L [H ₂ O ₂]=20mM [O7]=35mg/L radiation: 1000 W Tungsten Halogen Lamp	~100%	Au-CeO ₂	(Ge <i>et al.</i> 2014)

According to Navalon et al. (2011), the absorption of radiation causes the ejection of photo electrons, which in turn decompose hydrogen peroxide into free radicals. In a next step, H_2O_2 is also able to oxidize the gold to its initial state, thus forming a catalytic cycle. These radicals with high oxidative potential are the main intermediaries in the WP process, oxidizing the organic compounds according to a chain of reactions (Pignatello et al. 2006).

An overview about the existing studies regarding the use of Au based catalysts in photo assisted wet peroxidation are reviewed in Table 2.1.

Navalon *et al.* (2011) showed that the catalytic activity of a gold catalyst supported on diamond nanoparticles in wet peroxidation is promoted by irradiation of gold, either with monochromatic light or even with solar light. On the basis of the detection of photo-induced electron ejection, the experimentally observed catalytic enhancement can be attributed to the transfer of electrons from gold to hydrogen peroxide promoted by light. Taking advantage of this photo-assisted catalytic enhancement, wet peroxidation reaction in presence of radiation was made at moderate basic pH, conditions in which the dark catalytic process does not take place (Fig. 2.3).

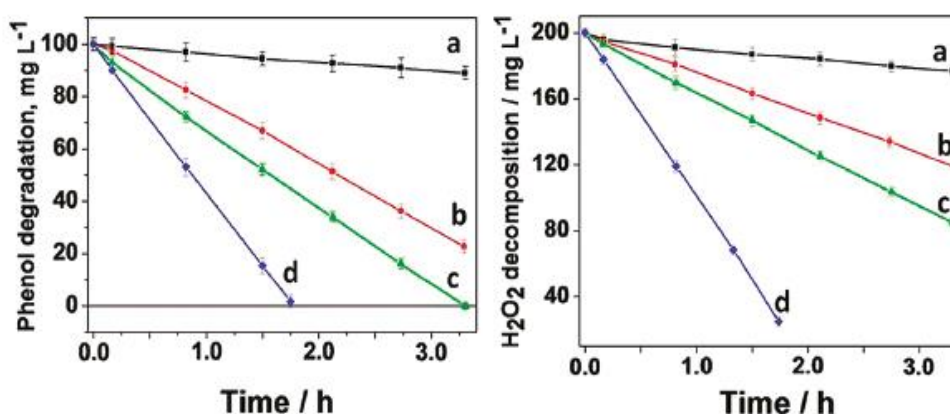


Figure 2.3 - Influence of the laser intensity on the catalytic activity of Au/HO-npD for the Fenton reaction of phenol degradation (left) and H_2O_2 decomposition (right). Reaction conditions for phenol degradation using increasing laser powers. (a) 0 mJ pulse⁻¹, (b) 20 mJ pulse⁻¹, (c) 38 mJ pulse⁻¹, and (d) 70 mJ pulse⁻¹. Reaction conditions: 100 mg L⁻¹ (1.06 mM) of phenol and 200 mg L⁻¹ (5.88 mM) of H_2O_2 and Au/HO-npD 1.0% 160 mg L⁻¹ (0.0056 mM) at pH = 4. (Navalon, de Miguel et al. 2011).

The same authors also evaluated the catalytic activity of a gold catalyst supported on diamond nanoparticles, assisted by sunlight (Navalon *et al.* 2011). As seen in Fig. 2.4, the reactions assisted by sunlight achieved total phenol degradation, however, the reactions in the dark only attained an insignificantly degradation. Regarding the H_2O_2 decomposition, the sunlight assisted processes were also more effective.

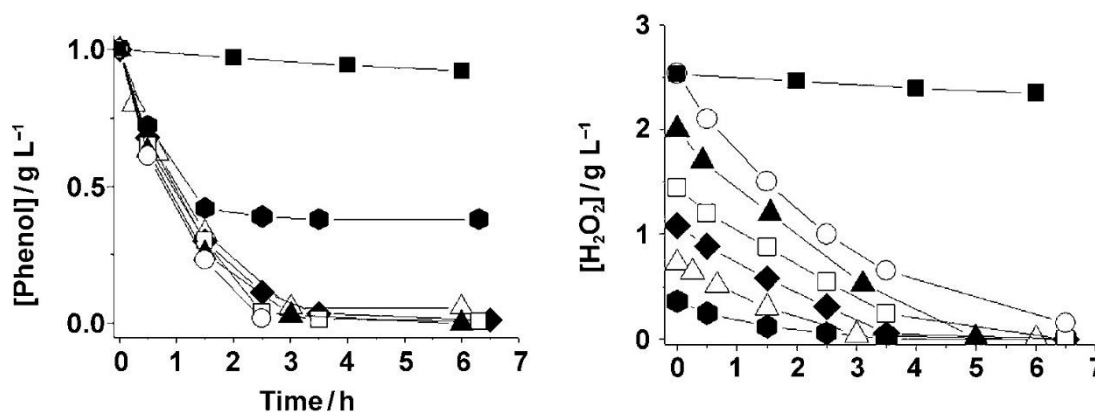


Figure 2.4 – Effect of irradiation and H_2O_2 /phenol molar ratio on phenol decomposition and H_2O_2 decomposition; H_2O_2 /phenol molar ratio: ●1.0; △2.0; ◆3.0; □4.0; ▲5.5 ; ○7.0; ■7.0 (dark). Reaction conditions: 1 g L⁻¹ phenol (10.64 mM), pH 4, 400 mg L⁻¹ catalyst (0.02 mM of gold) (Navalon, Martin *et al.* 2011).

The degradation of AO7 was employed by Ge *et al.* (2014) to evaluate the catalytic oxidation performance of the Au-CeO₂/H₂O₂ system. Fig. 2.5 shows the photo degradation of AO7 in pre-adsorbed mode (the catalyst powder was added into a quartz tube containing AO7 aqueous solution) under dark (A) and under visible irradiation (B), and in the pre-mixed mode (catalyst powder was mixed with H₂O₂ and mixed) under dark (C) and under visible irradiation (D).

The degradation rate of AO7 significantly increased with visible irradiation. In the pre-adsorbed mode, the degradation of the dye occurred in dark and under irradiation, however, it was much faster under irradiation. In the pre-mixed mode, with no radiation, the dye was not completely removed, though, the photo assisted process completely removed the dye. It was also possible to analyse that an Au concentration of 1.0% showed the best results.

Regarding the stability of the catalysts, in the study above mentioned, Navalon *et al.* (2011) stated that a gold based catalyst supported on diamond nanoparticles is in fact remarkably stable and that it can be reused four times without a decrease of the initial reaction activity (cf. Figure 2.6). It is also assumed that no leaching occurred, and this is the great advantage of such type of materials, as described above.

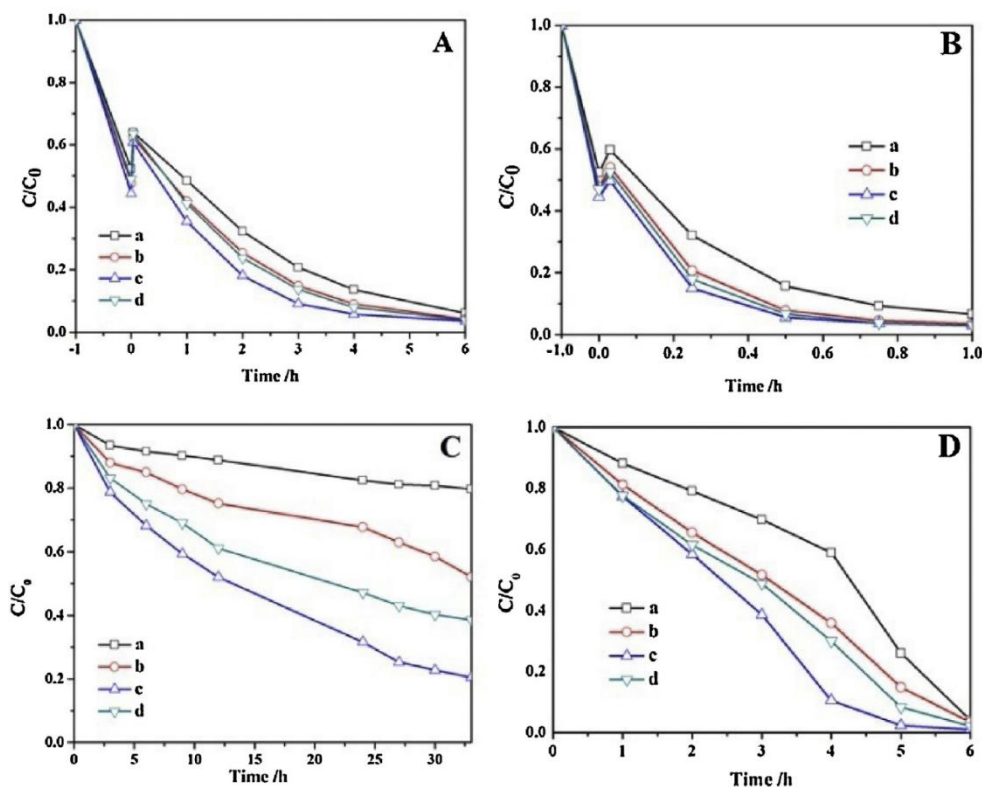


Figure 2.5 - Fenton-like degradation of AO7 aqueous solution with (a) bare CeO_2 , (b) 0.5 at.% Au- CeO_2 , (c) 1.0 at.% Au- CeO_2 , and (d) 2.0 at.% Au- CeO_2 in the pre-adsorbed mode (A) in dark and (B) under the visible irradiation, and in the pre-mixed mode (C) in dark and (D) under the visible irradiation. $[\text{CeO}_2] = 0.5 \text{ g/L}$, $[\text{H}_2\text{O}_2] = 20 \text{ mM}$, $[\text{AO7}] = 35 \text{ mg/L}$. (Ge *et al.* 2014)

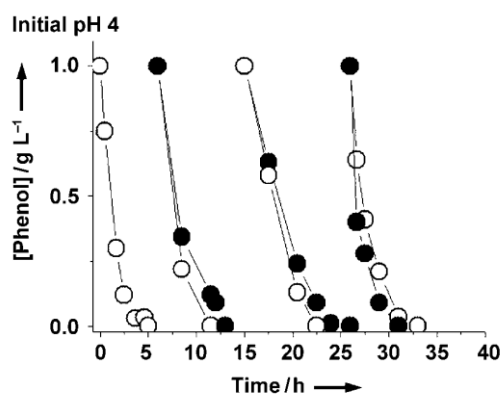


Figure 2.6 - Four consecutive cycles of phenol decomposition catalyzed by Au/DNPs. Open/closed symbols refer to fresh or reused catalyst, respectively. Reaction conditions: 1 g L⁻¹ phenol (10.64 mm), 2 g L⁻¹ (58.8 mm), pH as indicated, 400 mg L⁻¹ catalyst (0.02 mm of gold). (Navalon et al. 2011)

In the present work, different supports will be employed for depositing gold and their effect on the radiation-assisted wet peroxidation of a model compound (orange II azo dye) will be assessed. Up to the author's knowledge, no similar studies have been previously reported in the open scientific literature, putting into evidence the novelty of the current work.

3. Materials and Methods

3.1. Dye and dyeing effluent

The azo dye Orange II from Fluka was used in this study. Its chemical formula is $C_{16}H_{11}N_2NaO_4S$, molecular weight 350.33 g/mol and maximum absorbance at 486 nm.

A simulated industrial acrylic dyeing effluent was prepared, according to the procedure described in a previous publication (Rodrigues *et al.* 2013). Basically, it was taken into account the amount of Astrazon Blue FGGL 300% dye and auxiliaries used in the dyeing bath, the percentage of these products unfixed by the fibers (rejection percentage) and volume of clean water (Annex A).

3.2. Catalyst Preparation and Characterization

The following commercial supports were used: aluminium oxide (Al_2O_3) from Aldrich (< 50 nm), iron oxide (Fe_2O_3) from Sigma Aldrich (powder), titanium dioxide (TiO_2) from Evonik Degussa (P25) and zinc oxide (ZnO) from Evonik Degussa (AdNano VP 20). Gold was deposited on the supports by a deposition/precipitation method (Soria *et al.* 2014). It consisted in a solution (5×10^{-3} M) of $HAuCl_4$ (Sigma Aldrich, ACS reagent, $\geq 49.0\%$ Au basis, purity > 99.7%) being raised to pH 9 by addition of 1 M solution of NaOH (Sigma Aldrich, anhydrous, ACS reagent, $\geq 97\%$). Then the gold precursor solution was added to the support (1 g of support per 50 mL of Au solution), with continuous stirring at room temperature. The suspension was heated to 70 °C and vigorously stirred for 1 h. The catalyst obtained, after a 12 h cooldown, was filtered, washed with deionised water and then vacuum-dried at room temperature.

All catalysts were analysed by adsorption of N_2 at -196 °C, in a Quantachrom NOVA 4200e apparatus. Before analysis, all samples were previously degassed at 160 °C for 5 h. The specific surface area (S_{BET}) was calculated by the Brunauer–Emmett–Teller (BET) equation (Brunauer *et al.* 1938).

In order to determine the Au oxidation states, X-ray photoelectron spectroscopy (XPS) analyses were performed on a VG Scientific ESCALAB 200A spectrometer using Al

K α radiation (1486.6 eV). The charge effect was corrected taking the C1s peak as a reference (binding energy of 285 eV). CASAXPS software was used for data analysis.

The Au dispersion on catalyst samples was examined using high resolution transmission electron microscopy (HR-TEM) and was carried out with a Phillips CM-20 equipment. For the analysis, the powders were dispersed in ethanol and homogenized in an ultrasonic bath before use. A sample of catalysts particles was collected from the dispersion, and allowed to dry at ambient conditions before analysis. Nanoparticle sizes were measured from HR-TEM images, using the ImageJ program.

3.3. Analytical Methods

3.3.1. Total Organic Carbon (TOC)

The total organic carbon (TOC) was measured according the method 5310 D (APHA 1998), and for that catalytic oxidation was carried out at 680 °C in a Shimadzu TOC analyzer (model TOC-L), followed by quantification of the CO₂ formed by infra-red spectrometry. TOC was calculated as the difference between the total carbon (TC) and the inorganic carbon (IC) in the liquid samples, previously filtered with nylon filter membranes (0.45 µm of pore diameter).

3.3.2. Hydrogen Peroxide

The residual hydrogen peroxide was measured as described by Sellers (1980). The method is based on the measurement of the intensity of the yellow-orange colour resulting from the reaction of hydrogen peroxide with titanium oxalate. The samples were previously filtered through nylon filter membranes with pore diameter of 0.45µm.

3.3.3. Hydroxyl Radicals

To assess the presence of hydroxyl radicals in solution, 1,5-diphenyl carbazide (Sigma Aldrich) was oxidized into 1,5-diphenyl carbazone in the presence of hydrogen peroxide and each catalyst/support. The 1,5-diphenyl carbazone formed can be extracted by the mixed solution of benzene and carbon tetrachloride (50:50 % v/v) and identified measuring the absorbance at 563 nm (Wang *et al.* 2011).

3.3.4. Gold Concentration

Through atomic absorption spectrometry (AAS) - Method 3111 B (APHA 1998), the gold leaching from the catalyst samples along reaction experiments was measured, using an AAS UNICAM spectrophotometer (model 939/959), after filtrating the samples in nitrate cellulose membranes with 0.45 μm of porosity. The gold loading in solid catalyst was measured according with the above method of gold leaching, the samples being first digested with a mixture of concentrated nitric (65%, LabChem) and chloride (37%, Sigma Aldrich) acids at 140 °C during 2 h.

3.3.5. Toxicity

To assess the toxicity of the raw and treated dye solution and simulated effluent, the inhibition of *Vibrio fischeri* was measured, using a Microtox Modern Water model 500 analyzer. This was achieved according to the standard DIN/EN/ISO 11348-3 (Standardization 2005), by putting the bacteria in contact with samples at 15 °C and measuring the bioluminescence after a time of contact time of 5, 15 and 30 min.

3.3.6. Biodegradability

For the biodegradability assessment of the raw and treated dye-containing solution and simulated effluent, the samples were firstly inoculated with biomass from the activated sludge tank of Rabada a waste water treatment plant (WWTP) treating a mix of domestic and textile effluents; then the dissolved oxygen concentration was measured for 30 min (using a YSI Model 5300 B biological oxygen monitor) at 20 °C. The specific oxygen uptake rate (k') was calculated as the ratio between the oxygen concentration decay rate (which was linear in the above-mentioned period) and the volatile suspended solids (VSS) concentration after the addition of the inoculum (715 mg VSS/L) (Ramalho 1997, APHA 1998).

3.3.7. pH

The pH was measured using a selective electrode (WTW Sentix 81) and a pH meter (WTW Inolab pH 730).

3.3.8. Chemical Oxygen Demand (COD)

The determination of the chemical oxygen Demand (COD) was performed according to the method 5220 D (APHA 1998), which quantifies the $K_2Cr_2O_7$ reduction by oxidizable organic and inorganic compounds in a closed reflux digester (Thermoreactor TR 300), at 150 °C for 2 hours. Then the absorbance was measured in a Spectroquant Nova 60 spectrophotometer corresponding to the reduced chromium.

3.3.9. Biological Oxygen Demand (BOD₅)

The biochemical oxygen demand (BOD₅) quantifies the biodegradable organic matter. It was determined according to the procedure described in Method 5210 B (APHA 1998) This method is based on the difference between the initial and final dissolved oxygen concentration (assessed with BOD sensor System 6 from Velp Scientifica) after 5 days incubation at 20 °C, using a Velp Scientifica model FOC 225 E Refrigerator Incubator. The quantification of BOD₅ of wastewaters usually requires a previous dilution of samples.

