

UNIVERSIDADE FEDERAL DE UBERLÂNDIA
FACULDADE DE ENGENHARIA QUÍMICA
Programa de Pós-Graduação em Engenharia Química

IGOR GERALDO FIUZA COSTA

**DEVELOPMENT OF A SYSTEM CONTAINING TITANIUM DIOXIDE AND ALGAE
FOR HEXAVALENT CHROMIUM REDUCTION BY PHOTOCATALYSIS**

UBERLÂNDIA-BRAZIL

2022

IGOR GERALDO FIUZA COSTA

**DEVELOPMENT OF A SYSTEM CONTAINING TITANIUM DIOXIDE AND ALGAE
FOR HEXAVALENT CHROMIUM REDUCTION BY PHOTOCATALYSIS**

Tese de doutorado apresentada ao Programa de Pós-Graduação em Engenharia Química da Universidade Federal de Uberlândia como parte dos requisitos necessários para obtenção do título de Doutor em Engenharia Química, área de concentração em Pesquisa e Desenvolvimento de Processos Químicos.

Orientadoras: Prof^a. Dr^a. Fabiana Regina Xavier Batista

Prof^a. Dr^a. Miria Hespanhol Miranda Reis

Colaborador: Prof. Dr. Francisco Gabriel Acién Fernández

UBERLANDIA-BRAZIL

2022

Dados Internacionais de Catalogação na Publicação (CIP)
Sistema de Bibliotecas da UFU, MG, Brasil.

C837d Costa, Igor Geraldo Fiuza, 1992-
2022 Development of a system containing titanium dioxide and algae for hexavalent chromium reduction by photocatalysis [recurso eletrônico] / Igor Geraldo Fiuza Costa. - 2022.

Orientadora: Fabiana Regina Xavier Batista.

Coorientadora: Miria Hespanhol Miranda Reis.

Colaborador: Francisco Gabriel Ación Fernández.

Tese (Doutorado) - Universidade Federal de Uberlândia, Programa de Pós-Graduação em Engenharia Química.

Modo de acesso: Internet.

Disponível em: <http://doi.org/10.14393/ufu.te.2023.8022>

Inclui bibliografia.

Inclui ilustrações.

1. Engenharia Química. I. Batista, Fabiana Regina Xavier, 1976-, (Orient.). II. Reis, Miria Hespanhol Miranda, 1978-, (Coorient.). III. Ación Fernández, Francisco Gabriel, (Colab.). IV. Universidade Federal de Uberlândia. Programa de Pós-Graduação em Engenharia Química. V. Título.

CDU: 66.0

André Carlos Francisco
Bibliotecário - CRB-6/3408



UNIVERSIDADE FEDERAL DE UBERLÂNDIA
Coordenação do Programa de Pós-Graduação em Engenharia
Química

Av. João Naves de Ávila, 2121, Bloco 1K, Sala 206 - Bairro Santa Mônica, Uberlândia-MG,
CEP 38400-902 Telefone: (34)3239-4249 - www.ppgeq.feq.ufu.br - secppgeq@feq.ufu.br



ATA DE DEFESA - PÓS-GRADUAÇÃO

Programa de Pós-Graduação em:	Engenharia Química				
Defesa de:	Tese de Doutorado, 18/2022, PPGEQ				
Data:	22 de dezembro de 2022	Hora de início:	9:00	Hora de encerramento:	11:30
Matrícula do Discente:	11823EQU003				
Nome do Discente:	Igor Geraldo Fiuza Costa				
Título do Trabalho:	Development of a system containing titanium dioxide and algae for hexavalent chromium reduction by photocatalysis				
Área de concentração:	Desenvolvimento de Processos Químicos				
Linha de pesquisa:	Engenharia Ambiental				
Projeto de Pesquisa de vinculação:	Tratamento de efluentes empregando processos oxidativos e processos biológicos				

Reuniu-se por meio de webconferência, a Banca Examinadora, designada pelo Colegiado do Programa de Pós-graduação em Engenharia Química, assim composta: Francisco Gabriel Acién Fernández - UAL/Almería/Espanha; Ângela Maria Moraes - FEQ/UNICAMP; Adamo Ferreira Gomes do Monte - INFIS/UFU; Juliana de Souza Ferreira - PPGEQ/UFU; Miria Hespanhol Miranda Reis - PPGEQ/UFU, coorientadora e Fabiana Regina Xavier Batista - PPGEQ/UFU, orientadora do candidato.

Iniciando os trabalhos a presidente da mesa, Profa. Dra. Fabiana Regina Xavier Batista, apresentou a Comissão Examinadora e o candidato, agradeceu a presença do público, e concedeu ao Discente a palavra para a exposição do seu trabalho. A duração da apresentação do Discente e o tempo de arguição e resposta foram conforme as normas do Programa.

A seguir o senhor(a) presidente concedeu a palavra, pela ordem sucessivamente, aos(às) examinadores(as), que passaram a arguir o(a) candidato(a). Ultimada a arguição, que se desenvolveu dentro dos termos regimentais, a Banca, em sessão secreta, atribuiu o resultado final, considerando o(a) candidato(a):

Aprovado.

Esta defesa faz parte dos requisitos necessários à obtenção do título de Doutor.

O competente diploma será expedido após cumprimento dos demais requisitos, conforme as normas do Programa, a legislação pertinente e a regulamentação interna da UFU.

Nada mais havendo a tratar foram encerrados os trabalhos. Foi lavrada a presente ata que após lida e achada conforme foi assinada pela Banca Examinadora.



Documento assinado eletronicamente por **Fabiana Regina Xavier Batista, Professor(a) do Magistério Superior**, em 22/12/2022, às 11:36, conforme horário oficial de Brasília, com fundamento no art. 6º, §1º, do [Decreto nº 8.539, de 8 de outubro de 2015](#).



Documento assinado eletronicamente por **Juliana de Souza Ferreira, Professor(a) do Magistério Superior**, em 22/12/2022, às 11:39, conforme horário oficial de Brasília, com fundamento no art. 6º, §1º, do [Decreto nº 8.539, de 8 de outubro de 2015](#).



Documento assinado eletronicamente por **Adamo Ferreira Gomes do Monte, Professor(a) do Magistério Superior**, em 22/12/2022, às 11:51, conforme horário oficial de Brasília, com fundamento no art. 6º, § 1º, do [Decreto nº 8.539, de 8 de outubro de 2015](#).



Documento assinado eletronicamente por **Ângela Maria Moraes, Usuário Externo**, em 22/12/2022, às 14:51, conforme horário oficial de Brasília, com fundamento no art. 6º, § 1º, do [Decreto nº 8.539, de 8 de outubro de 2015](#).



Documento assinado eletronicamente por **Francisco Gabriel Acién Fernández, Usuário Externo**, em 22/12/2022, às 15:14, conforme horário oficial de Brasília, com fundamento no art. 6º, § 1º, do [Decreto nº 8.539, de 8 de outubro de 2015](#).



Documento assinado eletronicamente por **Miria Hespanhol Miranda Reis, Professor(a) do Magistério Superior**, em 29/12/2022, às 14:01, conforme horário oficial de Brasília, com fundamento no art. 6º, §1º, do [Decreto nº 8.539, de 8 de outubro de 2015](#).



A autenticidade deste documento pode ser conferida no site https://www.sei.ufu.br/sei/controlador_externo.php?acao=documento_conferir&id_orgao_acesso_externo=0, informando o código verificador **4158045** e o código CRC **10BC2FAD**.

*I dedicate this thesis to my friends, my family
and for all the amazing people I have met in
this journey.*

“If you want something to die, leave it alone”

Jorge Drexler

Acknowledgements

Aos meus pais Mauricio e Elianamar pela preocupação e cuidado, mesmo quando longe.

À minha irmã Amanda pela paciência e apoio incondicional.

Às minhas orientadoras Prof^a. Dr^a Fabiana Regina Xavier Batista e Prof^a. Dr^a. Miria Hespanhol Miranda Reis por terem me acolhido, pela paciência (principalmente), pela atenção, pelo conhecimento compartilhado e pelos puxões de orelha quando se faziam necessários.

À toda minha família, em especial à minha prima Gleice e minha tia Geusa por terem me recebido em Uberlândia e à minha tia Maria de Lourdes pela ajuda durante o começo do doutorado.

Aos professores do NUCBIO da Faculdade de Engenharia Química da UFU, em especial às Prof^a. Dr^a. Miriam Maria de Resende e Prof^a. Dr^a. Vicelma Luiz Cardoso pelas conversas rápidas, mas que me ajudaram muito.

Ao meu orientador Prof. Dr. Francisco Gabriel Ación Fernández e a toda a equipe do IFAPA pelo apoio na Espanha.

A todos os alunos de iniciação científica que me ajudaram com os experimentos.

Aos colegas de laboratório pelo companheirismo e pelas experiências trocadas, em especial ao Grupo de Processos de Separação por Membranas.

À Camila e à Stella pelo apoio e aprendizado em todas as etapas desse trabalho.

A todos os professores e funcionários da FEQUI/UFU e da UFV por tudo que contribuíram em minha trajetória desde a graduação, especialmente pela oportunidade a mim concedida de fazer parte de um Programa de Pós-graduação em Engenharia Química de tão alta qualidade.

À UFU, à CAPES, à FAPEMIG e ao CNPq pela estrutura e aporte financeiro.

Aos grupos Engenharia Integrada e Bolsistas CAPES pelos momentos de descontração.

Aos meus amigos, colegas e todos aqueles que, de alguma forma, colaboraram para esta vitória.

Summary

List of Figures.....	iv
List of Tables.....	vii
Resumo	viii
Abstract.....	ix
Chapter 1	1
Introduction and objectives.....	1
1.1 Introduction.....	1
1.2 Objectives.....	2
Chapter 2	3
Literature review.....	3
2.1 Heavy metals.....	3
2.2 Chromium	4
2.3 Chromium limits and health impacts.....	4
2.4 Usual treatments of wastewaters contaminated with chromium	5
2.5 Advanced Oxidative Processes	6
2.5.1 Doping of photocatalyst.....	8
2.6 Photocatalysis using algae	9
2.7 Membranes.....	10
2.8 Microalgal bioreactor configurations for wastewater remediation.....	12
2.9 Light penetration.....	16
2.9.1 Solar angles.....	18
2.9.2 Light relations at water.....	21

	<i>Summary</i>
2.9.3 Light attenuation.....	22
2.10 State of art of TiO ₂ and algae for Cr(VI) photoreduction.....	23
Chapter 3.....	26
Materials and methodology.....	26
3.1 Materials.....	26
3.2 Titanium dioxide doping and photocatalysis	28
3.2.1 Sonochemical synthesis of AgNP-TiO ₂ photocatalysts.....	28
3.2.2 Characterizations of AgNP-TiO ₂ particles.....	29
3.2.3 Photocatalytic test for Cr(VI) reduction using AgNP-TiO ₂	29
3.2.4 Immobilization of AgNP-TiO ₂	31
3.2.5 Photocatalytical test for reuse of immobilized AgNP-TiO ₂	32
3.3 <i>Scenedesmus obliquus</i> and <i>Scenedesmus acutus</i> photocatalysis using a raceway reactor and sun light as energy source	32
3.3.1 Raceway reactors.....	32
3.3.2 Light penetration.....	33
3.3.3 Photocatalytical tests for <i>Scenedesmus obliquus</i> and <i>Scenedesmus acutus</i>	33
3.4 <i>Scenedesmus obliquus</i> , <i>Scenedesmus acutus</i> and TiO ₂ photocatalysis using a cylindrical reactor and sun light as energy source for dissolved O ₂ tests.....	33
Chapter 4.....	35
Results and discussion.....	35
4.1 AgNP-TiO ₂	35
4.1.1 Characterization of the AgNP-TiO ₂ particles.	35
4.1.2 Photocatalytic tests	37
4.1.3 Impregnation and reuse	41
4.2 Light penetration.....	45

4.3 Photoreduction tests with raceway reactor	48
4.4 Photoreduction tests for dissolved oxygen.....	52
Chapter 5	54
Conclusions and next steps.....	54
References	56
Attachments	72
Anexo A – Calibration curves for Cr(VI) determination at 540 nm for a) AgNP-TiO ₂ and b) raceway reactors and dissolved O ₂ experiments.....	72

List of Figures

Figure 2.1 – Geometric arrangement of TiO ₂ crystal structures (SHANG-DI and CHING, 1995).....	7
Figure 2.2 – Photoactivation mechanism of a catalyst (adapted of SURI et al., 1993)	8
Figure 2.3 – Photoactivation mechanism of a doped catalyst (adapted from Chakhtouna et al., 2021).....	9
Figure 2.4 – Membrane classification according to the morphology (Based on SCOTT, 1995; HEBERT et al., 2006, LALIA et al., 2013 and STAROV et al. 2008....	11
Figure 2.5 – Categories of microalgal bioreactors for wastewater treatment	13
Figure 2.6 – Relevant angles. Solar position on sky: Solar azimuth (A), altitude (h) and zenith (θ_z) angles. Surface slope (β) and orientation (α).....	20
Figure 2.7 – Radiation relationships at the water surface.....	21
Figure 3.1 – Summary of the steps taken in this work.....	25
Figure 3.2 – AgNP-TiO ₂ Cr(VI) photocatalysis reactor	30
Figure 3.3 – Cr(VI) photocatalysis reactor with fibers(a) and fiber in the reactor (b).....	32
Figure 3.4 – Raceway reactor	33
Figure 3.5 – System for dissolved O ₂ experiments.....	34
Figure 4.1 – TEM images of (a) bare TiO ₂ particles and (b) TiO ₂ particles decorated with Ag nanoparticles at 30 wt% (AgNP30-TiO ₂).....	35
Figure 4.2 – XRD spectrum of Ag-decorated TiO ₂ particles.....	36
Figure 4.3 – Diffuse reflectance spectra of Ag-decorated TiO ₂ particles	37
Figure 4.4 – (a) Photocatalytic reduction of chromium (VI) with bare TiO ₂ and TiO ₂ decorated with 5, 10, 20 and 30 wt% of Ag nanoparticles as catalysts at 1 g/L for initial Cr(VI) concentration of 10 mg/L and (b) linear fitting of experimental data to the pseudo-first-order kinetic model.	38
Figure 4.5 - (a) Effect of the initial Cr(VI) concentration on the activity of the AgNP30-TiO ₂ catalyst at 1 g/L for Cr(VI) photoreduction and (b) linear fitting of experimental data to the pseudo-first-order kinetic model.....	40
Figure 4.6 – Adjustment of the Langmuir-Hinshelwood kinetic model for photocatalytic Cr(VI) reductions with the AgNP30-TiO ₂ catalyst at 1 g/L and at different initial Cr(VI) concentrations	41
Figure 4.7 - SEM images of the produced asymmetric alumina hollow fiber support: (a) overview, (b) cross-section, (c) cross-section with inner surface, (d) outer surface	42

Figure 4.8 – EDS images of the asymmetric alumina hollow fiber support impregnated internally with AgNP30-TiO ₂ ((a) oxygen, (b) aluminum, (c) titanium), (d) silver	43
Figure 4.9 - EDS images of the asymmetric alumina hollow fiber support impregnated externally with AgNP30-TiO ₂ ((a) oxygen, (b) aluminum, (c) titanium), (d) silver	43
Figure 4.10 – Photocatalytic reduction of chromium (VI) with 1g/L AgNP30-TiO ₂ dispersed, immobilized internal and externally for initial Cr(VI) concentration of 10 mg/L	44
Figure 4.11 – Efficiency of Cr(VI) reduction at sequential reuse cycles	45
Figure 4.12 – Light penetration in water without alga	45
Figure 4.13 – Linear fitting of experimental data to determine the light transfer function without alga.....	46
Figure 4.14 – Light penetration in water with <i>Scenedesmus obliquus</i>	47
Figure 4.15 – a) Linear fitting of experimental data to the Beer Lambert's law and b) correlation between the specific absorption coefficient and the algal concentration	47
Figure 4.16 – Influence of sunlight in Cr(VI) reduction	48
Figure 4.18 - Influence of pH and algal concentration for Cr(VI) photoreduction..	49
Figure 4.18 – Influence of algal specie in Cr(VI) photoreduction	49
Figure 4.19 – Influence of initial Cr(VI) concentration	50
Figure 4.20 – Influence of sunlight irradiation.....	50
Figure 4.21- Cr(VI) photoreduction using raceway reactor under initial 50mg/L Cr(VI), pH 3, 0.5 g/L <i>S.obliquus</i>	52
Figure 4.22 – Influence of dissolved O ₂ using 10 mg/L Cr(VI) pH 3 in the presence of a) TiO ₂ and b) <i>S. obliquus</i>	53

List of Tables

Table 2.1 – Main origin of heavy metal pollutants.....	3
Table 2.2 – Specific limits for total chromium, Cr (III) and Cr (VI) according to some regulations.....	5
Table 2.3 – Comparison of packing density of different types of modules	12
Table 2.4 Simplified expression for the incidence angle in special situations.....	20
Table 3.1 – Composition of bubble column media	27
Table 3.2 - Karentol® composition	27
Table 3.3 – Composition of the prepared photocatalysts	28
Table 4.1 - Linear fitting parameters of the pseudo-first-order kinetic model for Cr(VI) photoreductions with the different proposed catalysts at 1 g/L for initial Cr(VI) concentration at 10 mg/L	39
Table 4.2 – Linear fitting parameters to the pseudo-first-order kinetic model for Cr(VI) photoreductions with the AgNP30-TiO ₂ catalyst at 1 g/L for different initial Cr(VI) concentrations	40
Table 4.3 – Cr(VI) reduction (%) and reduction gradient for photocatalytical experiments using the raceway reactor.....	51

Resumo

Devido ao crescimento populacional, a fabricação de produtos tem aumentado e, consequentemente, a geração de efluentes com materiais tóxicos. Entre eles, o cromo(Cr) se destaca. Em seu estado de oxidação 6+, o cromo é tóxico e cancerígeno. Os tratamentos tradicionais de cromo demandam uma alta carga química, sendo importante a proposta de processos alternativos. Assim, os processos de fotocatalise ganharam destaque na área científica devido ao seu aspecto mais sustentável e eficiente. Em trabalho anterior, desenvolvemos um sistema híbrido de dióxido de titânio (TiO_2) e a alga verde *Chlorella vulgaris* imobilizados em fibras ocas de alumina assimétrica para a redução de cromo hexavalente (Cr(VI)) por fotocatalise. No entanto, alguns pontos precisavam ser melhorados e, por isso, decidimos focar em duas áreas diferentes: o TiO_2 e o reator. Para o TiO_2 , as partículas foram dopadas com nanopartículas de Ag a fim de reduzir o band-gap do catalisador utilizando um processo simples e ultrassom. Além disso, as partículas produzidas foram imobilizadas interna e externamente em uma membrana de fibra oca de alumina. Os experimentos foram realizados em um reator do tipo raceway utilizando a luz solar como fonte de energia e as microalgas *Scenedesmus acutus* e *Scenedesmus obliquus*. Para a análise da influência do oxigênio dissolvido, foi utilizado um sistema sob agitação magnética, injeção de oxigênio e nitrogênio e a comparação entre a eficiência do TiO_2 e da alga a 1 g/L. A metodologia ultrassônica produziu partículas de AgNP-TiO_2 com teor de 5 a 50% em peso de teor de Ag. Embora o conteúdo de Ag das partículas de AgNP40-TiO_2 e do AgNP50-TiO_2 tenham sido maiores, a eficiência dessas partículas é reduzida devido à oxidação do Ag. As metodologias de imobilização produziram fibras ocas com partículas imobilizadas. As partículas dispersas e imobilizadas tiveram desempenho semelhante. No entanto, após 10 ciclos de 12 h de reutilização, as partículas imobilizadas tiveram um desempenho superior, sendo uma boa alternativa para redução de custos. A penetração da luz solar no reator raceway seguiu a lei de Beer Lambert. A correlação entre o coeficiente de absorção específico e a concentração de alga foi determinada. Para condições de concentração inicial de Cr(VI) de 1, 5 e 10 g/L, pH 3 e 8, concentração de alga de 0,5 e 1g/L, *Scenedesmus acutus* e *Scenedesmus obliquus* e iluminação baixa e alta para experimentos de 3 h, a espécie de cultivo de algas foi o único fator que não apresentou influência significativa para a fotoredução do Cr(VI) . A partir das melhores condições obtidas de pH 3, 0.5 g/L *S. obliquus* e alta intensidade luminosa, utilizando 50 mg/L de Cr(VI) foi possível obter uma redução de 44.43% e um gradiente de redução de 22.22 mg/L Cr(VI) . A concentração de oxigênio dissolvido não influenciou a aplicação de TiO_2 enquanto a condição anaeróbica favoreceu o processo com alga.

Palavras-chave: cromo, dióxido de titânio, prata, nanopartículas, dopagem, fibra oca, fotocatalise, alga verde, reator raceway

Abstract

Due to population growth, the manufacture of products has increased and, consequently, the generation of effluents with toxic materials. Among them, chromium(Cr) stands out. In its 6+ oxidation state, chromium is toxic and carcinogenic. Traditional chromium treatments demand a high chemical load, and it is important to propose alternative processes. Thus, photocatalysis processes have gained prominence in the scientific area due to their more sustainable aspect and good yield. In a previous work, we developed a hybrid system of titanium dioxide (TiO₂) and the green alga *Chlorella vulgaris* immobilized in hollow asymmetric alumina fibers for the reduction of hexavalent chromium (Cr(VI)) by photocatalysis. However, some points needed to be improved, so we decided to focus on two different areas: TiO₂ and the reactor. For TiO₂, the particles were doped with Ag nanoparticles to reduce the bandgap of the catalyst using a simple process and the use of ultrasound. Furthermore, the produced particles were internally and externally immobilized on a hollow alumina fiber membrane. Finally, for the reactor, the experiments were carried out in a raceway reactor using sunlight as an energy source and the microalgae *Scenedesmus acutus* and *Scenedesmus obliquus*. For the influence of dissolved oxygen, a system under magnetic stirring, injection of oxygen and nitrogen and the comparison between the efficiency of TiO₂ and that of seaweed were used at 1 g/L. The ultrasonic methodology produced AgNP-TiO₂ particles with a content of 5 to 50% by weight of Ag content. Although the Ag content of AgNP40-TiO₂ and AgNP50-TiO₂ particles were higher, the efficiency of these particles is reduced due to Ag oxidation. Immobilization methodologies produced hollow fibers with immobilized particles. Dispersed and immobilized particles performed similarly. However, after 10 cycles of 12 h of reuse, the immobilized particles had a superior performance, being a good alternative for cost reduction. The penetration of sunlight into the raceway reactor followed Beer Lambert's law. The correlation between the specific absorption coefficient and the algal concentration was determined. For conditions of initial Cr(VI) concentration of 1, 5 and 10 g/L, pH 3 and 8, algal concentration of 0.5 and 1g/L, *Scenedesmus acutus* and *Scenedesmus obliquus* and low and high lighting for 3 h, the species of algal cultivation was the only factor that did not present a significant influence on Cr(VI) photoreduction. From the best pH 3 conditions, 0.5 g/L *S. obliquus* and high light intensity, using 50 mg/L of Cr(VI) it was possible to obtain a reduction of 44.43% and a reduction gradient of 22.22 mg/L Cr(VI). The dissolved oxygen concentration did not influence the application of TiO₂ while the anaerobic condition favored the process with seaweed.

Keywords: chromium, titanium dioxide, silver, nanoparticles, doping, hollow fiber, photocatalysis, green alga, raceway reactor.

Chapter 1

Introduction and objectives

1.1 Introduction

The evolution of humankind has affected nature, saving or harming it. In a negative side, the environment has been polluted due to population growth and, consequently, the generation of effluents. Therefore, proper management and toxic wastewater treatment are important to avoid negative environmental impacts. The industries have searched for alternative processes to address this issue. These processes are related with operational costs and generated products. Then, low cost, cleaner and sustainable processes are of interest.

There is a huge environmental concern about heavy metals due to the volume of effluent generated, their toxic nature and lack of water, as heavy metal concentration is one of the factors that regulates indirectly the reuse of treated wastewaters. In electroplating and tannery industries, one of the heavy metals that needs to be treated is chromium.

Chromium (Cr) can be found in natural waters and chromate industries. The Cr main oxidation states are +3 and +6, the latter being the most toxic one due to its higher mobility and solubility (ABREU, 2006).

Physicochemical and biological process treatments are the mainly used. Tannery industries treat their chromium effluents using the activated sludge technology, being necessary further treatments for color reduction. Electroplating industries use methods that involve chemical reduction of Cr(VI) to Cr(III), followed by neutralization and precipitation. However, these processes require high chemical loading and generate wastewater that needs to be treated (ARAÚJO, 2006; IRIKURA et al., 2018).