3.3.10. Color / Dye Concentration

The color of the samples was quantified by measuring the absorbance at the wavelengths of maximum absorbance (485 and 610 nm for dye solution and synthetic acrylic effluent, respectively), using a molecular absorption spectrophotometer (Thermo Electron Corporation, model Helios γ). For the dye-containing solutions, and because its oxidation by-products do not absorb in the visible region (Ramirez *et al.* 2007), a calibration curve allowed to correlated measured absorbances with orange II concentration. As the absorbance of the wastewaters varies with pH, this parameter was adjusted to the initial value (pH 3.0) in the treated synthetic effluent, whenever necessary, before measuring the absorbance.

In order to evaluate de compliance with the discharge limit as defined in Ordinance No. 423/97 of 25 June, the samples were diluted 40 times and the presence or absence of color was visually checked.

All parameters were measured in duplicate. The results obtained are the average and have the associated error bars (Annex B).

3.4 Experimental Procedures

The runs were carried out in a batch reactor equipped with a UV/visible high pressure mercury vapor lamp (Heraeus TQ 150 with 150 W, corresponding to an intensity of 500 W/m², which emits UV/visible radiation at wavelengths from 200 to ~600 nm - more information in Annex C), axially located inside a dip immersion quartz tube (see Figure 3.1), where 200 mL of dye solution (0.1 mM) or dyeing wastewater were added. This concentration of dye (corresponding to 35 mg/L) was chosen as this value is in the range of 10 to 50 mg/L, often found in real effluents (Herney-Ramirez *et al.* 2008). The reactor had a recirculating water jacket in a quartz tube, linked to a thermostatic bath (Hubber, polystat cc1), which maintained the temperature constant at ± 1.0 °C. After the solution reached the desired temperature, the pH was adjusted to the desired value (with 1 M sulfuric acid, from Labchem); then the support or catalyst was added, this being the time considered as zero for the adsorption experiments. In WPO runs, the initial instant ($t = 0$) coincided with the insertion of the desired hydrogen peroxide (30%, LabChem) dose, immediately after the catalyst or support. In the runs with radiation, the initial time corresponded to the addition of the oxidant and simultaneous turn on the mercury lamp. During the experiments, stirring (200 rpm) was ensured by a magnetic stir bar and a stir plate (VWR, model VS-C7). The absorbance at 486 nm for the Orange II dye (and 610 nm for the acrylic effluent) was analyzed after the times of 5, 10, 15, 30, 45, 60, 90 and 120 minutes, in order to assess the removal histories of the dye (or effluent color).

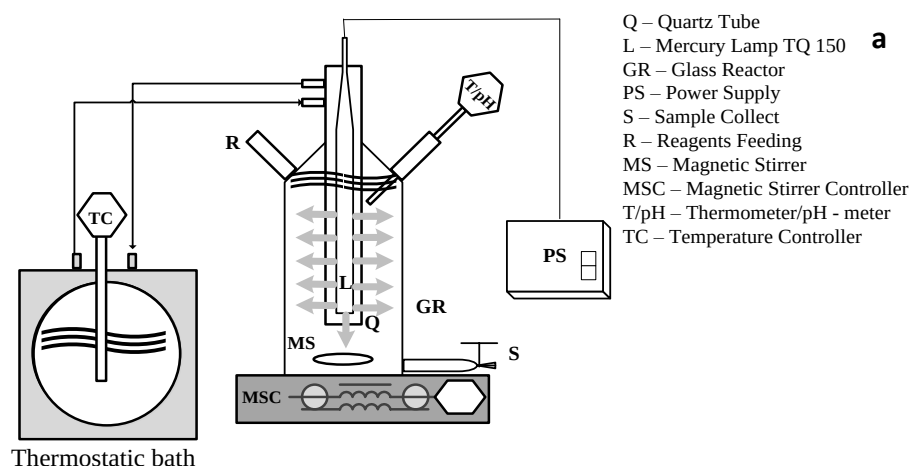


Figure 3.1 - Diagram (a) and photo (b) of the radiation assisted wet peroxidation set-up.

At the end of the reaction runs, the residual hydrogen peroxide, gold leaching and total organic carbon (TOC), after stopping the reaction with excess sodium sulphite that consumes residual H_2O_2 , were determined, using the methods described in the previous section. TOC was also measured for samples taken along reaction time. In the run with the simulated acrylic effluent, chemical oxygen demand (COD), biological oxygen demand after 5 days (BOD_5), toxicity and biodegradability of the treated solution were also assessed after 4 h of oxidation, after stopping the reaction by increasing the pH to 11 with subsequent neutralization with NaOH 10 M and H_2SO_4 1 M, respectively.

In the photo-assisted wet peroxidation tests the radiation that reached the wastewater was varied by circulating, in the jacket of the quartz tube, a solution of dye

Solophenyl Green BLE 155% with different concentrations, as described by Silva and Faria (2009). These concentrations have been previously determined by potassium ferrioxalate actinometry (Kuhn *et al.* 2004). Figure 3.2 shows the variation of the radiation intensity (measured with an UV radiometer Kipp & Zonen B.V., model CUV 5, and a visible radiometer - Delta OHM, model D9221 - placed outside and at mid-height of the dip immersion quartz tube) that reaches the solution to be treated as a function of the dye concentration in the solution circulating in the jacket.

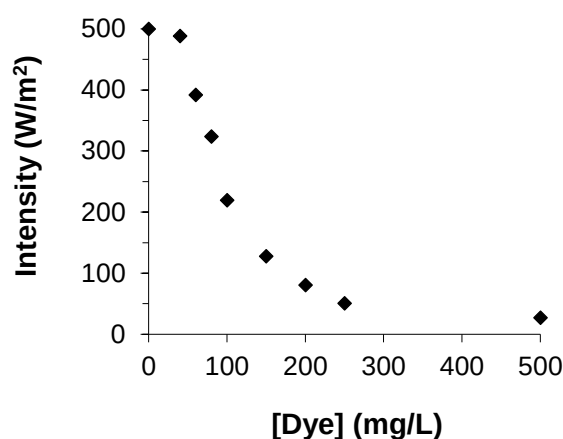


Figure 3.2 - Variation of the radiation intensity as a function of the dye concentration.

4. Results and Discussion

4.1. Materials Characterization

As mentioned before, in this thesis several gold-based materials have been used as catalysts in the photo-assisted wet peroxidation of a model azo dye, which mostly differ in the nature of the gold support used. In this section are included the results obtained from the characterization of the materials.

Concerning the supports, in Table 4.1 it is shown that Al_2O_3 has the highest surface area (211 g/m^2), Fe_2O_3 has the lowest (6 g/m^2), whereas TiO_2 and ZnO have intermediate values, 51 and 26 g/m^2 , respectively. Upon gold addition, the BET surface area of the oxides does not change significantly, most likely due to the low loading and low particle size of gold.

Regarding the average gold particle size, obtained from the histograms of particle size distribution through HR-TEM (HR-TEM images on Annex D), Au on ZnO provides the highest average (5.5 nm), the commercial catalyst provided by the World Gold Council (WGC) had an average of 3.6, as well as the $\text{Au-Al}_2\text{O}_3$, while TiO_2 and Fe_2O_3 are considered as “active supports” (Schubert *et al.* 2001), and have similar sizes of 2.2 and 2.3 nm, respectively. Concerning the gold loading, $\text{Au-Al}_2\text{O}_3$ and $\text{Au-Fe}_2\text{O}_3$ catalysts have the lowest (0.7 and 0.8% wt., respectively), while $\text{Au/Fe}_2\text{O}_3$ from WGC shows the largest (4.6% wt.), as expected, while Au-ZnO and Au-TiO_2 have intermediate values (1.2 and 1.6% wt., respectively).

By Au 4f XPS measurements it was possible to obtain information about the gold oxidation state. In Table 4.1 it is shown that gold is in the Au^+ state on $\text{Au-Fe}_2\text{O}_3$ and Au-TiO_2 catalysts, while for Au-ZnO and $\text{Au-Al}_2\text{O}_3$ the gold is in the Au^0 state (XPS spectra of the catalysts are showed in Annex D).

Table 4.1 - Characterisation of the gold supported materials: BET surface areas, gold loading, average gold nanoparticle sizes, gold oxidation state and gold dispersion.

Materials	BET Surface Area (m ² /g)	Au Loading (wt. %) ^a	Au Average Size (nm) ^b	Gold oxidation state ^c	DM (%)
Au-Fe₂O₃ (WGC)	41	4.0	3.6	Au ⁰	32.1
Au-Fe₂O₃	5	0.8	2.3	Au ⁺	50.3
Fe₂O₃	6	-	-	-	-
Au-ZnO	25	1.2	5.5	Au ⁰	25.7
ZnO	26	-	-	-	-
Au-TiO₂	49	1.6	2.2	Au ⁺	52.6
TiO₂	51	-	-	-	-
Au-Al₂O₃	210	0.7	3.6	Au ⁰	32.1
Al₂O₃	211	-	-	-	-

^a -determined by AAS; ^b - determined by TEM; ^c - determined by XPS Au4f (and XPS Au 4d for Au/ZnO).

The dispersion (was calculated according to equation 4.1) is higher for catalysts with smaller Au size (Au-Fe₂O₃ and Au-TiO₂), the Au-Al₂O₃ and Au-Fe₂O₃ WGC have the same DM value because theses catalysts present the same Au size and the catalysts with high Au size (Au-ZnO) has smaller DM.

$$DM (\%) = \frac{6 * n_s * MM * 1000}{\rho * N * dp} * 100 \quad 4.1$$

where, n_s is the number of atoms at the surface per unit area ($1.15 \times 10^{19} \text{ m}^{-2}$ for Au), MM is the molar mass of gold (196.97 g/mol), ρ is the density of gold (19.5 g/cm^3), N is Avogadro's number ($6.023 \times 10^{23} \text{ mol}^{-1}$), and dp is the average particle size (nm).

4.2. Orange II dye removal

4.2.1. Adsorption vs. Reaction without Radiation

To check the effect of the oxidant per se and to assess the contribution of the adsorption phenomenon, which might co-exist with the catalytic one, some control experiments, without radiation, were performed. Thus, for each catalyst, five runs were made where: i) only hydrogen peroxide was used, ii) and iii) the adsorption on the support and on the Au catalyst were analyzed, respectively; iv) and v) hydrogen peroxide was added to the support or Au catalyst, respectively. These same runs performed with

radiation are discussed later on. Regarding the use of hydrogen peroxide alone, very low dye and total organic carbon (TOC) removals can be seen after 2 hours of reaction in the dark (Figures 4.1 and 4.2, respectively). Such small efficiency is due to its low oxidation potential.

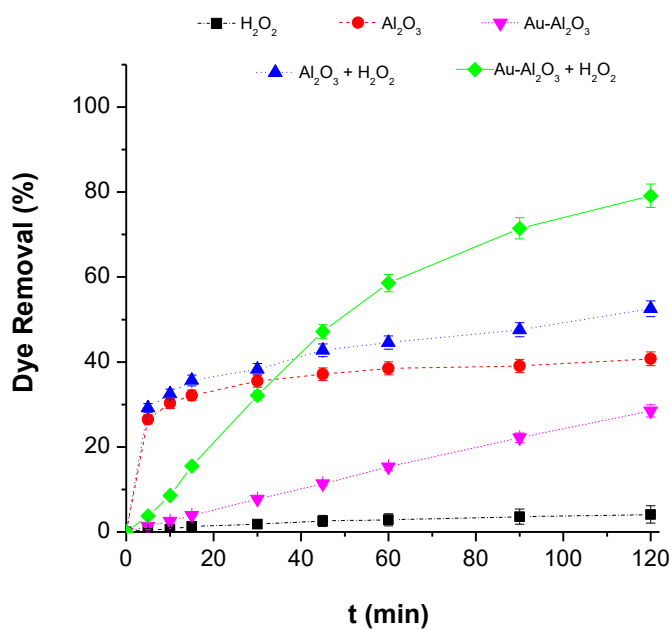


Figure 4.1 - Dye removal as a function of time for Al₂O₃ and 0.8% Au-Al₂O₃ (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM, when used).

Some dye removal, and consequently TOC elimination, occurs by adsorption, which is more relevant for the Al₂O₃ support than for the gold catalyst (Figures 4.1 and 4.2); similar results have been obtained when TiO₂ and ZnO are used (Figures 4.5 and 4.6, respectively). Taking into account the similar BET surface areas of both the supports and the Au catalysts (Table 4.1), the different adsorptive performance of these materials should be related to a larger difficulty of dye diffusion in the gold catalyst than in the support.

For all supports, in the presence of the oxidant, dye removal is apparently due to both adsorption over the support and oxidation by the peroxide itself. For example, by analyzing the kinetic curve of the Al₂O₃ support, plus the oxidant, along the 2 h (Figure 4.1) (the kinetic curves of the remaining supports are shown in Annex E), it is possible to

assume that this curve is the sum of the curves related with the support adsorption and the hydrogen peroxide per se. This is reinforced by the fact that in the presence of the Al_2O_3 support and H_2O_2 , no hydroxyl radicals were detected and no hydrogen peroxide was consumed in a blank run without dye (Figure 4.2b).

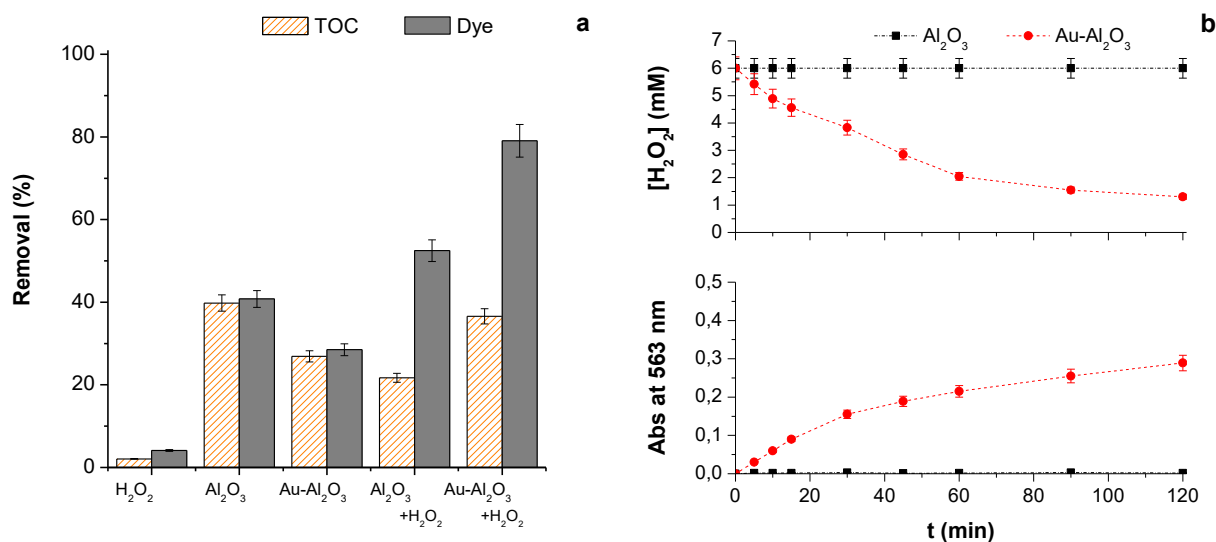


Figure 4.2 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for Al_2O_3 and $\text{Au-Al}_2\text{O}_3$ (pH=3.0, T= 30 °C, $[\text{H}_2\text{O}_2]$ = 6 mM, [Support or catalyst] = 2.0 g/L and $[\text{OII}]$ = 0.1 mM in a) and $[\text{OII}]$ = 0 in b)).

In the presence of gold and the oxidant, the efficiency of the process is considerably improved (cf. Figures 4.1 and 4.2 for the $\text{Au-Al}_2\text{O}_3$ system, although the same applies for all other systems – see Figures 4.3 to 4.6). The formation of hydroxyl radicals, through decomposition of hydrogen peroxide, in the presence of gold ($\text{X-Au}^0 + \text{H}_2\text{O}_2 \rightarrow \text{X-Au}^+ + \text{OH}^- + \text{HO}^\bullet$ (Quintanilla *et al.* 2012, Domínguez *et al.* 2014)), is responsible for the increase in removal. The formation of hydroxyl radicals can be seen by the results of the blank runs shown in Figure 4.2b for the case of the $\text{Au-Al}_2\text{O}_3$ system.

For the $\text{Au/Fe}_2\text{O}_3$ system, the WGC material with 4% Au led to a reduction in dye and TOC removals ($28.3 \pm 5.3\%$ and $24.5 \pm 5.6\%$, respectively) (Figure 4.3a) comparable to the 0.8% Au material ($34.0 \pm 5.1\%$ and $25.9 \pm 5.7\%$) (Figure 4.4a). The decay with the 4% Au catalyst is most likely due to scavenging radical reactions occurring due to the excess of gold ($\text{HO}^\bullet + \text{X-Au}^0 \rightarrow \text{X-Au}^+ + \text{HO}^-$), which is confirmed with less formation of radicals in the blanks with 4% Au than with 0.8% (Figures 4.3b and 4.4b).