Among the recent wastewater treatments, the Advanced Oxidative Processes (AOP) have been studied, mainly, to their low cost and long-term sustainability (SURI et al., 1993). Heterogeneous photocatalysis has been studied, mainly, using titanium dioxide (TiO₂) (PENG et al., 2012; XU et al., 2015; WANG et al., 2016; ACHARYA et

al., 2018) and microalgae (SIBI, 2016; LIU et al., 2016; SUZUKI et al., 2017; ARDILA et al., 2017) as photocatalysts.

As these photocatalysts are used dispersed, their immobilization is of interest as it makes possible the reuses, reducing operational costs (WANG et al, 2017, GARCIA-GARCIA and Li, 2013). Therefore, membranes are an alternative for it. Among the different kinds of membranes, ceramic hollow fibers are an option for wastewater treatment as the ceramic material has a higher resistance to more aggressive media and its geometry has a high-density packing. Also, ceramic hollow fibers can be produced by the inversion phase method followed by sinterization. This procedure will produce a membrane with an external sponge layer and an internal filamentous layer, where particles can be deposited (TERRA et al., 2016; TERRA et al., 2017; LEE et al., 2016). However, the evaluation of a proper assembling of catalysts in asymmetric hollow fibers was not yet systematically studied. There is a possible trade-off between supporting the catalyst particles on external and internal surfaces of the hollow fibers. Supporting of the catalyst on the external surface may potentialize the availability of the catalyst active sides to the light exposition, while supporting of the catalyst inside the hollow fiber microvoids may potentialize the reuse of the supported catalyst. To the best of the author knowledge, the evaluation of these both configurations was not yet presented in the literature.

In a previous research, Costa et al. (2019) studied a system with TiO_2 immobilized in alumina hollow fiber membranes coated with microalga *Chlorella vulgaris* for Cr(VI) photoreduction using a halogen tungsten lamp as energy source and noticed that some improvements could be done. These improvements are related to the TiO_2 band gap and the possibility of making the process more sustainable and technological.

1.2 Objectives

This research had as main objective the study of a photocatalytical system for Cr(VI) reduction focusing on modifying three different elements from Costa et al. (2019): the TiO_2 particles, the reactor and the light source. The innovations of this research are the application of a simple process and ultrasound for TiO_2 doping and the use of these particles for inorganic treatment, the immobilization in a ceramic hollow

fiber and, the application of a raceway reactor and sunlight for wastewater treatment.

And, as specific objectives:

- dope TiO_2 with Ag nanoparticles;
- evaluate the photoreduction efficiency of the doped particles in terms of Ag content, process time, pH and initial Cr(VI) concentration;
- immobilize the doped particles in alumina hollow fiber membranes and evaluate the reuse potential;
- evaluate the photoreduction efficiency of a system using a raceway reactor, sun light as energy source and the algae *Scenedesmus acutus* and *Scenedesmus obliquus* in terms of light, pH, Cr(VI) initial concentration and algal concentration
- evaluate the dissolved oxygen effect using TiO_2 and alga.

Chapter 2

Literature Review

This chapter contains the literature review for the fundamentalization of this research. In the following section, concepts and information about chromium, its usual treatments, photocatalysis, doping, membranes, algae, acclimation, sun light and algal reactors will be presented.

2.1 Heavy metals

Heavy metals are elements with atomic number superior to 20 or specific mass higher than 5 g/cm³. Although being essential to the physiology of animals and plants, a major part of the heavy metals are pollutants, since they are not biodegradable and tend to accumulate in living organisms, leading to diseases (BAILEY et al.,1999).

Heavy metals comprehend 65 metal elements. Among the most frequent studied ones are Cr, Cu, Fe, Mn, Mo, Zn, Ni, Cd and Hg, and radioactive elements such as U (GONÇALVES JR et al., 1999). Table 2.1 shows the origin of wastes containing some of these metals. The major environmental problem related to heavy metals is their accumulation in the food chain and its persistency in nature.

Table 2.1 – Main origin of heavy metal pollutants

POLLUTANTS	DISPOSAL ORIGIN
Chromium (hexavalent)	Ceramics, cooling water, dyeing in textile, explosives, galvanizing, mordant, papers, paints, pickling of metals, photography and tanneries industries
Copper (chloride)	Aluminum electroplating, indelible inks
Copper (nitrate)	Textile dyes, photographic prints, insecticides
Copper (sulfates)	Tanning, dyeing, electroplating
Mercury (chloride)	Manufacture of monomers
Mercury (nitrate)	Explosives
Nickel (chloride)	Electroplating and invisible ink
Nickel (ammonium sulfate)	Electroplating
Nickel (nitrate)	Galvanizing
Zinc	Galvanizing
Zinc (chloride)	Paper factory, inks

Source: adapted from Braile and Cavalcanti (1993).

Among the heavy metals, the study of chromium is important due to its toxicity for biological systems and its industrial application, as observed in Table 2.1.

2.2 Chromium

Chromium, in its pure state under natural temperature, is a gray metal, very resistant to corrosion (SILVA, 1998). This element was discovered by Nicolas Louis Vauquelin in 1797 in Siberia and isolated in 1798 (ROCHA, 1983). It was discovered from a red ore, crocoite, containing lead chromate (PbCrO_4). It is the seventh most abundant metal of the planet. Its name has Greek origins (*chroma* = color), because, due to its variable oxidation states, chromium compounds have intense and different colors (ROCHA, 1983). The chromium oxidations states vary between +2 to +6, being the trivalent and hexavalent the most stable (VAZ, 2007).

In non-contaminated aqueous systems, chromium has natural origins, as component of dissolved rocks. In the ground, its mainly in the form of insoluble $\text{Cr}(\text{OH})_3$ or $\text{Cr}(\text{III})$ adsorbed in soil components. Chromium is mainly found in the chromite ore ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$). Finally, in biological materials, it is mainly found in the trivalent and bivalent states (SILVA, 1998).

2.3 Chromium limits and health impacts

Chromium(VI), found, mainly, in the form of chromates and dichromats, has carcinogenic properties to human being. Fumes containing it can cause breathing diseases. The contact with the skin can cause allergic dermatitis and scarring. There is also the possibility to affect the immunological system (ABREU, 2006). Therefore, there are regulations that establish the maximum industrial discharge of chromium in different media, as shown by Table 2.2.

Trivalent chromium, however, is essential for man. It is recommended to consume 50 to 200 μg $\text{Cr}(\text{III})/\text{day}$. Fish, lobster, chicken and brewer's yeast are the highest $\text{Cr}(\text{III})$ containing foods. It has an important role in the metabolism of glucose, lipids and proteins. As so, its low consumption can generate diabetes symptoms, peripheral neuropathy, weight loss and high cholesterol levels (SCHENEIDER et al.,

2001).

Table 2.2 – Specific limits for total chromium, Cr (III) and Cr (VI) according to some regulations

REGULATION	MEDIA	LIMITS
NBR 10004	Solid (leached extract)	5 mg/L (total Cr)
	Ground	100 mg/Kg (Cr VI)
CONAMA	Water	0.50 mg/L (Cr III)
		0.05 mg/L (Cr VI)
U.S.EPA	Solid (leached extract)	5 mg/L (Cr VI)
	Human consumption water	50 µg/L (total Cr)
	Aquatic environments water	100 µg/L (total Cr)
European Legislation	Water	0.2-0.5 mg/L (Cr VI)
	Ground (dried)	150-250 mg/kg (Cr III)
Spain	Continental waters	5 g/L (total Cr)
		5 µg/L (Cr VI)
	Other waters	50 µg/L (Cr VI)
Germany	Ground	100 mg/kg (total Cr)
	Water	2 mg/L (total Cr)
		0.5 mg/L (Cr VI)
	Air	1-5 mg/m ³ (total Cr)

Source: (ABREU, 2006; MMAMRM, 2011)

2.4 Usual treatments of contaminated wastewater with chromium

Wastewater can be discharged if previously treated and/or if in accordance with regulatory parameters. Due to the pollutant potential and low degradability, the disposal of wastewater containing heavy metals is a problem. Therefore, looking for ways to reduce residue generation and costs, the industry has an interest in technologies for this demand.

Different technologies are used for chromium reduction and/or removal from industrial residues. Some of them has been used for decades, while some are recent innovations. Among the factors that affect the type of treatment to be chosen, there are chromium state and concentration, presence of other elements, removal level desired,

technique removal limit, residue generation and operation and disposal costs.

The main techniques for hexavalent chromium removal from industrial wastewaters are reduction, precipitation, ion exchange and evaporative techniques (TOCCHETTO, 2004). Basically, these methods are based on the chemical reduction of Cr(VI) to Cr(III), followed by de neutralization and precipitation. The reduction of hexavalent chromium process is done by adding a reducing agent, such as sodium bisulfite (NaHSO_3), in an acidic media, sulfuric acid (H_2SO_4) for example. Then the pH is increased using hydroxide until neutral pH to precipitate as $\text{Cr}(\text{OH})_3$. However, these treatments produce sludges containing metals that must be sent to controlled landfills for hazardous industrial waste (CIMM, 2005).

2.5 Advanced Oxidative Processes

Studies have been made looking for alternative technologies that enable the reduction of heavy metals from industrial wastewaters. The Advanced Oxidative Processes (AOP) have been recently studied and gained prominence in research as this technology has a higher long-term sustainability. Also, due to the formation of hydroxyl radicals, highly oxidizing agents, the AOPs can be used for a variety of compounds, generating less toxical substances like CO_2 and water (CANDAL et al., 2001). The usage of ozonium, hydrogen peroxide, catalytical decomposition of hydrogen peroxide in acidic media (Photon-Fenton reaction) and semiconductors are some examples of AOPs. The AOPs can be homogeneous or heterogeneous systems with the generation of hydroxyl radical with or without ultraviolet irradiation.

Among the AOPs, the heterogeneous photocatalysis has been studied for wastewater treatment. Fujishima and Honda (1972) described the oxidation of water in a TiO_2 suspension irradiated in a photoelectrochemical cell, producing hydrogen and oxygen. Since it, researches have been dedicated to the understanding of photocatalytical processes related to water oxidation and inorganic ions. Pruden and Ollis (1983a, 1983b) were two of pioneers in the of application of photocatalysis for wastewater treatment. In their works, they demonstrated total mineralization of chloroform and trichlorethylene from inorganic ions during the lighting of a TiO_2 suspension.

The main photocatalysts used in heterogeneous photocatalysis are transition

metal oxides, such as Fe_2O_3 , ZnO , ZnS , CdS and TiO_2 . Among them, titanium dioxide is mostly used due to its high photo sensibility, non-toxic nature, ideal band-gap value for UV radiation and sometimes for natural sunlight, high chemical stability, employability at room temperature and pressure, relatively low cost, easy obtainment and does not require the use of supporting reagents (SAKTHIVEL et al., 2004; ALBERICI and JARDIM, 1997). TiO_2 has three allotropic forms: anatase, rutile, and brookite (Figure 2.1). Anatase is the form that has the highest photoactivity and stability (CANDAL et al., 2001).

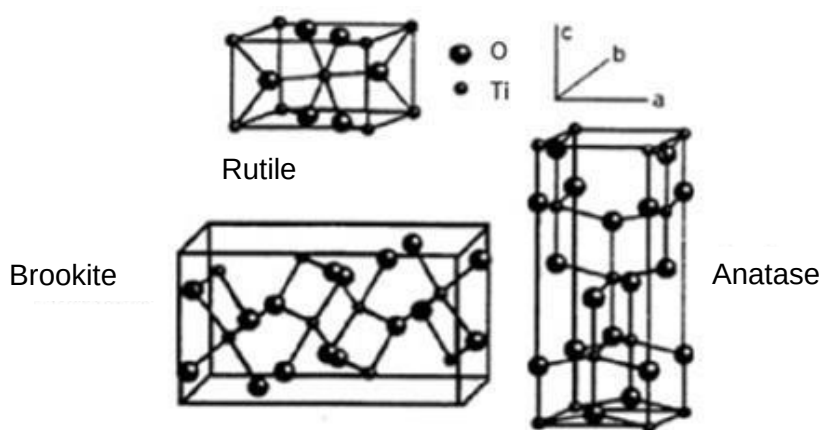


Figure 2.1 – Geometric arrangement of TiO_2 crystal structures (SHANG-DI and CHING, 1995)

In general terms, the heterogeneous photocatalytical process is based in the generation of hydroxyl radicals when a semiconductor solid (photocatalyst) is irradiated with an equal or higher energy radiation than the solid band-gap energy (Figure 2.2). With the absorption of the photon energy, an electron is transferred from the valence band (VB) to the conduction band (CB) forming oxidizing and reducing sites on its surface. The oxidizing sites can oxidize water adsorbed on the surface of the catalyst, generating hydroxyl radicals, which catalyze chemical reactions and reduce dissolved metals. On the other hand, the reducing sites react with dissolved O_2 , generating reactive species such as peroxide and superoxide anions, which oxidize organic compounds to CO_2 and H_2O (FERREIRA, 2005). The efficiency of this process depends mainly on the high probability of electron/hole recombination, which competes with the separation between the photogenerated charges (DOMENÈCH et al., 2001)

and the dissolved oxygen concentration (SAUER, 2002).

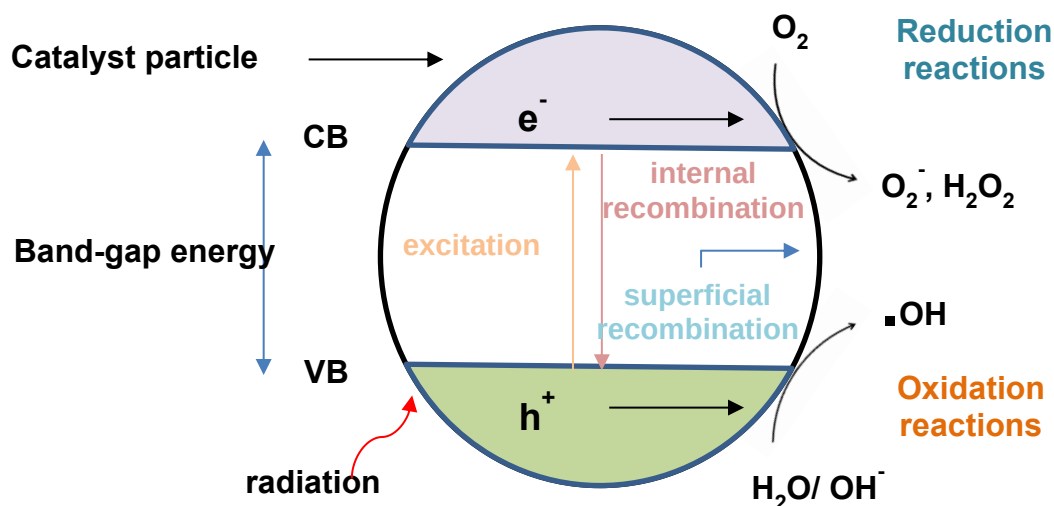


Figure 2.2 – Photoactivation mechanism of a catalyst (adapted of Suri et al., 1993)

2.5.1 Doping of photocatalyst

Despite its good properties, the use of sunlight as an energy source in photocatalytic processes with TiO_2 as catalyst is limited due to the relatively high TiO_2 band gap (3.2 eV) (SCHNEIDER et al., 2014). Also, the electron-hole charge (e^-/h^+) recombination should be considered, since it reduces the reactive of electron/hole pairs into interfacial charge-transfer reactions and, consequently, influences the TiO_2 photocatalytic efficiency (BAYRAK et al., 2016; CHOI et al., 1994). Therefore, noble metals, such as silver (Ag), gold (Au), palladium (Pd) and platinum (Pt), are suggested as electron traps (Figure 2.3), which stabilize the interfacial charge transfers and decrease the chances of e^-/h^+ recombination of TiO_2 particles (AL-MAMUN et al., 2019). TiO_2 particles decorated with Ag nanoparticles have greater visible light activity than bare TiO_2 particles mainly due to the surface plasmon band of Ag (SEERY et al., 2007).

Some procedures are reported in the literature for the synthesis of Ag nanoparticles (AgNPs) supported on TiO_2 , such as electrostatic self-assembly (LI et al., 2017), photoreduction of Ag salts (VIET et al., 2017), and preparation of Ag colloid- TiO_2 dispersions (YU et al., 2017). However, most of these processes for synthesis of AgNPs and their deposition on TiO_2 surface are multistep processes and use several chemical compounds.

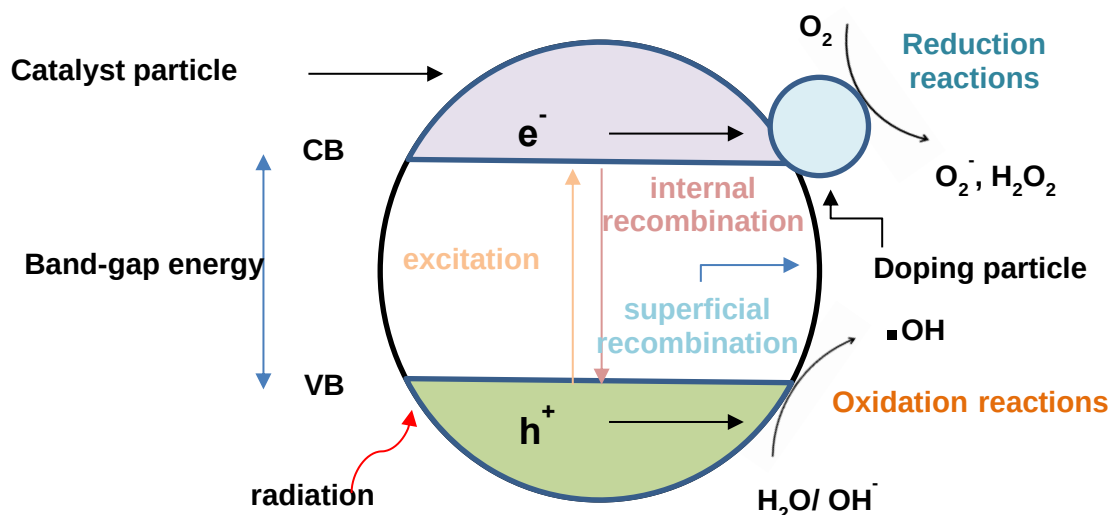


Figure 2.3 – Photoactivation mechanism of a doped catalyst (adapted from CHAKHTOUNA et al., 2021)

Ultrasound-assisted processes are suggested to potentialize the distribution of active phases on a support due to the generated ultrasound shock waves (BELOVA et al., 2011; COMAZZI et al., 2017). The collapse of the ultrasound bubbles, which are generated by acoustic cavitation, improves the nucleation rate in a solid/liquid dispersion (SUSLICK et al., 1995). Stucchi et al. (2018) showed that ultrasound prepared AgNP-TiO₂ catalysts presented greater acetone photodegradation than the catalysts prepared in the absence of ultrasound. However, the enhanced capacity of ultrasound synthesized AgNP-TiO₂ catalysts for Cr(VI) photoreduction was not yet presented in the literature.

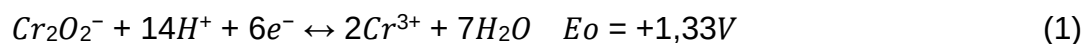
2.6 Photocatalysis using algae

There is a wide variety of biological materials of different structural compositions (bacteria, aquatic organisms, among others) being used for wastewaters with heavy metals treatment. The metal removal potential of these materials has been known for a long time, and their use as an indicator of water pollution is very common (VOLESKY, 2001; MURALEEDHARAN et al., 1991; KRATOCHVIL AND VOLESKY, 1998).

From an economic point of view, the use of algae as photocatalysts is a very advantageous alternative, since these materials are available in large quantities in nature and are relatively easily obtained. In addition, algae have a high efficiency in

removing metal ions from very dilute effluents. According to Pina (2011), the most studied seaweeds are chlorophytes (green algae), rhodophytes (red algae) and phaeophytes (brown algae).

During photoreduction, in acidic medium, chromium(VI) is reduced to chromium(III) according to the following equations (YUN et al. 2004):



It is observed that the algae use the protons existing in the aqueous medium in the reduction process. The electrons necessary for the reduction of chromium(VI) are provided by the biomass itself, resulting in the oxidation of organic compounds, which are partially released into the solution (YUN et al., 2004). Each alga grows in different media and has an ideal pH. Therefore, a different pH can impact the algae, in terms of morphology and metabolism.

2.7 Membranes

A membrane is a semipermeable barrier that separates two phases and partially or totally restricts the transport of one or more chemical species present in the phases. The application of membranes and their efficiency are directly related to their characteristics. The membranes can be classified according to the morphology as shown in Figure 2.4.

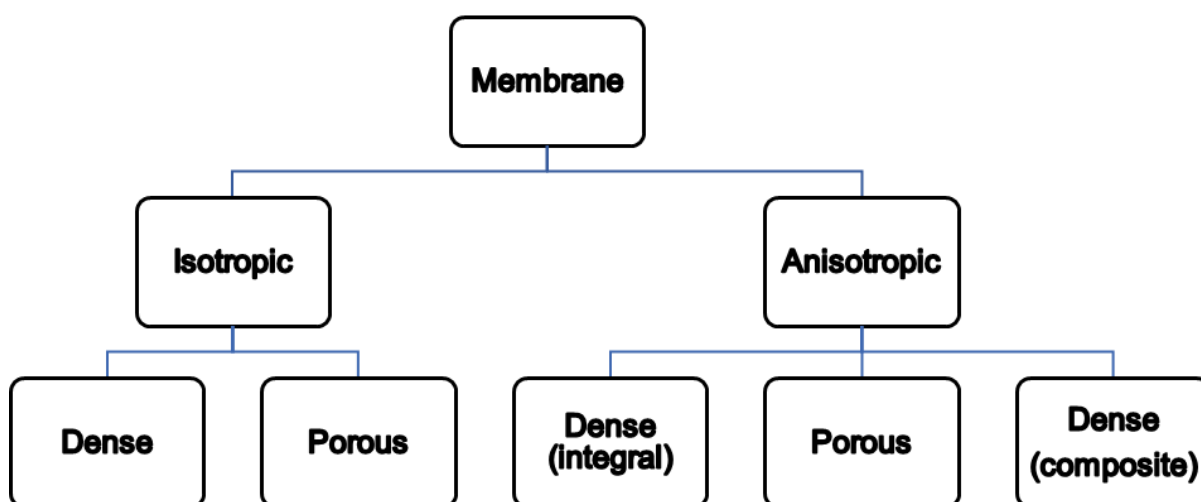


Figure 2.4 – Membrane classification according to the morphology (Based on SCOTT, 1995; HABERT et al., 2006, LALIA et al., 2013; STAROV, 2017)

Membranes can be divided into two major groups: biological or synthetic. Commercial membranes, or even those produced on a laboratory scale, are synthetic and are classified as those made of polymeric (organic) materials and those made of non-polymeric (inorganic) materials (MULDER, 1996). However, non-polymeric membranes are easier to clean and have greater durability due to resistance to conditions such as high temperature and acidic pH (HABERT et al., 2006).

Membranes have different geometries and are packaged in modules, which are defined as the central part of a membrane system. They must be chosen according to factors such as packing density.

Planar geometry membranes are obtained by precipitation from a polymeric solution. The manufacturing process is already widespread and must include all the steps necessary for the phase inversion process. In the manufacturing process, the membrane is conditioned in rolls or cut into slices for later assembly of permeation modules (HABERT, 2006).

The most used modules for flat membranes are plate and frame and spiral. In the board and frame module, the membranes are arranged in parallel, interspersed with spacers and supports. This module has a high manufacturing cost and a low relationship between the permeation area and the module volume, as shown in Table 2.3 (HABERT, 2006).

In the spiral module, the membrane is between two spacers, one of which acts

as a collecting channel for the permeate, while the other provides space for the feed solution to flow. The entire assembly is wrapped around a perforated duct into which the permeate flows, being sealed externally with epoxy resin. This module has a low manufacturing cost and a higher ratio between permeation area and module volume (HABERT, 2006).

Regarding the cylindrical geometry, the main modules are hollow fiber, capillary, and tubular. The technique of cold extrusion with precipitation by immersion is the most used technique for the manufacture of membranes in the form of hollow fibers and capillaries, as it allows greater flexibility to the membrane. The difference between fibers and capillaries is based on the external diameter, so if it is smaller than 0.5 mm, it is a fiber; if it is between 0.5 and 3.0 mm, it is a capillary. The main advantage of this geometry is that it does not need a support, which represents a reduction in the production cost of the module (HABERT, 2006).