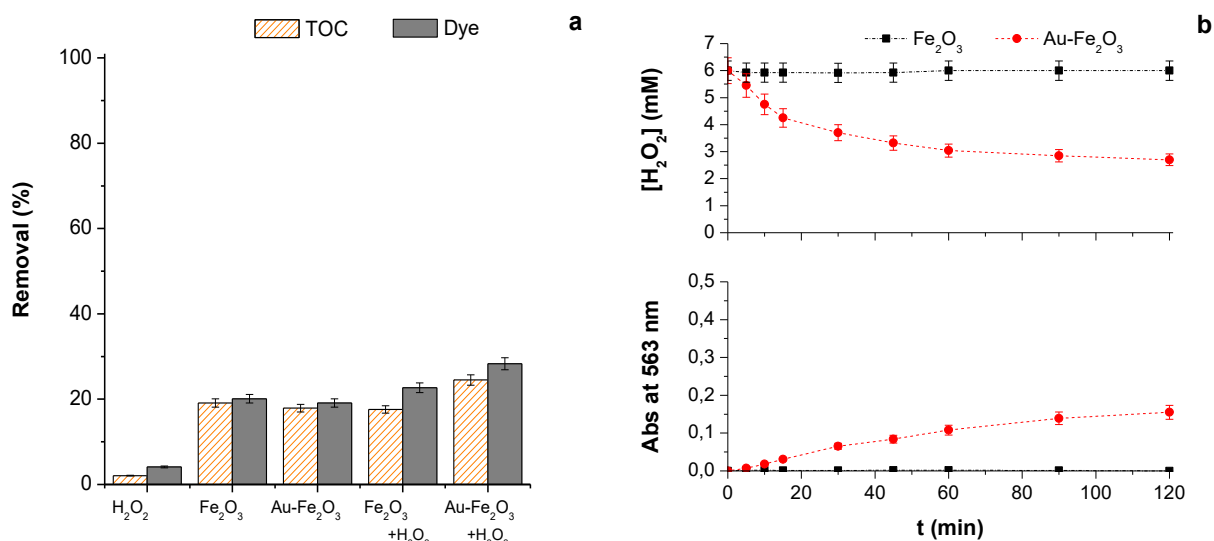


Figure 4.3 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for Fe₂O₃ and 4% Au-Fe₂O₃ (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM in a) and [OII] = 0 in b)).

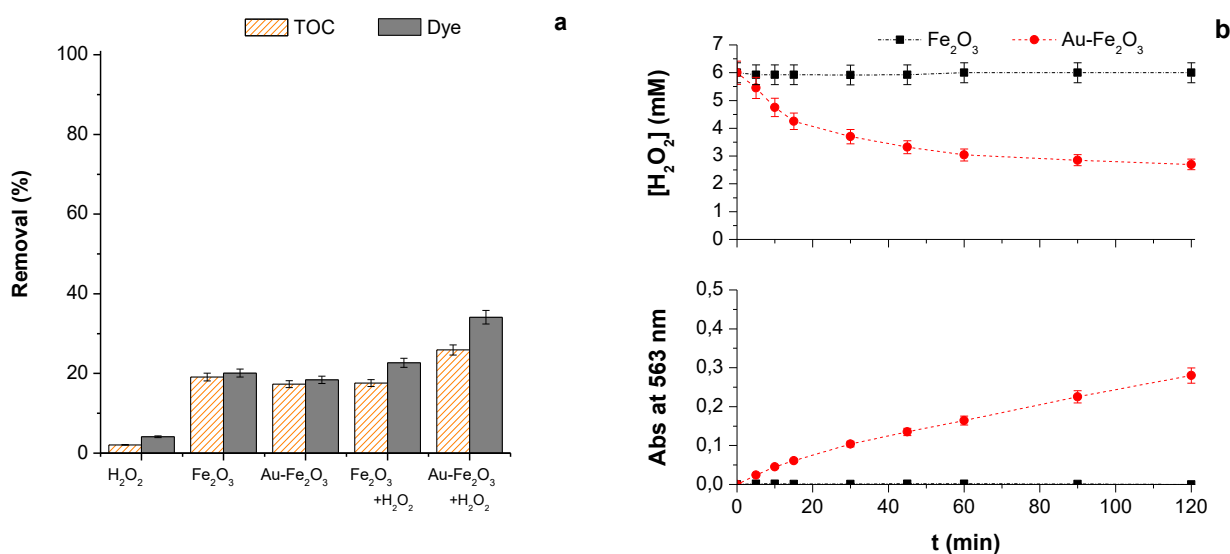


Figure 4.4 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for Fe₂O₃ and 0.8% Au-Fe₂O₃ (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM in a) and [OII] = 0 in b)).

Concerning the Au-TiO₂ and Au-ZnO catalysts, their efficiency was similar (40.5%5.4% and 19.9%5.8% for color and TOC, respectively, for Au-TiO₂ – Figure 4.5a - and 44.4%5.2% for color and 26.0%5.8% for TOC for Au-ZnO - Figure 4.6a). The amount

of hydroxyl radicals formed and hydrogen consumption in blank runs was also very similar (Figures 4.5b and 4.6b, for TiO_2 and ZnO , respectively).

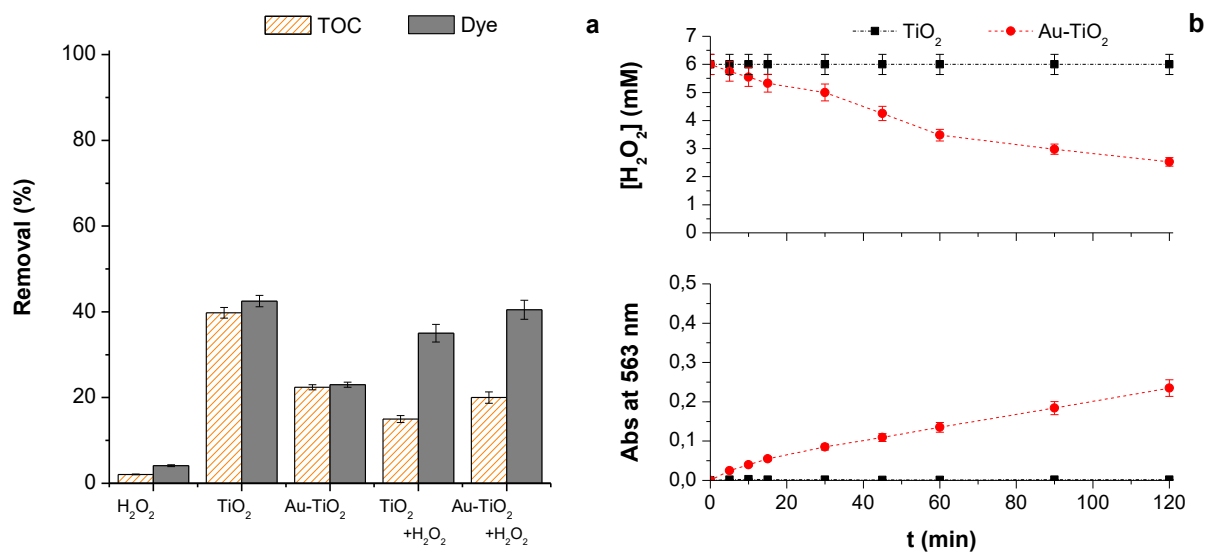


Figure 4.5 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for TiO_2 and Au-TiO_2 ($\text{pH}=3.0$, $T=30\text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2]=6\text{ mM}$, [Support or catalyst] = 2.0 g/L and $[\text{OII}]=0.1\text{ mM}$ in a) and $[\text{OII}]=0$ in b)).

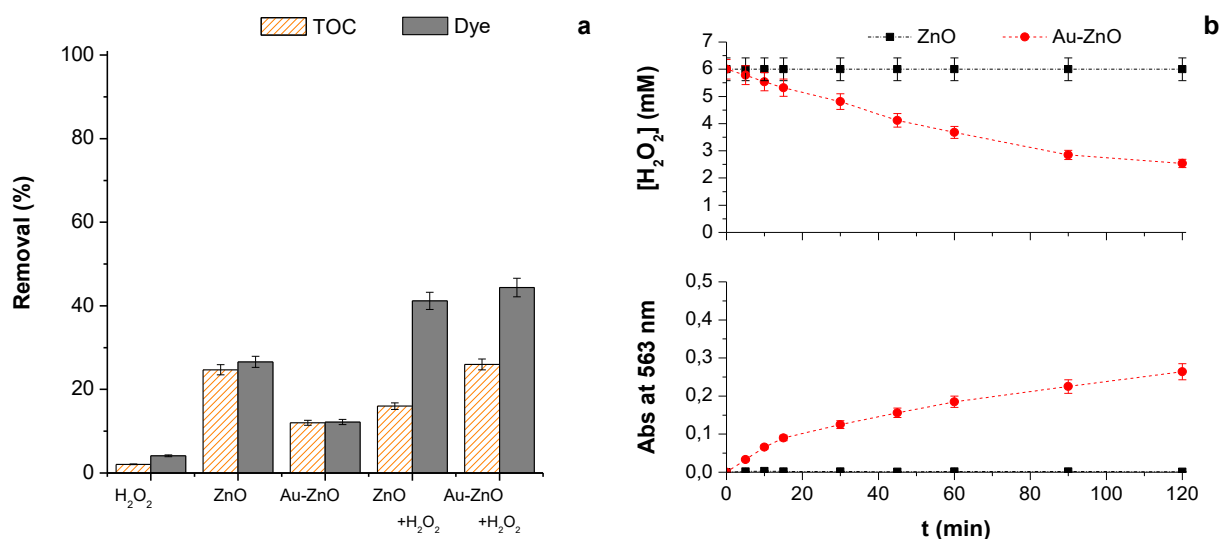


Figure 4.6 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for ZnO and Au-ZnO . ($\text{pH}=3.0$, $T=30\text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2]=6\text{ mM}$, [Support or catalyst] = 2.0 g/L and $[\text{OII}]=0.1\text{ mM}$ in a) and $[\text{OII}]=0$ in b)).

Nevertheless, the better performance, with a decolourization of 79.1%5.5% and 36.6%5.7% of TOC removal was obtained with Au-Al₂O₃ (Figure 4.2a), where a small increase in the generated hydroxyl radicals and consumption of oxidant, over the previous catalysts, was observed (Figure 4.2b).

4.2.2. Wet peroxidation vs. Wet peroxidation assisted with Radiation

The study started with the use of a high pressure mercury lamp (TQ 150) for comparing the performances of the materials making use of UV/visible radiation with the previous runs, without radiation; blank runs were also carried out without the support/catalyst but with radiation, to asses also the effect of the photolysis, with or without H₂O₂.

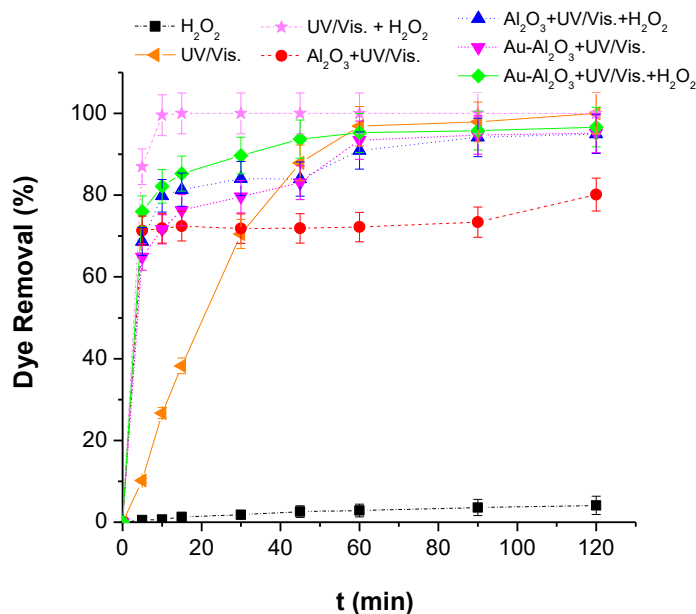


Figure 4.7 - Dye removal as a function of time for the Al₂O₃ and Au-Al₂O₃ system (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m², when used).

Figure 4.7 depicts the kinetics of the reaction for the Au-Al₂O₃ system (the kinetics of the remaining catalysts can be found in Annex F). It can be seen that the direct photolysis itself (UV/Vis only) promotes complete decolourization, and clearly enhances the efficiency of the previous runs. In the presence of radiation, the efficacy of the process is therefore considerably improved, which is even faster if the oxidant is added. The formation of hydroxyl radicals, through decomposition of hydrogen peroxide, in the

presence of radiation ($\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{HO}^\bullet$), as well as the regeneration of the catalyst assisted by radiation ($\text{X-Au}^+ + \text{H}_2\text{O}_2 + h\nu \rightarrow \text{X-Au}^0 + \text{HO}^\bullet + \text{H}^+$), are responsible for the increased performance. The formation of hydroxyl radicals can be seen by the result of the blank runs shown in Figure 4.8b, without the dye.

In the runs with the support (Al_2O_3) or gold-based catalyst ($\text{Au-Al}_2\text{O}_3$) assisted by radiation, it is observable a large enhancement in the TOC removals, compared to the others (direct photolysis, photolysis with H_2O_2) - Figure 4.8a. Such phenomenon is explained by the electrochemical properties of the supports, which enables the formation of hydroxyl radicals, as can be seen in Figure 4.8b. In the presence of radiation, hydrogen peroxide and the support/catalyst the performance is even better, particularly for the $\text{Au-Al}_2\text{O}_3$ sample (Figure 4.8a), which is related with the accelerated oxidant consumption and hydroxyl radicals formation (Figure 4.8b). Remarkable results were reached with this catalyst, with nearly complete dye removal and mineralization of ca. 80 ± 5.5 after 2 h of reaction.

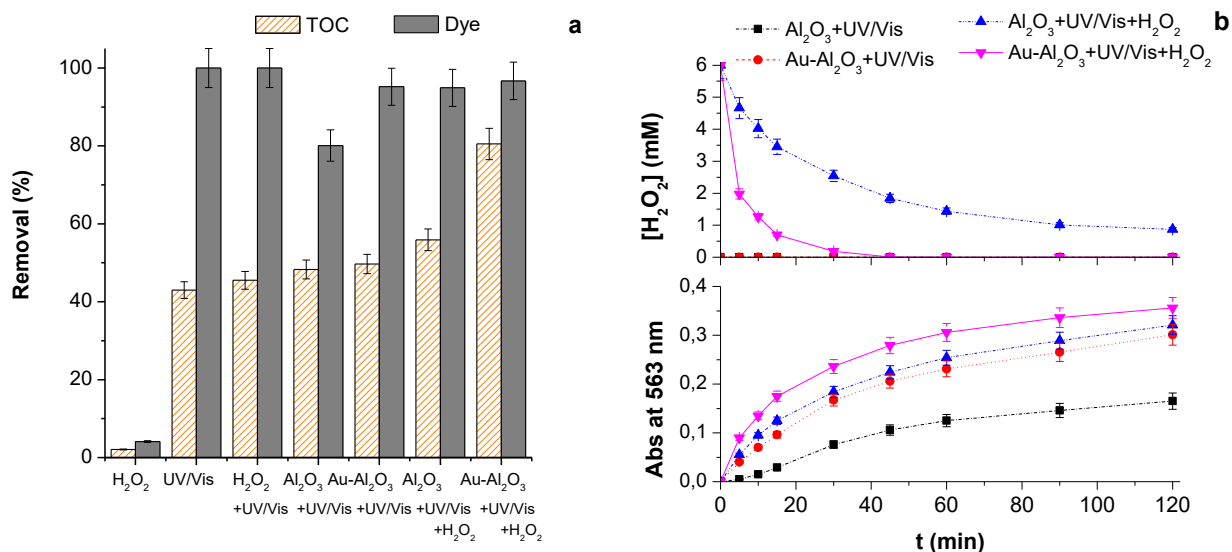


Figure 4.8 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for Al_2O_3 and $\text{Au-Al}_2\text{O}_3$. (pH=3.0, T= 30 °C, $[\text{H}_2\text{O}_2]$ = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m², when used).

For the $\text{Au-Fe}_2\text{O}_3$ system assisted by radiation and oxidant, the commercial material with 4% Au showed dye and TOC removals of $96.9 \pm 5.3\%$ and $58.4 \pm 5.8\%$, respectively (Figure 4.9a). Compared with the results obtained with the prepared 0.8%

Au-Fe₂O₃ sample (97.8±5.1% and 68.2±5.5%, for dye and TOC removals, respectively) (Figure 4.10a), there is a decay in performance that is explained by the excess of gold present, which acts as a scavenger, as previously explained. With radiation, and particularly in the presence of the catalyst and hydrogen peroxide, the formation of hydroxyl radicals is again notorious, which explains the more efficient removals (Figure 4.9b and Figure 4.10b).

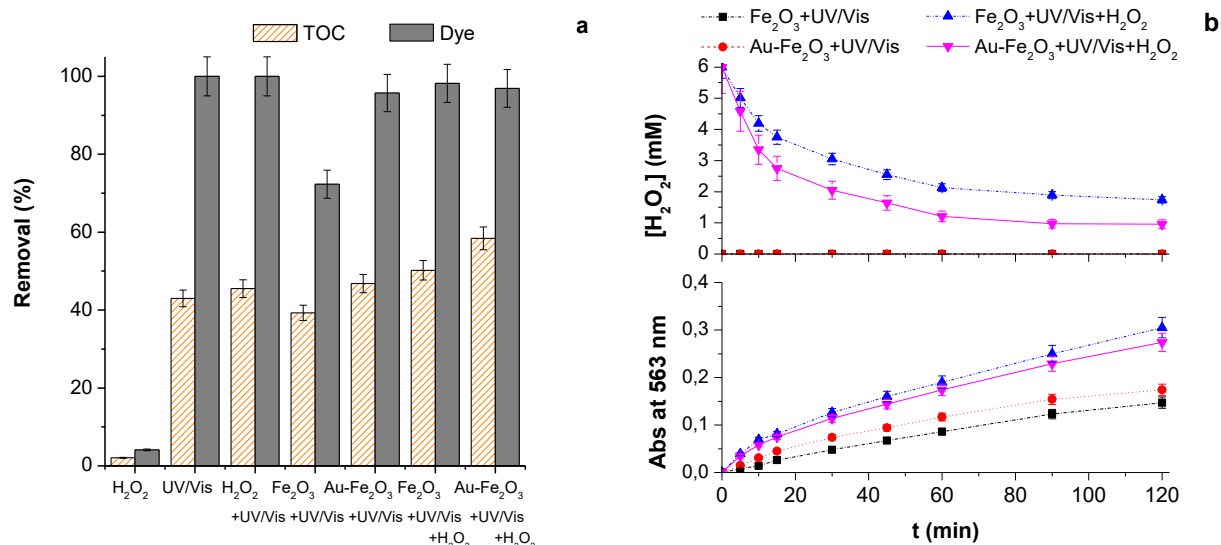


Figure 4.9 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for Fe₂O₃ and 4% Au/Fe₂O₃ (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation = 500 W/m², when used).