On the other hand, tubular membranes are produced in a semi-continuous manner by depositing a film of polymeric solution on the surface of a porous tube and causing this film to precipitate. The porous tube may be of ceramic material or a porous paper type. The module prepared from tubular membranes is similar to that of hollow and capillary fibers. Due to the use of a support to provide mechanical strength, the manufacturing cost is much higher (HABERT, 2006).

Table 2.3 – Comparison of packing density of different types of modules

MODULES	PACKING DENSITY (m^2/m^3)
Tubular	30
Plate/Frame	500
Spiral	900
Capilar	1000
Hollow fiber	10000

Source: (HABERT, 2006)

2.8 Microalgal bioreactor configurations for wastewater remediation

The assimilation of nutrients for growth is facilitated by the process of photosynthesis which is driven by the supply of inorganic carbon, light and temperature. Inorganic carbon, however, is often regarded as non-limiting within wastewater effluent (CROMAR AND FALLOWFIELD, 1997). It is the external factors

of light and temperature which have the greatest influence on growth and productivity and are considered the key design features in the operation of a microalgal bioreactor with studies focusing on light (MESECK et al., 2005; KIM et al., 2013; LEE et al., 2015).

Different bioreactor designs are available to enhance growth and facilitate biomass removal following treatment and include suspended and non-suspended systems with sub-categories of either open to the environment or enclosed (Figure 2.5).

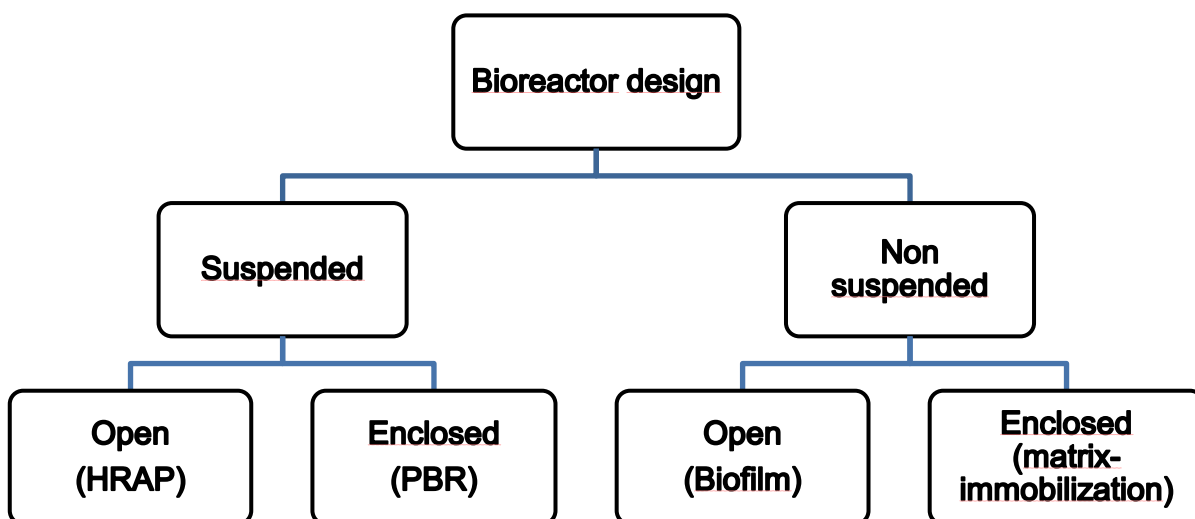


Figure 2.5 – Categories of microalgal bioreactors for wastewater treatment

Suspended cultures enable the microscopic algal cells to move freely within a body of water in dilute concentrations and are most used in microalgal wastewater treatment. The biomass concentration in suspended systems is reasonably low (<2 g/L) but can exceed 4.5 g/L in intensified systems when treating industrial sources (VAN WAGENEN et al., 2015).

Non-suspended systems can be further categorized into matrix-immobilization with microalgal biomass encapsulated in a hydrophilic polymer, reducing the challenges associated with harvesting increases issues related to cellular access to CO₂, nutrients, and photons (MORENO-GARRIDO, 2008). Such systems are considerably less well-established than the suspended systems and questions remain around their suitability and affordability for municipal wastewater treatment.

The suspended and non-suspended bioreactors are then further categorized into open and closed systems. Open systems rely on the external environmental

conditions to promote growth being characterized using solar radiation with sunlight hours and intensity affecting biomass productivity. Open systems are further influenced by external conditions including temperature; rainfall (leading to culture dilution) and contamination by opportunistic species resulting in variability in annual performance.

Alternatively, closed systems contain the biomass within the reactor, thereby minimizing opportunities for contamination and supporting the culture of a monocommunity through separation of the biomass from a potentially growth inhibiting environment. An enclosed system offers greater control of the parameters to optimize growth as irradiance, temperature, evapotranspiration, O₂ and CO₂ concentration, and pH. Also, it encourages increased specific growth greater infrastructure and operational costs limiting their scalability (UGWU et al., 2008).

The choice of bioreactor is evaluated upon performance at an economically acceptable cost, with examples including (but not limited to) high rate algal ponds (HRAP), photobioreactors (PBR), attached microalgal biofilms and matrix-immobilization.

A HRAP is a raceway configured open pond mixed via a paddle wheel to circulate the algal culture and prevent settlement. Sunlight is the primary method of irradiation and as such, culture depths of 20–60 cm are typical to enable optimal light penetration and maximize growth (GARCÍA et al., 2000). Their main advantages are their simplicity, ease of scale-up, and low construction costs. Indeed, raceway reactors are the most cost-effective cultivation system, and their low productivity is compensated by their low capital and operating costs (and high economic value of microalgae) (BANERJEE et al., 2017)

A photobioreactor (PBR) is an example of a closed, suspended system and is available in varying configurations including horizontal or vertical tubular (TPBR) or flat panel reactors (SIERRA et al., 2008). PBR encloses the culture in a series of narrow tubes or panels illuminated by sunlight and/or artificial sources. Enclosing the culture permits the growth of a target species through optimized growth parameters, facilitating an increased biomass concentration in comparison to a HRAP of up to 2.0 g/L when cultured/remediating domestic wastewater effluents. The culture is circulated through the reactor by pumping and degassing/bubbling processes. As a consequence of the sophistication of control, PBRs are expensive to install and operate (GUPTA et al., 2015) and are typically only employed in wastewater treatment as a plentiful source of

low-cost culture medium for growth of a species for the return of a high value product to cover the cost of operation (CANTRELL et al., 2008).

Two types of microalgal biofilm processes exist; these include the use of an inclined flow-way, as known as, algal turf scrubber with biofilm attachment to a surface or submersion of a substrate to support biofilm growth and development (JOHNSON AND WEN, 2010) with practical examples including rotating algal biofilm reactors (RABR). Biomass communities are heterogeneous and multi-layered and change seasonally with reported biomass productivity of up to 60.9 g/m²d and demonstrating enhanced metabolic activity (COHEN, 2001).

Matrix-immobilization is a variant of the attachment theme of reactors through the entrapment of living microalgae cells within a natural or artificial resin (MALLICK, 2002). These resins are hydrophilic in nature with small pores to enable the diffusion of wastewater to the entrapped microalgal cells. Immobilization enables intensification of a biomass concentration greater than a suspended bioreactor. Further benefits of immobilizing a microalgal culture includes the creation of a barrier around the selected species which prevents penetration by other organisms which could inhibit productivity or compete with the selected species (MORENO-GARRIDO, 2008); and following treatment, the biomass can be harvested through the low costing option of gravity settlement, eliminating chemical and energy costs associated with suspended systems. However, reduced space for mobility within the matrix leads to high shear stresses with the matrix imposing additional hindrance to photon accessibility as an area of concern along with the cost of the polymeric matrix when considered at full scale (ZENG et al, 2015).

2.9 Light penetration

The major factors that must be considered in the design of a high-density photobioreactor (PBR) are light, gas transfer into (CO₂) and out of the reactor, balancing medium components and removal of the potentially harmful secondary metabolites. Among these, light is undoubtedly the key parameter in designing a successful PBR.

Two properties of light energy are important for algal growth and metabolism: spectral quality and intensity. Spectral quality is defined by the absorption spectrum for

the chlorophyll and other photosynthetically active pigments, and the photosynthetic efficiency is a function of spectra quality (RABINOWITCH, 1961). The spectrum of emitted light from the light source, the delivery, and the distribution of the light into the culture, and the light scattering and attenuation in the culture must be considered. Supplying and delivering adequate amount of photosynthetically active radiation (PAR) into a photobioreactor offers many challenges.

However, distributing the delivered photons evenly over the illuminating surface and penetrating the photons deep into the culture are another problem. Antenna structures of microalgae are so efficient that they can absorb all the photons that hit them even though the cell cannot use all the photons in photosynthesis. This will cause mutual shading: the cells shielded from light by other cells cannot see the light, and thus consume oxygen by photorespiration. However, the photosynthetic photon flux (PPF) cannot be increased to infinity to overcome this mutual shading.

The effect of light intensities has been studied in connection with photosynthesis. The total amount of organic material which can be produced by growing plant cells from light energy increases as the light intensity increases up to a certain point (saturation intensity), but the amount produced per unit of light decreases rapidly as the intensity of light increases beyond that point. Light of high intensity apparently stimulates a process of photooxidation, which partially offsets some of photosynthesis (THACKER AND BABCOCK, 1957).

As a result, the growth rate shows the expected drop at higher optical densities and increasing the light intensity doesn't increase the growth rate. Further, higher light intensity normally damages the cells. As the cell concentration in the culture increases, the color of cells become lighter. The term 'photoinhibition' is frequently used for the damage caused by excess light (KYLE et al., 1987).

Photoinhibition is also a function of temperature and shows a coupled response with photorespiratory carbon metabolism. This mutual shading will decrease the portion of the cells exposed to the light. Thus, only the cells close to the illuminated surface 'see' the light at high cell densities regardless of supplied light intensity. As a result, apparent oxygen production rate (OPR) will decrease after the cell concentration reached a certain density.

Looking forward to a green technology, the application of natural sunlight as the light source is of interest as it is a clean and renewable energy. However, as

the light intensity is one of the factors that can influence the photocatalytical processes using microalgae, it is important to model the sunlight emission to estimate the light penetration.

2.9.1 Solar angles

Any location on Earth can be mapped on a grid system simply by giving its latitude and longitude angles. Latitude (L) is the angular location north or south of the equator (in general, north is taken as positive, $-90^\circ \leq L \leq 90^\circ$) and longitude is the angular distance of a place east or west of the Greenwich meridian. The position of the Sun relative to that plane is defined in terms of the latitude and several other main angles (Figure 2.6).

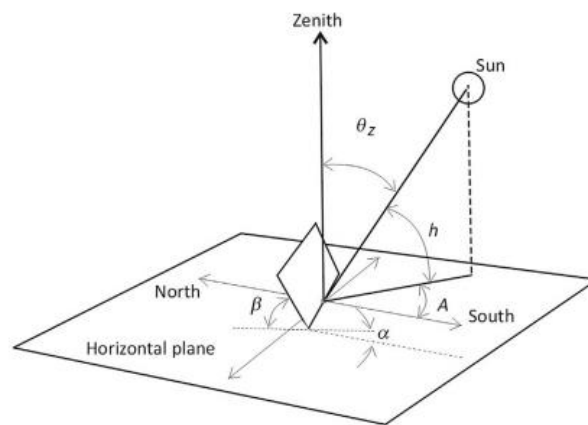


Figure 2.6 Relevant angles. Solar position on sky: Solar azimuth (A), altitude (h) and zenith (θ_z) angles. Surface slope (β) and orientation (α).

-Declination (δ): the angular position of the Sun at solar noon with respect to the plane of the equator (north positive, $-23.45^\circ \leq \delta \leq 23.45^\circ$). The solar noon is understood as the moment when the Sun is on the local meridian. The solar declination can be assumed as constant during any given day for engineering calculations. It varies throughout the year according to the equation of Cooper (Equation 5), angular magnitudes in degrees). It exclusively depends on the day n of the year, being January 1, $n = 1$ and December 31, $n = 365$.

$$\delta = 23.45 \sin \left[\frac{360}{365} (284 + n) \right] \quad (5)$$

-Slope (β): the angle between the plane of the considered surface (solar panel) and the horizontal. In general, $0^\circ \leq \beta \leq 90^\circ$, being slope 0 the surface on the horizontal and slope equal to 90 a façade. When the slope is higher, until 180° , it means that the surface has a downward facing component. It is not a common circumstance in solar systems, although they may appear in energy balances in buildings.

-Orientation (α): this angle is the deviation of the projection on a horizontal plane of the normal to the surface from the south. In most literature references, orientation equal to zero indicates south, east orientation is negative, and west orientation is positive. Differences in this criterion may, however, be found in some sources. The orientation angle is also called a surface azimuth angle.

-Hour angle (ω): angular displacement of the Sun east or west of the local meridian (zero due south, east negative, and west positive). This angle is generated by the rotation of the Earth around its axis, each hour is 15° (360° divided by 24 h), with a negative sign in the morning and positive in the afternoon, at noon $\omega = 0^\circ$ (Equation 6). For a correct calculation, the hour has to be introduced in 0–24 h format.

$$\omega = 15 (\text{hour} - 12) + \frac{\text{min}}{4} + \frac{\text{sec}}{240} \quad (6)$$

-Incidence angle (θ): the angle between the beam radiation on a surface and the normal to that surface (normal incidence is $\theta = 0$).

Two additional very important angles are those required to define the position of the Sun in the sky at any moment. They are the solar altitude angle and the solar azimuth angle. These angles are physical parameters of the position of the Sun with respect to a given place on Earth, and therefore are independent of the inclination and orientation of the surface.

-Solar altitude angle (h): the angle between the horizontal and the line to the Sun ($0^\circ \leq h \leq 90^\circ$) (Equation 7). The complement of this angle is the zenith angle (θ_z), that is defined by the vertical and the line to the Sun (i.e., the angle of incidence of beam radiation on a horizontal surface).

$$h = \arcsen (\sen L \sen + \cos L \cos \delta \cos \omega) \quad (7)$$

-Solar azimuth angle (A): angular displacement from south of the projection of beam radiation on the horizontal plane (Equation 8). In general, A = 0 equals south, A < 0 is east, and A > 0 is west. Different references may, however, be found in the literature.

$$A = \arccos \left(\frac{\cos \delta \cos \omega \sen h \cos L}{\cos h \sen L} \right) \quad (8)$$

The different mathematical relationships among the previously introduced angles allow the definition of the angle of incidence of beam radiation on a surface (θ) as a function of the latitude of the location, the declination, and hourly angle, and the slope and orientation of the surface as shown in Equation 9:

$$\cos \theta = \sin L \sin \delta \cos \beta - \cos L \sin \delta \sin \beta \cos \alpha + \cos L \cos \delta \cos \omega \cos \beta + \sin L \cos \delta \cos \omega \sin \beta \cos \alpha + \cos \delta \sin \omega \sin \beta \sin \alpha \quad (9)$$

Simpler forms of Equation 9 can be implemented for specific situations. Table 3.4 summarizes the common situation in solar applications.

Table 2.4 Simplified expression for the incidence angle in special situations

Particularity	Incidence angle	Comment
Horizontal surfaces $\beta = 0^\circ$	$\cos \theta_z = \sin L \sin \delta + \cos L \cos \delta \cos \omega$ (Eq. 10)	For the horizontal surface, the solar altitude h and the incidence angle θ_z are complementary angles. Then, $\cos \theta_z = \sen h$ (see Eq. 7)
Vertical surfaces $\beta = 90^\circ$	$\cos \theta = -\cos L \sin \delta \cos \alpha + \sin L \cos \delta \cos \omega \cos \alpha + \cos \delta \sin \omega \sin \beta$ (Eq 11)	This is the situation in façade
South-facing, tilted surface (northern hemisphere)	$\cos \theta = \sin (L - \beta) \sin \delta + \cos (L - \beta) \cos \delta \cos \omega$ (Eq 12)	Most fixed solar systems will be in this option. Low temperature solar thermal is the most common example. A similar expression can be used in southern hemisphere with $(L + \beta)$ instead of $(L - \beta)$

2.9.2 Light relations at water

The reflection and refraction of radiation at a water surface is schematically shown in Figure 3.

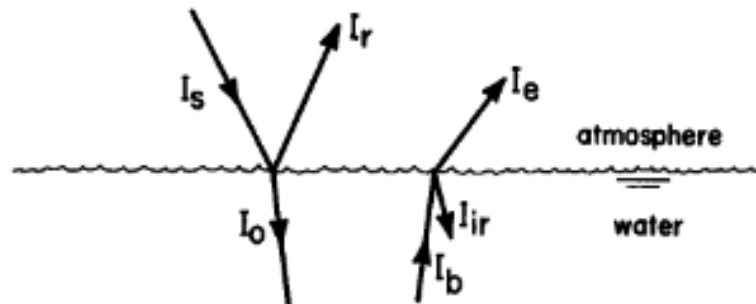


Figure 2.7 Radiation relationships at the water surface

Summarizing total radiation fluxes for all wavelengths into the water surface gives Equation 13.

$$I_s + I_b - I_r - I_e - I_o - I_{lr} = 0 \quad (13)$$

Where I_s is the incoming total radiation flux (all wavelengths), I_b is the back radiation upwelling from the water, I_r is the reflected incoming radiation, I_e is the emerging radiation, I_o is the refracted radiation downwelling into the water and I_{lr} the internally reflected back radiation.

The albedo is defined as the ratio of radiation flux going from the water to the atmosphere relative to the radiation flux from atmosphere to water (Equation 14).

$$albedo = \frac{I_r + I_e}{I_s} \quad (14)$$

Equation 13 may therefore be rewritten as Equation 15.

$$(1 - albedo) I_s = I_o + I_{lr} - I_b \quad (15)$$

The right-hand side of Equation 15 is the sum of all fluxes just beneath the water surface in both the downwelling and upwelling directions. Equation 15 specifies the light intensity below the water surface as a function of light intensity above the water.

Assuming the $I_{lr} \ll I_o$ and that backscattered radiation I_b is a function of

suspended particle concentration in the water, Equation 16 is obtained.

$$I_b = (a + b C) I_o \quad (16)$$

Where a and b are coefficients and C is the concentration (mass/volume) of suspended particles in water.

Therefore, using Equations 15 and 16, Equation 17 is obtained. This equation expresses the downwelling refracted radiation intensity I_o in the water just below the surface as a function of the total radiation I_s coming from the atmosphere. It is particularly useful to predict underwater light availability from total radiation measurements above the water. The albedo in Equation 17 is generally dependent on zenith angle, roughness of the water surface, and water color; i.e., a large zenith angle will increase the albedo.

$$I_o = I_s \frac{1-\text{albedo}}{1-a-bC} = I_s F(C) \quad (17)$$

Where $F(C)$ is the transfer function for total radiation through the water surface.

2.9.3 Light attenuation

Optical measurements of light intensity distribution within the photosynthetic culture are extremely difficult due to the complicated nature of scattering, such as reflection, refraction, and diffraction in addition to the light absorption by the cells. Beer-Lambert's law (Equation 18) is usually used to estimate light intensity within a culture medium.

$$\log \frac{I_o}{I} = a X x \quad (18)$$

where, I_o and I_x are the light intensities at the surface and depth of x (distance from the illuminating surface), respectively, X is the particle (or cell) concentration and a is the specific absorption coefficient.

2.10 State of art of TiO₂ and alga for Cr(VI) photoreduction

In the photoreduction of Cr(VI), the most recent works in relation to TiO₂ have focused mainly on the fabrication and doping of the material. Wang et al. (2016) studied the influence of calcination temperature on the manufacture of Ag/TiO₂ particles and its effect on Cr(VI) photocatalysis. The most promising result was obtained at a temperature of 350°C with about 100% reduction of Cr(VI) in the conditions of 1 g/L photocatalyst, 160 µmol/L Cr(VI) and pH 2. In addition, the catalyst remained stable after 5 cycles of 30 min each. Dozzi et al. (2012), in turn, have already studied the doping of TiO₂ with gold nanoparticles.

Xu et al. (2015) studied the photoreduction of Cr(VI) and the removal of Cr using Fe(II) doped TiO₂ hollow spheres. The methodology used involved a thermally easy process. An emulsion with TiOSO₄·2H₂O (1.46 g), absolute alcohol (22 mL), deionized water (4 mL), glycerol (9 mL) and FeSO₄·7H₂O (0.2 g) was mixed and stirred for 1 h. The emulsion was then moved to an autoclave and kept at 110°C for 24 h, followed by cooling to room temperature. Finally, the precipitate was removed from the autoclave, washed with alcohol and dried at 60°C for 1 h. The mass of FeSO₄·7H₂O was varied by 0; 0.1; 0.3 and 0.4 g). About 99.99% of Cr(VI) was reduced in the initial condition of 102.3 ppm and 99.01% to 153.4 ppm under 3 h of sunlight. The synergy between the photoelectrons generated by TiO₂, Fe(II) ions and reduced Fe contribute to the reduction of Cr(VI).

Acharya et al. (2017) performed Cr(VI) photoreduction using reduced graphene oxide doping. The modification in TiO₂ resulted in surface improvement, increased light absorption and electron promotion in the catalyst bands. The increase in the surface increased the adsorption of Cr(VI), facilitating the transport of electrons and reducing the recombination of charges. In this work, optimal conditions were defined for maximum reduction of pH ≤ 5.5, initial concentration of Cr(VI) 5.0–50.0 mg/L, catalyst dosage 0.2–1.0 g/L and time lighting 15–360 min.

Zhao et al. (2017) fabricated TiO₂ hollow spheres and studied the effect of this catalyst on Cr(VI) photoreduction. The spheres were obtained by a chemical induction process with alcohol and acidic medium and presented uniform diameter distribution and high specific area. In addition, they showed excellent activity in reducing Cr(VI), 100% in 30 min at pH 2 and initial concentration of 2.0 µg/mL and high resistance to

the action of interferents.

Wu et al. (2013) produced a film with TiO₂ and performed Cr(VI) photocatalysis under visible light. The Cr(VI) reduction efficiency was higher under acidic conditions in the absence of organic compounds and with the process time of 1h. The film showed a long duration and great capacity, being able to be used in favorable environmental conditions.

Jiang et al. (2012) fabricated TiO₂ nanotubes and studied the effect of calcination temperature on adsorption and photocatalytic activity. The results showed that both are strongly dependent on the calcination temperature. The photocatalytic process followed the first order kinetic model and the nanotubes calcined at 400 °C showed higher efficiency.

Regarding the alga, there is still no established mechanism for its activity, and photocatalysis phenomena are still being studied. Deng (2006) studied the photoreduction of Cr(VI) in the presence of the alga *C. vulgaris*. In this work, a metal halide lamp ($\lambda = 365$ nm, 250 W) was used. The photoreduction rate increased with increasing algal concentration, increasing light exposure time, decreasing initial Cr(VI) concentration and decreasing pH. At pH 6, no significant removal of Cr(VI) was observed.

Regarding hybrid systems, there are still not many works addressing the treatment of Cr. Wang et al. (2017) who fabricated a polymeric nanofiber membrane with alga and Ag-doped TiO₂. The addition of seaweed increased the photoremoval of Cr(VI) under visible light irradiation, and a mechanism for the process has even been proposed. The oxidative effect imposed by TiO₂/Ag on the alga was verified, which can cause the oxidation of lipids in the algal cell wall. Also, during the photocatalysis process, the alga presented two advantages: the release of substances that can inhibit electronic recombination and the release of organic matter due to photodegradation. The hybrid nanofiber was easy to recover and maintained a high photocatalytic activity after 5 cycles of reuse.

Costa et al. (2019) who fabricated a ceramic alumina hollow fiber membrane with TiO₂ and alga. The produced fiber created a barrier between the internal immobilized TiO₂ and the deposited alga, increasing the system activity. Also, an initial Cr(VI) concentration of 10 mg/L and dosages of 1 g/ L of TiO₂ and alga, the hybrid system resulted in total Cr(VI) reduction after 16 h of process. Additionally, the

efficiency of the hybrid system for Cr(VI) reduction was reduced in only 9% after 5 cycles of reuse and in 42% after 10 cycles of reuse.

Chapter 3

Materials and methods

In the chapter, the materials and the methodologies used in the development of this work are described. Figure 3.1 shows the stages of this work.

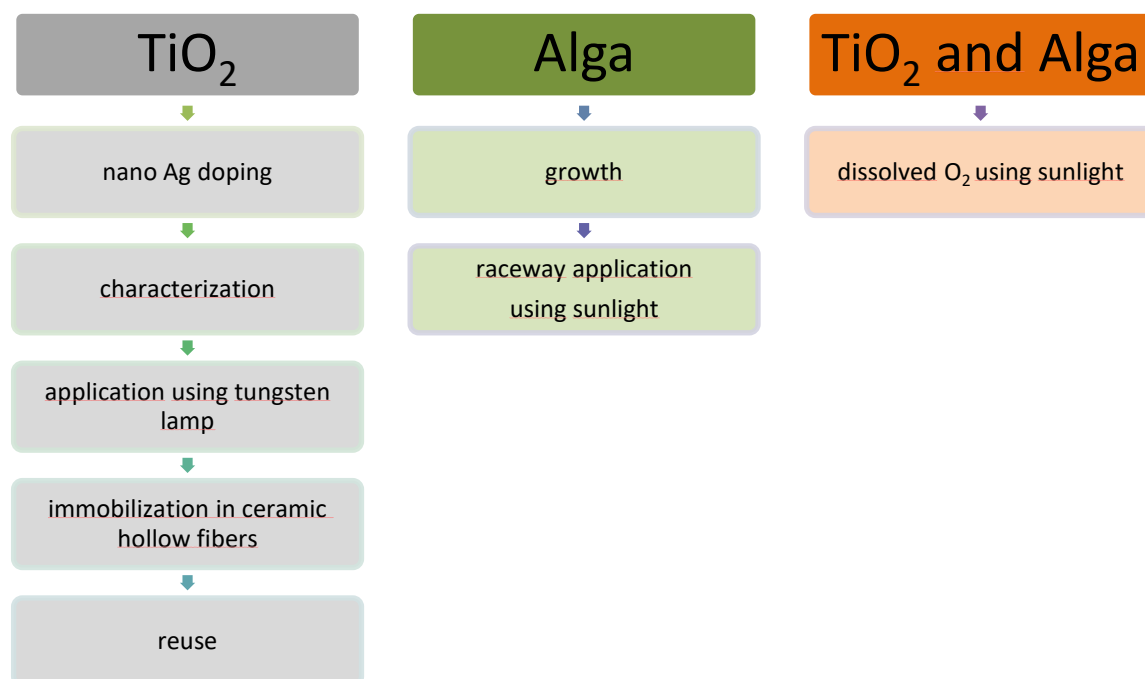


Figure 3.1 – Summary of the steps taken in this work

3.1 Materials

For the photocatalysis with doped particles, titanium dioxide (99% purity, Reagen) was used. Silver nitrate (AgNO_3 , 98%, Exodo Científica, Brazil) was used as a silver precursor. The other used materials were polyvinylpyrrolidone (PVP90, Fluka Chemika) and sodium borohydride (NaBH_4 , 98%, Exodo Científica, Brazil) was used to prepare the chromium solutions. For photocatalytic tests, potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, 99%, Vetec, Brazil) was used to prepare chromium solutions. Asymmetric hollow fibers were produced from a ceramic suspension composed of alumina (Al_2O_3 , 1.0 μm , alpha, 99.9% metal base, surface area 6-8 m^2/g , Alfa Aesar), dimethyl

sulfoxide (DMSO, Vetec, Brazil), poly(ethylene glycol) 30-dipoly(hydroxystearate) (Arlacel P135, Croda) and polyethersulfone (PES, Verdal 3000 P, Solvay). The halogen tungsten lamp (100 W, 220 V, FLC) was acquired in a local market.

The green algae *S. obliquus* (Hungary) and *S. acutus* (Peru) cultures were inoculated and grown in a sterile modified Arnon medium with the addition of NaNO_3 as a nitrogen source. The algae were kept in a 5 L batch mode, at 23 ± 2 °C, pH 8.0 ± 0.1 and $150 \mu\text{mol/m}^2\cdot\text{s}$ until the algal concentration reached 1 g/L. Then they were inoculated and grown in 85 L bubble columns in a media composed by fertilizers suggested by Morillas-España et al. (2022) (Table 3.1) at controlled pH 8 and ambient light illumination. The Karentol® fertilizer (Konegard, Barcelona, Spain) composition is shown in Table 3.2. The columns were refreshed each 7 days or when 40 L were used in the same period of time.

Table 3.1 – Composition of bubble column medium

Fertilizer	Solid mass (g) per liter of medium
NaNO_3	0.90
MgSO_4	0.18
HK_2PO_4	0.14
Karentol®	0.03

Table 3.2 - Karentol® composition

Reagents	Conc. (% m/m)
Bo	0.5
Cu	0.3
Cu EDTA	0.29
Fe	7.5
Fe EDTA	7.13
Mn	4
Mn EDTA	3.8
Mo	0.2
Zi	0.5
Zi EDTA	0.48

An experiment to evaluate the application of bare TiO₂ using the raceways reactors was done. Due to the particle characteristics and the raceway reactor hydrodynamic, the particles weren't properly dispersed and, therefore, further modifications are needed to be done. Therefore, the TiO₂ and the algae were used in another system to evaluate the dissolved O₂ effect.

The alumina fibers were produced by the research group in membrane separation process at FEQUI UFU. These fibers were manufactured by the phase inversion process followed by sintering (Terra et al., 2017). The ceramic suspension was prepared in the following proportion: 58% by weight of alumina (1.0 µm, alpha, 99.9% metallic base, surface area of 6-8 m²/g, Alfa Aesar); 36.1% by weight solvent (DMSO, P.A, Vetec); 0.4% by weight of Arlacel P135 (Croda, Brazil) and 5.5% by weight of polyethersulfone (PESf, Verdal 3000P, Solvay). The extrusion was performed using an extruder with 3 mm of external diameter and 1.2 mm of internal diameter with two inlets: one for the ceramic suspension and another for the internal fluid responsible for maintaining the internal lumen of the nascent fiber. Pure DMSO was used as the internal fluid. The flow of the ceramic suspension and of the internal fluid used during the spinning of the fibers were controlled and monitored using two pumps (Harvard Apparatus, model XHF) and were maintained at 15 mL/min. The fibers were directly discharged (zero air gap) into the external coagulation bath containing tap water. The fiber precursor was then sintered at 1350 °C in a muffle furnace (Carbolite TZF 15) following the following temperature ramp: from room temperature to 300 °C at 1 °C/min, from 300 to 600 °C at 2 °C/min, maintaining at 600 °C for 1 h, from 600 to 1350°C at 5°C/min, keeping at this temperature for 5 h, then reducing the ambient temperature to 5°C/min.

3.2 Titanium dioxide doping and photocatalysis

3.2.1 Sonochemical synthesis of AgNP-TiO₂ photocatalysts

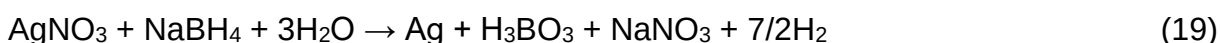
Decoration of micro-sized TiO₂ with Ag nanoparticles was based on the synthesis reported by Stucchi et al. (2018) and Goharshadi and Azizi-Toupkanloo (2013). Two precursor solutions were prepared. In the first solution, 0.02 g of PVP (stabilizing polymer), 2 g of TiO₂ and different amounts of AgNO₃ (Table 3.3) were added in 100 mL of distilled water. The second precursor solution was prepared by

dissolving NaBH₄ (the reducing agent) in MilliQ water to obtain a 0.1 M NaBH₄ solution.

Table 3.3 - Composition of the prepared photocatalysts.

Denomination	TiO ₂	AgNP5-TiO ₂	AgNP10-TiO ₂	AgNP20-TiO ₂	AgNP30-TiO ₂	AgNP40-TiO ₂	AgNP50-TiO ₂
Ag NP (wt %)	0	5	10	20	30	40	50

The first solution was magnetically stirred in an ice bath for 10 min followed by the addition of the NaBH₄ solution by dropping for 2 min. Equation 19 shows the chemical equation of the process. Afterward, an Erlenmeyer of 250 mL containing 115 mL of the mixed solution was placed in the middle of an ultrasound bath (power of 300 W, frequency of 40 kHz, bath volume of 9.5 L, Ultrasonic model Q9.5/40A, Brazil) for 2 h. The finished dispersion was washed at least 8 times with distilled water followed by centrifugation at 5000 rpm for 10 min. The separated solid particles were then dried at 100°C for 24 h and calcinated at 400°C for 2 h.



3.2.2 Characterizations of AgNP-TiO₂ particles

Morphological analyses of the produced AgNP-TiO₂ particles were performed by Transmission Electron Microscopy (TEM, HR, HITACHI Model HT7700). The AgNP-TiO₂ particles were characterized concerning their crystallinity in an X-ray diffractometer (XRD, Shimadzu, XRD - 6000) with an X-ray tube containing a copper anode (Cu-K α wavelength, λ = 1.54056 Å), at a scan rate of 2° min⁻¹, 2 θ ranging from 10 to 80° with step of 0.02°, the voltage at 40 kV and current at 30 mA. The diffraction peaks were compared to the ICDD Powder Diffraction File (PDF) database. Diffuse reflectance spectra were carried out in a Avantes AvaSpec-ULS2048CL-EVO spectrometer equipped with integrating sphere. Spectra were collected within 250-700 nm range and BaSO₄ was employed as 100% reflectance standard.

3.2.3 Photocatalytic tests for Cr(VI) reduction using AgNP-TiO₂

The photocatalytic experiments were carried out with individual dosages of TiO₂

or AgNP-TiO₂ at 1 g/L in a Cr(VI) solution at 10 mg/L, as suggested in the literature (COSTA et al., 2019). The pH of the medium was controlled at 2 by adding small volumes of 1N H₂SO₄ or 1N NaOH solutions (XIA et al., 2018). Additional experiments were carried out by varying the Cr(VI) initial concentration from 5 to 20 mg/L with the AgNP30-TiO₂ catalyst at 1g/L. For each experiment, the solution was mixed under magnetic stirring at 120 rpm in the dark for 30 min to reach adsorption-desorption equilibrium (XIA et al., 2018). After this time, the 150 mL glass reactor (100 mL working volume) was placed 10 cm away from the tungsten halogen lamp (100 W, 220 V, FLC, Brazil) (Figure 3.2). Individual photocatalytic tests were performed with pure TiO₂ or AgNP-TiO₂ catalysts for a total reaction time of 180 min. Aliquots of the Cr(VI) solution were withdrawn from the reactor at specific time intervals for analyses of chromium concentration according to the diphenylcarbazide method (SULE AND INGLE, 1996). Prior to Cr(VI) concentration analyses, samples were filtered through a 0.22 µm PTFE syringe filter.

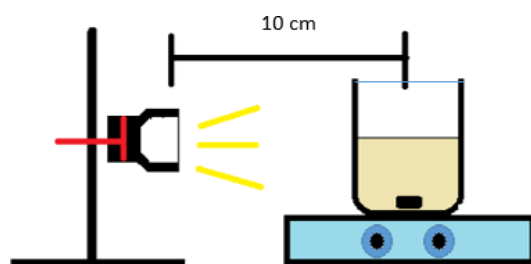


Figure 3.2 – AgNP-TiO₂ Cr(VI) photocatalysis reactor

Experimental data of Cr(VI) reductions were adjusted to the pseudo-first-order reaction model (Equation 20). The obtained apparent rate constants (k_{app}) at each initial Cr(VI) concentration were then adjusted to the Langmuir-Hinshelwood model (Equation 21).

$$\ln \frac{C_0}{C} = k_{app} t \quad (20)$$

Where C_0 is the initial concentration of Cr(VI) (mg/L), C is the concentration of Cr(VI) at the time t (mg/L), t is the reaction time (min) and k_{app} is the apparent rate constant (min⁻¹).

$$\frac{1}{k_{app}} = \frac{1}{k_r K_{LH}} + \frac{C_0}{k_r} \quad (21)$$

Where K_{LH} is the adsorption equilibrium constant (L/mg) and k_r is the reaction rate constant (mg/L min).

3.2.4 Immobilization of AgNP-TiO₂

As the asymmetric alumina hollow fibers have two accessible surfaces, the AgNP30-TiO₂ were immobilized internally and externally in these supports. For both immobilizations, the fibers were cut to measure 3.5 cm each. Internally, the AgNP30-TiO₂ particles were immobilized in the micro-voids of the produced supports according to the methodology proposed by Garcia-Garcia and Li (2013) with adaptations. Before the AgNP30-TiO₂ impregnation, one of the ends of each fiber was sealed with PTFE tape to avoid the flow of the AgNP30-TiO₂ dispersion. The AgNP30-TiO₂ dispersion was prepared to obtain a 50 mL dispersion at a concentration of 0.2 mg/mL and sonicated for 30 min. Then, the AgNP30-TiO₂ dispersion was manually injected to the open side of a fiber. This injection was repeated for approximately 3 times.

Externally, the alumina hollow fibers were coated with AgNP30-TiO₂ according to the vacuum assisted dip-coating methodology proposed by Ishak et al. (2020) with adaptations. Before the AgNP30-TiO₂ impregnation, one of the ends of each fiber was sealed with PTFE tape to avoid the flow of the AgNP30-TiO₂ dispersion. The AgNP30-TiO₂ dispersion was prepared to obtain a 50 mL dispersion at a concentration of 0.2 mg/mL and sonicated for 30 min. Then, the AgNP30-TiO₂ dispersion was added to a 25 ml graduated cylinder and a fiber connected to a vacuum bomb was put inside of the flask with the dispersion. The vacuuming was proceeded at 300 mmHg for 5 min and the volume inside the cylinder was maintained during the process.

Finally, for both AgNP30-TiO₂ impregnations, the fibers were dried at 80 °C for 12 h. The loading of AgNP30-TiO₂ in the fiber substrate was obtained by measuring the weight of the dried fiber before and after AgNP30-TiO₂ impregnation. The fibers before and after AgNP30-TiO₂ impregnation were also characterized by energy dispersive X-ray spectroscopy, as further described.

3.2.5 Photocatalytical tests for reuse of immobilized AgNP-TiO₂

For the TiO₂ and AgNP30-TiO₂, the dosage of 1g/L was used. For the impregnated systems, a total of 20 hollow fibers were assembled in a styrofoam holder, which was immersed in the Cr(VI) solution (Figure 3.3). This amount of 20 hollow fibers was accounted to contain 100 mg of AgNP30-TiO₂ particles. The active extension of the hollow fibers was at total contact with the Cr(VI) solution. The reuse of the hybrid system was evaluated in 10 sequential batch experiments of 12 h each one. Fresh Cr(VI) solutions were used in each batch experiment and the fibers were reused without any cleaning or other recovery procedures. For the systems using the particles not immobilized, the solutions were centrifuged at 4000 rpm for 10 min at the end of each batch for reuse.

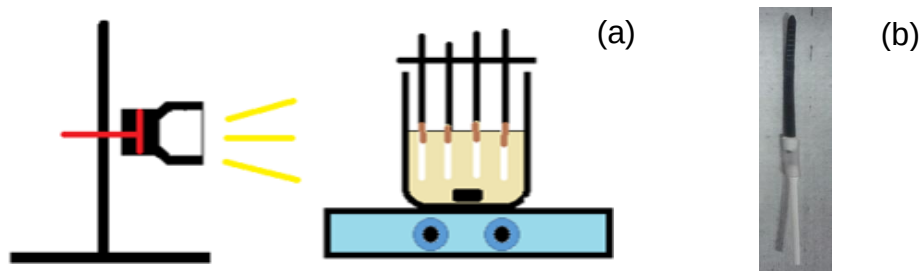


Figure 3.3 – Cr(VI) photocatalysis reactor with fibers (a) and fiber in the reactor (b)

3.3 *Scenedesmus obliquus* and *Scenedesmus acutus* photocatalysis using a raceway reactor and sun light as energy source

For the experiments in this section, K₂Cr₂O₇ (SIGMA-ALDRICH, 99.5% purity) was used as Cr(VI) source. The algal concentration was determined by dried weight filtering 25 ml of the sample in 1 µm filters followed by drying in an oven at 80 °C for 24 h. The Cr(VI) concentration was determined by the diphenylcarbazide colorimetric method (SULE AND INGLE, 1996) using a Genesys 10S UV-Vis spectrophotometer.

3.3.1 Raceway reactors

The following experiments were performed in three polyvinyl chloride (PVC) raceway reactors with 7.5 cm height, 100 cm length, 1740 cm² superficial area, 25 cm

external diameter and 13 cm internal diameter (Figure 3.4). Each one had a set of 6 acrylic stirrer paddles with 7.5 cm height and 11 cm length connected to a 12V adjustable engine.

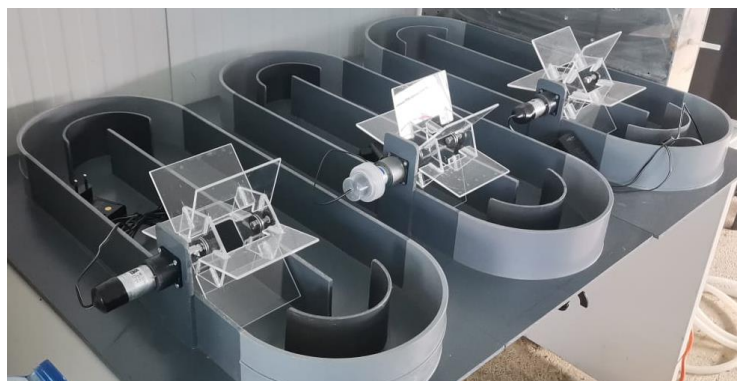


Figure 3.4 – Raceway reactor

3.3.2 Light penetration

The light intensity was measured with a ULM-500 Universal Light Meter with a ball pointed sensor. For no-algal conditions, the raceway reactors were filled with distilled water and the light intensity measured external and in each 1 cm depth for 5 h each hour. For algal conditions, 5 L of a culture was added to a reactor and the light intensity measured external and in each 1 cm depth for different dilutions. The data was then adjusted for the Beer-Lambert's law (Equation 5).

3.3.3 Photocatalytical tests for *S. obliquus* and *S. acutus*

5 L of an 0.5 g/L or 1 g/L algal culture was added to a reactor (3cm suspension height) and the pH adjusted to 3 or 8 using 10 %v/v H₂SO₄ and 1 M NaOH solution. Then, K₂Cr₂O₇ was added to obtain a concentration of 1 mg/L, 5 mg/L or 10 mg/L Cr(VI). Samples were collected each 20 min until 3 h of process. Using the best conditions, an experiment using 50 mg/L Cr(VI) was performed for comparison.

3.4 *Scenedesmus obliquus*, *Scenedesmus acutus* and TiO₂ photocatalysis using a cylindrical reactor and sun light as energy source for dissolved O₂ tests

As previously discussed, due to particle characteristics and the raceway reactor hydrodynamic, the particles TiO_2 were not properly dispersed and, therefore, experiments were not performed using the raceway reactor. Therefore, to evaluate the dissolved O_2 effect and compare the algal and TiO_2 application as catalysts, a different system was used. The system consisted of a cylindrical reactor 6 cm height and 24 cm diameter under magnetic stirring with inner gas dispersion (Figure 3.5). 1400 L of 1 g/L algal culture or TiO_2 dispersions were added to the reactor (3 cm suspension height). The dissolved O_2 concentration was adjusted to saturation and depletion using O_2 and N_2 gas cylinders. The pH was adjusted to 3 using 10 %v/v H_2SO_4 and 1 M NaOH solution. The $\text{K}_2\text{Cr}_2\text{O}_7$ was added to obtain a concentration of 10 mg/L Cr(VI). Samples were collected each 20 min until 3 h of process.



Figure 3.5 – System for dissolved O_2 experiments

Chapter 4

Results and discussion

4.1 AgNP-TiO₂ photocatalyst for Cr(VI) reduction

4.1.1 Characteristics of the AgNP-TiO₂ particles

TEM images were analyzed to verify the morphology, particle sizes and distribution of Ag nanoparticles on TiO₂ surface (Figure 4.1). The bare TiO₂ particles were in the form of aggregates with sizes varying from approximately 0.3 to 1 μm (Figure 4.1a). The ultrasound-assisted process enabled the decoration of single Ag nanoparticles on the surface of the micro-sized TiO₂ particles (Figure 4.1b). The acoustic cavitation, which was generated by ultrasound, caused a bubble nucleus grown, and these bubbles were imploded at the liquid-solid interface. With the implosion, transient hot spots were generated, which have enhanced the distribution of active sites for Ag deposition on TiO₂ surface.

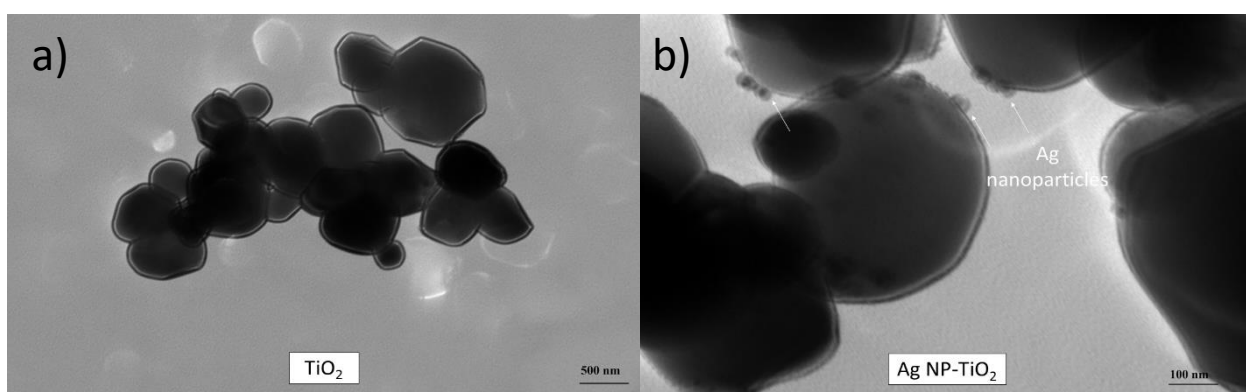


Figure 4.1 – TEM images of (a) bare TiO₂ particles and (b) TiO₂ particles decorated with Ag nanoparticles at 30 wt% (AgNP30-TiO₂).

Figure 4.2 shows the diffractogram of the TiO₂ particles decorated with Ag. The peaks at 2θ values of 38.1° , 44.3° , 64.44° , and 77.4° were attributed to the (111), (200), (220), and (311) planes of Ag (ICDD 04-0783), respectively, which confirmed the presence of metallic Ag nanoparticles (Pu et al., 2018). The other peaks were assigned to the TiO₂ anatase phase (ICDD 071-1166), which confirmed that the ultrasound

deposition did not affect the TiO₂ anatase phase.

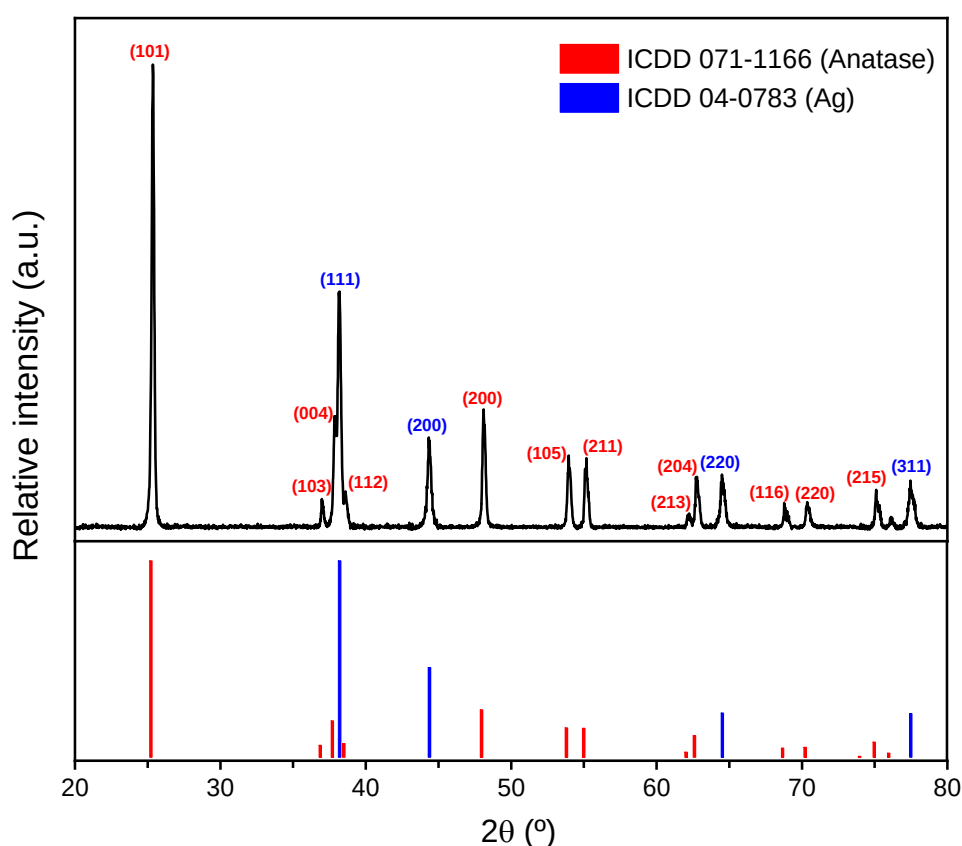


Figure 4.2 – XRD spectrum of Ag-decorated TiO₂ particles.