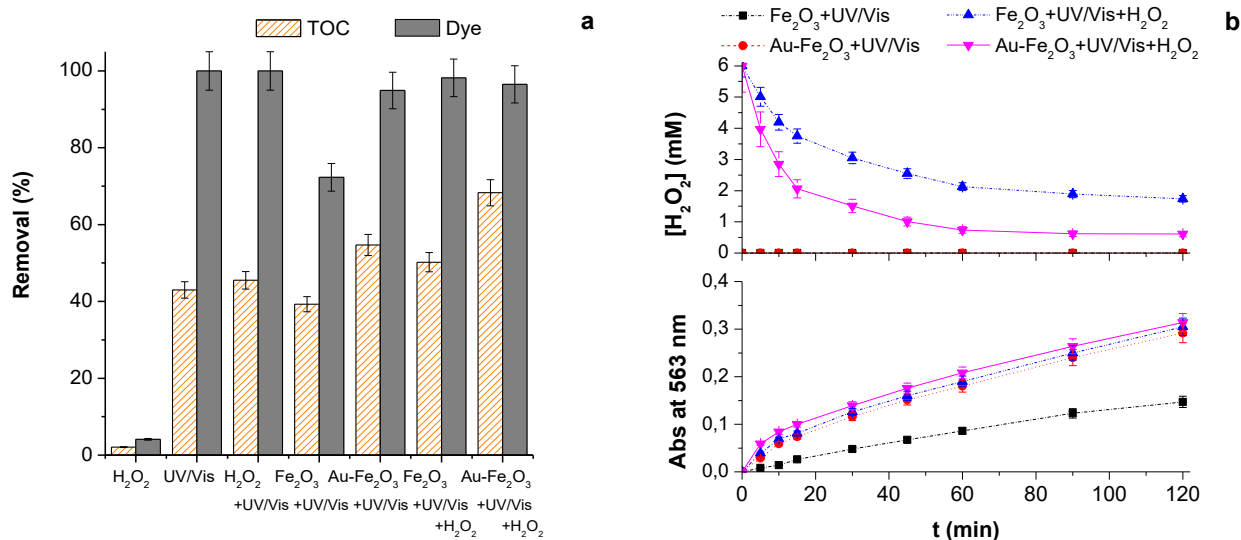


Figure 4.10 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for Fe₂O₃ and 0.8% Au-Fe₂O₃ (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m², when used).

Relatively to the Au-TiO₂ and Au-ZnO catalysts, their efficiency was, once again, similar (98.5±5.3% and 73.5±5.7% for color and TOC, respectively, for Au-TiO₂ – Figure 4.11a - and 99.8±5.2% for color and 73.4±5.5% for TOC for Au-ZnO - Figure 4.12a). The amount of hydroxyl radicals formed and hydrogen consumption in blank runs was also very similar (Figures 4.11b and 4.12b, for TiO₂ and ZnO, respectively).

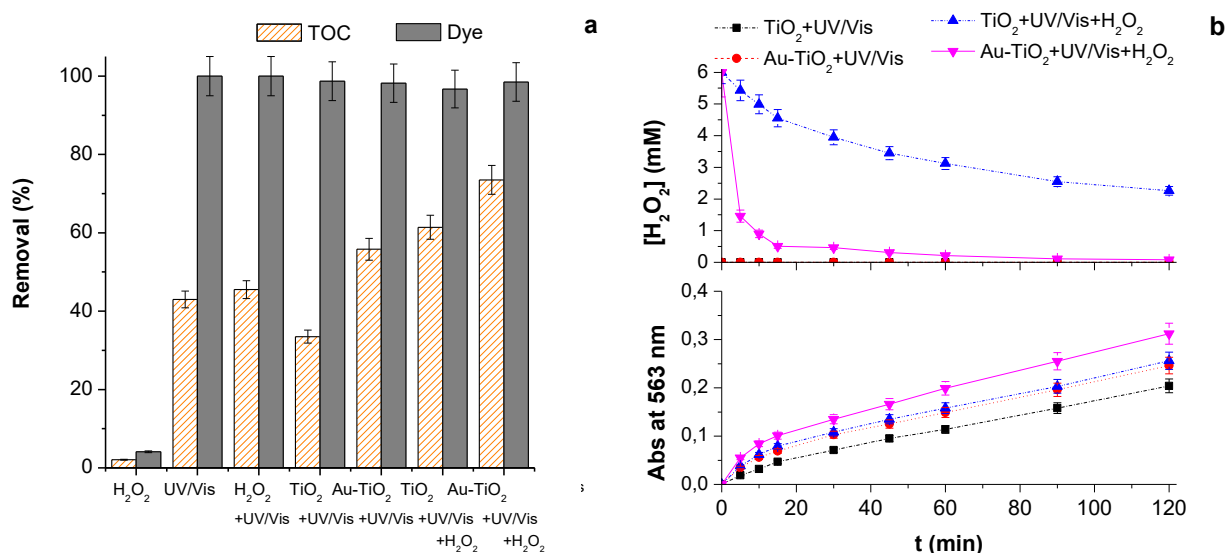


Figure 4.11 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for TiO₂ and Au-TiO₂ (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m², when used).

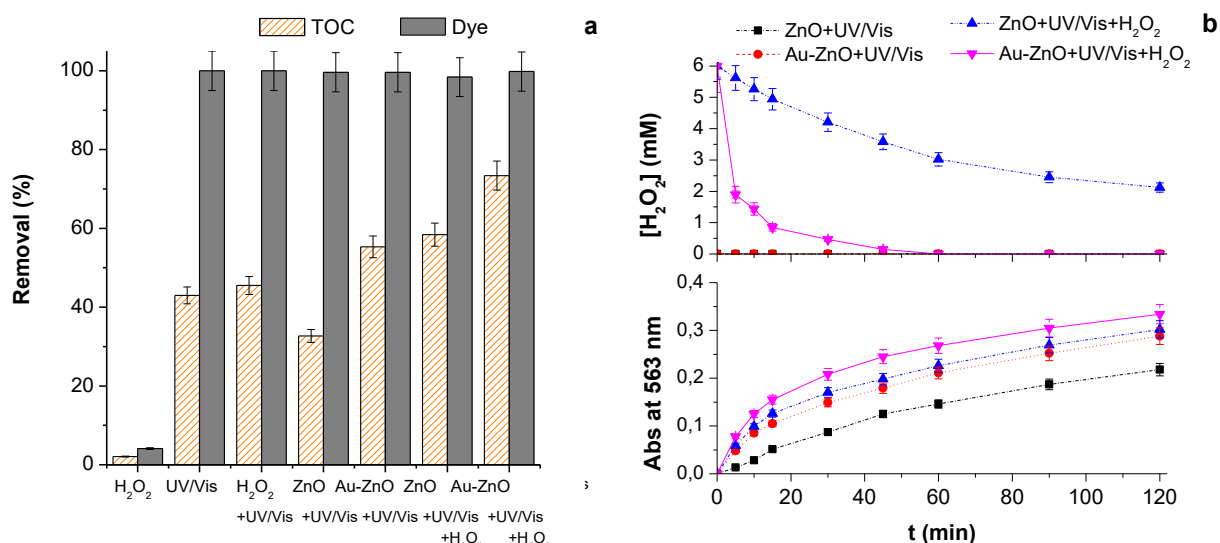


Figure 4.12 - Dye and TOC removals after 2 h (a) and consumption of hydrogen peroxide and hydroxyl radicals formation as a function of time (b) for ZnO and Au-ZnO (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m², when used).

Yet, the better performance, with a decolourization of 96.7±5.5% and 80.5±5.7% of TOC removal was obtained with Au-Al₂O₃ (Figure 4.8a), where a large increase in the generated hydroxyl radicals and consumption of oxidant was observed (Figure 4.8b).

4.2.3. Effect of Radiation Type

Another subject analysed was the radiation light spectrum. In order to analyse the implication of the UV radiation, runs with only visible radiation were carried out. For such, the quartz reactor was substituted by a glass one, so that it could block the UV radiation (transmittance of the glass reactor in Annex C).

Thus, 3 further runs were made for each catalyst using: i) only visible radiation; ii) the oxidant and the visible radiation and iii) the catalyst and hydrogen peroxide assisted by visible radiation. Figures below compare the runs with others shown before.

In Figure 4.13 it is possible to analyse that the visible radiation is not so significant as the UV/Vis radiation for the Au-Al₂O₃ system (the kinetics of the remaining catalyst systems are shown in Annex G). This radiation per se did not achieve a complete decolourization like the UV/Vis radiation, instead it only accomplished a 16%±5.3% of

OII removal. Similar conclusions of the radiation nature are reached in presence of the radiation and hydrogen peroxide.

Performances reached after 2 h, in terms of dye and TOC removal, are shown in Fig. 4.14 for all catalytic systems tested. Again, best performances are reached in presence of the alumina support loaded with 0.7wt.% of nanosized gold.

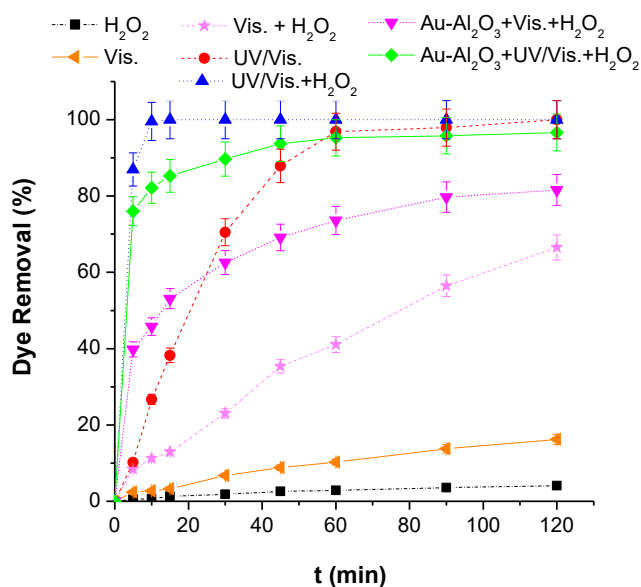


Figure 4.13 - Dye removal as a function of time for Au-Al₂O₃ (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [catalyst] = 2.0 g/L, [OII] = 0.1 mM and visible radiation= 500 W/m², when used).

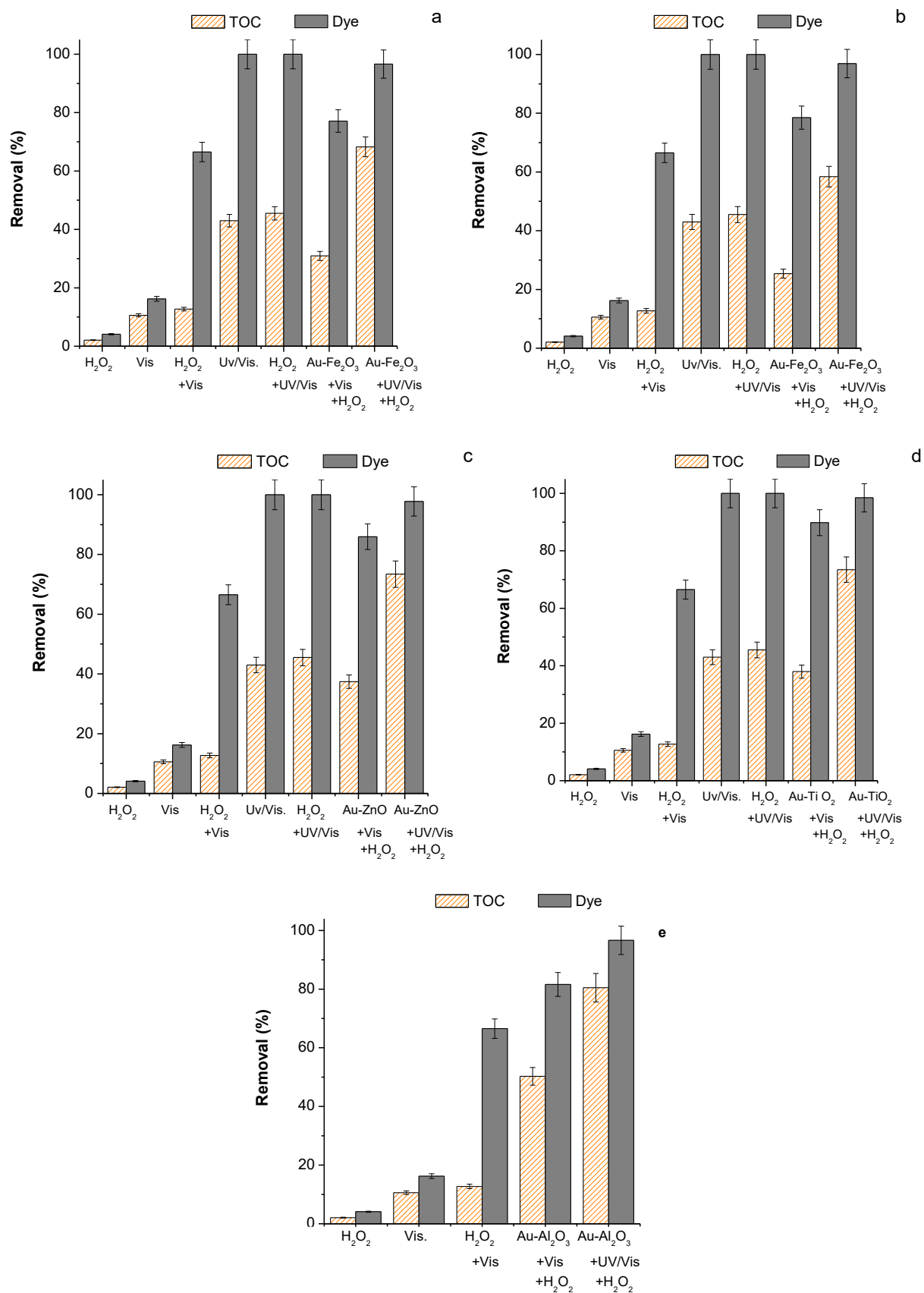


Figure 4.14 - Dye and TOC removals after 2 h for 0.8% Au-Fe₂O₃ (a), 4.0% Au-Fe₂O₃ (b), Au-ZnO (c), Au-TiO₂ (d) and Au-Al₂O₃ (e) (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and visible radiation= 500 W/m², when used).

4.2.4. Catalysts Stability

The catalysts stability was evaluated, with the exception of the commercial 4.0% Au-Fe₂O₃ material, since it showed low efficiency and low Turn Over Frequency (TOF) (as will be seen ahead).

In order to assess the catalysts stability, three consecutive reaction runs were performed under the same operating conditions (pH = 3, T = 30 °C, [H₂O₂] = 6 mM, [catalyst] = 2.0 g/L and radiation = 500 W/m²). The catalysts were recovered by filtration and, after drying, reused in the next run. As can be seen in Figure 4.15, the evolution of dye removal during the reaction does not change significantly by reusing the Au-Al₂O₃ catalyst, being this also observed for all other catalysts (Annex H). The TOC and dye removals, the hydrogen peroxide consumption and the efficiency of use (evaluated by the ratio between TOC conversion and H₂O₂ consumption – $X_{TOC}:X_{H_2O_2}$) are shown in Figure 4.16 for each catalytic test. The maximum variation of dye removal between cycles is less than 1.4%, for TOC is < 0.8%, < 2.3% for oxidant consumption and less than 1.7% for $X_{TOC}:X_{H_2O_2}$, for all catalysts tested.

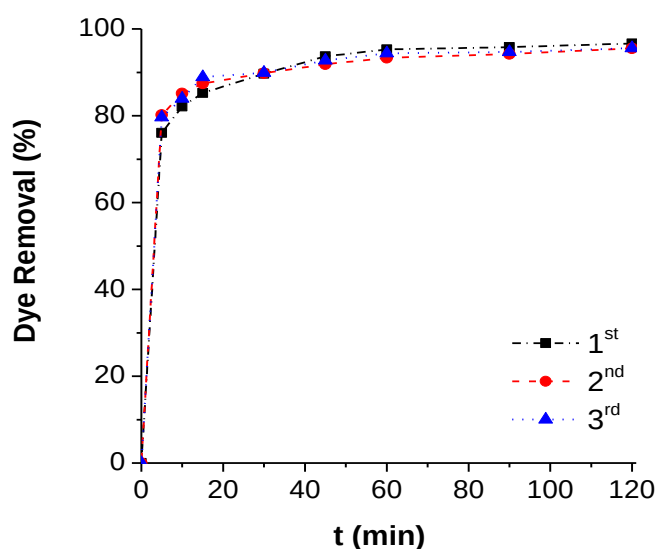


Figure 4.15 - Dye removal along time in 3 consecutive reaction cycles for Au-Al₂O₃ (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m²).

No leaching of gold was detected in all runs (unless it was below the detection limit of <0.5 mg/L – corresponding to a gold leaching level below 0.006% for 4.0% Au-Fe₂O₃, 0.02% for Au-TiO₂ and Au-ZnO, 0.03% for 0.8% Au-Fe₂O₃ and 0.04% for Au-Al₂O₃, as compared to the Au content initially present in the catalysts).