Optical characterization of the different samples was carried out by diffuse reflectance spectroscopy (Figure 4.3). For the pristine TiO₂, typical spectrum was observed with a broad band gap absorption band in the 250-420 nm range, which agrees well with the reported band gap energy of 3.2 eV (MACHADO et al., 2015). Following decoration, the TiO₂ particles with Ag nanoparticles turn visibly brownish. In the diffuse reflectance spectrum, a broad absorption in the visible range appears, which agrees well with the expected spectral feature for the oxide modified with Ag nanoparticles. It is also expected that the surface of the nanoparticles is partially oxidized and since Ag₂O has band gap of 1.3 eV (AKEL et al., 2018), a broad visible light absorption is expected to improve light-harvesting efficiency in relation to bare TiO₂. The close contact between the Ag/Ag₂O particles and TiO₂ leads then to the formation of heterojunctions, which should be beneficial to the charge separation efficiency and the photocatalytic activity.

According to Din et al. (2017), the Ag nanoparticles act as an electron trap capturing electrons transferred from the conduction band of TiO₂ semiconductor. Then

these electrons are transferred to the dissolved oxygen, which is converted into superoxide radicals. Consequently, the photogenerated holes in the valence band remaining on the TiO_2 react with water molecules and help in the formation of hydroxyl radicals used for photocatalytic oxidation.

Khana et al. (2015), Furube and Hashimoto (2017) and Pu et al. (2018) attributed this improvement to the surface plasmon resonance effect of spatially confined electrons in Ag nanoparticles and the interaction between Ag and TiO_2 particles, which extends the light absorption.

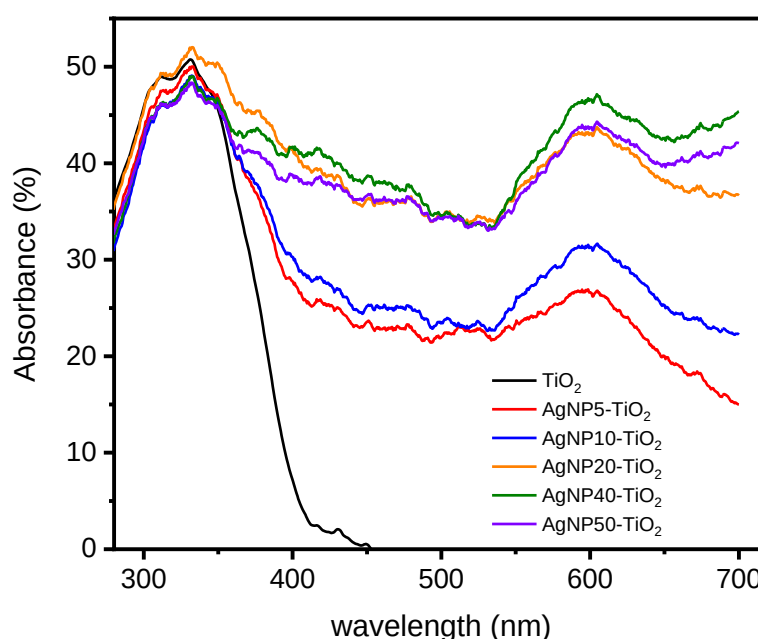


Figure 4.3 - Diffuse reflectance spectra of Ag-decorated TiO_2 particles.

4.1.2 Photocatalytic tests for Cr(VI) reduction

Figure 4.4 (a) presents the kinetic curves for Cr(VI) photoreduction during the photocatalytic tests at catalyst concentration of 1 g/L and initial Cr(VI) concentration of 10 mg/L. Bare TiO_2 and TiO_2 decorated with Ag nanoparticles at 5, 10, 20, 30, 40 and 50 wt% were used as catalysts. The fitting of experimental data to the pseudo-first-order kinetic model is presented in Figure 4.4 (b).

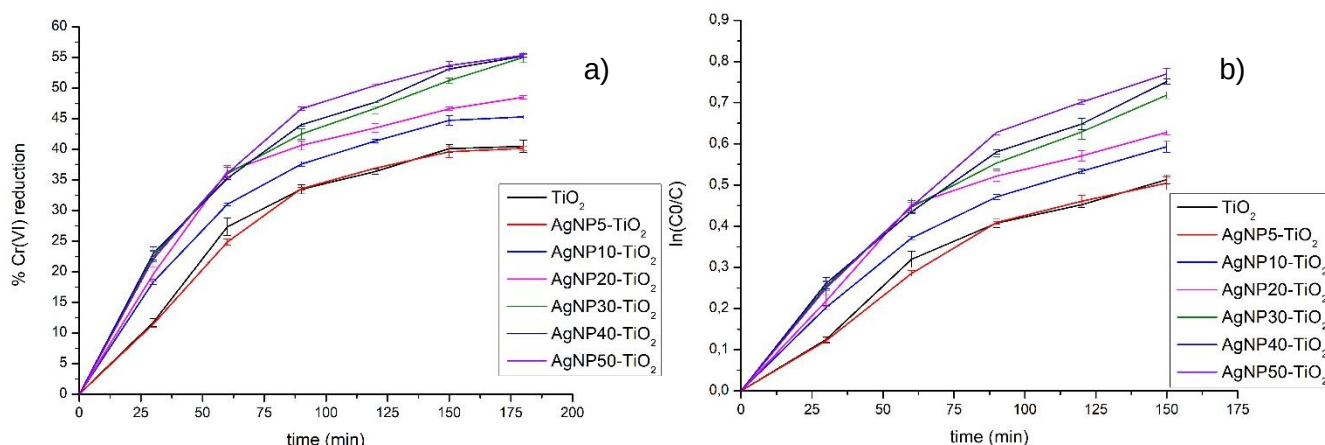
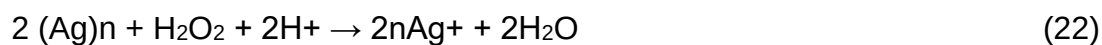


Figure 4.4 - (a) Photocatalytic reduction of chromium (VI) with bare TiO_2 and TiO_2 decorated with 5, 10, 20 and 30 wt% of Ag nanoparticles as catalysts at 1 g/L for initial Cr(VI) concentration of 10 mg/L and (b) linear fitting of experimental data to the pseudo-first-order kinetic model.

Bare TiO_2 and AgNP5- TiO_2 photocatalysts presented similar activities for Cr(VI) photoreduction, as their band-gap energy are similar as noticed by Table 4.1. However, the loading of Ag nanoparticles at mass ratios greater than 10% caused significant improvement on Cr(VI) photoreduction. After 180 min of reaction, Cr(VI) reductions were $40.49 \pm 0.99\%$ and $55.00 \pm 0.83\%$ with bare TiO_2 and with AgNP30- TiO_2 photocatalysts, respectively. The improvement in Cr(VI) reduction with the AgNP- TiO_2 composite catalyst is related to the increase in the light absorption capacity due to the plasmonic resonance of Ag nanoparticles. Moreover, the applied ultrasound-assisted process enabled the distribution of Ag nanoparticles on TiO_2 surface and, thus, the electron sink of Ag nanoparticles was favored (STUCCHI et al., 2018). Wang et al. (2017) reported a Cr(VI) photoreduction of about 50 wt% using Ag- TiO_2 particles and alga immobilized in a nanofiltration matrix by the electrospinning technique.

Although the AgNP40- TiO_2 and the AgNP50- TiO_2 particles presented higher band gap energy values (Table 4.1), high concentration of metals can, instead of dope a semiconductor particle, metalize it. Therefore, phase segregation occurs, and Ag clusters can be expelled from the bulk of the surface, reducing the AgNP- TiO_2 particles photoactivity (ROSARIO AND PEREIRA, 2014). Also, as the concentration of Ag nanoparticles on the surface increases, these particles are more susceptible to be oxidized in aqueous media, resulting in silver oxides or dissolved metal ions. One of the

oxidizing agents (Equation 22) is hydrogen peroxide (H_2O_2) (WEI et al., 2015) as this chemical can be produced during the photocatalysis process.



Experimental data of Cr(VI) photoreduction were adjusted to a rate expression of a pseudo-first-order reaction (Equation 7), as presented in Figure 4.4(b). As presented in Table 4.1, the apparent rate constant (k_{app} value) for bare TiO_2 is lower than for doped Ag- TiO_2 particles, which confirms the increase of photocatalytic activities and efficiencies of the doped particles. Similar values of apparent rate constant are reported in the literature for chromium photoreduction (ABDEL MONIEM et al., 2015).

Table 4.1 - Linear fitting parameters of the pseudo-first-order kinetic model for Cr(VI) photoreductions with the different proposed catalysts at 1 g/L for initial Cr(VI) concentration at 10 mg/L

Particle	$10^3 k_{\text{app}} (\text{min}^{-1})$	R^2
TiO_2	3.8	0.983
AgNP5- TiO_2	3.9	0.979
AgNP10- TiO_2	4.5	0.975
AgNP20- TiO_2	4.9	0.961
AgNP30- TiO_2	5.4	0.975
AgNP40- TiO_2	5.6	0.979
AgNP50- TiO_2	5.9	0.979

Figure 4.5 illustrates the effect of initial Cr(VI) concentration on the efficiency of the AgNP30- TiO_2 catalyst at 1 g/L for Cr(VI) photoreduction. The photocatalytic reduction of Cr(VI) decreased with the increase in the initial concentration of Cr(VI). Figure 4.5(a) shows the photocatalytic reduction of Cr(VI) decreased from 87.83% to 43.57% if increasing the initial Cr(VI) concentration from 5 to 20 mg/L at a reaction time of 180 min. This behavior was expected since the dosage of AgNP30- TiO_2 was fixed and, therefore, the catalytic sites were limited. The fitting of experimental data to the kinetic model of pseudo-first order is presented in Figure 4.5(b). The observed apparent rate constants (k_{app} values) for each initial Cr(VI) concentration were adjusted to the

Langmuir-Hinshelwood model (Table 4.3). As presented in Figure 4.6, the linear fitting of the apparent rate constants as a function of initial Cr(VI) concentrations were used to calculated values of k_r and K_{LH} as 0.061 mg/L min and 4.734 L/mg, respectively. These values are typical of the Langmuir-Hinshelwood model for heterogeneous photocatalysis (TREJO-VALDEZ et al., 2019).

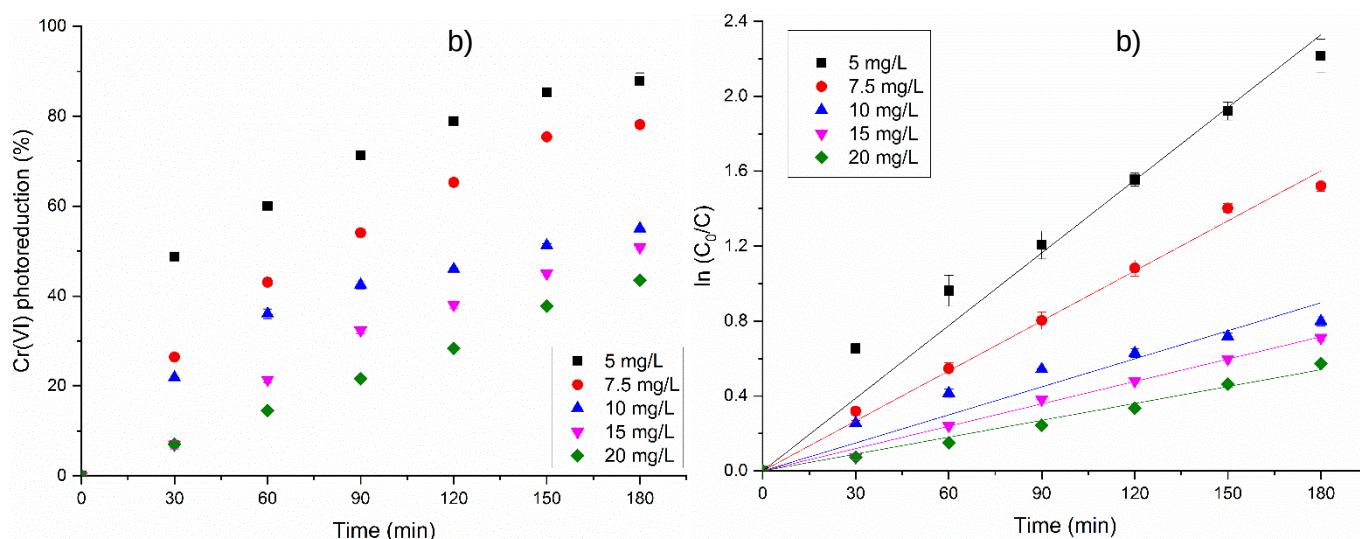


Figure 4.5 - (a) Effect of the initial Cr(VI) concentration on the activity of the AgNP30-TiO₂ catalyst at 1 g/L for Cr(VI) photoreduction and (b) linear fitting of experimental data to the pseudo-first-order kinetic model.

Table 4.2 Linear fitting parameters to the pseudo-first-order kinetic model for Cr(VI) photoreductions with the AgNP30-TiO₂ catalyst at 1 g/L for different initial Cr(VI) concentrations.

Initial Cr(VI) concentration (mg/L)	$10^3 \text{ kapp (min}^{-1}\text{)}$	R^2
5	12.92	0.989
7.5	8.91	0.997
10	5.00	0.975
15	4.03	0.997
20	3.15	0.973

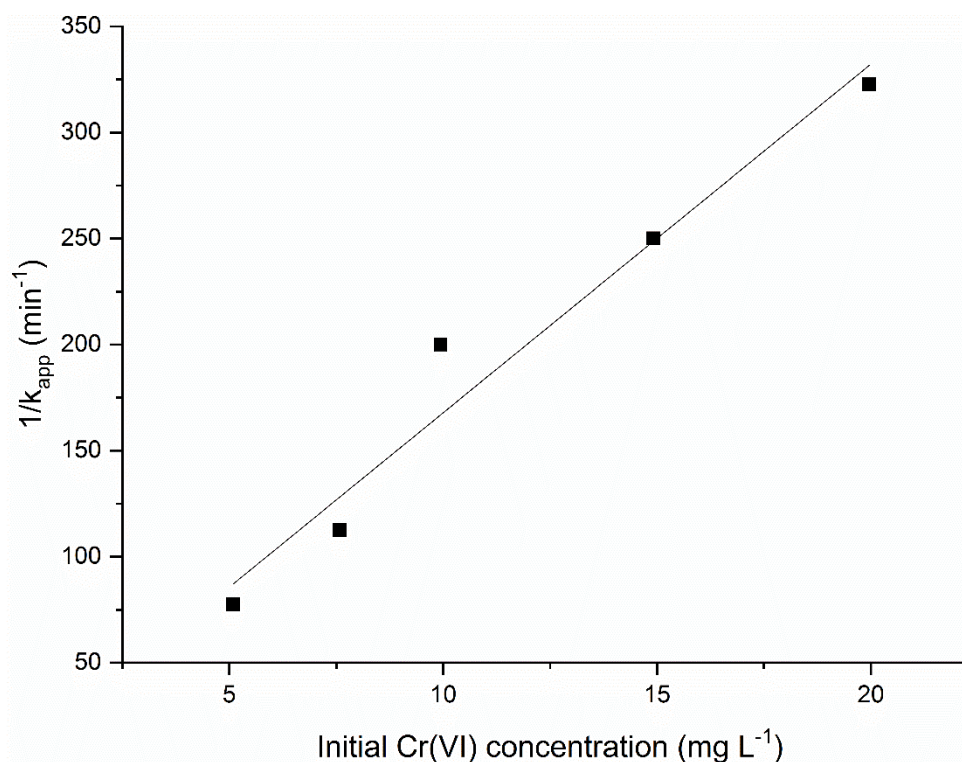


Figure 4.6 - Fitting of the Langmuir-Hinshelwood kinetic model for photocatalytic Cr(VI) reductions with the AgNP30-TiO₂ catalyst at 1 g/L and at different initial Cr(VI) concentrations.

4.1.3 Impregnation and reuse

The produced asymmetric alumina hollow fiber support is shown in Figure 4.7 by the SEM images. The fibers had inner and outer diameters of 1.79 ± 0.02 and 2.25 ± 0.01 mm, respectively (Figure. 4.7a). As observed in Figure 4.7b, asymmetric pore size distribution was obtained and micro-voids were formed due to the viscous fingering phenomenon (BENJAMIN AND KINGSBURI, 2009) or due to interfacial instabilities described by the Rayleigh-Taylor theory (LEE et al., 2015). The internal bore fluid was pure solvent and therefore the formation of micro-voids was from the outer surface of the fiber. The micro-void formations were potentialized by the zero airgap applied between the fiber nascent and the coagulation bath. As shown in Fig 4.7c, the micro-voids remained open in the lumen side of the fiber being ideal for a catalyst impregnation. Finally, as observed in Fig 4.7d, since the fiber was not in contact with air, a very thin outer sponge irregular layer was formed on the fiber outer surface, being

ideal for coating.

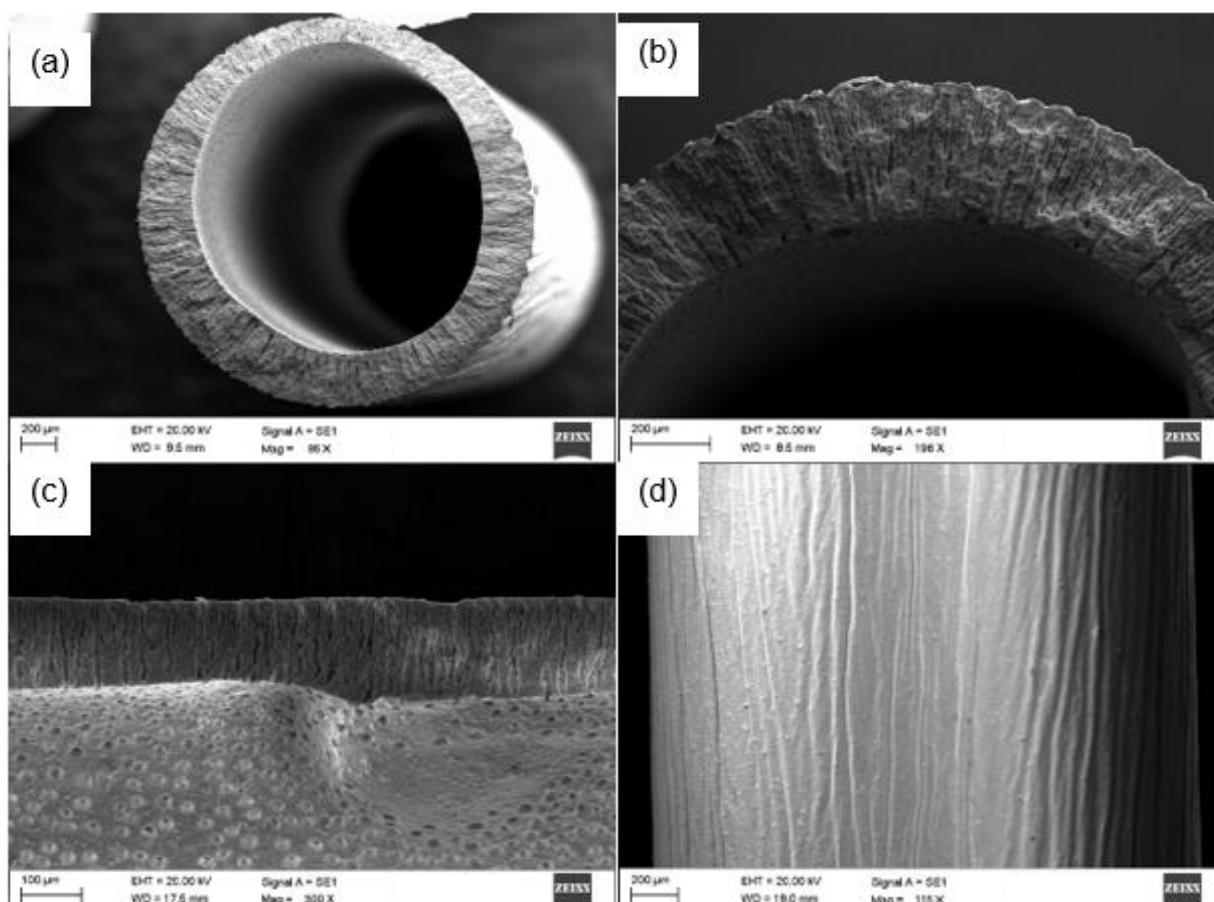


Figure 4.7 - SEM images of the produced asymmetric alumina hollow fiber support: (a) overview, (b) cross-section, (c) cross-section with inner surface, (d) outer surface.

Figures 4.8 and 4.9 show the aluminum and oxygen composition of the fibers, which are related to the ceramic material (alumina, Al_2O_3). In both situations, the distribution of titanium was observed as regular. Also, the distribution of silver was observed mainly in the side of the specific aimed immobilization and in the other parts of the fiber, reflecting the nano size of the Ag particles. The AgNP- TiO_2 particles were impregnated within the fiber micro-voids probably due to capillarity forces while externally by the liquid pressure. Prasetya et al. (2017) and Garcia-Garcia and Li (2013) showed that asymmetric alumina hollow fibers are suitable substrates for internal deposition of catalysts while Sousa et al (2022) and Pan et al (2003) showed that for external immobilization.

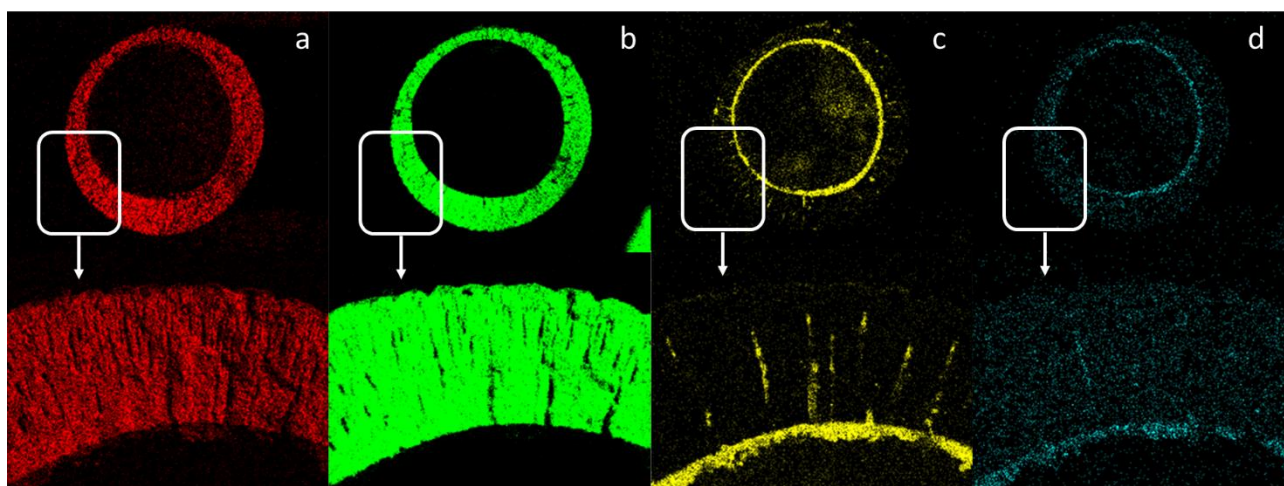


Figure 4.8 – EDS images of the asymmetric alumina hollow fiber support impregnated internally with AgNP30-TiO₂ ((a) oxygen, (b) aluminum, (c) titanium), (d) silver.