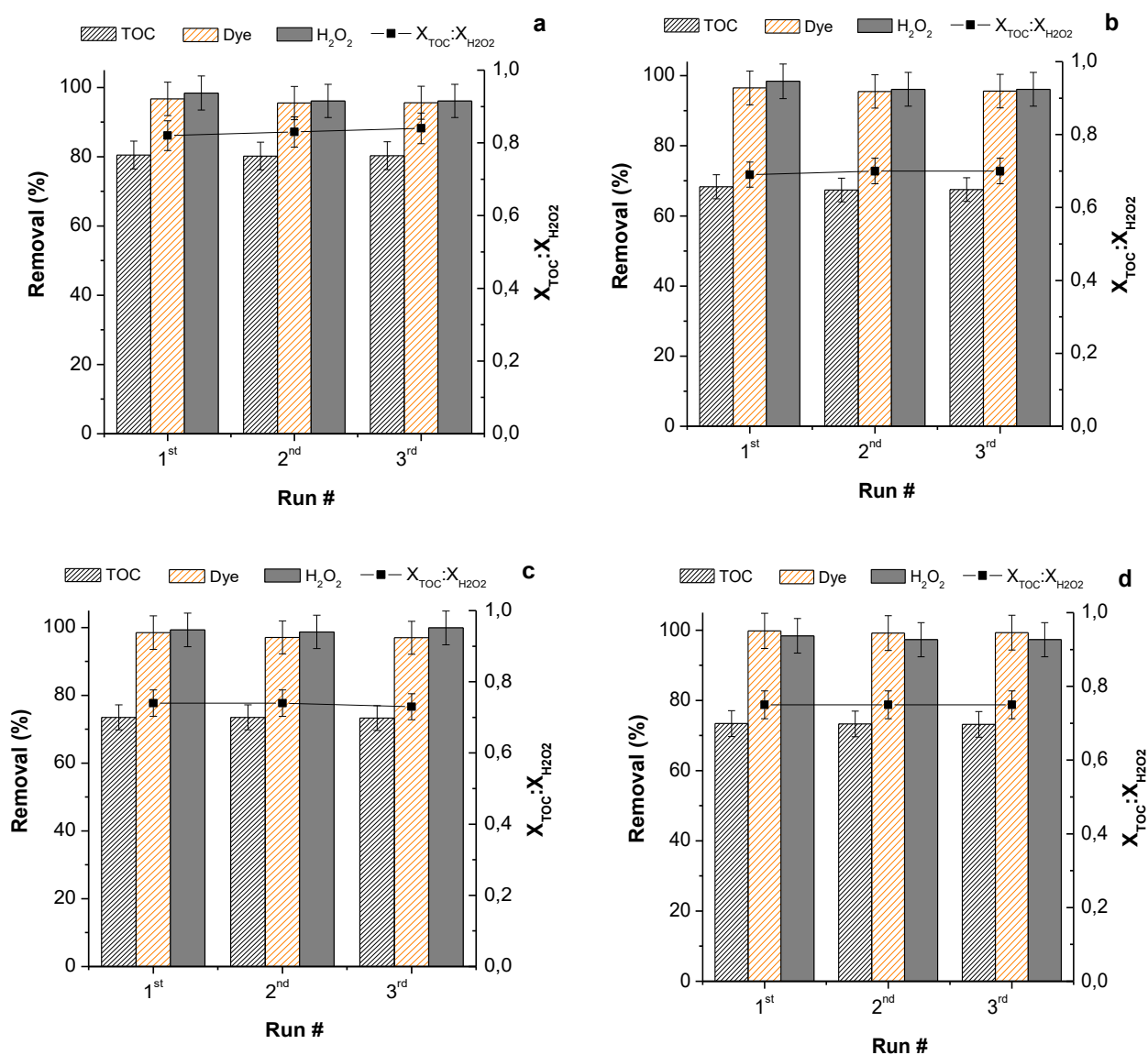


Figure 4.16 - TOC and dye removal, hydrogen peroxide consumption and its efficiency of use after 2 h of reaction in 3 consecutive reaction cycles for Au-Al₂O₃ (a), Au-Fe₂O₃ (b), Au-TiO₂ (c) and Au-ZnO (d) (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m²).

In summary, the results obtained allowed us to conclude that the catalysts are stable, and this is a crucial aspect for a potential industrial application of these materials.

4.2.5. Turn Over Frequency (TOF)

To compare the catalysts that have different gold loadings (an aspect that is inherent to the preparation method used) and select the one with better performance, the Turn Over Frequencies (TOF) for dye and TOC removals were determined.

TOF was calculated by equation 4.2, taking into account the dispersion of gold particles (DM) – cf. equation 4.1, the conversion of dye (or TOC) and the amount of gold present in each catalyst:

$$TOF (s^{-1}) = \frac{\frac{C * V * X}{1000}}{\frac{DM}{100} * n * t} \quad 4.2$$

where C is the dye concentration (mmol/L), V is the volume of dye solution (L), X is the dye (or TOC) conversion, n is the moles of gold used and t is the reaction time (s) at which the conversion (and TOF) and calculated (2 h).

The TOF results can be found in Figure 4.17. For both dye and TOC removal, the Au-Al₂O₃ catalyst gave the highest value, followed by Au-ZnO, 0.8% Au-Fe₂O₃, Au-TiO₂ and 4.0% Au-Fe₂O₃. The catalyst with highest TOF (Au-Al₂O₃) was the one with better performances of dye and TOC removals (Figure 4.8a), which also generated more radicals (Figure 4.8b) and presents the highest BET area (see Table 4.1).

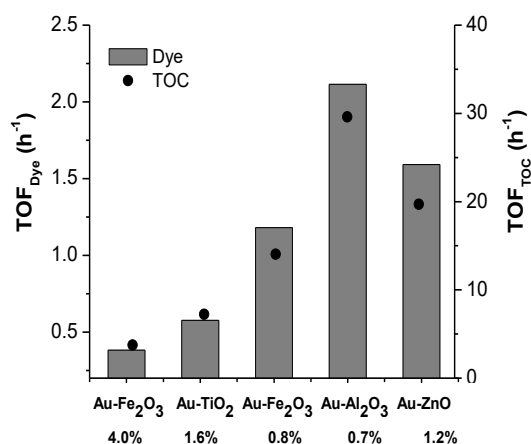


Figure 4.17 – TOFs for dye and TOC removals for all gold catalysts prepared.

4.2.6. Optimization

Since the Au-Al₂O₃ catalyst gave the highest TOF values, this material was chosen to optimize the process, in a traditional parametric study changing one-factor-at-a-time, regarding parameters such hydrogen peroxide concentration, catalyst concentration, pH, temperature and radiation intensity. Statistically-based strategies like design of experiments were not employed to have a better understanding of the effect of each parameter analyzed.

4.2.6.1. Hydrogen Peroxide Concentration

The hydrogen peroxide concentration has a substantial impact on the performance of this process and on the operating cost. Consequently, it is necessary to optimize this parameter in order to increase the efficiency. For this purpose, four runs were carried out, in which the hydrogen concentration was varied in the range of 1,5-12 mM.

The initial dye oxidation rate increases with the dose of oxidant until ca. 6 mM (Figure 4.18a). Figure 4.18b shows that, in terms of dye and TOC removal after 2 h of reaction and oxidant use (assessed by the ratio $X_{TOC}:X_{H_2O_2}$), the best performance is achieved for a 3 mM dose of oxidant (respectively 96.8%±5.1%, 85.9%±5.5% and 0.91±0.05). The existence of an optimum concentration of hydrogen peroxide can be explained by the scavenging of the hydroxyl radicals. When using an excess of oxidant, the parallel and undesirable scavenging of the hydroxyl radicals may occur, leading to their consumption by the H₂O₂ molecules in excess ($HO^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet$) (Walling 1975), thus decreasing the number of radicals available to oxidize the organic matter. As can be seen in the equation above, perhydroxyl radicals are formed, however, their oxidation potential is much smaller than that of the hydroxyl ones. This explanation is also supported by the nearly complete conversion of H₂O₂ shown in Figure 4.18b, for doses higher than 3 mM, in which dye and TOC removals do not increase, or even decrease.

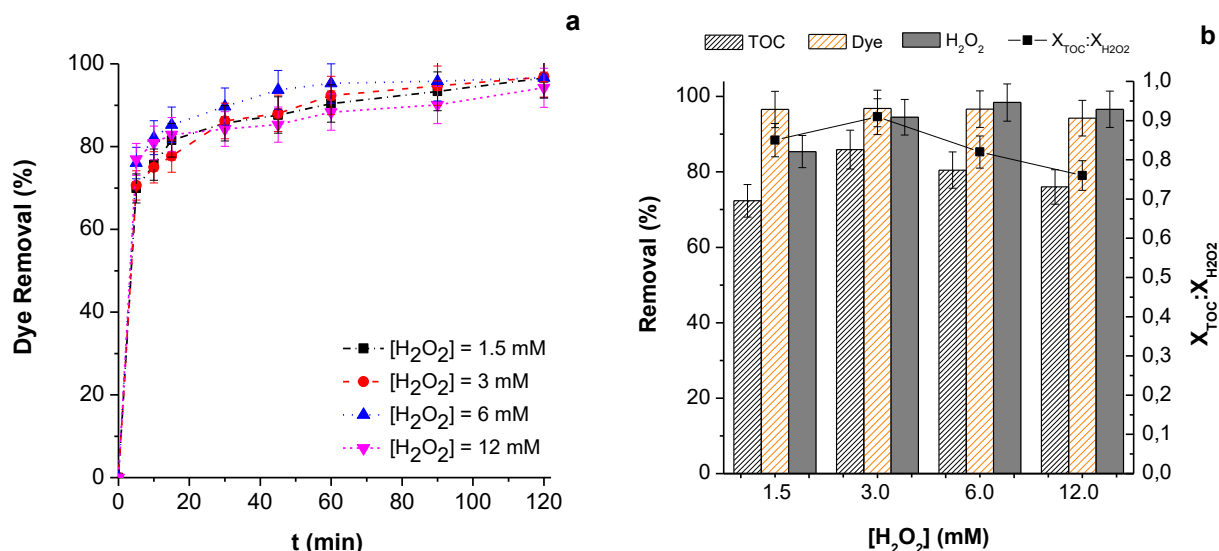


Figure 4.18— Effect of hydrogen peroxide concentration in dye removal as a function of reaction time (a), and in TOC and dye removal, in overall hydrogen peroxide consumption and in its efficiency of use after 2 h of reaction (b) (pH=3.0, T= 30 °C, [catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m²).

4.2.6.2. Catalyst Concentration

In Figure 4.19a it is shown that, at first, the oxidation reaction accelerates when the concentration of Au-Al₂O₃ is increased until 2.0 g/L (because more radicals are generated), declining for a catalyst dosage of 2.5 g/L. For this dose of catalyst, the final TOC and dye removal performance (75.2±5.4% and 81.3±5.6%, respectively) declines, compared to the catalyst concentration of 2.0 g/L (85.9±5.2% and 96.8±5.9% for TOC and dye removal, respectively) (Figure 4.19b). About the efficiency of the hydrogen peroxide used ($X_{TOC}:X_{H_2O_2}$), it is evident that the catalyst with a concentration of 2.0 g/L shows the best result, $X_{TOC}:X_{H_2O_2} = 0.90 \pm 0.05$.

The existence of an optimal catalyst amount is common in wet peroxidation processes (assisted or not with radiation) and is explained by the scavenging reaction of hydroxyl radicals with excess of catalyst (gold): $HO^\bullet + X-Au^0 \rightarrow X-Au^+ + HO^-$. This is also confirmed by the results that show that the highest consumption of hydrogen peroxide, found for the catalyst concentration of 2.5 g/L (97.0±5.2% - Figure 4.19b), does not result in an increased process efficiency. On the other hand, excessive amount of catalyst in

suspension in the slurry reactor can difficult the radiation to penetrate so efficiently and reach the catalyst, hydrogen peroxide or organic molecules.

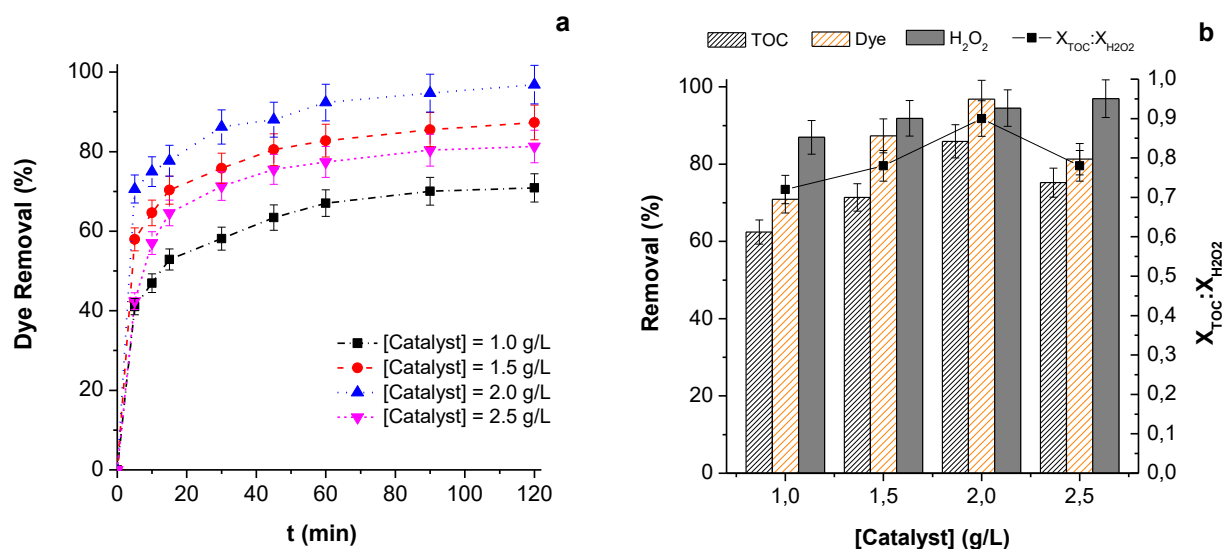


Figure 4.19 - Influence of catalyst dose in dye removal as a function of reaction time (a), and in TOC and dye removal, in overall hydrogen peroxide consumption and its efficiency of use after 2 h of reaction (b) (pH=3.0, $T = 30\text{ }^{\circ}\text{C}$, $[H_2O_2] = 6\text{ mM}$, $[OII] = 0.1\text{ mM}$ and radiation= 500 W/m^2).

One aspect to highlight is that the leaching of gold was less than 0.07%, 0.05%, 0.04%, 0.03% for the catalyst concentrations 1.0 g/L, 1.5 g/L, 2.0 g/L, 2.5 g/L, respectively, (detection limit of $<0.5\text{ mg/L}$).

4.2.6.3. pH

Acidic conditions are usually more favorable to the WP process; however, some literature suggests that applying high pH values when using Au based catalysts is advantageous (Morais 2005, Martín *et al.* 2011, Domínguez *et al.* 2014). In this work, the initial pH was varied in the range of 1.5 to 5.0. Figures 4.20a and 4.20b show that there was an optimum pH at 3, at which $85.9 \pm 5.8\%$ of TOC removal and $96.8 \pm 5.3\%$ of OII removal were reached in 2 h, with a $X_{TOC}:X_{H_2O_2}$ ratio of 0.90 ± 0.05 . However, at the end of the reaction, the pH of the solution was at 4, which may indicate the real optimal pH, which is the ideal value described in other studies (Navalon *et al.* 2011). Regarding hydrogen peroxide consumption, it increased progressively with the initial pH increase

(from 89.9% at pH 1.5 to 98.1% at pH 5 – Figure 4.20b). The leaching of gold was less than 0.04% for all the pH values tested (i.e., no gold was found in solution; the detection limit being <0.5 mg/L).

The existence of an optimum pH is explained by the fact that, at higher values, the decomposition of hydrogen peroxide into water and oxygen occurs (as corroborated by data in Figure 4.20b), leading to a reduction in the amount of oxidant available for hydroxyl radical's formation. A pH < 2.5 the protons tends to act like a scavenger due to the following equation: $HO^{\bullet} + H^{+} + e^{-} \rightarrow H_2O$.

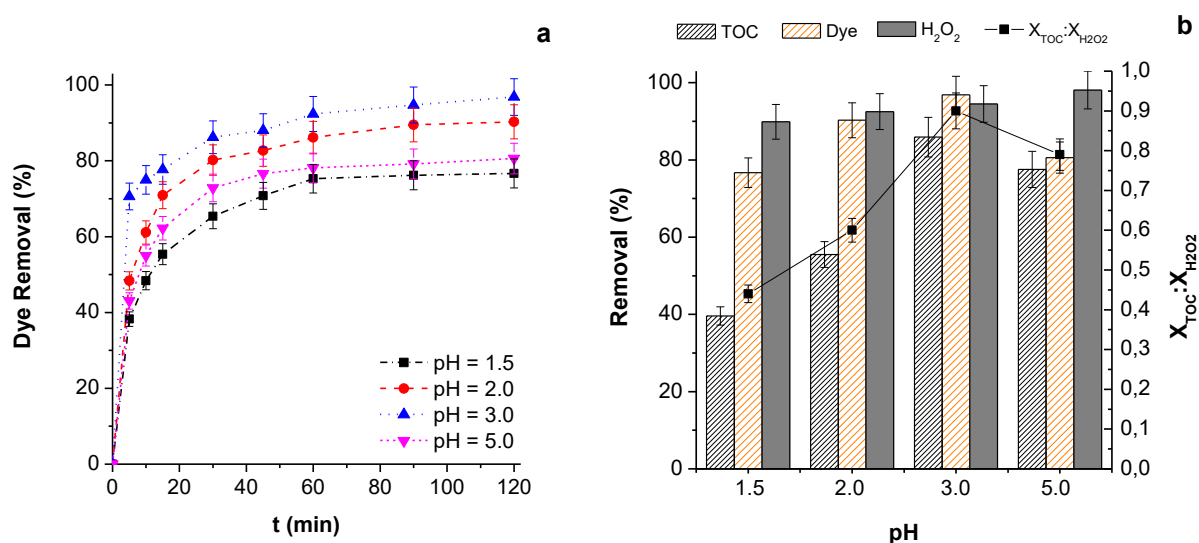


Figure 4.20 - Influence of initial pH in the Orange II dye removal as a function of reaction time (a), in TOC and dye removal, overall hydrogen peroxide consumption and its efficiency of use after 2 h of reaction (b) ($T = 30\text{ }^{\circ}\text{C}$, $[\text{H}_2\text{O}_2] = 6\text{ mM}$, $[\text{catalyst}] = 2.0\text{ g/L}$, $[\text{OII}] = 0.1\text{ mM}$ and radiation = 500 W/m^2).

4.2.6.4. Radiation Intensity

Since one of the disadvantages of the photo assisted wet peroxidation is the cost related to the energy dispended for the radiation, runs with an intensity of 130 W/m^2 and 100 W/m^2 were also made, since this is the maximum and minimum intensity of radiation incident in the northern region of Portugal (Miranda 2008). By simulating as close as possible the natural intensity of solar light, it is possible to get an idea of how this process would work with solar energy.

In Figure 4.21, it is observable that, with these intensities of radiation, the process loses performance as compared to the one employed previously, of 500 W/m². With an intensity of 130 W/m², there is a 63±5.0% and 52±5.7% of dye and TOC removals at the end of the run, while with 100 W/m² there are 53±5.2% and 42±5.6% of dye and TOC removals. These removals are clearly less effective than the ones obtained with an intensity of 500 W/m². However, the use of solar radiation should be much cheaper, so, a study regarding the performance:cost ratio is needed. Even so, it is worth mentioning that only with 500 W/m² was possible to reach nearly complete decolorization, with an outstanding mineralization degree.

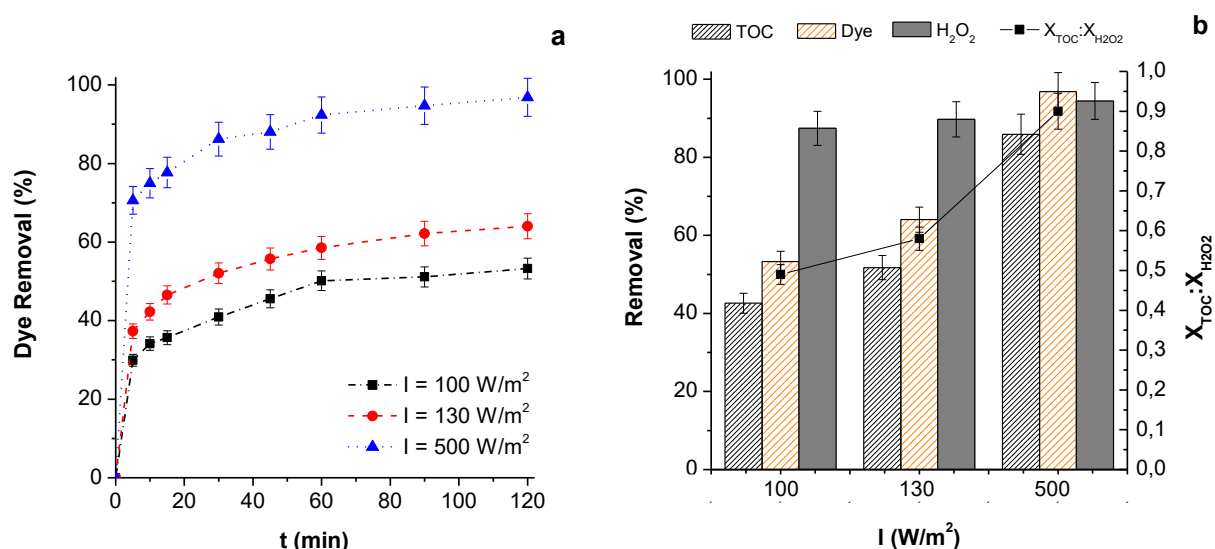


Figure 4.21 - Influence of the radiation intensity in the dye removal as a function of reaction time (a), in TOC and dye removal, overall hydrogen peroxide consumption and its efficiency of use after 2 h of reaction (b) (pH= 3.0, [H₂O₂] = 6 mM, T= 30 °C, [catalyst] = 2.0 g/L and [OII] = 0.1 mM).

4.2.6.5. Reaction Temperature

Another important parameter in this process is the temperature; so, runs were carried out in the temperature range of 10 to 70 °C. Figures 4.22a and 4.22b show that the temperature has a strong effect in the efficiency of the process. The removals of dye and TOC were significantly improved when the temperature was raised from 10 to 30 °C, and a small increase was found when the temperature was raised to 50 °C. However, at 70 °C the mineralization performances are negatively affected. The efficiency of

peroxide use ($X_{TOC}:X_{H_2O_2}$) also follows this trend. The dye and TOC removals ($99.3\pm4.9\%$ and $90.9\pm5.7\%$, respectively) obtained at 50 °C indicate that this temperature was the optimal one.

The reaction rates increase with temperature (Figure 4.22a) due to the increasing kinetic constants, according to the Arrhenius law but, on the other hand, for temperatures above ca. 50 °C, thermal decomposition of hydrogen peroxide into water and oxygen occurs (Walling 1975). This explains the worse performances obtained at 70 °C. Again, no leaching of gold was found to the solutions at any temperature.

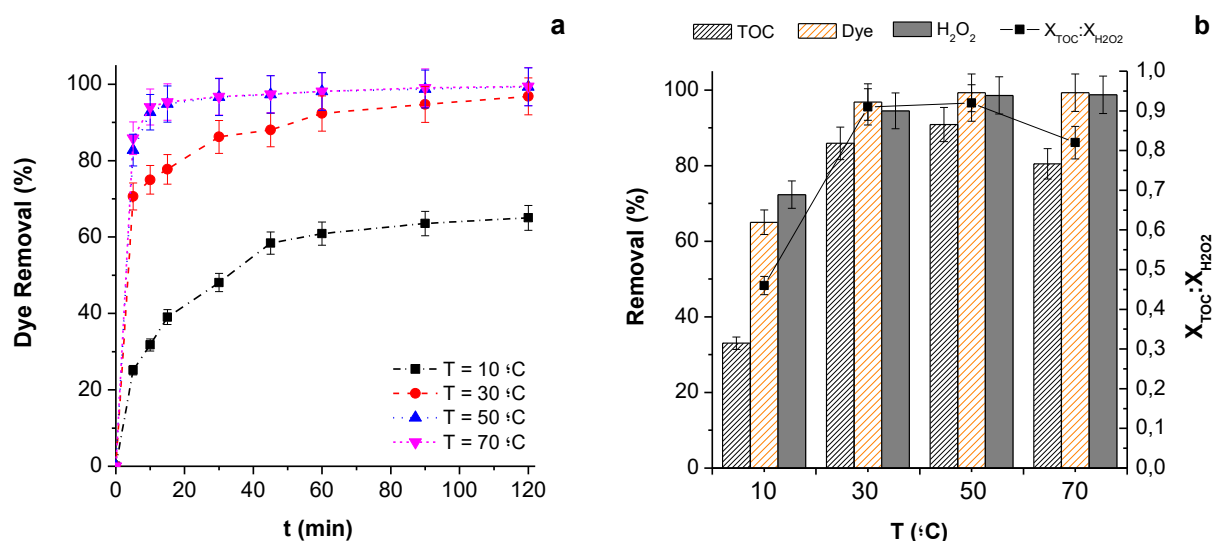


Figure 4.22 - Influence of reaction temperature in the dye removal as a function of reaction time (a), in TOC and dye removal, overall hydrogen peroxide consumption and its efficiency of use after 2 h of reaction (b) ($pH=3.0$, $[H_2O_2]=6$ mM, $[catalyst]=2.0$ g/L, $[OII]=0.1$ mM and radiation=500 W/m²).

4.3. Acrylic Dye Treatment

In order to assess the applicability of this process to industrial wastewater treatment, a catalytic run was performed using a simulated acrylic dyeing effluent at pH 3, 50 °C, employing 2 g/L of the 0.7 wt.% Au-Al₂O₃ catalyst and using a radiation with intensity of 500 W/m² - which were the best conditions found in the dye degradation experiments. In this case, 3.52 g/L of oxidant were used (twice the stoichiometric amount of COD – 796.8 ± 4.0 mgO₂/L).

An impressive performance was reached with the photo assisted wet peroxidation, with removals in only 2 h of reaction up to $100\pm1.5\%$, $72.4\pm2.2\%$ and $70.0\pm1.0\%$ for color, TOC and COD, respectively (see Figure 4.23 and Table 4.2). Moreover, there was an improvement in the biodegradability of the effluent ($BOD_5:COD$ ratio increased from $<0.002\pm4.5$ for untreated wastewater to 0.50 ± 3.0 after the radiation-assisted wet peroxidation, and the specific oxygen uptake rate (k') increased from $<0.2\pm6.5$ to $17.9\pm5.7 \text{ mgO}_2/(\text{g}_{\text{VSS}} \text{ h})$ – see Figure 4.23b. Regarding the toxicity, the final effluent was non-toxic (the inhibition of *Vibrio fischeri* was $0.0\pm4.0\%$, indicating that no toxic intermediates have been generated). For easier comprehension, these results are summarized in Table 4.2.

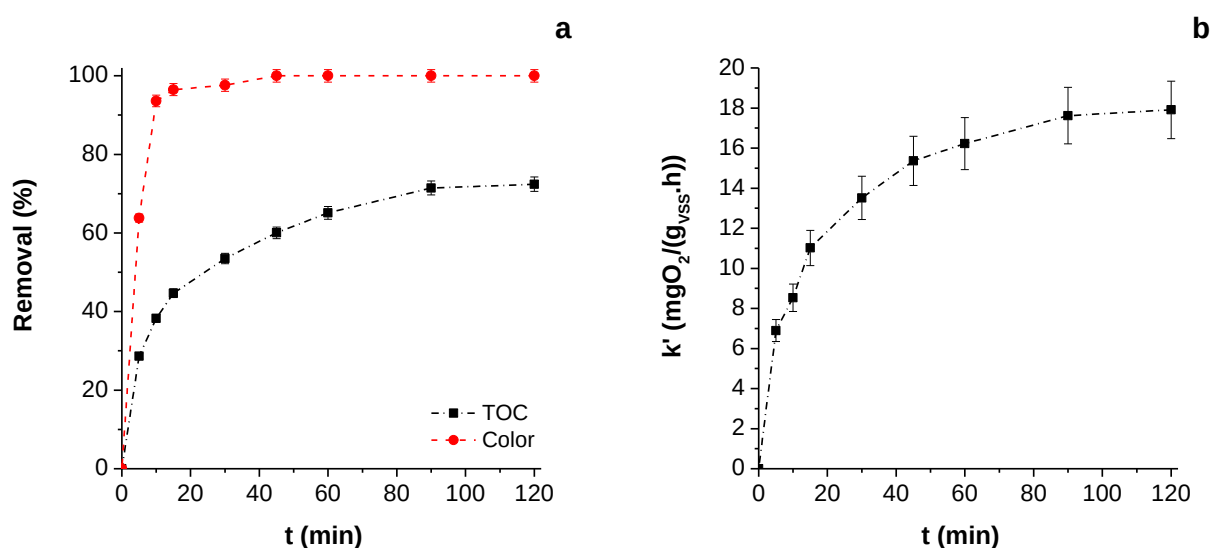


Figure 4.23 – Dye an TOC removal (a) and specific oxygen uptake rate (k') (b) as a function of reaction time during degradation of the industrial acrylic effluent ($T= 50\text{ }^{\circ}\text{C}$, $\text{pH}= 3.0$, $[\text{H}_2\text{O}_2] = 3.52 \text{ g/L}$, $[\text{catalyst}] = 2.0 \text{ g/L}$ and radiation= 500 W/m^2).

The heterogeneous wet peroxidation photo-assisted process generated a treated effluent that does not comply with the legal discharge limits, since the BOD_5 concentration is slightly higher than the maximum allowable value (M.A.V.) - see Table 4.2 – set by discharge legislation for textile wastewater. However, the process generated a wastewater clearly far more biodegradable and non-toxic, which can be combined with biological degradation.

Table 4.2 Characterization of the synthetic acrylic dyeing effluent before and after photo-assisted wet peroxidation and removal efficiencies.

	Initial State	After Treatment	Removal (%)	M.A.V. *
Absorbance at 610 nm (a.u.)	2.078±2.3	0.00±2.9	100.0±1.5	-
TOC	334.5±4.0	92.3±4.5	72.4±2.2	-
COD (mg O₂/L)	796.8±4.0	239.3±3.6	70.0±1.0	250
BOD₅ (mg/L)	< 1±5.0	120.7±6.6	-	100
BOD₅:COD	< 0.002±4.5	0.5±3.0	-	-
Inhibition of <i>V. fischeri</i> 5 min(%)	92±4.3	0±3.9	100±2.1	-
Inhibition of <i>V. fischeri</i> 15 min(%)	94±4.2	0±4.4	100±2.3	-
Inhibition of <i>V. fischeri</i> 30 min(%)	96±3.8	0±4.0	100±2.9	-
SOUR (mgO₂/g_{SSV} h)	< 0.2±6.5	17.9±5.7	-	-
Visible color after dilution 1:40	Visible	Not visible		Not visible

* Ordinance No. 423 of June 25, 1997

5. Conclusions and Suggestions for Future Work

The main purpose of this work was to analyze the efficiency of different metal oxides (namely Al_2O_3 , Fe_2O_3 , TiO_2 and ZnO) as supports for Au-based catalysts in the radiation-assisted peroxidation of an organic model compound. Testing the stability of the catalysts was also a key objective. This study also aimed to analyze the influence of some parameters in the process, such as, radiation type, temperature, pH, hydrogen peroxide concentration, catalyst concentration and radiation intensity. The final goal of this work was to apply the optimized process to a simulated acrylic dyeing effluent.

Photo assisted wet peroxidation using nanosized gold-based catalysts proved to be a promising technique for the degradation of the model recalcitrant compound Orange II dye. This work allowed to conclude that the used supports have an important role in the efficiency of the process. The comparison of the efficiencies of the different supports regarding their dye and TOC removals, as well as their TOF values, allowed to conclude that the best catalyst tested was gold supported on alumina, which is the one with higher BET surface area; other characteristics determined through different techniques didn't seem to be so critical.

The use of radiation had a considerable effect in the wet peroxidation, considerably enhancing the reaction kinetics and process performance, through a notorious increase in the formation rate of hydroxyl radicals.

The stability of all catalysts was confirmed, and above all, no leaching was found for any of the catalysts. Through optimization of the process the following parameters were considered as being the best: $T = 50\text{ }^\circ\text{C}$, $\text{pH } 3.0$, $[\text{H}_2\text{O}_2] = 3.0\text{ mM}$, $[\text{catalyst}] = 2.0\text{ g/L}$ and radiation = 500 W/m^2 .

In the treatment of a simulated industrial acrylic dyeing wastewater, removals of $100 \pm 1.5\%$, $72.4 \pm 2.2\%$ and $70.0 \pm 1.0\%$ for color, TOC and COD, respectively, were obtained. Moreover, there was an improvement in the biodegradability of the effluent, as well as a no toxic effluent was generated.

Thus, the use of gold-based catalysts in a wet peroxidation process assisted with radiation shows potential to become a new method to treat wastewater, since these catalysts showed great efficiency and excellent stability.

Although this process already shows great efficacy, some future studies can still be made in order to fully optimize this method to treat wastewater. One of the subjects that can be further investigated is the test of other supports, because it was shown that different oxides have a large influence in the efficiency of the procedure. Employing further physical-chemical characterization techniques, of both fresh and used catalysts, could lead to a better comprehension regarding the path to follow to reach even better catalysts. Another parameter that can also be considered is the variation of the gold loading in the oxide. Different amounts of gold could be tested for every material, or at least for the most promising. Finally, this process should be applied to a continuous reactor, which can be a challenging task to accomplish, but it should be tested, in order to envisage the possibility to implement this process in the wastewater treatment industry. For that, strategies have to be considered to minimize gold loading (to reduce costs), while reaching good catalytic performances, and find a way to have these materials in pellets or in structured configurations (e.g. monoliths, foams, etc.).