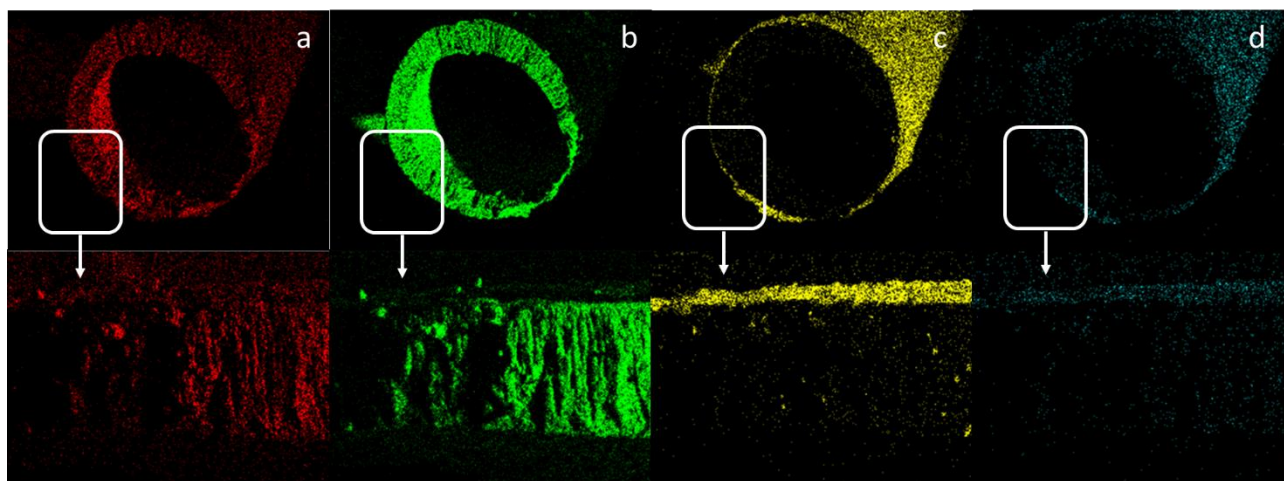


Figure 4.9 – EDS images of the asymmetric alumina hollow fiber support impregnated externally with AgNP30-TiO₂ ((a) oxygen, (b) aluminum, (c) titanium), (d) silver.

Figure 4.10 shows the photoactivity of different immobilization systems with AgNP-TiO₂. In 1440 min of process, all the systems achieved 100% percent of Cr(VI) photoreduction. Until 1080 min, the system with AgNP30-TiO₂ immobilized externally showed a slightly higher activity. The homogeneous distribution in the surface is favorable for the process as it maximizes the absorption of the light photons by the catalyst and promote a better contact between the particles and the Cr(VI). Also, the suspended and the internal systems showed similar behaviors as the results obtained by Costa et al. (2019).

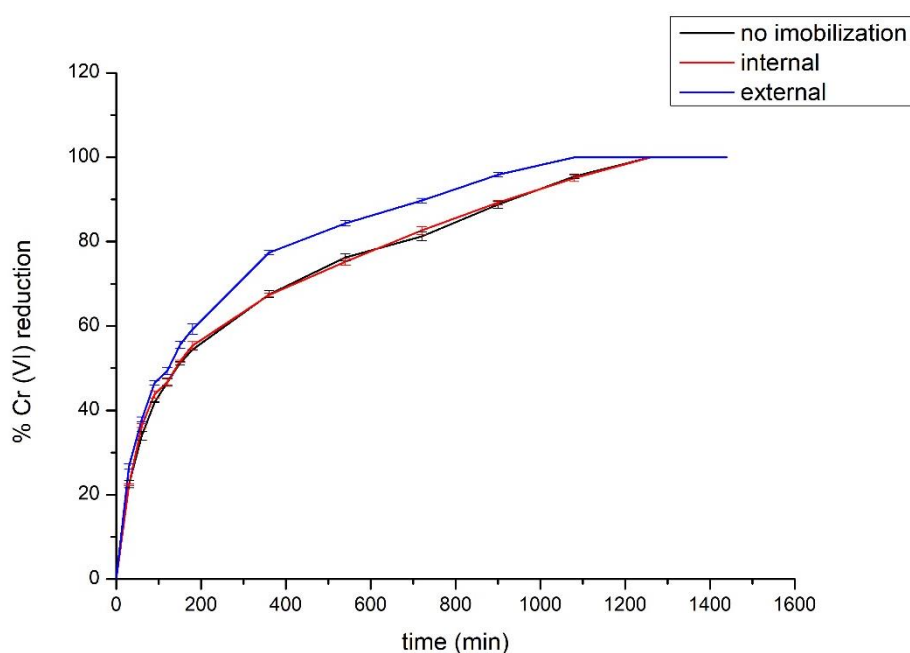


Fig 4.10. Photocatalytic reduction of chromium (VI) with 1g/L AgNP30-TiO₂ dispersed, immobilized internal and externally for initial Cr(VI) concentration of 10 mg/L

Figures 4.11 shows the activity of different systems for reuses of 12 hours each. After 10 sequential reuses, the photoreduction activity of suspended TiO₂ and suspended AgNP30-TiO₂ decreased from $61.34 \pm 0.85\%$ to $47.32 \pm 0.71\%$ and from $81.82 \pm 1.05\%$ to $66.94 \pm 0.37\%$, respectively. For the same number of reuses, the photoreduction activity of internal and external immobilized AgNP30-TiO₂ decreased from $81.98 \pm 0.73\%$ to $66.53 \pm 0.92\%$ and from $89.44 \pm 0.56\%$ to 65.70 ± 0.64 , respectively. One of the reasons for the reduction of activity is the decrease of the active sites of the catalyst related to the deposition of Cr(OH)₃ generated after photocatalytic reactions Sun et al (2014). Also, during the reuses some TiO₂ particles were probably released from the fiber. The AgNP30-TiO₂ systems showed similar behavior. However, the reuse of suspended particles requires centrifugation as recovery process while supported catalysts can be used without any pretreatment. Also, the internal immobilization requires more labor work and time to be produced while the external requires more energy represented by the vacuum pump. After the 10th cycle of reuse, EDS analysis was carried out to confirm the presence of AgNP30-TiO₂ on the fibers and the sequential reuses did not cause visual detachment.

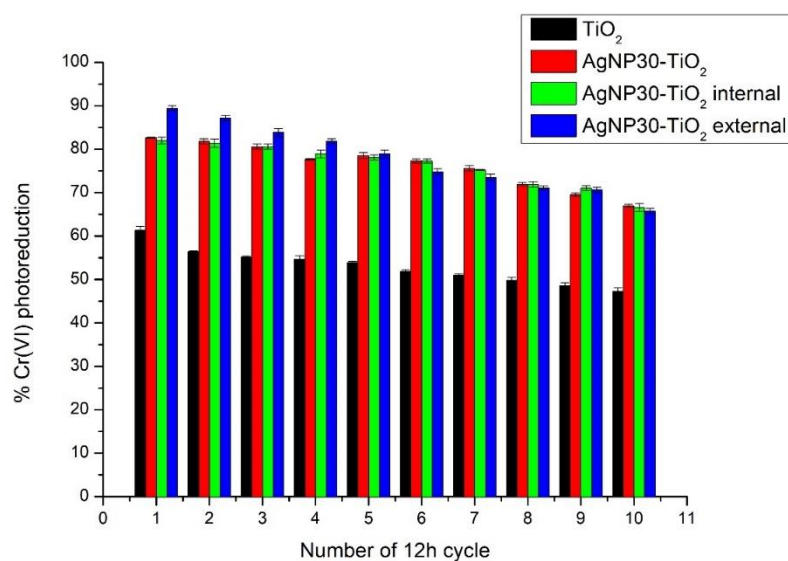


Figure 4.11 - Efficiency of Cr(VI) reduction at sequential reuse cycles

4.2 Light penetration

Figure 4.12 shows the variation of the light intensity outside the reactor and in different depths without particles. As time increases, the incident light increases as well and higher light penetration. As the sun moves, the incidence angle on the surface decreases, decreasing the light path in water.

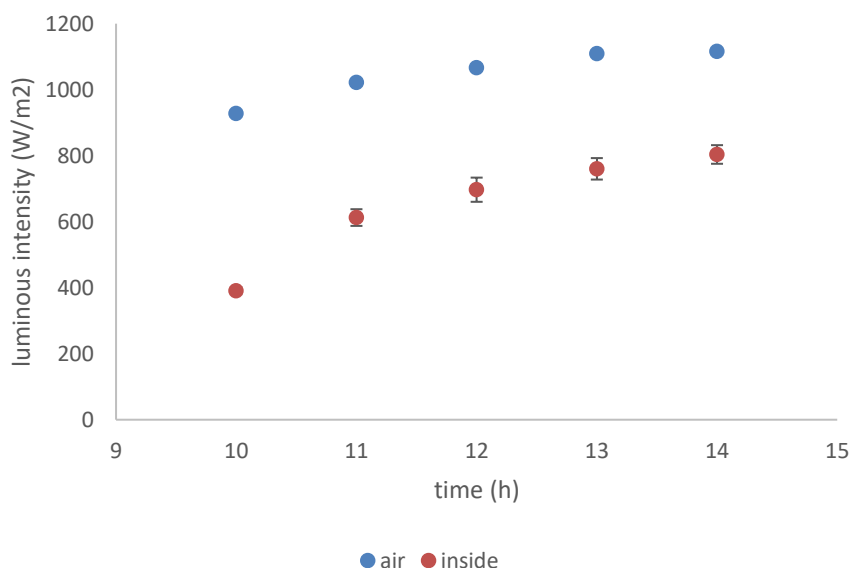


Figure 4.12 – Light penetration in water without alga

Experimental data of light penetration without alga were linear fitted to Equation 17 as presented in Figure 4.13. The transfer function for total radiation through the water surface correlation was expressed by Equation 23.

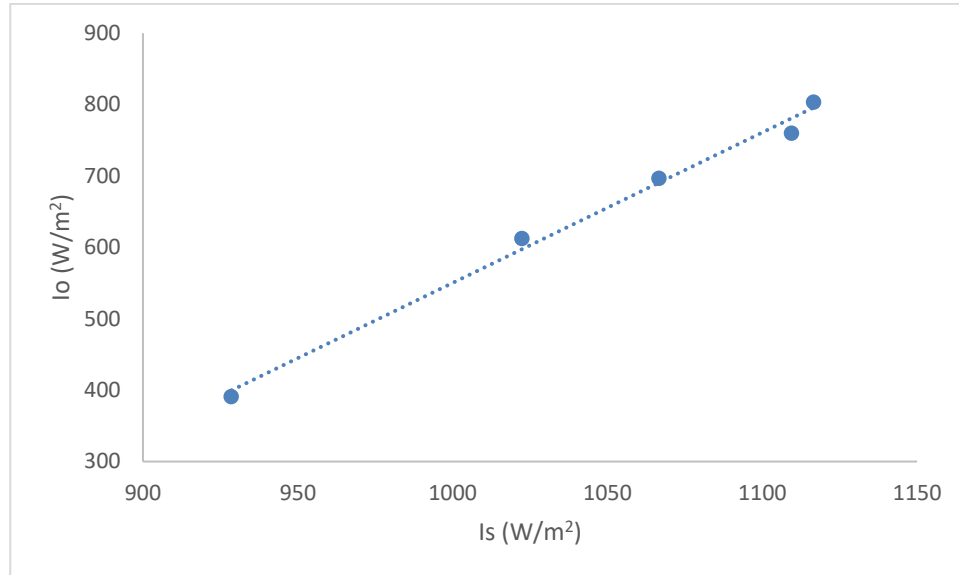


Figure 4.13 – Linear fitting of experimental data to transfer function without alga

$$I_o = 2,107 I_s - 1556.8 \quad (R^2 = 0.9921) \quad (23)$$

Figure 4.14 shows the light penetration in water with alga in different depth and dilution factor from a 0.5 g/L *Scenedesmus obliquus* culture. At the same dilution factor, the light penetration increases with deeper depths as the number of dispersed particles increase. Also, for the same depth, the light penetration increases with lower concentrations due to the reduced turbidity, showing that for photobioreactor, lower concentration as there is more access to illumination for the processes.

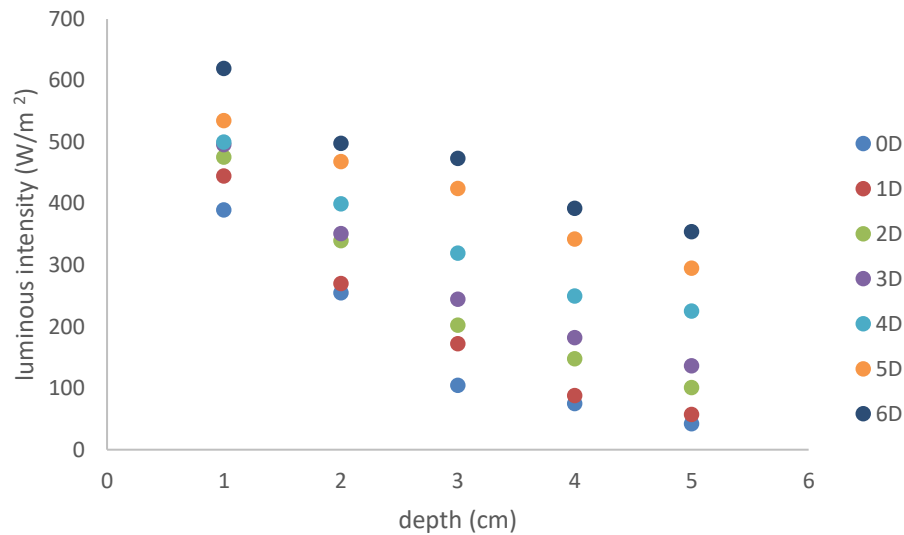


Figure 4.14 – Light penetration in water with *Scenedesmus obliquus* under different dilutions

Experimental data of light penetration was linear fitted to the Beer-Lambert's law (Equation 18), as presented in Figure 4.15a. Using the fitting parameters, the specific absorption coefficient (α) for each dilution was determined and related with the concentration Figure 4.15b. The correlation between the specific absorption coefficient and the algal concentration was obtained (Equation 24). As expected, the higher the algal concentration, the higher the turbidity and, therefore, lower the specific absorption coefficient.

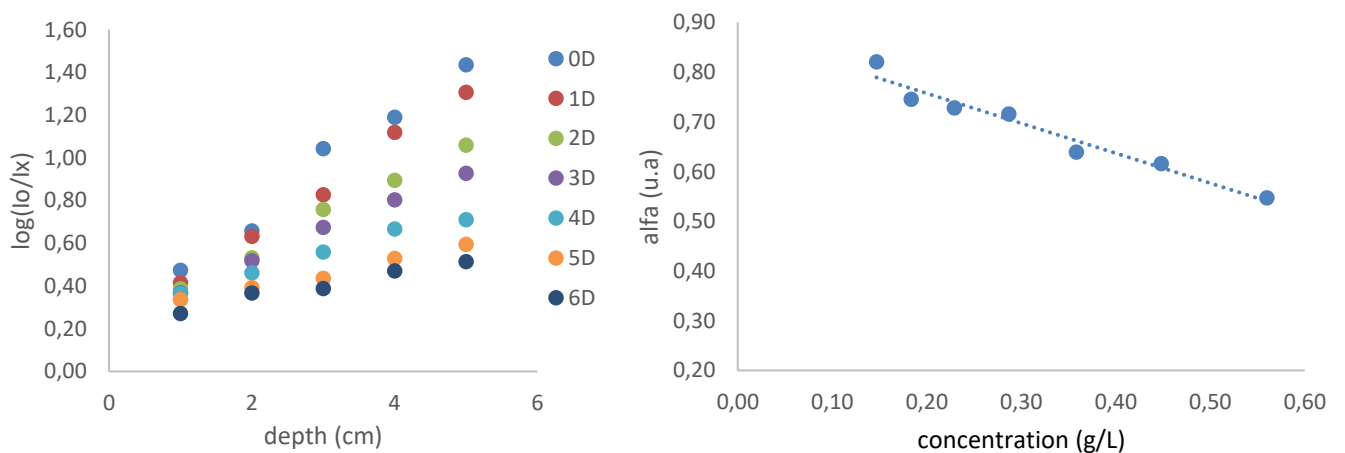


Figure 4.15 – a) Linear fitting of experimental data to the Beer Lambert's law and b) correlation between the specific absorption coefficient and the algal concentration.

$$a = -0.602 \text{ Algal concentration (g/L)} + 0.878 \quad (R^2=0.954) \quad (24)$$

4.3 Photoreduction tests with raceway reactor

Figure 4.16 shows the photoreduction of Cr(VI) without alga under pHs 3 and 8. For the time process of 3 h, the effect of light is low, justifying the need of a photocatalyst to improve it. Also, the influence of pH for this system is not significant. During the process, it was noticed that the pH did not vary significantly showing that the sunlight did not affect the pH media.

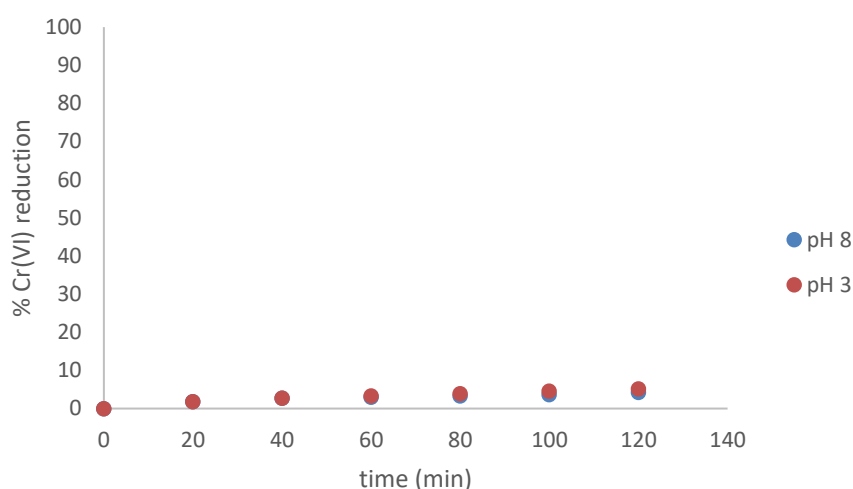


Figure 4.16 – Influence of sunlight in Cr(VI) reduction without catalyst

Figure 4.17 shows the influence of pH and algal concentration for *Scenedesmus obliquus* with the same sunlight irradiation. As previously observed, the lower the algal concentration, the higher the light penetration and, therefore, more light is accessible for the alga to reduce chromium. At acidic conditions, the green microalgae can generate more free electrons and acid organic matter, such as oxalic acid and oleic acid, improving the photoreduction process (DELLAGRECA et al., 2010, DENG et al., 2006, LIU et al. 2016).

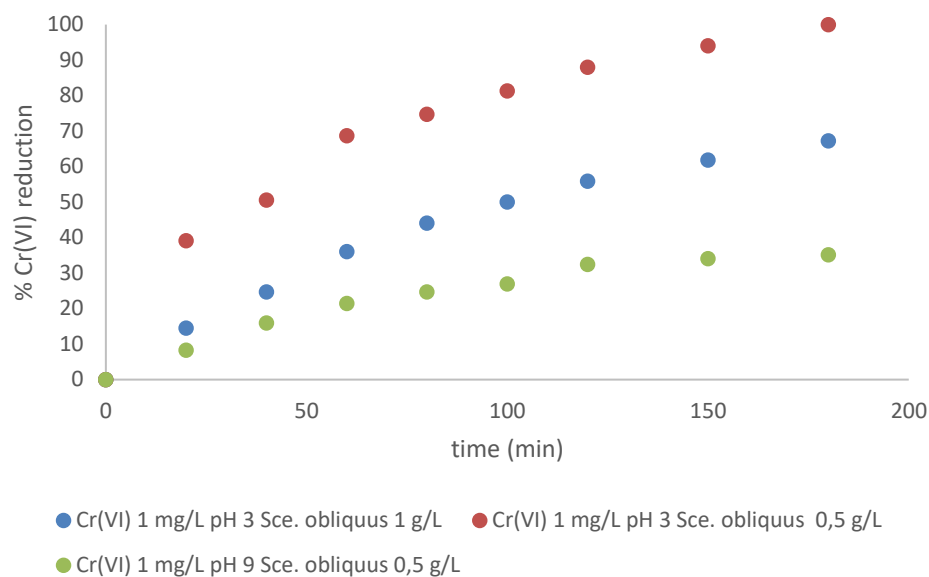


Figure 4.17 – Influence of pH and algal concentration for Cr(VI) photoreduction

Also, Figure 4.18 shows the influence of the alga under the same light irradiation. The *Scenedesmus acutus* and *Scenedesmus obliquus* are green algae with similar metabolisms being the main difference their morphology. *Scenedesmus acutus* has elongated fusiform cells, concave middle and convex ends of outer cells, smooth cell wall while *Scenedesmus obliquus* are cylindrical cells usually in one series and outer cells with long curved spines at each pole (AKGÜL et al. 2017).

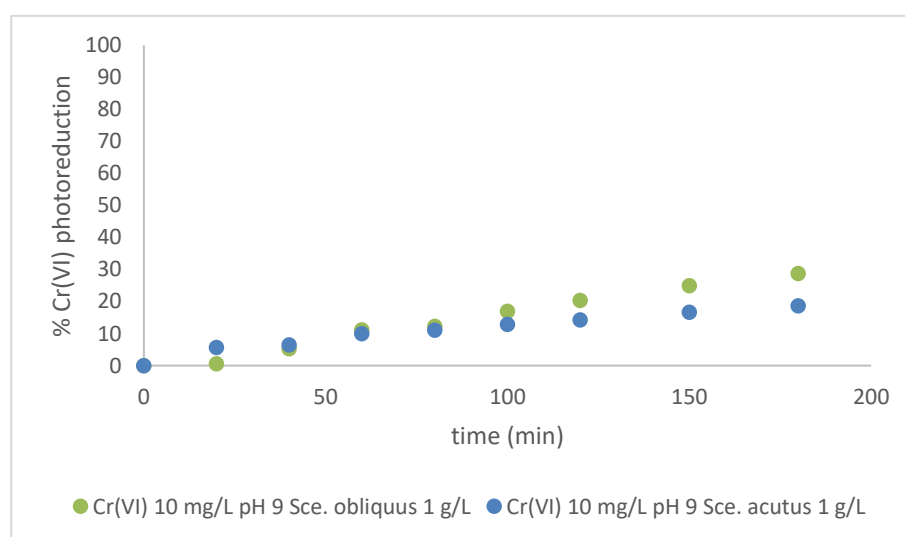


Figure 4.18 - Influence of algal type Cr(VI) photoreduction

Figure 4.19 shows the influence of Cr(VI) initial concentration. As verified by Deng et al. (2006), the photoreduction of Cr(VI) decreases with the initial Cr(VI) concentration, as there will be more Cr(VI) to be treated for the same amount of alga.

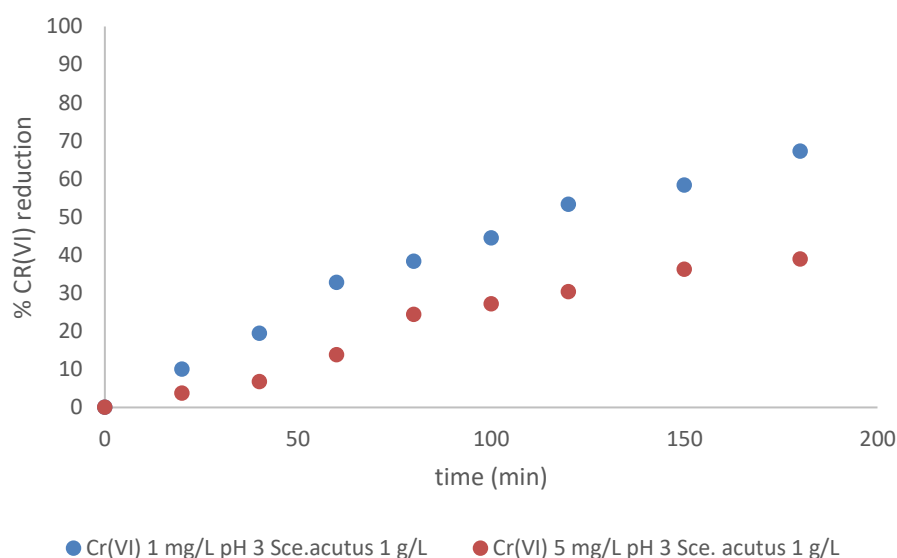


Figure 4.19 – Influence of initial Cr(VI) concentration

Figure 4.20 shows the influence of light irradiation for Cr(VI) photoreduction. As higher the time, more light penetrates in the system, improving Cr(VI) photoreduction. Under the same conditions, the system illuminated with the higher illumination external irradiance, showed the higher efficiency.

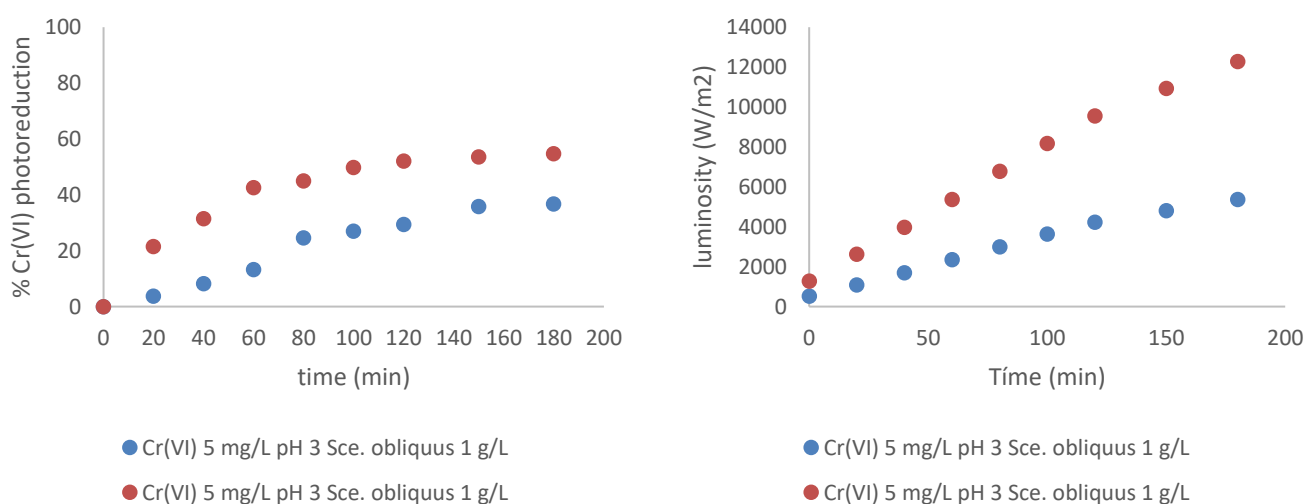


Figure 4.20 – Influence of sunlight irradiation

Therefore, Table 4.3 shows Cr(VI) reduction (%) and the reduction gradient

obtained for the photocatalytical experiments under the variation of the initial Cr(VI) concentration, the pH, the algal concentration, the algal specie and the total light incident intensity. Although the total Cr(VI) reduction occurred for the conditions of 1 mg/L Cr(VI), pH 3, 0.5 mg/L *S. obliquus* and 10967 W/m² light intensity, the higher reduction gradient (7.094 mg/L Cr(VI)) was obtained for 10 mg/L, pH 3, 0.5 g/L *S. obliquus* and 10897 W/m² light intensity. This shows that under acidic conditions and lower algal concentration, the absolute amount of Cr(VI) reduced can be increased.

Table 4.3 – Cr(VI) reduction (%) and reduction gradient for photocatalytical experiments using the raceway reactor

Cr(VI) (mg/L)	pH	Algal conc. (g/L)	Algal specie	Total light (W/m ²)	Reduc (%)	Reduc. Grad. (mg/L)
1	3	1	<i>S. obliquus</i>	10967	67.20	0.733
1	3	0.5	<i>S. obliquus</i>	10967	100	1
1	9	0.5	<i>S. obliquus</i>	10967	35.16	0.375
10	3	1	<i>S. obliquus</i>	10897	58.87	5.875
10	3	0.5	<i>S. obliquus</i>	10897	70.35	7.094
10	3	0.5	<i>S. acutus</i>	10897	66.51	6.637
5	3	1	<i>S. obliquus</i>	5120	36.78	1.835
5	3	0.5	<i>S. acutus</i>	5120	39.43	1.947
10	9	1	<i>S. obliquus</i>	5120	21.80	2.158
10	8	0.5	<i>S. obliquus</i>	11319	33.80	3.377
10	8	0.5	<i>S. acutus</i>	11319	31.02	3.096
5	8	0.5	<i>S. obliquus</i>	11319	34.74	1.741
10	9	1	<i>S. obliquus</i>	11742	28.77	2.885
10	9	1	<i>S. acutus</i>	11742	18.67	1.841
10	3	1	<i>S. acutus</i>	11742	46.53	4.632
1	3	0.5	<i>S. acutus</i>	11336	98.70	0.926
5	8	0.5	<i>S. acutus</i>	11336	37.69	1.876
1	8	1	<i>S. obliquus</i>	11336	33.70	0.358
5	8	1	<i>S. obliquus</i>	11700	34.90	1.741
5	8	1	<i>S. acutus</i>	11700	30.86	1.536
5	3	1	<i>S. obliquus</i>	11700	54.72	2.756
5	3	0.5	<i>S. obliquus</i>	11614	41.53	2.070
5	3	0.5	<i>S. acutus</i>	11641	41.20	2.058
1	8	0.5	<i>S. acutus</i>	11614	32.96	0.346
1	8	1	<i>S. acutus</i>	11700	26.32	0.264
1	3	1	<i>S. acutus</i>	11700	67.22	0.709
5	3	1	<i>S. acutus</i>	11700	38.92	1.947

Using the best conditions from the analyzed ones, the amount of initial Cr(VI) concentration was increased to 50 mg/L and the data obtained was plotted in Figure 4.20. Under 3 hours of experiment, the final Cr(VI) reduction was 44.43% and a Cr(VI) reduction gradient of 22.22 mg/L Cr(VI) showing that the absolute reduction of Cr(VI) can be increased.

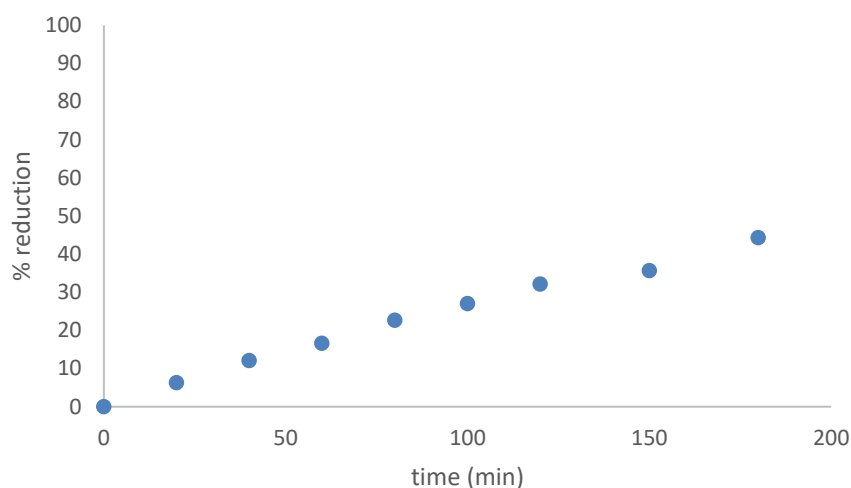


Figure 4.21 – Cr(VI) photoreduction using raceway reactor under initial 50 mg/L Cr(VI), pH 3, 0,5 g/L *S. obliquus*

4.4 Photoreduction tests for dissolved oxygen

Figure 4.22 shows the photoreduction of Cr(VI) in the presence of a) TiO₂ and b) *S. obliquus* under different dissolved O₂ conditions after 3 hours using 1 g/L catalyst, pH 3 and initial 10 mg/L Cr(VI). As seen in Figure 4.22 a), the dissolved O₂ does not significantly affects the photoreduction of Cr(VI) in the presence of TiO₂. As discussed by Chen and Ray (2001), at pH 3, Cr(VI) and O₂ have similar reduction potential and therefore, they will not compete for the reduction sites of the TiO₂. However, the influence of dissolved oxygen in the photoreduction of Cr(VI) using TiO₂ still not clear as positive (KHALIL et al., 1998), negative (MUNOZ & DOMENECH, 1990; LIN, WEI, & RAJESH-WAR, 1993), and no effects (AGUADO, GIMENEZ, & CERVERA-MARCH, 1991) were reported. The difference of the results is related to the experimental conditions performed by the researchers. However, in the presence of alga, the depletion of O₂ increased the Cr(VI) photoreduction. As algae require nutrients such as nitrates, phosphates and sulfur to produce and convert them into proteins, fats and

carbohydrates, the increase of N₂ will induce the growth of the algae and the production of these metabolists which have a positive effect for the Cr(VI) photoreduction. Similar results were obtained by Deng et al. (2006).

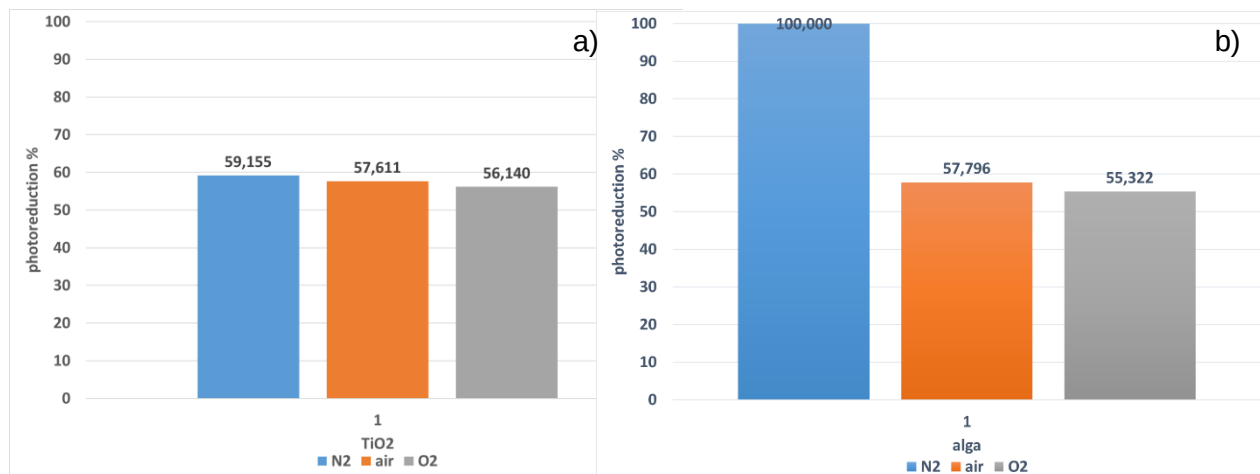


Figure 4.22 – Influence of dissolved O₂ using 10 mg/L Cr(VI) pH 3 in the presence of 1g/L a) TiO₂ and b) *S. obliquus*

Chapter 5

Conclusions and suggestions

In this chapter, the conclusions obtained in this work are presented, as well as the next steps.

The results in this work could allow the following conclusions:

- The ultrasound-assisted technique enabled to produce the composite catalyst formed by TiO_2 and Ag nanoparticles in a single and simplified process.
- The composite AgNP- TiO_2 catalyst presented higher radiation absorption than bare TiO_2 particles and, thus, the required energy for the photocatalytic reduction was reduced with the doping of Ag nanoparticles on TiO_2 surface.
- According to photocatalytic experiments for Cr(VI) reductions, Ag nanoparticles at concentrations greater than 5 wt% are necessary to increase the efficiency of the bare TiO_2 catalyst.
- The increase in the concentration of Ag nanoparticles increased Cr(VI) photoreductions.
- The efficiency of the composite AgNP- TiO_2 catalyst was decreased with the increase in the initial Cr(VI) concentration.
- The AgNP- TiO_2 particles were successfully immobilized internal and externally in the asymmetric alumina hollow fiber.
- The raceway reactor had hydrodynamics issues for TiO_2 application.
- Sunlight had a low efficiency for Cr(VI) photoreduction without photocatalysts.
- Initial Cr(VI) concentration, sunlight intensity, algal concentration and pH influence the Cr(VI) photoreduction.
- Higher Cr(VI) concentration leads to lower Cr(VI) photoreduction but higher photoreduction gradient.

- Higher sunlight intensity increases Cr(VI) photoreduction as more light penetrates in the dispersion.
- Lower algal concentration increases Cr(VI) photoreduction.
- Lower pH increases Cr(VI) photoreduction.
- The dissolved O₂ does not significantly affect the photoreduction process using TiO₂, however, the depletion of O₂ had a positive effect under the presence of alga.

For further studies, the following experiments could be done:

1. Evaluation of different membrane materials;
2. Evaluation of acclimated *C. vulgaris* for Cr(VI) photoreduction;
3. Evaluation of acidophilic microalga for Cr(VI) photoreduction;
4. Evaluation of the process for other heavy metals;
5. Modification of TiO₂ for application in raceway reactor.

References

ABDEL, S.M.; ALI, M.E.M.; GAD-ALLAH, T.A.; KHALIL, A.S.G.; ULBRICHT, M.; EL-SHAHAT, M.F.; ASHMAWY, A.M.; IBRAHIM, H.S. Detoxification of hexavalent chromium in wastewater containing organic substances using simonkolleite-TiO₂ photocatalyst. *Process Safety and Environmental Protection*, 95, 247-254, 2015. Available in "<https://doi.org/10.1016/j.psep.2015.03.010>"

ABREU, M.A. Reciclagem do resíduo de cromo da indústria do curtume como pigmentos cerâmicos. Tese de Doutorado da Escola Politécnica da Universidade de São Paulo, 2006. Available in "https://www.teses.usp.br/teses/disponiveis/3/3133/tde-16092010-111529/publico/Tese_Miriam_Abreu.pdf"

ACHARYA, R.; NAIK, B.; PARIDA, K. Cr(VI) remediation from aqueous environment through modified-TiO₂-mediated photocatalytic reduction. *Beilstein Journal of Nanotechnology*, 9, 1448-1470, 2018. Available in "<https://doi.org/10.3762/bjnano.9.137>"

AGUADO, M. A.; GIMENEZ, J.; CERVERA-MARCH, S. Continuous photocatalytic treatment of Cr(VI) effluents with semiconductor powders. *Chemical Engineering and Communication*, 104, 71-85. 1991. Available in "<https://doi.org/10.1080/00986449108910875>"

AKEL, S.; DILLERT, R.; BALAYERA, N.O.; BOUGHALED, R.; KOCH, J.; AZZOUZI, M.E.; BAHNEMANN, D.W. Ag/Ag₂O as a Co-Catalyst in TiO₂ Photocatalysis: Effect of the Co-Catalyst/Photocatalyst Mass Ratio. *Catalysts*, 8, 12, 647, 2018. Available in "<https://doi.org/10.3390/catal8120647>"

AKGÜL, F.; KIZILKAYA, I.T.; AKGÜL, R.; ERDUĞAN, H. Morphological and Molecular Characterization of *Scenedesmus*-Like Species from Ergene River Basin (Thrace, Turkey). *Turkish Journal of Fisheries and Aquatic Sciences*, 17, 3, 609-619, 2017. Available in "https://doi.org/10.4194/1303-2712-v17_3_17"

ALBERICI, R.M.; JARDIM, W.F. Photocatalytic destruction of VOCs in the gas-phase using titanium dioxide. *Applied Catalysis B: Environmental*, 14, 1-2, 55-68, 1997. Available in "[https://doi.org/10.1016/S0926-3373\(97\)00012-X](https://doi.org/10.1016/S0926-3373(97)00012-X)"

AL-MAMUN, M.R.; KADER, S.; ISLAM, M.S.; KHAN, M.Z.H. Photocatalytic activity improvement and application of UV-TiO₂ photocatalysis in textile wastewater treatment: A review. *Journal of Environmental Chemical Engineering*, 7, 2019. Available in "<https://doi.org/10.1016/j.jece.2019.103248>"

ARAÚJO, N.V.S. de. Galvanoplastia com cromo, diagnósticos das condições ambientais e ocupacionais em pequenas empresas. 2006. 119f. Dissertação (Mestrado em Engenharia Civil). Universidade Federal de Pernambuco, Recife, 2006. Available in "<https://repositorio.ufpe.br/handle/123456789/5389>"

ARDILA, L.; GODOY, R.; MONTENEGRO, L. Sorption Capacity Measurement of *Chlorella vulgaris* and *Scenedesmus acutus* to Remove Chromium from Tannery Wastewater. 2nd International Conference on Green Energy Technology, 2017. Available in "<https://iopscience.iop.org/article/10.1088/1755-1315/83/1/012031>"

BAILEY, S.E.; OLIN, T.J.; BRICKA, R.M.; ADRIAN, D. A review of potentially low-cost sorbents for heavy metals. *Water Research.*, v.33, p.2469-2479, 1999. Available in "[https://doi.org/10.1016/S0043-1354\(98\)00475-8](https://doi.org/10.1016/S0043-1354(98)00475-8)"

BANERJEE, S.; RAMASWAMY, S. Dynamic process model and economic analysis of microalgae cultivation in open raceway ponds. *Algal Res*, 26, 330–340, 2017. Available in “<https://doi.org/10.1016/j.algal.2017.08.011>”

BAYRAK, R.; ALBAY, C.; KOÇ, M.; ALTIN, İ.; DEĞİRMENCIOĞLU, İ.; SÖKMEN, M. Preparation of phthalocyanine/TiO₂ nanocomposites for photocatalytic removal of toxic Cr(VI) ions. *Process Safety and Environmental Protection*, 102, 294-302, 2016. Available in “<https://doi.org/10.1016/j.psep.2016.03.023>”

BELOVA, V.; GORIN, D.A.; SHCHUKIN, D.G.; MÖHWALD, H. Controlled Effect of Ultrasonic Cavitation on Hydrophobic/Hydrophilic Surfaces. *Acs Appl Mater Inter* 3, 417-425, 2011. Available in “<https://doi.org/10.1021/am101006x>”

BENJAMIN, F.K.; KINGSBURY, K.L. A morphological study of ceramic hollow fiber membranes. *Journal of Membrane Science*, 328, 1–2, 134-140, 2009. Available in “<https://doi.org/10.1016/j.memsci.2008.11.050>”

BRAILE, P.M.; CAVALCANTI, J.E.W.A., Manual de tratamento de águas residuárias industriais, CETESB, 1993, apud HA YASHI, A. M., Remoção de cromo hexavalente através de processos de bio sorção em algas marinhas, Tese de Doutorado da Faculdade de Engenharia Química, Unicamp, Campinas, SP, 2001. Available in “https://www.cetesb.sp.gov.br/aguas-interiores/wp-content/uploads/sites/12/2013/11/Cetesb_QualidadeAguasInteriores_2017_02-06_VF.pdf”

CANDAL, R.J.; RODRÍGUEZ, J.; COLÓN, G.; GELOVER, S.; SANTOS, E.V. Eliminación de Contaminantes por Fotocatálisis Heterogênea. Blesa, M., ed.; Red CYTED VIII-G, Argentina, cap. 7, 2001. ISBN 9789874338099 e 9874338091

CANTRELL, K.B. Livestock waste to bioenergy generation opportunities. *Bioresource Technology*, 99, 17, 7941-7953, 2008. Available in "<https://doi.org/10.1016/j.biortech.2008.02.061>"

CHAKHTOUNA, H.; BENZEID, H.; Nadia, Z. Recent progress on Ag/TiO₂ photocatalysts: photocatalytic and bactericidal behaviors. *Environmental Science and Pollution Research*, 28, 33, 1-29, 2021. Available in "<https://link.springer.com/article/10.1007/s11356-021-14996-y>"

CHEN, D.; RAY, A.K. Removal of toxic metal ions from wastewater by semiconductor Photocatalysis. *Chemical Engineering Science*, 56, 1561-1570, 2001. Available in "[https://doi.org/10.1016/S0009-2509\(00\)00383-3](https://doi.org/10.1016/S0009-2509(00)00383-3)"

CHOI, W.; TERMIN, A.; HOFFMANN, M.R. The Role of Metal Ion Dopants in Quantum-Sized TiO₂: Correlation between Photoreactivity and Charge Carrier Recombination Dynamics. *The Journal of Physical Chemistry* 98, 13669-13679, 1994. Available in "<https://doi.org/10.1021/j100102a038>"

CHUGUNOV, S.; LI, C. Parallel implementation of inverse adding-doubling and monte carlo multi-layered programs for high performance computing systems with shared and distributed memory. *Computer Physics Communications*, 194, 64-75, 2015. Available in "<https://doi.org/10.1016/j.cpc.2015.02.029>"

CIMM (CENTRO DE INFORMAÇÃO METAL MECÂNICA. Efluentes industriais. 2001. Available in "http://www.cimm.com.br/construtordepaginas/htm/3_24_5267.htm"

COHEN, Y. Biofiltration – the treatment of fluids by microorganisms immobilized into the filter bedding material: a review. *Bioresource Technology*, 77, 3, 257-274, 2001. Available in "[https://doi.org/10.1016/S0960-8524\(00\)00074-2](https://doi.org/10.1016/S0960-8524(00)00074-2)"

COMAZZI, A.; PIROLA, C.; LONGHI, M.; BIANCHI, C.L.M.; SUSLICK, K.S. Fe-based heterogeneous catalysts for the Fischer-Tropsch reaction: Sonochemical synthesis and bench-scale experimental tests. *Ultrason. Sonochem.*, 34, 774-780, 2017. Available in "<https://doi.org/10.1016/j.ultsonch.2016.07.012>"

FUJISHIMA, A.; HONDA, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature*, 238, 37, 1972. Available in "<https://doi.org/10.1038/238037a0>"

COSTA, I.G.F.; TERRA, N.M.; CARDOSO, V.L.; BATISTA, F.R.X.; REIS, M.H.M. Photoreduction of chromium(VI) in microstructured ceramic hollow fibers impregnated with titanium dioxide and coated with green algae *Chlorella vulgaris*. *J Hazard Mater* 379, 120837, 2019. Available in "<https://doi.org/10.1016/j.jhazmat.2019.120837>"

CROMAR, N. J.; FALLOWFIELD, H. J. Effect of nutrient loading and retention time on performance of high-rate algal ponds. *Journal of Applied Phycology*, 9, 4, 301-309, 1997. Available in "<https://doi.org/10.1023/A:1007917610508>"

DENG, L.; WANG, H.; DENG, N. Photoreduction of chromium(VI) in the presence of algae, *Chlorella vulgaris*. *Journal of Hazardous Materials*, B138, 288–292, 2006. Available in "<https://doi.org/10.1016/j.jhazmat.2006.04.062>"

DIN, M.I.; KHALID, R.; HUSSAIN, Z.. Minireview: silver doped titanium dioxide and silver doped zinc oxide photocatalysts. *Analytical Letters*, 51, 2719–2907, 2017. Available in "<http://dx.doi.org/10.1080/00032719.2017.1363770>"

DOZZI, M.V.; SACCOMANNI, A.; SELLI, E. Cr(VI) photocatalytic reduction: Effects of simultaneous organics oxidation and of gold nanoparticles photodeposition on TiO₂. *Journal of Hazardous Materials*, 211– 212, 188-195, 2012. Available in

[“https://doi.org/10.1016/j.jhazmat.2011.09.038”](https://doi.org/10.1016/j.jhazmat.2011.09.038)

GARCÍA, J. High-rate algal pond operating strategies for urban wastewater nitrogen removal. *Journal of Applied Phycology*, 12, 3-5, 331-339, 2000. Available in [“https://doi.org/10.1023/A:1008146421368”](https://doi.org/10.1023/A:1008146421368)

GARCIA-GARCIA, F.R; LI, K. New catalytic reactors prepared from symmetric and asymmetric ceramic hollow fibers. *Applied Catalysis A: General*, 456, p.1-10, 2013. Available in [“https://doi.org/10.1016/j.apcata.2013.01.031”](https://doi.org/10.1016/j.apcata.2013.01.031)

GOHARSHADI, E.K.; AZIZI-TOUPKANLOO, H. Silver colloid nanoparticles: Ultrasound-assisted synthesis, electrical and rheological properties. *Powder Technol* 237, 97-101, 2013. Available in [“https://doi.org/10.1016/j.powtec.2012.12.059”](https://doi.org/10.1016/j.powtec.2012.12.059)

GONÇALVES JR, A.C.; LUCHESE, E.B.; LENZI, E. Avaliação da fito disponibilidade de cádmio, chumbo e crômio, em soja cultivada em latossolo vermelho escuro tratado com fertilizantes comerciais. *Química Nova*, 23, 173-177, 1999. Available in [“https://doi.org/10.1590/S0100-40422000000200006”](https://doi.org/10.1590/S0100-40422000000200006)

GUPTA, P.L. A mini review: photobioreactors for large scale algal cultivation. *World Journal of Microbiology and Biotechnology*, 31, 9, 1409-1417, 2015. Available in [“http://dx.doi.org/10.1007/s11274-015-1892-4”](http://dx.doi.org/10.1007/s11274-015-1892-4)

FURUBE, A.; HASHIMOTO, S. Insight into plasmonic hot-electron transfer and plasmon molecular drive : new dimensions in energy conversion and nanofabrication. *NPG Asian Materials* 9, 424-454, 2017. Available in [“https://doi.org/10.1038/am.2017.191”](https://doi.org/10.1038/am.2017.191)

HABERT, A. C. Processos de Separação por Membranas. E-papers, 2006. ISBN 9788576500858. Available in "<https://books.google.com.br/books?id=P-7kje1EincC>"

IRIKURA, K.; GUERRA, M.B.B; BOCCHI, N.; ROCHA-FILHO, R.C.; KIKUTI, E. Uso de palha de aço comercial para o tratamento de efluentes contendo cromo hexavalente provenientes de processos de eletrocoloração de aços inoxidáveis. Química Nova, 41, n.3, 2018. Available in "<https://doi.org/10.21577/0100-4042.20170150>"

ISHAK, N. F.; HASHIM, N. A.; OTHMAN, M. H. D. Antifouling properties of hollow fiber alumina membrane incorporated with graphene oxide frameworks. Journal of Environmental Chemical Engineering, 8, 4, 104059, 2020. Available in "<https://doi.org/10.1016/j.jece.2020.104059>"

JOHNSON, M. B.; WEN, Z. Development of an attached microalgal growth system for biofuel production. Applied Microbiology and Biotechnology, 85, 3, 525-534, 2010. Available in "<https://doi.org/10.1007/s00253-009-2133-2>"

KHALIL, L. B.; MOURAD, W. E.; ROPHAEL, M. W. Photocatalytic reduction of environmental pollutant Cr(VI) over some semiconductors under UV/visible light illumination. Applied Catalysis B: Environmental, 17, 267-273, 1998. Available in "[https://doi.org/10.1016/S0926-3373\(98\)00020-4](https://doi.org/10.1016/S0926-3373(98)00020-4)"

KHANA, M.R.; CHUANA, T.W.; YOUSUF, A.; CHOWDHURY, M.N.K.; CHENG, C.K. Schottky barrier and surface plasmonic resonance phenomena towards the photocatalytic reaction: Study of their mechanisms to enhance the photocatalytic activity. Catalysis Science Technology, 5, 2522–2531, 2015. Available in "<https://doi.org/10.1039/C4CY01545B>"

KIM, J. Removal of Ammonia from Wastewater Effluent by *Chlorella vulgaris*. *Tsinghua Science and Technology*, 15, 4, 391-396, 2010. Available in "[https://doi.org/10.1016/S1007-0214\(10\)70078-X](https://doi.org/10.1016/S1007-0214(10)70078-X)"

KRATOCHVIL, D.; PIMENTEL, P.; VOLESKY, B. Removal of trivalent and hexavalent chromium by seaweed biosorbent. *Environmental Science and Technology*, 32, 2963-2698, 1998. Available in "<https://doi.org/10.1021/es971073u>"

KYLE, D.J.; OSMOND, C.B.; ARNTZEN, C.J. *Photoinhibition*. Elsevier. Amsterdam, Netherlands, 1987. ISBN 978-044-4415-96-7

LALIA, B.S. A review on membrane fabrication: Structure, properties and performance relationship. *Desalination*, 326, supplement C, 77-95, 2013. ISSN:0011-9164.