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Annex

A. Acrylic Dyeing Effluent

Table A.1 – Components of the simulated acrylic dyeing effluent

<i>Component</i>	Dyeing stage use	Dyeing stage Concentration	Amounts used in every stage	Rejection	Amounts rejected	Concentration in the initial effluent
Sera con N-VS	Dyeing	0.4 mL/L	1204 mL	100%	1204 mL	0.13 mL/L
Sera sperse M-IW	Dyeing	0.5 g/L	1505 g	100%	1505 g	0.17 g/L
Sera tard A-AS	Dyeing	1 g/L	3010 g	100%	3010 g	0.33 g/L
Sodium sulphate	Dyeing	3 g/L	9030 g	90%	8127 g	0.9 g/L
Sera lube M-CF	Dyeing	2 g/L	6020 g	100%	6020 g	0.67 g/L
Astrazon Blue FGGL 300% 03	Dyeing	1.5% (w dye/w fiber)	4515 g	5 %	225 g	0.025 g/L
Water	Dyeing	100% (v/v)	3010 L	100%	3010 L	---
Water	Washing	100% (v/v)	6020 L	100%	6020 L	---

B. Determination of Standard Deviation

The confidence interval for the values obtained is given by:

$$x_m \pm t_{student} \times \frac{s}{\sqrt{n}}$$

x_m : medium valour of both measures

$t_{student}$: t-student factor for a determined confidence interval (in this case, $t_{student} = 1$ and confidence interval = 50%).

s : standard deviation

n : number of measures

The standard deviations (S_y) were calculated through the formulas of errors propagation by subtraction (D.1) and division (D.2)

$$S_y = \sqrt{S_{x1}^2 + S_{x2}^2} \quad (D.1)$$

$$S_y = y \times \sqrt{\left(\frac{S_{x1}}{x1}\right)^2 + \left(\frac{S_{x2}}{x2}\right)^2} \quad (D.2)$$

C. Radiation

Abb. 5: relativ spektraler Strahlungsfluß des UV-Strahlers im Tauchrohr
 Fig. 5: relativ spectral radiant flux of UV-immersion lamp in immersion tube
 Illu. 5: spectre d'émission (unités relatives) d'émetteur positionné dans le tube d'immersion

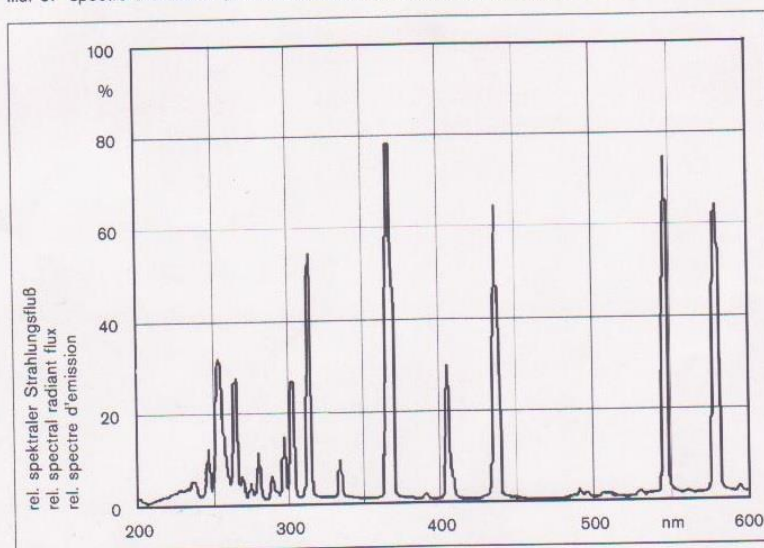


Figure C.1 – Emission spectrum of Heraeus TQ 150 mercury lamp.

Abb. 6: Transmission von Quarzglas und Duran 50
 Fig. 6: transmission from quartz glass and Duran 50
 Illu. 6: transmission de verre en quartz et Duran 50

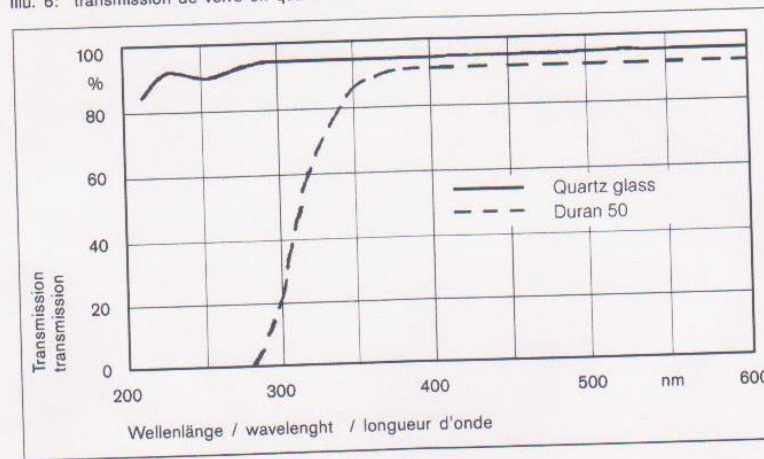


Figure C.2 – Transmittance from quartz and Duran 50 reactors.

D. Catalysts Characterization

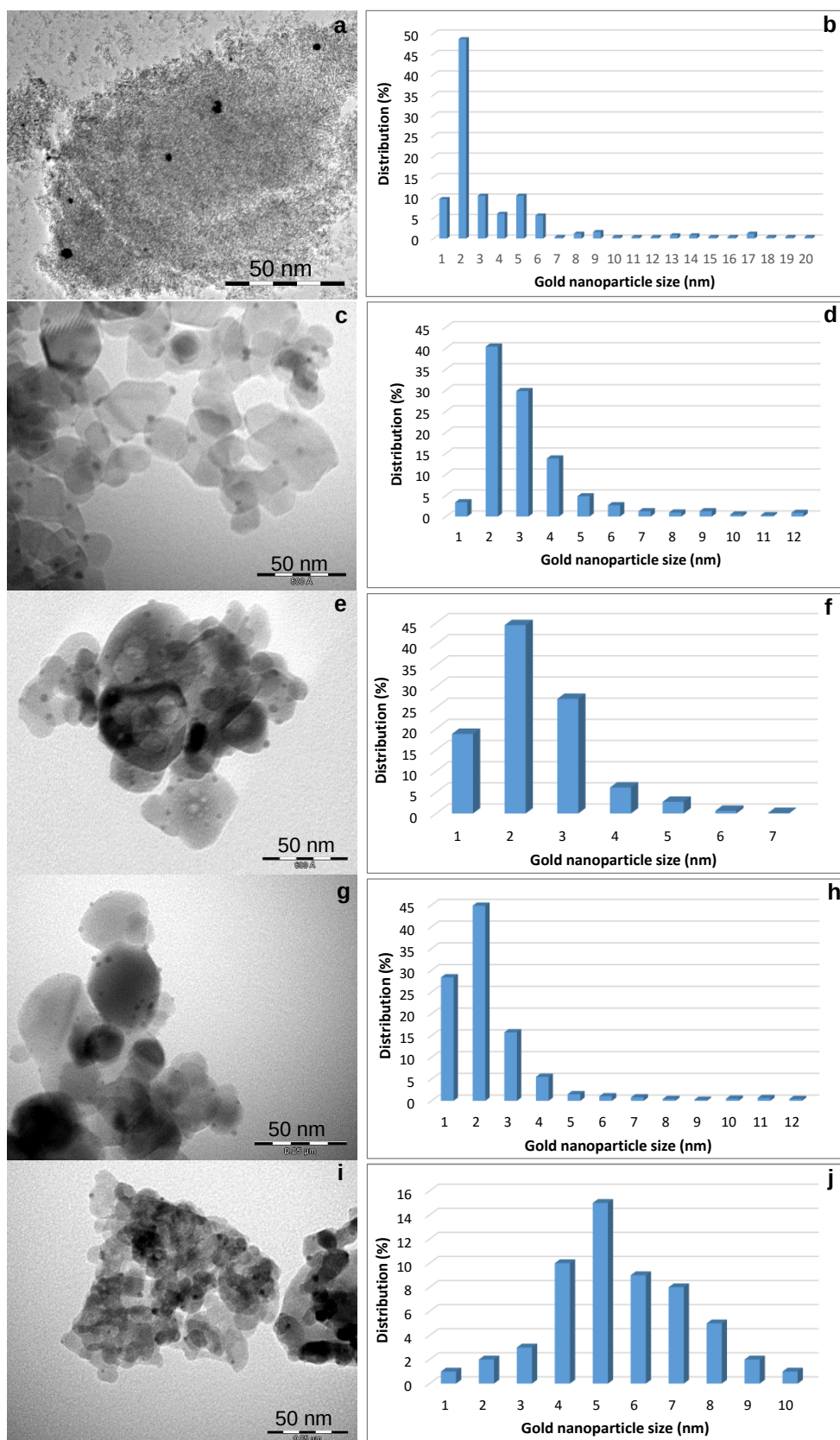


Figure D.1 - HRTEM images of Au-Al₂O₃ (a), Au-Fe₂O₃ WGC (c), of Au-Fe₂O₃ (e), Au/TiO₂ (g) and Au/ZnO (i) along with the corresponding gold nanoparticle size distribution histograms (b,d,f,h,j).

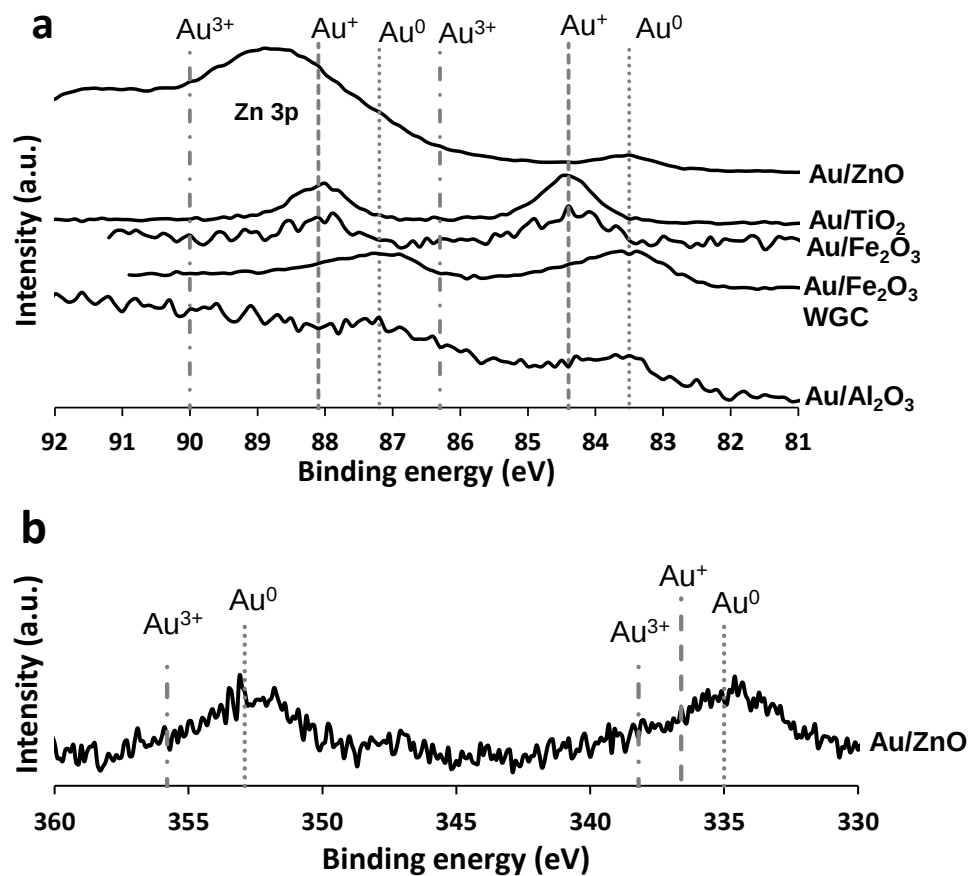


Figure D.2 - Au 4f XPS spectra of Au supported on Al₂O₃, Fe₂O₃, TiO₂ and ZnO (a) and Au 4d XPS spectra of Au-ZnO (b).

E. Adsorption vs. Reaction without Radiation

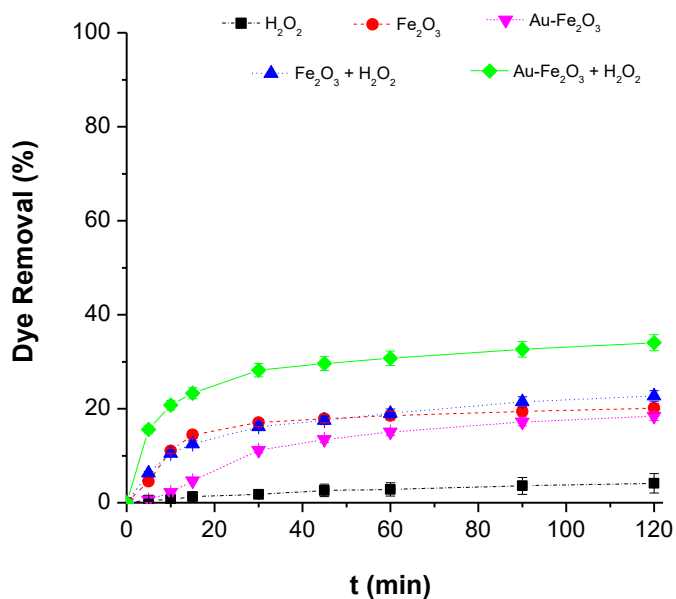


Figure E.1 - Dye removal as a function of time for Fe₂O₃ and 0.8% Au-Fe₂O₃ (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM, when used).

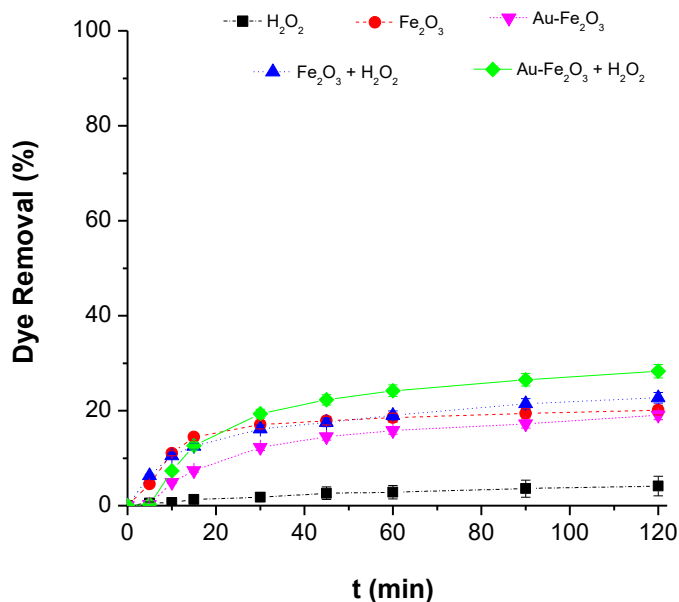


Figure E.2 - Dye removal as a function of time for Fe₂O₃ and 4.0% Au-Fe₂O₃ (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM, when used).

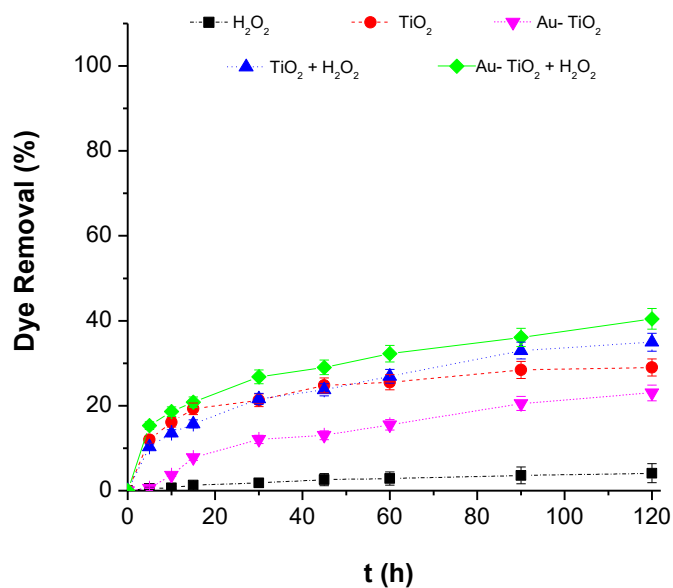


Figure E.3 - Dye removal as a function of time for TiO₂ and Au-TiO₂ (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM, when used).

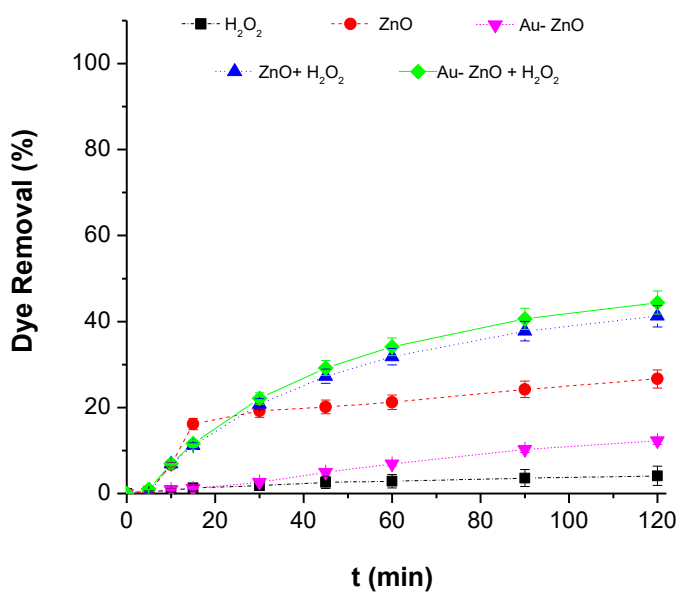


Figure E.4 - Dye removal as a function of time for ZnO and Au-ZnO (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [Support or catalyst] = 2.0 g/L and [OII] = 0.1 mM, when used).

F. Wet Peroxidation vs. Wet Peroxidation assisted with Radiation

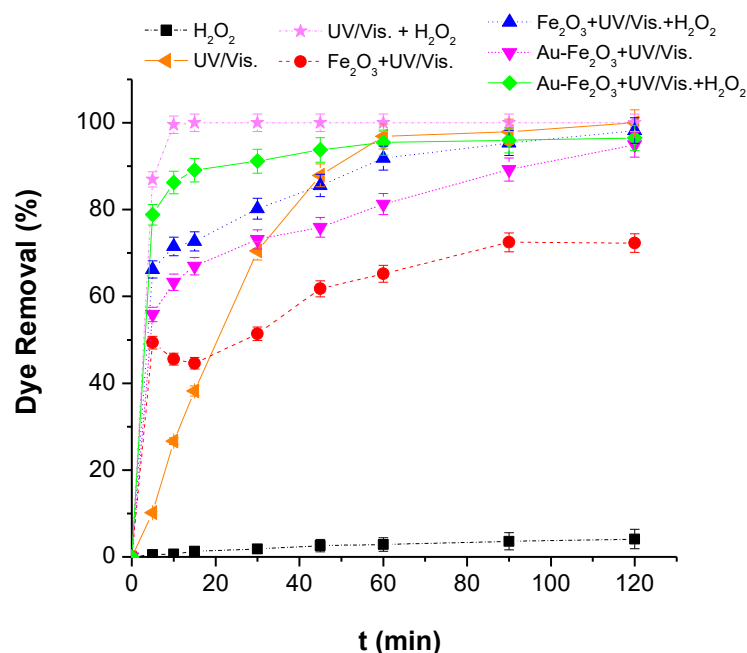


Figure F.1 - Dye removal as a function of time for Fe_2O_3 and 0.8% $\text{Au-Fe}_2\text{O}_3$ (pH=3.0, $T=30\text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2] = 6\text{ mM}$, [Support or catalyst] = 2.0 g/L, $[\text{OII}] = 0.1\text{ mM}$ and radiation= 500 W/m^2 , when used).

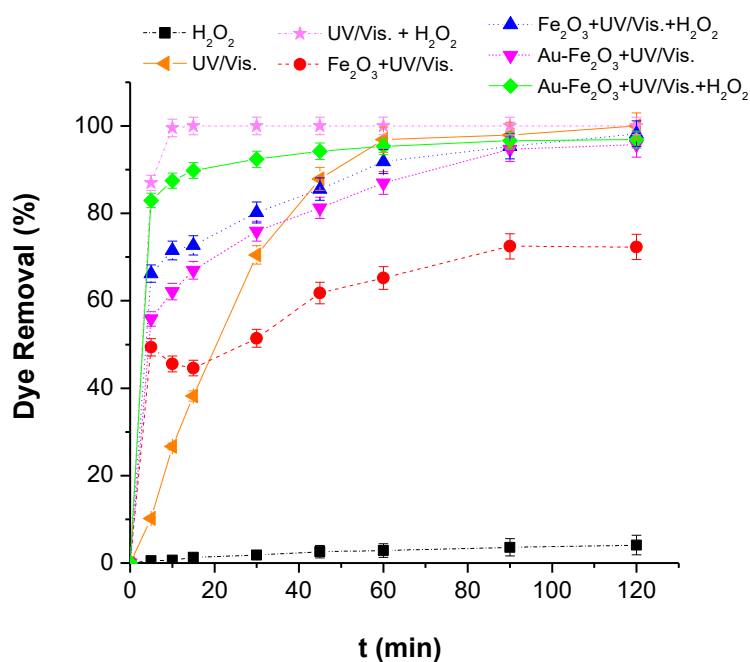


Figure F.2 - Dye removal as a function of time for Fe_2O_3 and 4.0% $\text{Au-Fe}_2\text{O}_3$ (pH=3.0, $T=30\text{ }^\circ\text{C}$, $[\text{H}_2\text{O}_2] = 6\text{ mM}$, [Support or catalyst] = 2.0 g/L, $[\text{OII}] = 0.1\text{ mM}$ and radiation= 500 W/m^2 , when used).

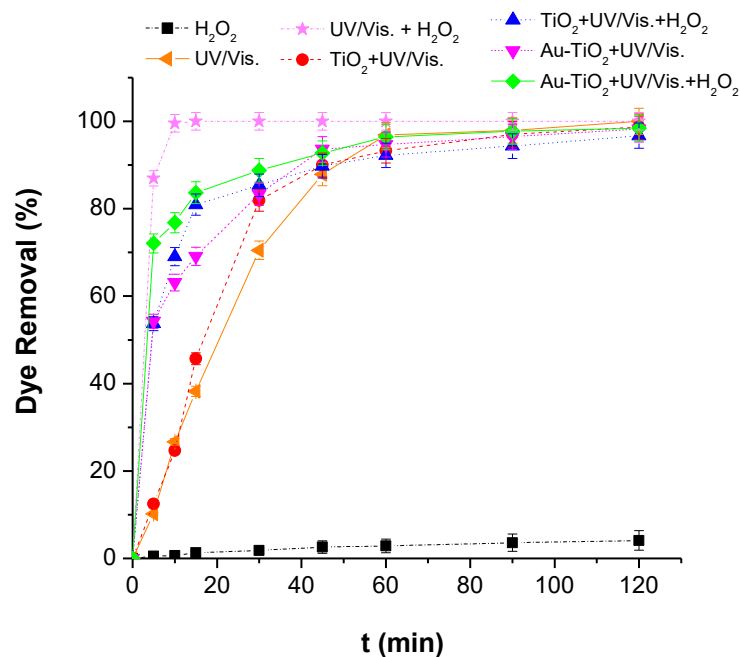


Figure F.3 - Dye removal as a function of time for TiO_2 and Au-TiO_2 ($\text{pH}=3.0$, $T=30^\circ\text{C}$, $[\text{H}_2\text{O}_2] = 6\text{ mM}$, $[\text{Support or catalyst}] = 2.0\text{ g/L}$, $[\text{OII}] = 0.1\text{ mM}$ and radiation= 500 W/m^2 , when used).

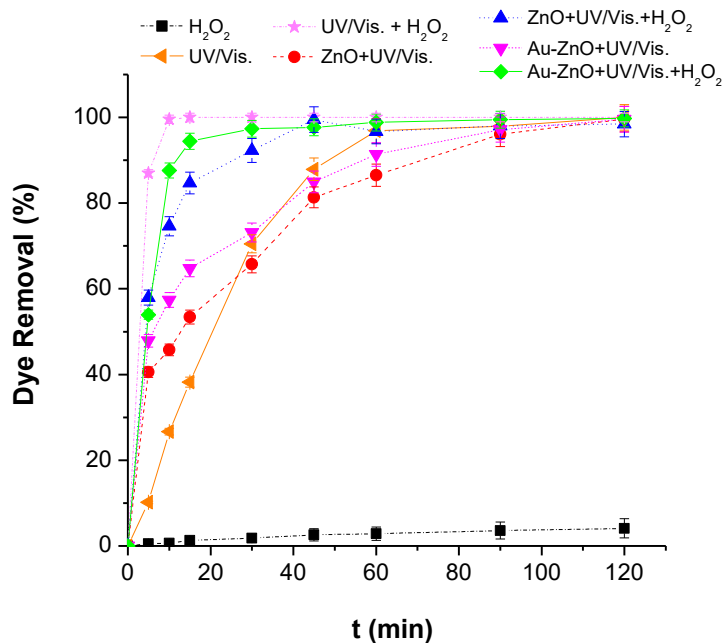


Figure F.4 - Dye removal as a function of time for ZnO and Au-ZnO ($\text{pH}=3.0$, $T=30^\circ\text{C}$, $[\text{H}_2\text{O}_2] = 6\text{ mM}$, $[\text{Support or catalyst}] = 2.0\text{ g/L}$, $[\text{OII}] = 0.1\text{ mM}$ and radiation= 500 W/m^2 , when used).

G. Effect of Radiation Type

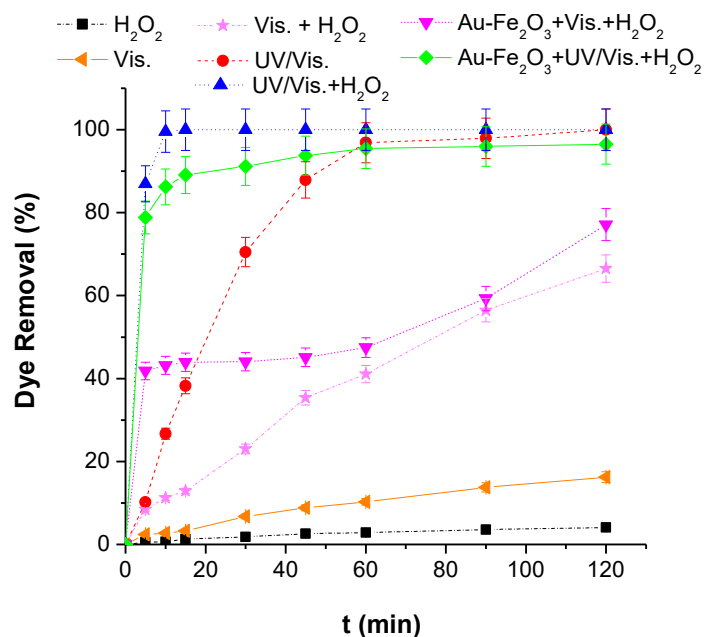


Figure G.1 - Dye removal as a function of time for Fe_2O_3 and 0.8% $\text{Au-Fe}_2\text{O}_3$ with visible radiation ($\text{pH}=3.0$, $T=30^\circ\text{C}$, $[\text{H}_2\text{O}_2]=6\text{ mM}$, $[\text{Support or catalyst}]=2.0\text{ g/L}$, $[\text{OII}]=0.1\text{ mM}$ and radiation= 500 W/m^2 , when used).

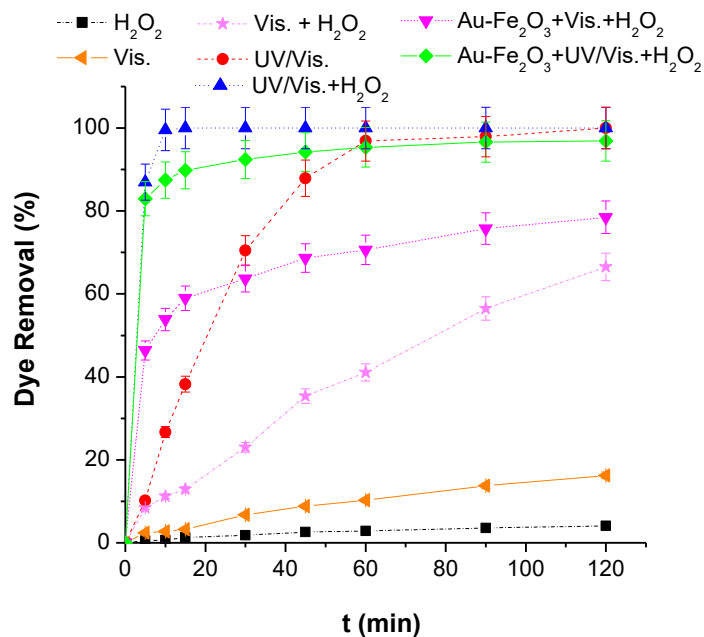


Figure G.2 - Dye removal as a function of time for Fe_2O_3 and 4.0% $\text{Au-Fe}_2\text{O}_3$ with visible radiation ($\text{pH}=3.0$, $T=30^\circ\text{C}$, $[\text{H}_2\text{O}_2]=6\text{ mM}$, $[\text{Support or catalyst}]=2.0\text{ g/L}$, $[\text{OII}]=0.1\text{ mM}$ and radiation= 500 W/m^2 , when used).

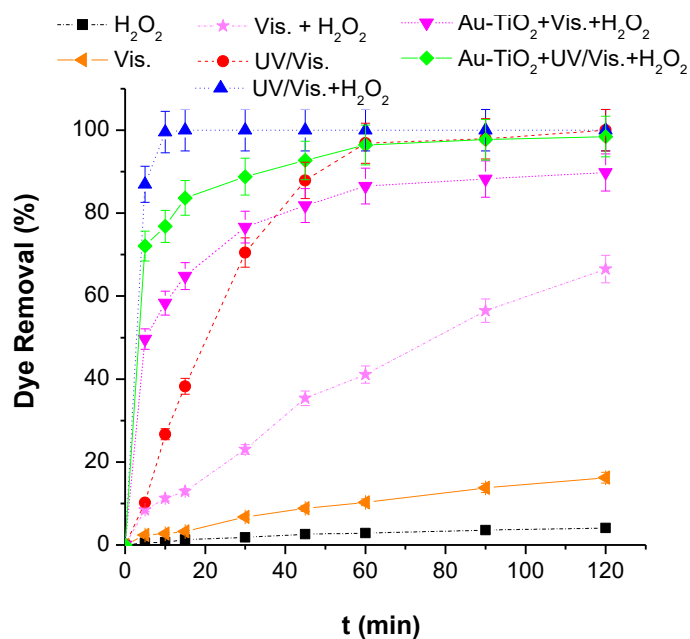


Figure G.3 - Dye removal as a function of time for TiO₂ and Au-TiO₂ assisted with visible radiation (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m², when used).

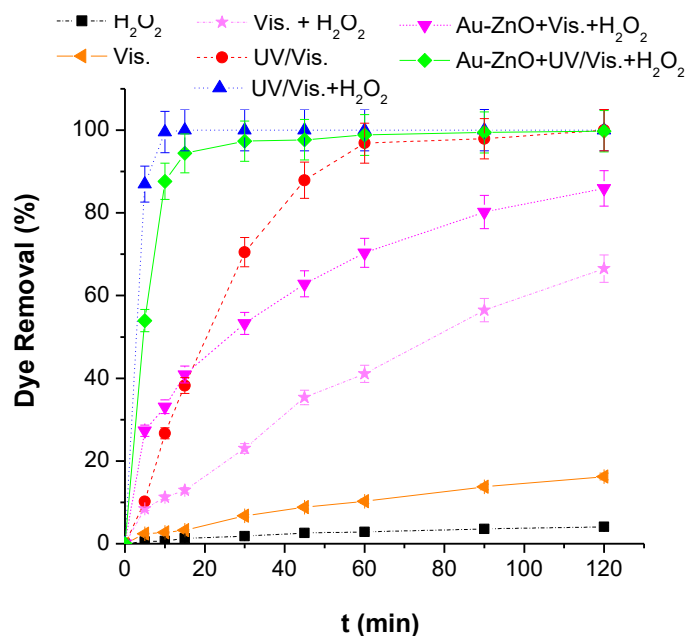


Figure G.4 - Dye removal as a function of time for ZnO and Au-ZnO assisted with visible radiation (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [Support or catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m², when used).

H. Catalyst Stability

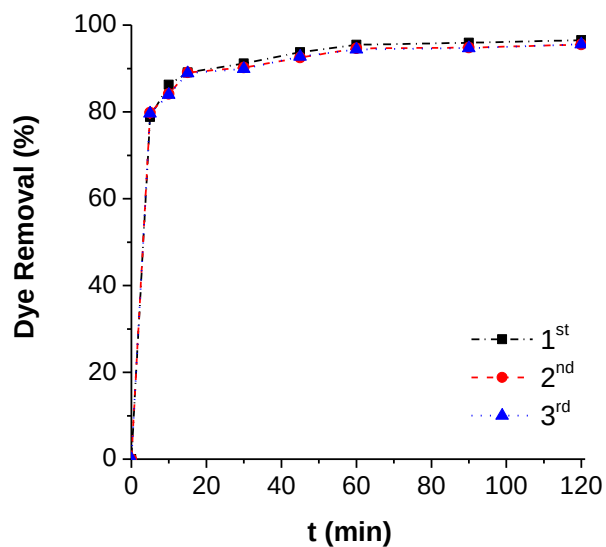


Figure H.1 - Dye removal along time in 3 consecutive reaction cycles for Au-Fe₂O₃ (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m²).

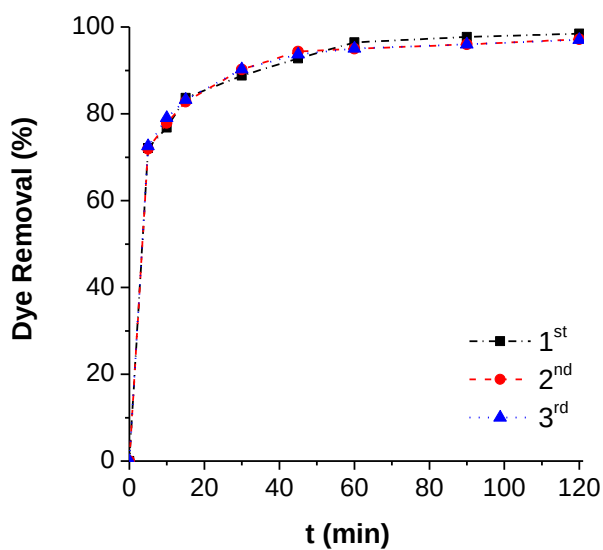


Figure H.2 - Dye removal along time in 3 consecutive reaction cycles for Au-TiO₂ (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m²).

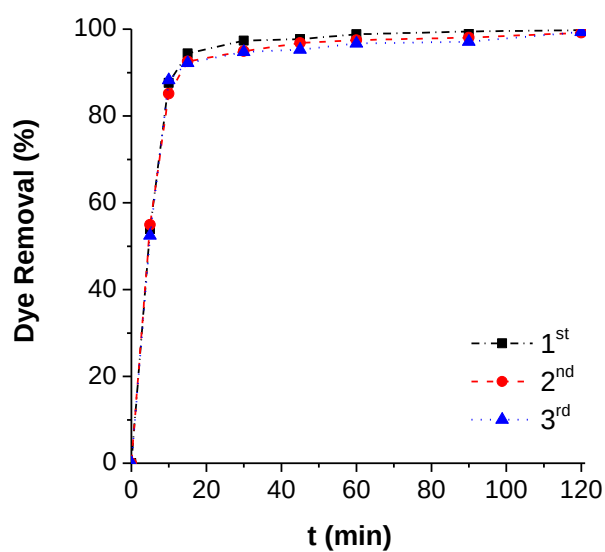


Figure H.3 - Dye removal along time in 3 consecutive reaction cycles for Au-ZnO (pH=3.0, T= 30 °C, [H₂O₂] = 6 mM, [catalyst] = 2.0 g/L, [OII] = 0.1 mM and radiation= 500 W/m²).