LEE, C.S. Effects of photoperiod on nutrient removal, biomass production, and algal-bacterial population dynamics in lab-scale photobioreactors treating municipal wastewater. *Water Research*, 68, 680-691, 2015. Available in "<https://doi.org/10.1016/j.watres.2014.10.029>"

LEE, M.; WANG, B.; LI, K. New designs of ceramic hollow fibers toward broadened applications. *Journal of Membrane Science*, 503, 48-58, 2016. Available in "<https://doi.org/10.1016/j.memsci.2015.12.047>"

LEE, M. WANG, B., WU, Z., LI, K. Formation of micro-channels in ceramic membranes – Spatial structure, simulation, and potential use in water treatment. *Journal of Membrane Science*, 483, 1-14, 2015. Available in "<https://doi.org/10.1016/j.memsci.2015.02.023>"

LI, Y.; WANG, P.; HUANG, C.; YAO, W.; WU, Q.; XU, Q. Synthesis and photocatalytic activity of ultrafine Ag₃PO₄ nanoparticles on oxygen vacated TiO₂. Applied Catalysis B: Environmental 205, 489-497, 2017. Available in "<https://doi.org/10.1016/j.apcatb.2016.12.059>"

LIN, W.Y.; WEI, C.; RAJESHWAR, K. Photocatalytic reduction and immobilization of hexavalent chromium at titanium-dioxide in aqueous basic-media. Journal of Electrochemical Society, 140, 2477. 1993. Available in "<https://iopscience.iop.org/article/10.1149/1.2220847>"

LIU, L.; POHNERT, G; WEI, D. Extracellular Metabolites from Industrial Microalgae and Their Biotechnological Potential. Marine Drugs, 14, 10, 191, 2016. Available in "<https://doi.org/10.3390%2Fmd14100191>"

MACHADO, W.A.; SANTOS, L.M.; FRANCA, M.D.; BORGES, K.A.; PANIAGO, R.M.; PATROCINIO, A.O.T.; MACHADO, A.E.H. Structural characterization of Ag-doped TiO₂ with enhanced photocatalytic activity. RSC Advances, 5, 125, 103752-103759, 2015. Available in "<https://doi.org/10.1039/C5RA22647C>"

MALLICK, N. Biotechnological potential of immobilized algae for wastewater N,P and metal removal: A review. Biometals, 15, 4, 377-390, 2002. Available in "<https://doi.org/10.1023/A:1020238520948>"

MESECK, S.L. Photoperiod and light intensity effects on growth and utilization of nutrients by the aquaculture feed microalga, Tetraselmis chui(PLY429). Aquaculture, 246, 1, 393-404, 2005. Available in "<https://doi.org/10.1016/j.aquaculture.2005.02.034>"

MMAMRM - Real Decreto 60/2011, de 21 de enero, sobre las normas de calidad ambiental en el ámbito de la política de aguas. Ministerio de Medio Ambiente, y Medio

Rural y Marino «BOE» núm. 19, de 22 de enero de 2011. Available in “<https://www.boe.es/eli/es/rd/2011/01/21/60>”

MORENO-GARRIDO, I. Microalgae immobilization: Current techniques and uses. Bioresource Technology, 99, 10, 3949-3964, 2008. Available in “<https://doi.org/10.1016/j.biortech.2007.05.040>”

MORILLAS-ESPAÑA, A.; VILLARÓ, S.; CIARDI, M.; ACIÉN, G.; LAFARGA, T. Production of *Scenedesmus almeriensis* Using Pilot-Scale Raceway Reactors Located inside a Greenhouse Phycology, 2, 1, 76-85, 2022. Available in “<http://dx.doi.org/10.3390/phycology2010005>”

MULDER, M. Basic Principals of Membrane Technology. Dordrech, Netherlands: Kluwer Academic Publishers, 1996. ISBN: 978-94-009-1766-8

MUNOZ, J.; DOMENECH, X. TiO₂ catalyzed reduction of Cr(VI) in aqueous solutions under ultraviolet illumination. Journal of Applied Electrochemistry, 20, 518-521, 1990. Available in “<https://doi.org/10.1007/BF01076066>”

MURALEEDHARAN, T.R.; YENGAR, L.I.; VENKOBACHAR, C. Biosorption: an attractive alternative for metal removal and recovery. Current Science, 61, 6, 379-385, 1991. Available in “<https://www.jstor.org/stable/24095078>”

PAN, X.L.; STROH, N.; BRUNNER, H.; XIONG, G.X.; SHENG, S.S. Deposition of sol-gel derived membranes on α -Al₂O₃ hollow fibers by a vacuum-assisted dip-coating process. Journal of Membrane Science 226, 1–2, 111-118, 2003. Available in “<https://doi.org/10.1016/j.memsci.2003.07.019>”

PINA, F.R.D.S. Tratamento de águas contaminadas com crómio(VI) por biossorção em algas marinhas. Dissertação submetida para obtenção do grau de Mestre Em Engenharia Do Ambiente – Ramo De Gestão. Mestrado Integrado Em Engenharia Do Ambiente. Faculdade de Engenharia da Universidade do Porto, Portugal, 2011. Available in “<https://repositorio-aberto.up.pt/bitstream/10216/61695/1/000149215.pdf>”

PENG, Y.H.; HUANG, G.F.; HUANG, W.Q. Visible-light absorption and photocatalytic activity of Cr-doped TiO₂ nanocrystal films. *Advanced Powder Technology*, 23, 8-12, 2012. Available in “<https://doi.org/10.1016/j.appt.2010.11.006>”

PRASETYA, N.; WU, Z.; GIL, A.G.; LI, K. Compact hollow fiber reactors for efficient methane conversion. *Journal of the European Ceramic Society*, 37, 16, 5281-5287. , 2017. Available in “<https://doi.org/10.1016/j.jeurceramsoc.2017.04.011>”

PRUDEN, A.L.; OLLIS, D.F. Photoassisted heterogeneous catalysis: The degradation of trichloroethylene in water. *Journal of Catalysis*, 83, 404, 1983. Available in “[https://doi.org/10.1016/0021-9517\(83\)90207-5](https://doi.org/10.1016/0021-9517(83)90207-5)”

PRUDEN, A.L.; OLLIS, D. F. Degradation of chloroform by photoassisted heterogeneous catalysis in dilute aqueous suspensions of titanium dioxide. *Environmental Science Technology*, v.17, n.628, 1983. Available in “<https://doi.org/10.1021/es00116a013>”

PU, S.; HOU, Y.; CHEN, H.; DENG, D.; YANG, Z.; XUE, S.; ZHU, R.; DIAO, Z.; CHU, W. An Efficient Photocatalyst for Fast Reduction of Cr(VI) by Ultra-Trace Silver Enhanced Titania in Aqueous Solution. 8, 251 , 2018. Available in “<http://dx.doi.org/10.3390/catal8060251>”

RABINOWITCH, E. Spectral efficiency of photosynthesis, p. 274-298. In: Campbell, P. A. (ed.), Medical and Biological Aspects of the Energies of Space. Columbia University Press. New York, NY, 1961. Available in "[https://doi.org/10.1016/0005-2728\(68\)90061-3](https://doi.org/10.1016/0005-2728(68)90061-3)"

ROCHA, J. C. Determinação Seqüencial de Cr (III) e de Cr(VI), por injeção em fluxo contínuo. Dissertação de Mestrado da Universidade de Campinas - Instituto de Química, 1983. Available in "<https://hdl.handle.net/20.500.12733/1581314>"

ROSARIO, A.V.; PEREIRA, E.C. The role of Pt addition on the photocatalytic activity of TiO₂ nanoparticles: The limit between doping and metallization. Applied Catalysis B: Environmental, 144, 840–845, 2014. Available in "<https://doi.org/10.1016/j.apcatb.2013.07.029>"

SAKTHIVEL, S.; SHANKAR, M.V.; PALANICHAMY, M.; ARABINDOO, B.; BAHNEMANN, D.W.; MURUGESAN, V. Enhancement of photocatalytic activity by metal deposition: characterization and photonic efficiency of Pt, Au and Pd deposited on TiO₂ catalyst. Water Research, 38, 13, 3001-3008, 2004. Available in "<https://doi.org/10.1016/j.watres.2004.04.046>"

SCHNEIDER, J.; MATSUOKA, M.; TAKEUCHI, M.; ZHANG, J.; HORIUCHI, Y.; ANPO, M.; BAHNEMANN, D.W. Understanding TiO₂ Photocatalysis: Mechanisms and Materials. Chem Rev, 114, 9919-9986, 2014. Available in "<https://doi.org/10.1021/cr5001892>"

SCHNEIDER, V.E.; COSTA, A.R.; MUNIZ, L.A.R.; BEAL, L.L.; PANAROTTO, V.T. Diagnostico de resíduos industriais perigosos no município de Caxias do Sul – Fase II: caracterização de resíduos galvânicos e de pintura industrial com vistas à valorização e à recuperação. Instituto de saneamento Ambiental, Departamento de Engenharia Química da Universidade de Caxias do Sul, 2001.

SCOTT, K. Membrane Materials, Preparation and Characterization. In: (Ed.). Handbook of Industrial Membranes. Amsterdam: Elsevier Science, 187-269, 1995. ISBN 978-1-85617-233-2.

SEERY, M.K.; GEORGE, R.; FLORIS, P.; PILLAI, S.C. Silver doped titanium dioxide nanomaterials for enhanced visible light photocatalysis. Journal of Photochemistry and Photobiology A: Chemistry, 189, 258-263, 2007. Available in "<https://doi.org/10.1016/j.jphotochem.2007.02.010>"

SHANG-DI, M; CHING, W.Y. Electronic and optical properties of three phases of titanium dioxide: Rutile, anatase, and brookite. Physical Review B, 51, 13023, 1995. Available in "<https://doi.org/10.1103/PhysRevB.51.13023>"

SIBI, G. Biosorption of Chromium from Electroplating and Galvanizing Industrial effluents under Extreme Conditions using *Chlorella vulgaris*. Green Energy & Environment, 2016. Available in "<https://doi.org/10.1016/j.gee.2016.08.002>"

SIERRA, E. Characterization of a flat plate photobioreactor for the production of microalgae. Chemical Engineering Journal, 138, 1–3, 136-147, 2008. Available in "<https://doi.org/10.1016/j.cej.2007.06.004>"

SILVA, C.S. Um estudo crítico sobre a saúde dos trabalhadores de galvanicas, por meio das relações entre as avaliações ambientais, biológicas e otorrinolaringológicas. São Paulo: Fundacentro, 1998. ISBN 978-85-98117-55-3

SOUSA, T.S.; FERREIRA, E.P.; VIEIRA, P.A.; REIS, M.H.M. Decoration of alumina hollow fibers with zinc oxide: improvement of the photocatalytic system for methylene blue degradation. Environmental Science Pollution Research, 2022. Available in "<https://doi.org/10.1007/s11356-022-20397-6>"

STAROV, V.M. Membrane Fabrication. Desalination, 402, n. supplement C, 173, 2017. ISSN 0011-9164.

STUCCHI, M.; BIANCHI, C.L.; ARGIRUSIS, C.; PIFFERI, V.; NEPPOLIAN, B.; CERRATO, G.; BOFFITO, D.C. Ultrasound assisted synthesis of Ag-decorated TiO₂ active in visible light. Ultrason Sonochem, 40, 282-288, 2018. Available in "<https://doi.org/10.1016/j.ultsonch.2017.07.016>"

SULE, P.A.; INGLE, J.D. Determination of the speciation of chromium with an automated two-column ion-exchange system. Anal Chim Acta 326, 85-93, 1996. Available in "[https://doi.org/10.1016/0003-2670\(96\)00041-4](https://doi.org/10.1016/0003-2670(96)00041-4)"

SUN, Q.; LI, H.; ZHENG, S.; SUN, Z. Characterizations of nano-TiO₂/diatomite composites and their photocatalytic reduction of aqueous Cr (VI). Applied Surface Science 311, 369-376, 2014. Available in "<https://doi.org/10.1016/j.apsusc.2014.05.070>"

SURI, R.P.S.; LIU, J.; HAND, D.W.; CRITTENDEN, J.C.; PERRAM, D.L.; MULLINS, M.E. Heterogeneous Photocatalytic Oxidation of Hazardous Organic Contaminants in Water. Water Environment Research. v.65, n.5, p.665-673, 1993. Available in "<https://doi.org/10.2175/WER.65.5.9>"

SUSLICK, K.S.; HYEON, T.; FANG, M.; CICHOWLAS, A.A. Sonochemical synthesis of nanostructured catalysts. Materials Science and Engineering: A 204, 186-192, 1995. Available in "[https://doi.org/10.1016/0921-5093\(95\)09958-1](https://doi.org/10.1016/0921-5093(95)09958-1)"

SUZUKI, N.; SANADA, T.; TERASHIMA, C.; SUZUKI, T.; ARAI, T.; SAITOU, S.; KAWASHIMA, T.; MIZUTANI, A.; SAITOU, T.; NAKATA, K.; KATSUMATA, K.; KONDO, T.; YUASA, M.; FUJISHIMA, A. Systematic studies of TiO₂-based

photocatalysts anti-algal effects on *Chlorella vulgaris*. *Journal of Applied Electrochemistry*, 47, 2, 197–203, 2017. Available in “<https://link.springer.com/article/10.1007/s10800-016-1031-4>”

TERRA, N.M.; BESSA, L.P.; CARDOSO, V.L.; REIS, M.H.M. Graphite coating on alumina substrate for the fabrication of hydrogen selective membranes. *International Journal of Hydrogen Energy*, 2017. Available in “<https://doi.org/10.1016/j.ijhydene.2017.10.179>”

TERRA, N.M.; LEMOS, C.O.T.; DA SILVA, F.B.; CARDOSO, V.L.; REIS, M.H.M. Characterization of asymmetric alumina hollow fibers: application for hydrogen permeation in composite membranes. *Brazilian Journal of Chemical Engineering*, 33, 5, 567-576, 2016. Available in “<https://doi.org/10.1590/0104-6632.20160333s20150074>”

THACKER, D. R.; BABCOCK, H. The mass culture of algae. *J. Sol. Energy Science. Eng.* 1: 37-49, 1957. Available in “[https://doi.org/10.1016/0038-092X\(57\)90054-3](https://doi.org/10.1016/0038-092X(57)90054-3)”

TOCCHETTO, M.R.L. Implantação de gestão ambiental em grandes empresas com atividade galvânica no Rio Grande do Sul.- Tese de Doutorado em Engenharia Metalúrgica - Universidade Federal do Rio Grande do Sul (UFRGS). Santa Maria (RS), 2004. Available in “<https://lume.ufrgs.br/handle/10183/6408>”

TREJO-VALDEZ, M.; HERNÁNDEZ-GUZMÁN, S.R.; MANRIQUEZ-RAMÍREZ, M.E.; SOBRAL, H.; MARTÍNEZ-GUTIÉRREZ, H.; TORRES-TORRES, C. Removal of aqueous chromium and environmental CO₂ by using photocatalytic TiO₂ doped with tungsten. *J Hazard Mater* 370, 196-202, 2019. Available in “<https://doi.org/10.1016/j.jhazmat.2018.05.008>”

UGWU, C.U. Photobioreactors for mass cultivation of algae. *Bioresource Technology*, 70

99, 10, 4021-4028, 2008. Available in "<https://doi.org/10.1016/j.biortech.2007.01.046>"

VAZ, L.G.L. Performance do processo de coagulação/floculação no tratamento do efluente líquido gerado na galvanoplastia. Trabalho de Pós-Graduação da Universidade Estadual do Oeste do Paraná, 2007. Available in "<https://livros01.livrosgratis.com.br/cp134520.pdf>"

VIET, P.V.; PHAN, B.T.; THI, C.M.; HIEU, L.V. Controlled Formation of Silver Nanoparticles on TiO₂ Nanotubes by Photoreduction Method. J Nanosci Nanotechnol 17, 1497-1503, 2017. Available in "<http://dx.doi.org/10.1166/jnn.2017.12645>"

VOLESKY, B. Detoxification of metal-bearing effluents: biosorption for the next century. Hydrometallurgy, 59, 203-216, 2001. Available in "[https://doi.org/10.1016/S0304-386X\(00\)00160-2](https://doi.org/10.1016/S0304-386X(00)00160-2)"

WAGENEN, J.V. Characterization of nutrient removal and microalgal biomass production on an industrial waste-stream by application of the deceleration-stat technique. Water Research, 75, 301-311, 2015. Available in "<https://doi.org/10.1016/j.watres.2015.02.022>"

WANG, L.; ZHANG, C.; GAO, F.; MAILHOT, G.; PAN, G. Algae decorated TiO₂/Ag hybrid nanofiber membrane with enhanced photocatalytic activity for Cr(VI) removal under visible light. Chem Eng J 314, 622-630, 2017. Available in "<https://doi.org/10.1016/j.cej.2016.12.020>"

WANG, Q.; SHI, X.; XU, J.; CRITTENDEN, J.C.; LIU, E.; ZHANG, Y.; CONG, Y. Highly enhanced photocatalytic reduction of Cr(VI) on AgI/TiO₂ under visible light irradiation: Influence of calcination temperature. Journal of Hazardous Materials, 307, 213-220, 2016. Available in "<https://doi.org/10.1016/j.jhazmat.2015.12.050>"

WANG, Y.; JIANG, L.; FENG, C. Effect of additives on photocatalysis of Cr(VI)-methyl orange. *Procedia Environmental Sciences*, 18, 625-631, 2013. Available in “<https://doi.org/10.1016/j.proenv.2013.04.086>”

WEI, L.; LU, J.; XU, H.; PATEL, A.; CHEN, Z.; CHEN, G. Silver nanoparticles: synthesis, properties, and therapeutic applications. *Drug Discovery Today* 20, 5, 595–601, 2015. Available in “<https://doi.org/10.1016/j.drudis.2014.11.014>”

XIA, Q.; HUANG, B.; YUAN, X.; WANG, H.; WU, Z.; JIANG, L.; XIONG, T.; ZHANG, J.; ZENG, G.; WANG, H. Modified stannous sulfide nanoparticles with metal-organic framework: Toward efficient and enhanced photocatalytic reduction of chromium (VI) under visible light. *J Colloid Interf Sci*, 530, 481-492, 2018. Available in “<https://doi.org/10.1016/j.jcis.2018.05.015>”

XU, S.C.; PAN, S.S.; XU, Y.; LUO, Y.Y.; ZHANG, Y.X.; LI, G.H. Efficient removal of Cr(VI) from wastewater under sunlight by Fe(II)-doped TiO₂ spherical shell. *Journal of Hazardous Materials*, 283, 7-13, 2015. Available in “<https://doi.org/10.1016/j.jhazmat.2014.08.071>”

YU, A.; WANG, Q.; WANG, J.; CHANG, C. Rapid synthesis of colloidal silver triangular nanoprisms and their promotion of TiO₂ photocatalysis on methylene blue under visible light. *Catal Commun* 90, 75-78, 2017. Available in “<https://doi.org/10.1016/j.catcom.2016.11.004>”

YUN, Y.S.; PARK, D.; PARK, J.M. Reduction of Hexavalent chromium with the brown seaweed *Ecklonia* Biomass. *Environmental Science & Technology*, 38, 18, 4860-4864, 2004. Available in “<https://doi.org/10.1021/es035329+>”

ZENG, X. Bioprocess considerations for microalgal-based wastewater treatment and

biomass production. Renewable and Sustainable Energy Reviews, 42, 1385-1392, 2015. Available in "<https://doi.org/10.1016/j.rser.2014.11.033>"

ZHAOA, Y.; CHANG, W.; HUANG, Z.; FENG, X.; MA, L.; QI, X.; LI, Z. Enhanced removal of toxic Cr(VI) in tannery wastewater by photoelectrocatalysis with synthetic TiO₂ hollow spheres. Applied Surface Science, 405, 102-110, 2017. Available in "<https://doi.org/10.1016/j.apsusc.2017.01.306>"

Attachments

This chapter shows the calibration curves used in this work.

Attachment A – Calibration curves for Cr(VI) determination

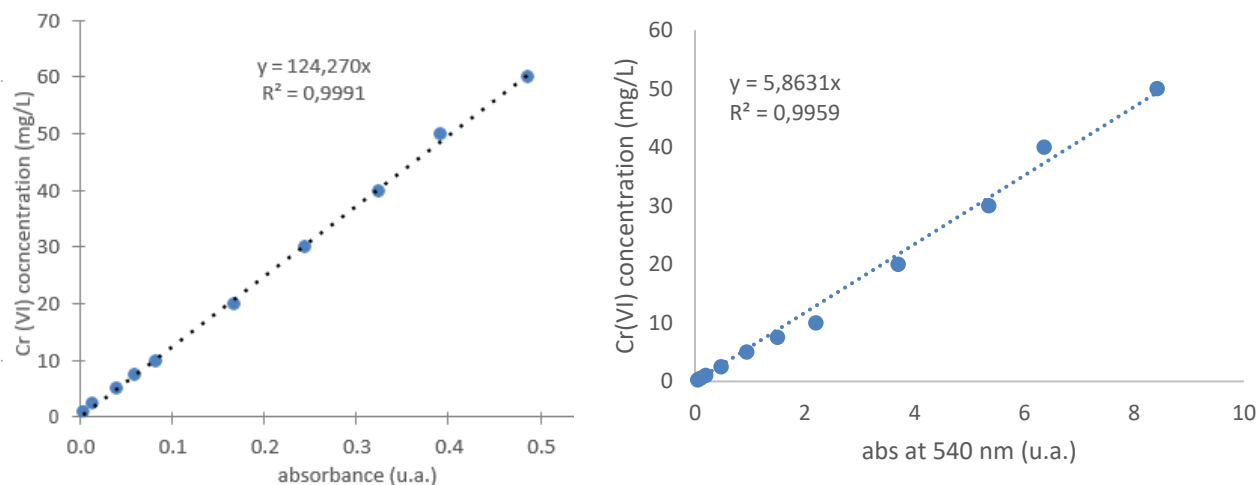


Figure A.1 – Calibration curves for Cr(VI) determination at 540 nm for a) AgNP-TiO₂ and b) raceway reactors and dissolved O₂ experiments